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Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry Supplement IV

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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This paper updates and extends previous critical evaluations of the kinetics and photochemistry of gas phase chemical reactions of neutral species involved in atmosphere chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989)]. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 489 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed, and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available data on enthalpies of formation of the reactant and product species.

Key words: air pollution; atmospheric chemistry; chemical kinetics; data evaluation; gas phase; photoabsorption cross-section, photochemistry; quantum yield; rate coefficient.

Contents

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1. Preface

This paper is the fourth supplement to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Gas Phase Chemical Kinetics in 1980[1] and subsequently updated by the first supplement in 1982,[2] and the second supplement in 1984.[3] The original evaluation and the first two supplements were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) set up a group to continue and enlarge upon the work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry is chaired by J. A. Kerr and is part of the Commission on Chemical Kinetics (I.4) of the IUPAC Physical Chemistry Division.

This subcommittee produced the third supplement in 1989,[4] in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry, it was decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms. The present fourth supplement has continued this policy in considering the reactions of organic species.

This publication differs from the previous supplements in that here we provide a data sheet for each reaction whether or not new data have been published since the previous publication. For reactions for which no new data have been published since the last data sheet was presented, we have largely reproduced that data sheet, merely updating the Reviews and Evaluations. For reactions for which new data have subsequently appeared since the data sheet was last published, we have followed our previous practice of listing only the new data, together again with updated Reviews and Evaluations. We have also prepared a large number of data sheets for "new" reactions, which were not previously included in our evaluations.

For each reaction the data sheet includes the preferred rate coefficient with a statement of the error limits, a comment giving the basis for the recommendation, and a list of the relevant references. To the extent that this information suffices, the reader can use this publication without need to refer to the previous publications. However, it should be noted that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation[1] and the three supplements.[2-4] Consequently, for many reactions, to obtain the overall picture and background to the preferred rate parameters the present supplement must be read in conjunction with its predecessors.[1-4]

It should also be noted that a number of reactions contained in our previous evaluations have been omitted from the data sheets in this evaluation, on the grounds that they are unimportant in atmospheric chemistry. These reactions are, however, still included in the Summary of Reactions, where, for each, the entry from the 1989 publication[4] is given, with a reference to the most recent evaluation containing a data sheet.

Unfortunately it has not been possible for us to include an evaluation of atmospheric heterogeneous reactions involving aerosol particles, now known to play an important role particularly in the chemistry of nitrogen and chlorine in the stratosphere. We intend to evaluate such reactions in our next updated review. In the meantime we have omitted from the Summary Table and the data sheets our previous evaluations of the homogeneous gas-phase reactions $ClONO_2 + H_2O \rightarrow HOCl + HONO_2$ and $ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$. The experimental data reported for these gas-phase reactions are influenced by the much more rapid heterogeneous reactions. The data indicate that the gas-phase reactions are too slow to be significant.

The cutoff point for literature searching for this supplement was May 1991. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Summary of Reactions and Preferred Rate Data

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	O_x Reactions						
1148	$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34} [O_2]	(k_0)	± 0.05	$6.0 \times 10^{-34}(T/300)^{-2.8}[O_2]$	100–300	$\Delta n = \pm 0.5$
		5.6×10^{-34} [N_2]	(k_0)	± 0.05	$5.6 \times 10^{-34}(T/300)^{-2.8}[N_2]$	100–300	$\Delta n = \pm 0.5$
*	$O + O_2 \rightarrow O_3^*$	See previous evaluation					
*	$O_3^* + M \rightarrow O_3 + M$	See previous evaluation					
1149	$O + O_3 \rightarrow 2\ O_2$	8.0×10^{-15}		± 0.08	$8.0 \times 10^{-12}\exp(-2060/T)$	200–400	± 200
*	$O + O_3^* \rightarrow$ products	See previous evaluation					
1150	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	4.0×10^{-11}		± 0.05	$3.2 \times 10^{-11}\exp(67/T)$	200–350	± 100
1151	$O(^1D) + O_3 \rightarrow O_2 + 2\ O(^3P)$	1.2×10^{-10}		± 0.1	2.4×10^{-10}	100–400	$\Delta\log k = \pm 0.05$
	$\rightarrow 2\ O_2(^3\Sigma_g^-)$	1.2×10^{-10}		± 0.1			
1152	$O_2^* + O_3 \rightarrow O + 2\ O_2$	See data sheet					
1152	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	1.6×10^{-18}	($M = O_2$)	± 0.2	$3.0 \times 10^{-18}\exp(-200/T)$	100–450	± 200
		$\leq 1.4 \times 10^{-19}$	($M = N_2$)				
		5×10^{-18}	($M = H_2O$)	± 0.3			
		$\leq 2 \times 10^{-20}$	($M = CO_2$)				
*	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	See previous evaluation					
*	$O_2(^1\Sigma_g^+) + O_3 \rightarrow$ products	See previous evaluation					
*	$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$	See previous evaluation					
1153	$O_2 + h\nu \rightarrow$ products	See data sheets					
1155	$O_3 + h\nu \rightarrow$ products	See data sheets					
	HO_x Reactions						
1157	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}		± 0.5	5.6×10^{-12}	245–300	$\Delta\log k = \pm 0.5$
	$\rightarrow 2\ HO$	7.2×10^{-11}		± 0.1	7.2×10^{-11}	245–300	$\Delta\log k = \pm 0.1$
	$\rightarrow H_2O + O$	2.4×10^{-12}		± 0.5	2.4×10^{-12}	245–300	$\Delta\log k = \pm 0.5$
1158	$H + O_2 + M \rightarrow HO_2 + M$	$6.2 \times 10^{-32}[N_2]$	(k_0)	± 0.05	$6.2 \times 10^{-32}(T/300)^{-1.6}[N_2]$	200–600	$\Delta n = \pm 0.6$
		7.5×10^{-11}	(k_∞)	± 0.3	7.5×10^{-11}	200–300	$\Delta n = \pm 0.6$
		$F_c = 0.55$		$\Delta F_c = \pm 0.15$	$F_c = \exp(-T/498)$	200–300	
*	$H + O_3 \rightarrow HO + O_2$	See previous evaluation					
*	$H + O_3 \rightarrow HO^\dagger + O_2$	See previous evaluation					
*	$O + H_2 \rightarrow HO + H$	See previous evaluation					
1159	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		± 0.1	$2.3 \times 10^{-11}\exp(110/T)$	220–500	± 100
1160	$O + HO_2 \rightarrow HO + O_2$	5.8×10^{-11}		± 0.08	$2.7 \times 10^{-11}\exp(224/T)$	200–400	± 100
1161	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}		± 0.3	$1.4 \times 10^{-12}\exp(-2000/T)$	250–390	± 1000
1162	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}		± 0.1	1.1×10^{-10}	200–350	± 100
1163	$O(^1D) + H_2O \rightarrow 2\ HO$	2.2×10^{-10}		± 0.1	2.2×10^{-10}	200–350	± 100
1164	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		± 0.1	$7.7 \times 10^{-12}\exp(-2100/T)$	200–450	± 200
*	$HO + H_2(v=1) \rightarrow H_2O + H$	See previous evaluation					
1165	$HO + HO \rightarrow H_2O + O$	1.9×10^{-12}		± 0.15	$4.2 \times 10^{-12}\exp(-240/T)$	250–500	± 240

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1165	$HO + HO + M \rightarrow H_2O_2 + M$	$8 \times 10^{-31}[N_2]$ (k_0)	±0.3	$8 \times 10^{-31}(T/300)^{-0.8}[N_2]$	200–300	$\Delta n = \pm 0.5$
		3×10^{-11} (k_∞)	±0.3	3×10^{-11}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$F_c = 0.5$	200–300	
1167	$HO + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}	±0.1	$4.8 \times 10^{-11}\exp(250/T)$	250–400	±200
1168	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}	±0.1	$2.9 \times 10^{-12}\exp(-160/T)$	240–460	±100
1169	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}	±0.15	$1.9 \times 10^{-12}\exp(-1000/T)$	220–450	±300
*	$HO^* + M \rightarrow HO + M$	See previous evaluation				
*	$HO^* + O_3 \rightarrow$ products	See previous evaluation				
1170	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.6×10^{-12}	±0.15	$2.2 \times 10^{-13}\exp(600/T)$	230–420	±200
1170	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	5.2×10^{-32} $[N_2]$	±0.15	$1.9 \times 10^{-33}\exp(980/T)[N_2]$	230–420	±300
		4.5×10^{-32} $[O_2]$	±0.15			
		See data sheets for effect of H_2O				
1171	$HO_2 + O_3 \rightarrow HO + 2\,O_2$	2.0×10^{-15}	±0.2	$1.4 \times 10^{-14}\exp(-600/T)$	250–350	+500 −100
1172	$H_2O + h\nu \rightarrow HO + H$	See data sheets				
1173	$H_2O_2 + h\nu \rightarrow 2\,HO$	See data sheets				
	NO_x Reactions					
1175	$O + NO + M \rightarrow NO_2 + M$	1.0×10^{-31} $[N_2]$ (k_0)	±0.1	$1.0 \times 10^{-31}(T/300)^{-1.6}[N_2]$	200–300	$\Delta n = \pm 0.3$
		3.0×10^{-11} (k_∞)	±0.3	$3.0 \times 10^{-11}(T/300)^{0.3}$	200–1500	$\Delta n = \pm 0.3$
		$F_c = 0.85$	$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1850)$	200–300	
1176	$O + NO_2 \rightarrow O_2 + NO$	9.7×10^{-12}	±0.06	$6.5 \times 10^{-12}\exp(120/T)$	230–350	±120
1177	$O + NO_2 + M \rightarrow NO_3 + M$	9.0×10^{-32} $[N_2]$ (k_0)	±0.1	$9.0 \times 10^{-32}(T/300)^{-2.0}[N_2]$	200–400	$\Delta n = \pm 1$
		2.2×10^{-11} (k_∞)	±0.2	2.2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.8$	$\Delta F_c = \pm 0.1$	$F_c = \exp(-T/1300)$	200–400	
1178	$O + NO_3 \rightarrow O_2 + NO_2$	1.7×10^{-11}	±0.3			
*	$O + N_2O_5 \rightarrow$ products	See previous evaluation				
1178	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}	±0.1	$1.8 \times 10^{-11}\exp(107/T)$	200–350	±100
1179	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}	±0.15	4.4×10^{-11}	200–350	±100
	$\rightarrow 2\,NO$	7.2×10^{-11}	±0.15	7.2×10^{-11}	200–350	±100
*	$N + HO \rightarrow NO + H$	See previous evaluation				
*	$N + O_2 \rightarrow NO + O$	See previous evaluation				
*	$N + O_2(^1\Delta_g) \rightarrow NO + O$	See previous evaluation				
*	$N + O_3 \rightarrow NO + O_2$	See previous evaluation				
*	$N + NO \rightarrow N_2 + O$	See previous evaluation				
*	$N + NO_2 \rightarrow N_2O + O$	See previous evaluation				
1181	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}	±0.1	$3.5 \times 10^{-12}\exp(-925/T)$	230–450	±200
1181	$HO + HONO \rightarrow H_2O + NO_2$	4.9×10^{-12}	±0.3	$1.8 \times 10^{-11}\exp(-390/T)$	280–340	±400
1182	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.5×10^{-13} (1 bar)	±0.1	See data sheets		
1183	$HO + HO_2NO_2 \rightarrow$ products	5.0×10^{-12}	±0.2	$1.5 \times 10^{-12}\exp(360/T)$	240–340	$^{+300}_{-600}$

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
1184	$HO + NO + M \rightarrow HONO + M$	7.4×10^{-31} [N_2]	(k_0)	±0.1	$7.4 \times 10^{-31}(T/300)^{-2.4}[N_2]$	200–300	$\Delta n = \pm0.5$
		3.2×10^{-11}	(k_∞)	±0.3	3.2×10^{-11}	200–400	$\Delta\log k = \pm0.3$
		$F_c = 0.8$					
1185	$HO + NO_2 + M \rightarrow HONO_2 + M$	2.6×10^{-30} [N_2]	(k_0)	±0.1	$2.6 \times 10^{-30}(T/300)^{-2.9}[N_2]$	200–300	$\Delta n = \pm0.5$
		6.0×10^{-11}	(k_∞)	±0.1	6.0×10^{-11}	200–300	$\Delta n = \pm0.5$
		$F_c = 0.43$					
1186	$HO + NO_3 \rightarrow HO_2 + NO_2$	2.3×10^{-11}		±0.2			
1187	$HO_2 + NO \rightarrow HO + NO_2$	8.3×10^{-12}		±0.1	$3.7 \times 10^{-12}\exp(240/T)$	230–500	±100
1188	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	1.8×10^{-31} [N_2]	(k_0)	±0.1	$1.8 \times 10^{-31}(T/300)^{-3.2}[N_2]$	200–300	$\Delta n = \pm1$
		4.7×10^{-12}	(k_∞)	±0.2	4.7×10^{-12}	200–300	$\Delta n = \pm1$
		$F_c = 0.6$			$F_c = 0.6$		
1189	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	1.3×10^{-20} [N_2]	(k_0/s^{-1})	±0.3	$5 \times 10^{-6}\exp(-10000/T)[N_2]$	260–300	±500
		0.34	(k_∞/s^{-1})	±0.5	$2.6 \times 10^{15}\exp(-10900/T)$	260–300	±500
		$F_c = 0.6$					
1190	$HO_2 + NO_3 \rightarrow O_2 + HONO_2$ $\rightarrow HO + NO_2 + O_2$ }	4.3×10^{-12}		±0.2			
*	$NH_2 + HO \rightarrow$ products	See previous evaluation					
*	$NH_2 + HO_2 \rightarrow$ products	See previous evaluation					
1191	$NH_2 + O_2 \rightarrow$ products	$<3 \times 10^{-18}$					
1192	$NH_2 + O_3 \rightarrow$ products	1.7×10^{-13}		±0.5	$4.9 \times 10^{-12}\exp(-1000/T)$	250–380	±500
1193	$NH_2 + NO \rightarrow$ products	1.6×10^{-11}		±0.2	$1.6 \times 10^{-11}(T/298)^{-1.5}$	210–500	$\Delta n = \pm0.5$
1194	$NH_2 + NO_2 \rightarrow$ products	2.0×10^{-11}		±0.2	$2.0 \times 10^{-11}(T/298)^{-2.0}$	250–500	$\Delta n = \pm0.7$
1195	$2\,NO + O_2 \rightarrow 2\,NO_2$	2.0×10^{-38} (cm^6 molecule^{-2} s^{-1})		±0.1	$3.3 \times 10^{-39}\exp(530/T)$	273–600	±400
1196	$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}		±0.08	$1.8 \times 10^{-12}\exp(-1370/T)$	195–304	±200
1197	$NO + NO_3 \rightarrow 2\,NO_2$	2.6×10^{-11}		±0.1	$1.8 \times 10^{-11}\exp(110/T)$	220–400	±100
1198	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}		±0.06	$1.2 \times 10^{-13}\exp(-2450/T)$	230–360	±150
1199	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$2.7 \times 10^{-30}[N_2]$	(k_0)	±0.1	$2.7 \times 10^{-30}(T/300)^{-3.4}[N_2]$	200–400	$\Delta n = \pm0.5$
		2.0×10^{-12}	(k_∞)	±0.2	$2.0 \times 10^{-12}(T/300)^{0.2}$	200–500	$\Delta n = \pm0.6$
		$F_c = 0.33$			$F_c = [\exp(-T/250) + \exp(-1050/T)]$	200–500	
1200	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$1.6 \times 10^{-19}[N_2]$	(k_0/s^{-1})	±0.2	$2.2 \times 10^{-3}(T/300)^{-4.4} \exp(-11080/T)[N_2]$	220–300	$\Delta n = \pm0.5$
		6.9×10^{-2}	(k_∞/s^{-1})	±0.3	$9.7 \times 10^{14}(T/300)^{0.1} \exp(-11080/T)$	200–300	$\Delta n = \pm0.2$
		$F_c = 0.33$			$F_c = [\exp(-T/250) + \exp(-1050/T)]$	200–300	
1201	$N_2O_5 + H_2O \rightarrow 2\,HONO_2$	$<2 \times 10^{-21}$					
1202	$HONO + h\nu \rightarrow$ products	See data sheets					
1204	$HONO_2 + h\nu \rightarrow$ products	See data sheets					
1205	$HO_2NO_2 + h\nu \rightarrow$ products	See data sheets					
*	$NO + h\nu \rightarrow$ products	See previous evaluation					
1206	$NO_2 + h\nu \rightarrow$ products	See data sheets					
1208	$NO_3 + h\nu \rightarrow$ products	See data sheets					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1212	$N_2O + h\nu \rightarrow$ products	See data sheets				
1213	$N_2O_5 + h\nu \rightarrow$ products	See data sheets				
	Organic Reactions					
1214	$O + CH_3 \rightarrow HCHO + H$	1.4×10^{-10}	± 0.1	1.4×10^{-10}	200–900	± 100
*	$O + CN \rightarrow CO + N(^2D)$	See previous evaluation				
	$\rightarrow CO + N(^4S)$	See previous evaluation				
1215	$O(^1D) + CH_4 \rightarrow HO + CH_3$	1.35×10^{-10}	± 0.1	1.35×10^{-10}	200–300	± 100
	$\rightarrow HCHO + H_2$	1.5×10^{-11}	± 0.1	1.5×10^{-11}	200–300	± 100
1216	$HO + CH_4 \rightarrow H_2O + CH_3$	7.0×10^{-15}	± 0.10	$3.9 \times 10^{-12}\exp(-1885/T)$	240–300	± 100
1217	$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$	$5 \times 10^{-30}[N_2]$ (k_0)	± 0.1	$5 \times 10^{-30}(T/300)^{-1.5}[N_2]$	200–300	$\Delta n = \pm 1.5$
		9.0×10^{-13} (k_∞)	± 0.1	$9.0 \times 10^{-13}(T/300)^2$	200–300	$\Delta n = \pm 1$
		$F_c = 0.62$		$F_c = \exp(-T/623)$	200–300	
1219	$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$	$7 \times 10^{-29}[N_2]$ (k_0)	± 0.3	$7 \times 10^{-29}(T/300)^{-3.1}[N_2]$	200–300	$\Delta n = \pm 2$
		9×10^{-12} (k_∞)	± 0.3	9×10^{-12}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.7$				
1221	$HO + C_2H_6 \rightarrow H_2O + C_2H_5$	2.5×10^{-13}	± 0.10	$7.8 \times 10^{-12}\exp(-1020/T)$	240–300	± 100
1222	$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$	$8 \times 10^{-27}[N_2]$ (k_0)	± 1	$8 \times 10^{-27}(T/300)^{-3.5}[N_2]$	200–300	$\Delta n = \pm 1$
		3.0×10^{-11} (k_∞)	± 0.1	3.0×10^{-11}	200–300	$\Delta n = \pm 1$
		$F_c = 0.5$				
1223	$HO + C_3H_8 \rightarrow H_2O + C_3H_7$	1.14×10^{-12}	± 0.10	$9.8 \times 10^{-12}\exp(-640/T)$	~300	± 150
1225	$HO + CO \rightarrow H + CO_2$	1.5×10^{-13} (1 + 0.6 P/bar)	± 0.1	1.5×10^{-13}(1 + 0.6 P/bar)	200–300	± 300
1226	$HO + HCHO \rightarrow H_2O + HCO$	9.6×10^{-12}	± 0.10	$8.8 \times 10^{-12}\exp(25/T)$	240–300	± 150
1227	$HO + CH_3CHO \rightarrow H_2O + CH_3CO$	1.6×10^{-11}	± 0.10	$5.6 \times 10^{-12}\exp(310/T)$	240–530	± 200
1228	$HO + C_2H_5CHO \rightarrow$ products	2.0×10^{-11}	± 0.15			
1229	$HO + (CHO)_2 \rightarrow$ products	1.1×10^{-11}	± 0.3			
1229	$HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO$	8.0×10^{-12}	± 0.3			
	$\rightarrow H_2O + HOCHCHO$	2.0×10^{-12}	± 0.3			
1230	$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$	1.7×10^{-11}	± 0.3			
1231	$HO + CH_3COCH_3 \rightarrow H_2O + CH_2COCH_3$	2.3×10^{-13}	± 0.2	$1.7 \times 10^{-12}\exp(-600/T)$	240–440	± 300
1232	$HO + CH_3OH \rightarrow H_2O + CH_2OH$	7.8×10^{-13}	± 0.15 }	$3.3 \times 10^{-12}\exp(-380/T)$	240–300	± 200
	$\rightarrow H_2O + CH_3O$	1.4×10^{-13}	± 0.15 }			
1233	$HO + C_2H_5OH \rightarrow H_2O + CH_2CH_2OH$	1.6×10^{-13}	± 0.15 }			
	$\rightarrow H_2O + CH_3CHOH$	2.9×10^{-12}	± 0.15 }	$4.1 \times 10^{-12}\exp(-70/T)$	270–340	± 200
	$\rightarrow H_2O + CH_3CH_2O$	1.6×10^{-13}	± 0.15 }			
1235	$HO + n\text{-}C_3H_7OH \rightarrow$ products	5.5×10^{-12}	± 0.2			
1235	$HO + i\text{-}C_3H_7OH \rightarrow$ products	5.7×10^{-12}	± 0.2	5.7×10^{-12}	240–440	± 200
1236	$HO + CH_3COCH_2OH \rightarrow$ products	3.0×10^{-12}	± 0.3			
1237	$HO + CH_3OOH \rightarrow H_2O + CH_2OOH$	1.9×10^{-12}	± 0.2	$1.0 \times 10^{-12}\exp(190/T)$	220–430	± 150
	$\rightarrow H_2O + CH_3OO$	3.6×10^{-12}	± 0.2	$1.9 \times 10^{-12}\exp(190/T)$	220–430	± 150
1238	$HO + HCOOH \rightarrow$ products	4.5×10^{-13}	± 0.15	4.5×10^{-13}	290–450	± 250
1239	$HO + CH_3COOH \rightarrow$ products	8×10^{-13}	± 0.3			

2. Summary of Reactions and Preferred Rate Data – Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
1239	$HO + CH_3ONO_2 \rightarrow$ products	3.5×10^{-13}	(1 bar)	±0.10	$1.0 \times 10^{-14}\exp(1060/T)$ (1 bar)	290–400	±500
1240	$HO + C_2H_5ONO_2 \rightarrow$ products	4.9×10^{-13}	(1 bar)	±0.15	$4.4 \times 10^{-14}\exp(720/T)$ (1 bar)	290–380	±500
1241	$HO + n\text{-}C_3H_7ONO_2 \rightarrow$ products	7.3×10^{-13}	(1 bar)	±0.15	7.3×10^{-13} (1 bar)	290–370	±500
1242	$HO + i\text{-}C_3H_7ONO_2 \rightarrow$ products	4.9×10^{-13}	(1 bar)	±0.25			
1242	$HO + CH_3CO_3NO_2 \rightarrow$ products	1.1×10^{-13}		±0.2	$9.5 \times 10^{-13}\exp(-650/T)$	270–300	±400
1243	$HO + HCN \rightarrow$ products	3×10^{-14}	(1 bar)	±0.5	$1.2 \times 10^{-13}(-400/T)$ (1 bar)	290–440	±300
1244	$HO + CH_3CN \rightarrow$ products	2.2×10^{-14}	(1 bar)	±0.15	$8.1 \times 10^{-13}\exp(-1080/T)$ (1 bar)	250–390	±200
1245	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$	5.2×10^{-12}		±0.3	$3.8 \times 10^{-13}\exp(780/T)$	225–580	±500
1246	$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H$ $\rightarrow O_2 + HCO_2H + H_2O$ }	1.2×10^{-11}		±0.3	$5.6 \times 10^{-15}\exp(2300/T)$	275–335	±1500
1247	$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$	5.8×10^{-12}		±0.2	$6.5 \times 10^{-13}\exp(650/T)$	240–380	±200
1248	$HO_2 + CH_3CO_3 \rightarrow O_2 + CH_3CO_3H$	4.2×10^{-12}		±0.3	$1.3 \times 10^{-13}\exp(1040/T)$	250–370	±500
	$\rightarrow O_3 + CH_3CO_2H$	1.0×10^{-11}		±0.3	$3.0 \times 10^{-13}\exp(1040/T)$	250–370	±500
1249	$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products	1.0×10^{-11}		±0.3			
1250	$HO_2 + HCHO \rightarrow HOCH_2OO$	7.9×10^{-14}		±0.3	$9.7 \times 10^{-15}\exp(625/T)$	275–333	±600
1251	$HOCH_2OO \rightarrow HO_2 + HCHO$	1.5×10^{2}	(k/s^{-1})	±0.3	$2.4 \times 10^{12}\exp(-7000/T)$	275–333	±2000
1252	$NO_3 + C_2H_2 \rightarrow$ products	$<1 \times 10^{-16}$					
1252	$NO_3 + C_2H_4 \rightarrow$ products	2.1×10^{-16}		±0.2	$3.3 \times 10^{-12}\exp(-2880/T)$	270–330	±500
1253	$NO_3 + C_3H_6 \rightarrow$ products	9.4×10^{-15}		±0.2			
1254	$NO_3 + HCHO \rightarrow HNO_3 + HCO$	5.8×10^{-16}		±0.3			
1256	$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$	2.7×10^{-15}		±0.2	$1.4 \times 10^{-12}\exp(-1860/T)$	260–370	±500
1257	$NO_3 + CH_3OH \rightarrow$ products	2.4×10^{-16}		±0.5	$1.3 \times 10^{-12}\exp(-2560/T)$	290–480	±700
1257	$NO_3 + C_2H_5OH \rightarrow$ products	$<2 \times 10^{-15}$					
1258	$NO_3 + i\text{-}C_3H_7OH \rightarrow$ products	$<5 \times 10^{-15}$					
1258	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$1.0 \times 10^{-30}[N_2]$	(k_0)	±0.2	$1.0 \times 10^{-30}(T/300)^{-3.3}[N_2]$	200–300	$\Delta n = \pm1$
		2.2×10^{-12}	(k_∞)	±0.3	$2.2 \times 10^{-12}(T/300)^{1.0}$	200–300	$\Delta n = \pm1$
		$F_c = 0.27$					
1259	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	3.8×10^{-15}	(1 bar air)	±0.5			
		1.9×10^{-14}	(0.133 bar air)	±0.5			
1260	$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$	$5.9 \times 10^{-29}[N_2]$	(k_0)	±0.3	$5.9 \times 10^{-29}(T/300)^{-3.8}[N_2]$	200–300	$\Delta n = \pm1$
		7.8×10^{-12}	(k_∞)	±0.2	7.8×10^{-12}	200–300	$\Delta\log k = \pm0.2$
		$F_c = 0.54$			$F_c = \{0.58\exp(-T/1250) + 0.42\exp(-T/183)\}$	200–300	
1262	$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$	8×10^{-12}	(k_∞)	±0.2	8×10^{-12}	200–300	$\Delta\log k = \pm0.2$
1263	$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$	1.1×10^{-11}	(k_∞)	±0.3	1.1×10^{-11}	200–300	$\Delta\log k = \pm0.3$
1263	$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$	1.5×10^{-12}	(k_∞)	±0.5			
1264	$HCO + O_2 \rightarrow CO + HO_2$	5.5×10^{-12}		±0.15	5.5×10^{-12}	200–400	±150
1265	$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$	5.0×10^{-12}	(k_∞)	±0.5	5.0×10^{-12}	200–300	$\Delta\log k = \pm0.5$
1265	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	9.4×10^{-12}		±0.12			
1266	$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$	1.9×10^{-11}		±0.3			
1267	$CH_2CH_2OH + O_2 \rightarrow$ products	3.0×10^{-12}		±0.3			
1267	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}		±0.2	$7.2 \times 10^{-14}\exp(-1080/T)$	298–610	±300
1268	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	9.5×10^{-15}		±0.2	$6.0 \times 10^{-14}\exp(-550/T)$	295–425	±300
1269	$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$	8×10^{-15}		±0.5			
1270	$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$	8×10^{-15}		±0.3	$1.5 \times 10^{-14}\exp(-200/T)$	290–390	±200

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1270	$CH_3 + O_3 \rightarrow$ products	2.5×10^{-12}		± 0.3	$5.1 \times 10^{-12}\exp(-210/T)$	240–400	± 200
1271	$CH_3O + NO + M \rightarrow CH_3ONO + M$	$1.6 \times 10^{-29}[N_2]$	(k_0)	± 0.1	$1.6 \times 10^{-29}(T/300)^{-3.5}[N_2]$	200–400	$\Delta n = \pm 0.5$
		3.6×10^{-11}	(k_∞)	± 0.5	$3.6 \times 10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.6$					
1271	$CH_3O + NO \rightarrow HCHO + HNO$	4×10^{-12}			$4 \times 10^{-12}(T/300)^{-0.7}$	200–400	$\Delta n = \pm 0.5$
1272	$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$	4.4×10^{-11}	(k_∞)	± 0.3	4.4×10^{-11}	200–300	$\Delta n = \pm 0.5$
1272	$C_2H_5O + NO \rightarrow CH_3CHO + HNO$	1.3×10^{-11}					
1273	i-$C_3H_7O + NO + M \rightarrow i$-$C_3H_7ONO + M$	3.4×10^{-11}	(k_∞)	± 0.3	3.4×10^{-11}	200–300	$\Delta n = \pm 0.5$
1273	i-$C_3H_7O + NO \rightarrow CH_3COCH_3 + HNO$	6.5×10^{-12}		± 0.5			
1274	$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$	$2.8 \times 10^{-29}[N_2]$	(k_0)	± 0.3	$2.8 \times 10^{-29}(T/300)^{-4.5}[N_2]$	200–400	$\Delta n = \pm 1$
		2×10^{-11}	(k_∞)	± 0.3	2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.44$					
1274	$CH_3O + NO_2 \rightarrow HCHO + HONO$	See data sheets					
1275	$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M$	2.8×10^{-11}	(k_∞)	± 0.3	2.8×10^{-11}	200–300	$\Delta n = \pm 0.5$
1275	$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO$	See data sheets					
1276	i-$C_3H_7O + NO_2 + M \rightarrow i$-$C_3H_7ONO_2 + M$	3.5×10^{-11}	(k_∞)	± 0.3	3.5×10^{-11}	200–300	$\Delta n = \pm 0.5$
1276	i-$C_3H_7O + NO_2 \rightarrow CH_3COCH_3 + HONO$	See data sheets					
1276	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.6×10^{-12}		± 0.1	$4.2 \times 10^{-12}\exp(180/T)$	240–360	± 180
1277	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.9×10^{-12}		± 0.3			
1277	$C_2H_5O_2 + NO\ (+M) \rightarrow C_2H_5ONO_2\ (+M)$	$\leq 1.3 \times 10^{-13}$	(1 bar)				
1278	n-$C_3H_7O_2 + NO \rightarrow n$-$C_3H_7O + NO_2$	8.7×10^{-12}		± 0.3			
1278	n-$C_3H_7O_2 + NO\ (+M) \rightarrow n$-$C_3H_7ONO_2$ $(+M)$	1.8×10^{-13}	(1 bar)	± 0.5			
1279	i-$C_3H_7O_2 + NO \rightarrow i$-$C_3H_7O + NO_2$	8.5×10^{-12}		± 0.5			
1279	i-$C_3H_7O_2 + NO\ (+M) \rightarrow i$-$C_3H_7ONO_2$ $(+M)$	3.7×10^{-13}	(1 bar)	± 0.5			
1280	$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	2.0×10^{-11}		± 0.2	2.0×10^{-11}	280–325	± 600
1281	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	$2.5 \times 10^{-30}[N_2]$	(k_0)	± 0.3	$2.5 \times 10^{-30}(T/300)^{-5.5}[N_2]$	250–350	$\Delta n = \pm 1$
		7.5×10^{-12}	(k_∞)	± 0.3	7.5×10^{-12}	250–350	$\Delta n = \pm 0.5$
		$F_c = 0.4$					
1282	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$	$6.8 \times 10^{-19}[N_2]$	(k_0/s^{-1})	± 0.3	$9 \times 10^{-5}\exp(-9690/T)[N_2]$	250–300	± 500
		4.5	(k_∞/s^{-1})	± 0.3	$1.1 \times 10^{16}\exp(-10560/T)$	250–300	± 500
		$F_c = 0.4$					
1283	$C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2 + M$	$1.3 \times 10^{-29}[N_2]$	(k_0)	± 0.3	$1.3 \times 10^{-29}(T/300)^{-6.2}[N_2]$	200–300	$\Delta n = \pm 1$
		8.8×10^{-12}	(k_∞)	± 0.3	8.8×10^{-12}	200–300	$\Delta\log k = \pm 0.3$
		$F_c = 0.31$			$F_c = 0.31$	250–300	
1285	$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$	$1.4 \times 10^{-17}[N_2]$	(k_0/s^{-1})	± 0.5	$4.8 \times 10^{-4}\exp(-9285/T)[N_2]$	250–300	± 1000
		5.4	(k_∞/s^{-1})	± 0.5	$8.8 \times 10^{15}\exp(-10440/T)$	250–300	± 1000
		$F_c = 0.31$			$F_c = 0.31$	250–300	
1286	$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$	$2.7 \times 10^{-28}[N_2]$	(k_0)	± 0.4	$2.7 \times 10^{-28}(T/300)^{-7.1}[N_2]$	250–300	$\Delta n = \pm 2$
		1.2×10^{-11}	(k_∞)	± 0.2	$1.2 \times 10^{-11}(T/300)^{-0.9}$	250–300	$\Delta n = \pm 1$
		$F_c = 0.3$					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
1287	$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$	$1.1 \times 10^{-20}[N_2]$ (k_0/s^{-1})	±0.4	$4.9 \times 10^{-3}\exp(-12100/T)[N_2]$	300–330	±1000
		6.1×10^{-4} (k_∞/s^{-1})	±0.2	$4.0 \times 10^{16}\exp(-13600/T)$	280–330	±200
		$F_c = 0.3$				
1288	$CH_3O_2 + NO_3 \rightarrow$ products	No recommendation (see data sheets)				
1289	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$					
	$\rightarrow 2\ CH_3O + O_2$	3.7×10^{-13}	±0.12	$1.1 \times 10^{-13}\exp(365/T)$	200–400	±200
	$\rightarrow CH_3OOCH_3 + O_2$					
1291	$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2$					
	$+ O_2$	5.5×10^{-12}	±0.5			
	$\rightarrow CH_3CO_2H + HCHO$					
	$+ O_2$	5.5×10^{-12}	±0.5			
1292	$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH +$					
	$CH_2(OH)_2 + O_2$	7.0×10^{-13}	±0.3	$5.7 \times 10^{-14}\exp(750/T)$	275–325	±750
	$\rightarrow 2\ HOCH_2O + O_2$	5.5×10^{-12}	±0.3			
1293	$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2$					
	$\rightarrow 2\ C_2H_5O + O_2$	6.8×10^{-14}	±0.12	$9.8 \times 10^{-14}\exp(-110/T)$	250–450	$^{+300}_{-100}$
	$\rightarrow C_2H_5OOC_2H_5 + O_2$					
1294	$CH_3CO_3 + CH_3CO_3 \rightarrow 2\ CH_3CO_2 + O_2$	1.6×10^{-11}	±0.5	$2.8 \times 10^{-12}\exp(530/T)$	250–370	±500
1295	$HOCH_2CH_2O_2 + HOCH_2CH_2O_2$					
	$\rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2$	1.5×10^{-12}	±0.3			
	$\rightarrow 2\ HOCH_2CH_2O + O_2$	8.3×10^{-13}	±0.3			
1296	$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH +$					
	$C_2H_5CHO + O_2$	3×10^{-13}	±0.5			
	$\rightarrow 2\ n\text{-}C_3H_7O + O_2$					
1297	$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH$					
	$+ CH_3COCH_3 + O_2$	4.4×10^{-16}	±0.3			
	$\rightarrow 2\ i\text{-}C_3H_7O$			$1.6 \times 10^{-12}\exp(-2200/T)$	300–400	±300
	$+ O_2$	5.6×10^{-16}	±0.3			
1298	$CH_3COCH_2O_2 + CH_3COCH_2O_2$					
	$\rightarrow CH_3COCH_2OH + CH_3COCHO + O_2$	$\leq 1 \times 10^{-11}$				
	$\rightarrow 2\ CH_3COCH_2O + O_2$					
1299	$RCHOO + H_2O \rightarrow RCOOH + H_2O$					
1299	$RCHOO + NO_2 \rightarrow RCHO + NO_3$	No recommendations (see data sheets)				
1299	$RCHOO + SO_2 \rightarrow$ products					
1299	$RCHOO + HCHO \rightarrow$ products					
*	$CN + O_2 \rightarrow$ products	See previous evaluation				
1301	$O_3 + C_2H_2 \rightarrow$ products	1×10^{-20}	±1.0			
1302	$O_3 + C_2H_4 \rightarrow$ products	1.7×10^{-18}	±0.10	$1.2 \times 10^{-14}\exp(-2630/T)$	180–360	±100
1304	$O_3 + C_3H_6 \rightarrow$ products	1.2×10^{-17}	±0.15	$6.5 \times 10^{-15}\exp(-1880/T)$	230–370	±400
1306	$HCHO + h\nu \rightarrow$ products	See data sheets				
1308	$CH_3CHO + h\nu \rightarrow$ products	See data sheets				

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1309	$C_2H_5CHO + h\nu \rightarrow$ products	See data sheets					
1310	$(CHO)_2 + h\nu \rightarrow$ products	See data sheets					
1312	$CH_3COCHO + h\nu \rightarrow$ products	See data sheets					
1313	$CH_3COCH_3 + h\nu \rightarrow$ products	See data sheets					
1315	$CH_3OOH + h\nu \rightarrow$ products	See data sheets					
1316	$CH_3ONO_2 + h\nu \rightarrow$ products	See data sheets					
1317	$C_2H_5ONO_2 + h\nu \rightarrow$ products	See data sheets					
1318	n-$C_3H_7ONO_2 + h\nu \rightarrow$ products	See data sheets					
1319	i-$C_3H_7ONO_2 + h\nu \rightarrow$ products	See data sheets					
1320	$CH_3O_2NO_2 + h\nu \rightarrow$ products	See data sheets					
1321	$CH_3CO_3NO_2 + h\nu \rightarrow$ products	See data sheets					
	SO_x Reactions						
*	$O + H_2S \rightarrow HO + HS$	See previous evaluation					
1323	$O + CS \rightarrow CO + S$	2.1×10^{-11}		±0.1	$2.7 \times 10^{-10}\exp(-760/T)$	150–300	±250
1324	$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$	5.0×10^{-11}		±0.1	$1.3 \times 10^{-11}\exp(409/T)$	270–560	±100
1325	$O + CS_2 \rightarrow SO + CS$	3.6×10^{-12}		±0.2	$3.2 \times 10^{-11}\exp(-650/T)$	200–500	±100
1326	$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$	1.3×10^{-10}		±0.3	$5.5 \times 10^{-11}\exp(250/T)$	290–570	±100
1327	$O + OCS \rightarrow SO + CO$	1.2×10^{-14}		±0.2	$1.6 \times 10^{-11}\exp(-2150/T)$	220–500	±150
1328	$O + SO_2 + M \rightarrow SO_3 + M$	$1.4 \times 10^{-33}[N_2]$	(k_0)	±0.3	$4.0 \times 10^{-32}\exp(-1000/T)[N_2]$	200–400	±200
1329	$S + O_2 \rightarrow SO + O$	2.1×10^{-12}		±0.2	2.1×10^{-12}	230–400	±200
1329	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}		±0.3			
1330	$Cl + H_2S \rightarrow HCl + HS$	5.7×10^{-11}		±0.3	5.7×10^{-11}	210–350	±100
1331	$HO + H_2S \rightarrow H_2O + HS$	4.8×10^{-12}		±0.08	$6.3 \times 10^{-12}\exp(-80/T)$	200–300	±80
1332	$HO + SO_2 + M \rightarrow HOSO_2 + M$	$4.0 \times 10^{-31}[N_2]$	(k_0)	±0.3	$4.0 \times 10^{-31}(T/300)^{-3.3}[N_2]$	300–400	$\Delta n = \pm1$
		$F_c = 0.8$					
		2×10^{-12}	(k_∞)	±0.3	2×10^{-12}	200–300	$\Delta\log k = \pm0.3$
		$F_c = 0.45$					
1333	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	4.0×10^{-13}		±0.1	$1.3 \times 10^{-12}\exp(-330/T)$	290–420	±200
1334	$HO + OCS \rightarrow$ products	2.0×10^{-15}		±0.3	$1.1 \times 10^{-13}\exp(-1200/T)$	250–500	±500
1335	$HO + CS_2 + M \rightarrow HOCS_2 + M$	$8 \times 10^{-31}[N_2]$	(k_0)	±0.5	$8 \times 10^{-31}[N_2]$	270–300	$\Delta\log k = \pm0.5$
		8×10^{-12}	(k_∞)	±0.5	8×10^{-12}	250–300	$\Delta\log k = \pm0.5$
		$F_c = 0.8$					
1335	$HO + CS_2 \rightarrow HS + OCS$	$<2 \times 10^{-15}$					
1337	$HOCS_2 + M \rightarrow HO + CS_2 + M$	$4.8 \times 10^{-14}[N_2]$	(k_0/s^{-1})	±0.5	$1.6 \times 10^{-6}\exp(-5160/T)[N_2]$	250–300	±500
		4.8×10^{5}	(k_∞/s^{-1})	±0.5	$1.6 \times 10^{13}\exp(-5160/T)$	250–300	±500
		$F_c = 0.8$					
1338	$HOCS_2 + O_2 \rightarrow$ products	2.8×10^{-14}		±0.3	2.8×10^{-14}	240–300	$\Delta\log k = \pm0.3$
1340	$HO + CH_3SH \rightarrow$ products	3.3×10^{-11}		±0.10	$9.9 \times 10^{-12}\exp(356/T)$	240–430	±100
1341	$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$	4.4×10^{-12}		±0.10	$9.6 \times 10^{-12}\exp(-234/T)$	250–400	±300
	$\rightarrow CH_3S(OH)CH_3$	See data sheets					
1342	$HO + CH_3SSCH_3 \rightarrow$ products	2.0×10^{-10}		±0.10	$6.0 \times 10^{-11}\exp(380/T)$	250–370	±300
1343	$HO_2 + SO_2 \rightarrow$ products	$\leq 1 \times 10^{-18}$					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/ K
1344	$NO_3 + H_2S \rightarrow$ products	$<1 \times 10^{-15}$				
1344	$NO_3 + CS_2 \rightarrow$ products	$<1 \times 10^{-15}$				
1345	$NO_3 + OCS \rightarrow$ products	$<1 \times 10^{-16}$				
1345	$NO_3 + SO_2 \rightarrow$ products	$<1 \times 10^{-19}$				
1346	$NO_3 + CH_3SH \rightarrow$ products	9.2×10^{-13}	± 0.15	9.2×10^{-13}	250–370	± 400
1347	$NO_3 + CH_3SCH_3 \rightarrow$ products	1.1×10^{-12}	± 0.15	$1.9 \times 10^{-13}\exp(520/T)$	250–380	± 200
1348	$NO_3 + CH_3SSCH_3 \rightarrow$ products	7×10^{-13}	± 0.3	7×10^{-13}	300–380	± 500
*	$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$	See previous evaluation				
	$\rightarrow CH_3O_2SO_2$	See previous evaluation				
1349	$HS + O_2 \rightarrow$ products	$\leq 4 \times 10^{-19}$				
1350	$HS + O_3 \rightarrow HSO + O_2$	3.7×10^{-12}	± 0.2	$9.5 \times 10^{-12}\exp(-280/T)$	290–450	± 250
1351	$HS + NO + M \rightarrow HSNO + M$	$2.4 \times 10^{-31}[N_2]$ (k_0)	± 0.3	$2.4 \times 10^{-31}(T/300)^{-2.5}[N_2]$	200–300	$\Delta n = \pm 1$
		2.7×10^{-11} (k_∞)	± 0.5	2.7×10^{-11}	200–300	$\Delta\log k = \pm 0.5$
		$F_c = 0.6$				
1352	$HS + NO_2 \rightarrow HSO + NO$	5.8×10^{-11}	± 0.3	$2.6 \times 10^{-11}\exp(240/T)$	220–450	± 200
1353	$HSO + O_2 \rightarrow$ products	$\leq 2.0 \times 10^{-17}$				
1353	$HSO + O_3 \rightarrow$ products	1.1×10^{-13}	± 0.3			
1354	$HSO + NO \rightarrow$ products	$\leq 1.0 \times 10^{-15}$				
1355	$HSO + NO_2 \rightarrow$ products	9.6×10^{-12}	± 0.3			
1355	$HSO_2 + O_2 \rightarrow$ products	3.0×10^{-13}	± 0.8			
1356	$SO + O_2 \rightarrow SO_2 + O$	6.7×10^{-17}	± 0.15	$1.4 \times 10^{-13}\exp(-2280/T)$	230–420	± 500
1357	$SO + O_3 \rightarrow SO_2 + O_2$	8.9×10^{-14}	± 0.10	$4.5 \times 10^{-12}\exp(-1170/T)$	230–420	± 150
1357	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}	± 0.1	1.4×10^{-11}	210–360	± 100
1358	$SO_3 + H_2O \rightarrow$ products	$<6 \times 10^{-15}$				
1359	$CS + O_2 \rightarrow$ products	2.9×10^{-19}	± 0.6			
1360	$CS + O_3 \rightarrow OCS + O_2$	3.0×10^{-16}	± 0.5			
1360	$CS + NO_2 \rightarrow OCS + NO$	7.6×10^{-17}	± 0.5			
1361	$CH_3S + O_2 \rightarrow$ products	$<2.5 \times 10^{-18}$				
1362	$CH_3S + O_3 \rightarrow$ products	4.1×10^{-12}	± 0.5			
1363	$CH_3S + NO + M \rightarrow CH_3SNO + M$	$3.2 \times 10^{-29}[N_2]$ (k_0)	± 0.3	$3.2 \times 10^{-29}(T/298)^{-4}[N_2]$	250–450	$\Delta n = \pm 2$
		4×10^{-11} (k_∞)	± 0.5	4×10^{-11}	250–450	$\Delta\log k = \pm 0.5$
		$F_c = 0.50$		$F_c = \exp(-T/580)$		
1364	$CH_3S + NO_2 \rightarrow CH_3SO + NO$	5.6×10^{-11}	± 0.2			
1365	$CH_3SO + O_3 \rightarrow$ products	1×10^{-12}	± 0.7			
1365	$CH_3SO + NO_2 \rightarrow$ products	1.2×10^{-11}	± 0.5			
1366	$O_3 + CH_3SCH_3 \rightarrow$ products	$<1 \times 10^{-18}$				
1366	$OCS + h\nu \rightarrow$ products	See data sheets				
1368	$CS_2 + h\nu \rightarrow$ products	See data sheets				
1369	$CH_3SSCH_3 + h\nu \rightarrow$ products	See data sheets				
1370	$CH_3SNO + h\nu \rightarrow$ products	See data sheets				

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	FO_x Reactions					
1372	$O + FO \rightarrow O_2 + F$	5×10^{-11}	±0.5			
1372	$O + FO_2 \rightarrow O_2 + FO$	5×10^{-11}	±0.7			
1372	$O(^1D) + HF \rightarrow HO + F$ $\rightarrow O(^3P) + HF$	1×10^{-10}	±0.5			
1373	$O(^1D) + COF_2 \rightarrow CO_2 + F_2$	2.2×10^{-11}	±0.2			
	$\rightarrow O(^3P) + COF_2$	5.2×10^{-11}	±0.2			
1374	$O(^1D) + CH_3F \rightarrow$ products	1.4×10^{-10}	±0.5			
1374	$O(^1D) + CH_2F_2 \rightarrow$ products	9×10^{-11}	±0.5			
1374	$O(^1D) + CHF_3 \rightarrow$ products	8.4×10^{-12}	±0.5			
1374	$O(^1D) + CH_3CHF_2 \rightarrow$ products	1×10^{-10}	±0.7			
1374	$O(^1D) + CH_3CF_3 \rightarrow$ products	1×10^{-10}	±0.5			
1374	$O(^1D) + CH_2FCF_3 \rightarrow$ products	1×10^{-10}	±0.7			
1374	$O(^1D) + CHF_2CF_3 \rightarrow$ products	5×10^{-11}	±0.5			
1375	$F + H_2 \rightarrow HF + H$	2.6×10^{-11}	±0.1	$1.4 \times 10^{-10}\exp(-500/T)$	200–375	±200
1376	$F + H_2O \rightarrow HF + HO$	1.4×10^{-11}	±0.1	1.4×10^{-11}	240–370	±200
1377	$F + O_2 + M \rightarrow FO_2 + M$	$3.7 \times 10^{-33}[N_2]$ (k_0)	±0.3	$3.7 \times 10^{-33}(T/300)^{-1}[N_2]$	300–400	$\Delta n = \pm 0.5$
1378	$FO_2 + M \rightarrow F + O_2 + M$	No recommendation (see data sheets)				
1378	$F + O_3 \rightarrow FO + O_2$	1.3×10^{-11}	±0.3	$2.8 \times 10^{-11}\exp(-230/T)$	250–365	±200
1379	$F + HONO_2 \rightarrow HF + NO_3$	2.3×10^{-11}	±0.1	$6.0 \times 10^{-12}\exp(400/T)$	260–320	±200
*	$F + NO_2 + M \rightarrow FONO + M$	See previous evaluation				
1380	$F + CH_4 \rightarrow HF + CH_3$	8×10^{-11}	±0.2	$3.0 \times 10^{-10}\exp(-400/T)$	250–450	±200
1380	$HO + CH_3F \rightarrow H_2O + CH_2F$	1.7×10^{-14}	±0.10	$3.7 \times 10^{-12}\exp(-1600/T)$	270–340	±300
1381	$HO + CH_2F_2 \rightarrow H_2O + CHF_2$	1.1×10^{-14}	±0.10	$2.0 \times 10^{-12}\exp(-1545/T)$	240–300	±200
1382	$HO + CHF_3 \rightarrow H_2O + CF_3$	2.4×10^{-16}	±0.5	$1.0 \times 10^{-12}\exp(-2490/T)$	270–340	±500
1383	$HO + CH_3CH_2F \rightarrow$ products	2.3×10^{-13}	±0.3			
1384	$HO + CH_3CHF_2 \rightarrow$ products	3.6×10^{-14}	±0.10	$1.0 \times 10^{-12}\exp(-990/T)$	240–300	±200
1385	$HO + CH_3CF_3 \rightarrow H_2O + CH_2CF_3$	1.3×10^{-15}	±0.15	$1.05 \times 10^{-12}\exp(-1990/T)$	240–300	±300
1386	$HO + CH_2FCHF_2 \rightarrow$ products	1.8×10^{-14}	±0.3			
1386	$HO + CH_2FCF_3 \rightarrow H_2O + CHFCF_3$	4.9×10^{-15}	±0.2	$8.4 \times 10^{-13}\exp(-1535/T)$	240–300	±300
1387	$HO + CHF_2CHF_2 \rightarrow H_2O + CF_2CHF_2$	5.7×10^{-15}	±0.3			
1388	$HO + CHF_2CF_3 \rightarrow H_2O + CF_2CF_3$	1.9×10^{-15}	±0.2	$4.9 \times 10^{-13}\exp(-1655/T)$	240–300	±300
1389	$HO + CF_3CHO \rightarrow H_2O + CF_3CO$	1.1×10^{-12}	±0.3			
1389	$FO + O_3 \rightarrow$ products	No recommendation (see data sheets)				
1390	$FO + NO \rightarrow F + NO_2$	2.6×10^{-11}	±0.3			
*	$FO + NO_2 + M \rightarrow FONO_2 + M$	See previous evaluation				
1391	$FO + FO \rightarrow$ products	1.5×10^{-11}	±0.3			
1392	$COF_2 + h\nu \rightarrow$ products	See data sheets				
1392	$HCOF + h\nu \rightarrow$ products	See data sheets				
1393	$CF_3COF + h\nu \rightarrow$ products	See data sheets				

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	ClO_x Reactions						
*	$O + HCl \rightarrow HO + Cl$	See previous evaluation					
1395	$O + HOCl \rightarrow HO + ClO$	No recommendation (see data sheets)					
1395	$O + ClO \rightarrow Cl + O_2$	3.8×10^{-11}		±0.1	3.8×10^{-11}	200–300	±250
1396	$O + OClO \rightarrow O_2 + ClO$	1.0×10^{-13}		±0.3	$2.5 \times 10^{-12}\exp(-950/T)$	240–400	±300
1397	$O + OClO + M \rightarrow ClO_3 + M$	$1.8 \times 10^{-31}[N_2]$	(k_0)	±0.3	$1.8 \times 10^{-31}(T/298)^{-1}[N_2]$	250–300	$\Delta n = \pm0.5$
		3.1×10^{-11}	(k_∞)	±0.3	$3.1 \times 10^{-11}(T/298)^{1}$	250–300	$\Delta n = \pm1$
		$F_c = 0.48$					
1398	$O + Cl_2O \rightarrow ClO + ClO$	3.5×10^{-12}		±0.15	$2.9 \times 10^{-11}\exp(-630/T)$	235–300	±200
1399	$O + ClONO_2 \rightarrow$ products	2.0×10^{-13}		±0.1	$3.0 \times 10^{-12}\exp(-800/T)$	213–295	±200
1400	$O(^1D) + CHF_2Cl \rightarrow$ products	9.5×10^{-11}		±0.2	9.5×10^{-11}	175–340	$\Delta\log k = \pm0.2$
1400	$O(^1D) + CHFCl_2 \rightarrow$ products	1.9×10^{-10}		±0.2	1.9×10^{-10}	175–340	$\Delta\log k = \pm0.2$
1400	$O(^1D) + CH_3CF_2Cl \rightarrow$ products	1.4×10^{-10}		±0.3			
1400	$O(^1D) + CH_3CFCl_2 \rightarrow$ products	1.5×10^{-10}		±0.5			
1400	$O(^1D) + CH_2ClCF_3 \rightarrow$ products	1.5×10^{-10}		±0.3			
1400	$O(^1D) + CH_2ClCF_2Cl \rightarrow$ products	1.6×10^{-10}		±0.3			
1400	$O(^1D) + CHFClCF_3 \rightarrow$ products	1.0×10^{-10}		±0.5			
1400	$O(^1D) + CHCl_2CF_3 \rightarrow$ products	2.2×10^{-10}		±0.3			
1401	$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}		±0.1			
1402	$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}		±0.1			
1403	$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}		±0.1			
1404	$O(^1D) + COFCl \rightarrow$ products	1.9×10^{-10}		±0.3			
1405	$O(^1D) + COCl_2 \rightarrow$ products	3.6×10^{-10}		±0.3			
1405	$Cl + H_2 \rightarrow HCl + H$	1.6×10^{-14}		±0.1	$3.7 \times 10^{-11}\exp(-2300/T)$	200–300	±200
1406	$Cl + HO_2 \rightarrow HCl + O_2$	3.2×10^{-11}		±0.2	$1.8 \times 10^{-11}\exp(170/T)$	250–420	±250
	$\rightarrow ClO + HO$	9.1×10^{-12}		±0.3	$4.1 \times 10^{-11}\exp(-450/T)$	250–420	±250
1407	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.1×10^{-13}		±0.2	$1.1 \times 10^{-11}\exp(-980/T)$	265–424	±500
1408	$Cl + O_2 + M \rightarrow ClOO + M$	$1.4 \times 10^{-33}[N_2]$	(k_0)	±0.2	$1.4 \times 10^{-33}(T/300)^{-3.9}[N_2]$	160–300	$\Delta n = \pm1$
		$1.6 \times 10^{-33}[O_2]$	(k_0)	±0.2	$1.6 \times 10^{-33}(T/300)^{-2.9}[O_2]$	160–300	$\Delta n = \pm1$
1409	$ClOO + M \rightarrow Cl + O_2 + M$	$6.2 \times 10^{-13}[N_2]$	(k_0/s^{-1})	±0.3	$2.8 \times 10^{-10}\exp(-1820/T)[N_2]$	200–300	±200
1410	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}		±0.06	$2.9 \times 10^{-11}\exp(-260/T)$	205–298	±100
1411	$Cl + HONO_2 \rightarrow HCl + NO_3$	$<2.0 \times 10^{-16}$					
1411	$Cl + NO_3 \rightarrow ClO + NO_2$	2.6×10^{-11}		±0.3	2.6×10^{-11}	200–300	±400
1412	$Cl + OClO \rightarrow ClO + ClO$	5.8×10^{-11}		±0.1	$3.4 \times 10^{-11}\exp(160/T)$	298–450	±200
1413	$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}		±0.1	9.8×10^{-11}	200–300	±250
1414	$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO$	1.0×10^{-10}		±0.3	1.0×10^{-10}	230–298	±300
1415	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$	1.2×10^{-11}		±0.12	$6.8 \times 10^{-12}\exp(160/T)$	219–298	±200
1416	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}		±0.08	$9.6 \times 10^{-12}\exp(-1350/T)$	200–300	±250
1417	$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$	$6 \times 10^{-30}[N_2]$	(k_0)	±0.3	$6 \times 10^{-30}(T/300)^{-3.5}[N_2]$	200–300	$\Delta n = \pm1$
		2.3×10^{-10}	(k_∞)	±0.5	2.3×10^{-10}	200–300	$\Delta n = \pm1$
		$F_c = 0.6$					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1419	$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$	1.6×10^{-29}[air] (k_0)	±0.5	$1.6 \times 10^{-29}(T/298)^{-3.5}$[air]	250–300	$\Delta n = \pm 1$
		3×10^{-10} (k_∞)	±0.3	3×10^{-10}	250–300	$\Delta n = \pm 1$
		$F_c = 0.6$				
1420	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.9×10^{-11}	±0.06	$8.2 \times 10^{-11}\exp(-100/T)$	220–600	±100
1421	$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}	±0.12	$1.2 \times 10^{-10}\exp(40/T)$	220–600	±200
1422	$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}	±0.06	$8.2 \times 10^{-11}\exp(-34/T)$	200–500	±100
1423	$Cl + CH_3CHO \rightarrow HCl + CH_3CO$	7.2×10^{-11}	±0.15	7.2×10^{-11}	210–340	±300
1424	$Cl + C_2H_5CHO \rightarrow$ products	1.2×10^{-10}	±0.3			
1424	$Cl + CH_3COCH_3 \rightarrow HCl + CH_3COCH_2$	3.5×10^{-12}	±0.3			
1425	$Cl + CH_3OH \rightarrow HCl + CH_2OH$	5.3×10^{-11}	±0.15	5.3×10^{-11}	200–500	±200
1426	$Cl + C_2H_5OH \rightarrow$ products	9.4×10^{-11}	±0.2			
1426	$Cl + n\text{-}C_3H_7OH \rightarrow$ products	1.5×10^{-10}	±0.2			
1427	$Cl + i\text{-}C_3H_7OH \rightarrow$ products	8.4×10^{-11}	±0.3			
1427	$Cl + CH_3OOH \rightarrow$ products	5.9×10^{-11}	±0.5			
1428	$Cl + HCOOH \rightarrow$ products	2.0×10^{-13}	±0.2			
1428	$Cl + CH_3COOH \rightarrow$ products	2.8×10^{-14}	±0.3			
1429	$Cl + CH_3ONO_2 \rightarrow$ products	2.4×10^{-13}	±0.3			
1429	$Cl + C_2H_5ONO_2 \rightarrow$ products	4.7×10^{-12}	±0.2			
1430	$Cl + n\text{-}C_3H_7ONO_2 \rightarrow$ products	2.7×10^{-11}	±0.2			
1431	$Cl + i\text{-}C_3H_7ONO_2 \rightarrow$ products	5.8×10^{-12}	±0.3			
1431	$Cl + CH_3CO_3NO_2 \rightarrow$ products	$<2 \times 10^{-14}$				
1432	$Cl + CH_3CN \rightarrow$ products	$\leq 2 \times 10^{-15}$				
1433	$Cl + HCOCl \rightarrow HCl + ClCO$	7.8×10^{-13}	±0.15	$1.2 \times 10^{-11}\exp(-815/T)$	265–325	±300
1434	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}	±0.15	$3.3 \times 10^{-11}\exp(-1250/T)$	233–322	±300
1435	$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$	4.1×10^{-13}	±0.25	$8.7 \times 10^{-12}\exp(-910/T)$	270–330	±400
1436	$Cl + CHCl_3 \rightarrow HCl + CCl_3$	7.6×10^{-14}	±0.3	$4.9 \times 10^{-12}\exp(-1240/T)$	240–330	±400
1437	$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$	$<4 \times 10^{-14}$				
1437	$HO + HCl \rightarrow H_2O + Cl$	8.1×10^{-13}	±0.1	$2.4 \times 10^{-12}\exp(-330/T)$	200–300	±150
1438	$HO + HOCl \rightarrow ClO + H_2O$	5.0×10^{-13}	±0.5	$3.0 \times 10^{-12}\exp(-500/T)$	200–300	±500
1439	$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$	1.7×10^{-11}	±0.2	$1.1 \times 10^{-11}\exp(120/T)$	200–373	±150
1440	$HO + OClO \rightarrow HOCl + O_2$	7.0×10^{-12}	±0.3	$4.5 \times 10^{-13}\exp(800/T)$	290–480	±200
1441	$HO + ClNO_2 \rightarrow HOCl + NO_2$	3.5×10^{-14}	±0.3			
1441	$HO + ClONO_2 \rightarrow$ products	3.9×10^{-13}	±0.2	$1.2 \times 10^{-12}\exp(-330/T)$	246–387	±200
1442	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.3×10^{-14}	±0.10	$1.8 \times 10^{-12}\exp(-1115/T)$	240–300	±200
1443	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	4.4×10^{-14}	±0.10	$2.0 \times 10^{-12}\exp(-1135/T)$	240–300	±200
1444	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.6×10^{-15}	±0.10	$7.8 \times 10^{-13}\exp(-1530/T)$	240–300	±200
1445	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	3.0×10^{-14}	±0.10	$8.8 \times 10^{-13}\exp(-1010/T)$	240–300	±200
1446	$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	1.4×10^{-13}	±0.10	$4.4 \times 10^{-12}\exp(-1030/T)$	240–300	±250
1447	$HO + CHCl_3 \rightarrow H_2O + CCl_3$	1.0×10^{-13}	±0.10	$3.3 \times 10^{-12}\exp(-1030/T)$	240–300	±100
1448	$HO + CFCl_3 \rightarrow HOCl + CFCl_2$	$<5 \times 10^{-18}$		$<1 \times 10^{-12}\exp(-3650/T)$	250–480	
1449	$HO + CF_2Cl_2 \rightarrow HOCl + CF_2Cl$	$<7 \times 10^{-18}$		$<1 \times 10^{-12}\exp(-3540/T)$	250–478	
1450	$HO + CCl_4 \rightarrow HOCl + CCl_3$	$<5 \times 10^{-16}$		$<1 \times 10^{-12}\exp(-2260/T)$	250–300	
1451	$HO + C_2HCl_3 \rightarrow$ products	2.2×10^{-12}	±0.10	$5.0 \times 10^{-13}\exp(445/T)$	230–420	±200

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1452	$HO + C_2Cl_4 \rightarrow$ products	1.7×10^{-13}	±0.10	$9.4 \times 10^{-12}\exp(-1200/T)$	300–420	±200
1453	$HO + CH_3CF_2Cl \rightarrow H_2O + CH_2CF_2Cl$	3.0×10^{-15}	±0.10	$9.2 \times 10^{-13}\exp(-1705/T)$	240–300	±200
1454	$HO + CH_3CFCl_2 \rightarrow H_2O + CH_2CFCl_2$	5.9×10^{-15}	±0.2	$7.0 \times 10^{-13}\exp(-1425/T)$	240–300	±300
1455	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	9.5×10^{-15}	±0.10	$1.2 \times 10^{-12}\exp(-1440/T)$	240–300	±200
1456	$HO + CH_2ClCF_3 \rightarrow H_2O + CHClCF_3$	1.3×10^{-14}	±0.2	$5.2 \times 10^{-13}\exp(-1100/T)$	260–380	±250
1457	$HO + CH_2ClCF_2Cl \rightarrow H_2O + CHClCF_2Cl$	1.6×10^{-14}	±0.3	$3.2 \times 10^{-12}\exp(-1580/T)$	250–350	±500
1458	$HO + CHFClCF_3 \rightarrow H_2O + CFClCF_3$	9.5×10^{-15}	±0.10	$5.4 \times 10^{-13}\exp(-1205/T)$	240–300	±200
1459	$HO + CHCl_2CF_3 \rightarrow H_2O + CCl_2CF_3$	3.6×10^{-14}	±0.15	$5.5 \times 10^{-13}\exp(-815/T)$	240–300	±200
1460	$HO + CHCl_2CF_2CF_3 \rightarrow H_2O + CCl_2CF_2CF_3$	2.5×10^{-14}	±0.15	$1.1 \times 10^{-12}\exp(-1130/T)$	270–400	±300
1460	$HO + CHFClCF_2CF_2Cl \rightarrow H_2O + CFClCF_2CF_2Cl$	8.9×10^{-15}	±0.10	$5.5 \times 10^{-13}\exp(-1230/T)$	290–400	±300
1461	$HO + CH_3CF_2CFCl_2 \rightarrow H_2O + CH_2CF_2CFCl_2$	2.4×10^{-15}	±0.3	$7.0 \times 10^{-13}\exp(-1690/T)$	290–370	±300
1462	$HO + HCOCl \rightarrow H_2O + ClCO$	$<5 \times 10^{-13}$				
1462	$HO + COCl_2 \rightarrow$ products	$<5 \times 10^{-15}$				
1463	$HO + CH_2ClCHO \rightarrow$ products	3.0×10^{-12}	±0.3			
1463	$HO + CHCl_2CHO \rightarrow$ products	2.4×10^{-12}	±0.3			
1464	$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$	1.4×10^{-12}	±0.3			
1464	$HO + CH_3COCl \rightarrow H_2O + CH_2COCl$	9×10^{-15}	±1.0			
1465	$HO + CHF_2OCHClCF_3 \rightarrow$ products	2.1×10^{-14}	±0.5			
1465	$HO + CHF_2OCF_2CHFCl \rightarrow$ products	1.6×10^{-14}	±0.5	$6.1 \times 10^{-13}\exp(-1080/T)$	300–430	±500
1466	$NO_3 + C_2HCl_3 \rightarrow$ products	2.9×10^{-16}	±0.3			
1466	$NO_3 + C_2Cl_4 \rightarrow$ products	$<1 \times 10^{-16}$				
1467	$ClO + HO_2 \rightarrow HOCl + O_2$; $\rightarrow HCl + O_3$	5.0×10^{-12}	±0.15	$4.6 \times 10^{-13}\exp(710/T)$	200–300	±300
*	$ClO + O_2(^1\Delta_g) \rightarrow sym\text{-}ClO_3$	See previous evaluation				
1468	$ClO + O_3 \rightarrow ClOO + O_2$	$<1.5 \times 10^{-17}$				
	$\rightarrow OClO + O_2$	$<1 \times 10^{-18}$				
1469	$ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}	±0.1	$6.2 \times 10^{-12}\exp(294/T)$	202–415	±100
1470	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$1.6 \times 10^{-31}[N_2]$ (k_0)	±0.1	$1.6 \times 10^{-31}(T/300)^{-3.4}[N_2]$	200–300	$\Delta n = \pm 1$
		2×10^{-11} (k_∞)	±0.3	2×10^{-11}	200–300	$\Delta\log k = \pm 0.3$
		$F_c = 0.5$		$F_c = \exp(-T/430)$	200–300	
1472	$ClO + NO_3 \rightarrow ClOO + NO_2$; $\rightarrow OClO + NO_2$	4.0×10^{-13}	±0.3			
*	$ClO + HCHO \rightarrow$ products	See previous evaluation				
1473	$ClO + ClO \rightarrow Cl + ClOO$	3.4×10^{-15}	±0.3			
	$\rightarrow Cl + OClO$	1.7×10^{-15}	±0.3			
	$\rightarrow Cl_2 + O_2$	4.9×10^{-15}	±0.3			
1474	$ClO + ClO + M \rightarrow Cl_2O_2 + M$	$1.7 \times 10^{-32}[N_2]$ (k_0)	±0.1	$1.7 \times 10^{-32}(T/300)^{-4}[N_2]$	200–260	$\Delta n = \pm 1.5$
		5.4×10^{-12} (k_∞)	±0.3	5.4×10^{-12}	200–300	$\Delta\log k = \pm 0.3$
		$F_c = 0.6$				

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1475	$Cl_2O_2 + M \rightarrow ClO + ClO + M$	$2.7 \times 10^{-18}[N_2]$	(k_0/s^{-1})	±0.3	$1.35 \times 10^{-5}(T/300)^{-5}$ $\exp(-8720/T)[N_2]$	200–300	±900
		8.7×10^{2}	(k_∞/s^{-1})	±0.3	$1.8 \times 10^{15}\exp(-8450/T)$	200–300	±900
		$F_c = 0.6$					
1476	$ClO + OClO + M \rightarrow Cl_2O_3 + M$	$2.8 \times 10^{-31}[N_2]$	(k_0; 226 K)	±0.5 (226 K)			
1477	$Cl_2O_3 + M \rightarrow ClO + OClO + M$	$2.8 \times 10^{-18}[N_2]$	(k_0/s^{-1}; 226 K)	±0.5 (226 K)			
1477	$ClO + CH_3O_2 \rightarrow ClOO + CH_3O$	$<4 \times 10^{-12}$	(200 K)				
	$\rightarrow OClO + CH_3O$	$<1 \times 10^{-15}$	(200 K)				
1478	$OClO + O_3 \rightarrow ClO_3 + O_2$	3.0×10^{-19}		±0.4	$2.1 \times 10^{-12}\exp(-4700/T)$	262–298	±1000
1479	$OClO + NO \rightarrow NO_2 + ClO$	3.4×10^{-13}		±0.3			
1479	$Cl_2O_2 + O_3 \rightarrow ClO + ClOO + O_2$	$<1 \times 10^{-19}$	(200 K)				
1480	$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$	$1.9 \times 10^{-29}[N_2]$	(k_0)	±0.2	$1.9 \times 10^{-29}(T/300)^{-4.7}[N_2]$	200–300	$\Delta n = \pm1$
		1.0×10^{-11}	(k_∞)	±0.3	1.0×10^{-11}	200–400	$\Delta\log k = \pm0.3$
		$F_c = 0.6$					
1481	$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$	$1.4 \times 10^{-29}[N_2]$	(k_0)	±0.5	$1.4 \times 10^{-29}(T/300)^{-5}[N_2]$	200–300	$\Delta n = \pm2$
		9×10^{-12}	(k_∞)	±0.5	9×10^{-12}	200–300	$\Delta\log k = \pm0.5$
		$F_c = 0.6$					
1482	$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$	$5.5 \times 10^{-30}[N_2]$	(k_0)	±0.3	$5.5 \times 10^{-30}(T/300)^{-6}[N_2]$	200–300	$\Delta n = \pm2$
		9×10^{-12}	(k_∞)	±0.5	9×10^{-12}	200–300	$\Delta n = \pm1$
		$F_c = 0.6$					
1483	$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$	$1.6 \times 10^{-30}[N_2]$	(k_0)	±0.3	$1.6 \times 10^{-30}(T/300)^{-6}[N_2]$	200–300	$\Delta n = \pm2$
		3.6×10^{-12}	(k_∞)	±0.5	3.6×10^{-12}	200–300	$\Delta\log k = \pm0.5$
		$F_c = 0.6$					
1485	$CF_3O \rightarrow COF_2 + F$	$<10^{-5}$	(k_∞/s^{-1})				
1485	$CF_2ClO \rightarrow COF_2 + Cl$	7×10^{5}	(k/s^{-1})	±1.0	$3 \times 10^{13}\exp(-5250/T)$	220–300	±1000
1485	$CFCl_2O \rightarrow COFCl + Cl$	7×10^{5}	(k/s^{-1})	±1.0	$3 \times 10^{13}\exp(-5250/T)$	220–300	±1000
1485	$CCl_3O \rightarrow COCl_2 + Cl$	8×10^{6}	(k/s^{-1})	±1.0	$4 \times 10^{13}\exp(-4600/T)$	220–300	±1000
1486	$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	1.6×10^{-11}		±0.2	$1.6 \times 10^{-11}(T/300)^{-\ 2}$	230–430	$\Delta\log k = \pm0.2$
1486	$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	1.6×10^{-11}		±0.3	$1.6 \times 10^{-11}(T/300)^{-\ 5}$	230–430	$\Delta\log k = \pm0.3$
1486	$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	1.5×10^{-11}		±0.2	$1.5 \times 10^{-11}(T/300)^{-\ .3}$	230–430	$\Delta\log k = \pm0.2$
1486	$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	1.8×10^{-11}		±0.2	$1.8 \times 10^{-11}(T/300)^{-\ 0}$	230–430	$\Delta\log k = \pm0.2$
1487	$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$	$4.5 \times 10^{-29}[N_2]$	(k_0)	±0.3	$4.5 \times 10^{-29}(T/300)^{-4.4}[N_2]$	220–300	$\Delta n = \pm1$
		7.5×10^{-12}	(k_∞)	±0.5	7.5×10^{-12}	200–300	$\Delta\log k = \pm0.5$
		$F_c = 0.28$			$F_c = 0.28$	220–300	
1489	$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M$	$3.6 \times 10^{-19}[N_2]$	(k_0/s^{-1})	±0.4	$5 \times 10^{-1}(T/300)^{-6}$ $\exp(-12460/T)[N_2]$	233–373	±500
		5.6×10^{-2}	(k_∞/s^{-1})	±0.5	$1.2 \times 10^{17}\exp(-12580/T)$	233–373	±500
		$F_c = 0.28$			$F_c = 0.28$	220–300	
1490	$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$	$1.4 \times 10^{-28}[N_2]$	(k_0)	±0.5	$1.4 \times 10^{-28}(T/300)^{-6.4}[N_2]$	200–300	$\Delta n = \pm2$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	200–300	$\Delta\log k = \pm0.3$
		$F_c = 0.26$			$F_c = 0.26$	220–300	
1491	$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$	$9.0 \times 10^{-19}[N_2]$	(k_0/s^{-1})	±0.3	$1.8 \times 10^{-3}\exp(-10500/T)[N_2]$	260–300	±500
		5.4×10^{-2}	(k_∞/s^{-1})	±0.3	$1.6 \times 10^{16}\exp(-11990/T)$	260–300	±500
		$F_c = 0.26$			$F_c = 0.26$	250–300	

2. Summary of Reactions and Preferred Rate Data – Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1492	$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$	$1.7 \times 10^{-28}[N_2]$	(k_0)	±0.3	$1.7 \times 10^{-28}(T/300)^{-6.7}[N_2]$	230–300	$\Delta n = \pm2$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–300	$\Delta\log k = \pm0.3$
		$F_c = 0.23$			$F_c = 0.23$	230–300	
1494	$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$	$1.5 \times 10^{-18}[N_2]$	(k_0/s^{-1})	±0.3	$1.0 \times 10^{-2}\exp(-10860/T)$	250–300	±500
		9.6×10^{-2}	(k_∞/s^{-1})	±0.3	$6.6 \times 10^{16}\exp(-12240/T)$	250–300	±500
		$F_c = 0.23$			$F_c = 0.23$	250–300	
1495	$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$	$3.2 \times 10^{-28}[N_2]$	(k_0)	±0.5	$3.2 \times 10^{-28}(T/300)^{-7.7}[N_2]$	230–300	$\Delta n = \pm3$
		7.5×10^{-12}	(k_∞)	±0.3	7.5×10^{-12}	250–300	$\Delta\log k = \pm0.3$
		$F_c = 0.21$			$F_c = 0.21$	250–300	
1496	$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2 + M$	$7.6 \times 10^{-18}[N_2]$	(k_0/s^{-1})	±0.3	$6.3 \times 10^{-3}\exp(-10235/T)[N_2]$	250–300	±500
		0.29	(k_∞/s^{-1})	±0.3	$4.8 \times 10^{16}\exp(-11820/T)$	250–300	±500
		$F_c = 0.20$			$F_c = 0.20$	250–300	
1498	$O_3 + C_2HCl_3 \rightarrow$ products	$<5 \times 10^{-20}$					
1498	$O_3 + C_2Cl_4 \rightarrow$ products	$<10^{-21}$					
1499	$HCl + h\nu \rightarrow$ products	See data sheets					
1499	$HOCl + h\nu \rightarrow$ products	See data sheets					
1500	$OClO + h\nu \rightarrow$ products	See data sheets					
1501	$Cl_2O + h\nu \rightarrow$ products	See data sheets					
1501	$Cl_2O_2 + h\nu \rightarrow$ products	See data sheets					
1503	$Cl_2O_3 + h\nu \rightarrow$ products	See data sheets					
1503	$ClNO + h\nu \rightarrow$ products	See data sheets					
1504	$ClONO + h\nu \rightarrow$ products	See data sheets					
1505	$ClNO_2 + h\nu \rightarrow$ products	See data sheets					
1505	$ClONO_2 + h\nu \rightarrow$ products	See data sheets					
1507	$Cl_2 + h\nu \rightarrow$ products	See data sheets					
1507	$CH_3Cl + h\nu \rightarrow$ products	See data sheets					
1508	$CHF_2Cl + h\nu \rightarrow$ products	See data sheets					
1509	$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheets					
1510	$CFCl_3 + h\nu \rightarrow$ products	See data sheets					
1511	$CCl_4 + h\nu \rightarrow$ products	See data sheets					
1512	$CH_3CF_2Cl + h\nu \rightarrow$ products	See data sheets					
1512	$CH_3CFCl_2 + h\nu \rightarrow$ products	See data sheets					
1513	$CH_3CCl_3 + h\nu \rightarrow$ products	See data sheets					
1514	$CF_3CHFCl + h\nu \rightarrow$ products	See data sheets					
1514	$CF_3CHCl_2 + h\nu \rightarrow$ products	See data sheets					
1515	$CF_2ClCFCl_2 + h\nu \rightarrow$ products	See data sheets					
1516	$CF_2ClCF_2Cl + h\nu \rightarrow$ products	See data sheets					
1516	$CF_3CF_2Cl + h\nu \rightarrow$ products	See data sheets					
1517	$CF_3CF_2CHCl_2 + h\nu \rightarrow$ products	See data sheets					
1518	$CF_2ClCF_2CHFCl + h\nu \rightarrow$ products	See data sheets					
1518	$HCOCl + h\nu \rightarrow$ products	See data sheets					
1519	$COFCl + h\nu \rightarrow$ products	See data sheets					
1520	$COCl_2 + h\nu \rightarrow$ products	See data sheets					
1520	$CCl_3CHO + h\nu \rightarrow$ products	See data sheets					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1521	$CF_3COCl + h\nu \rightarrow$ products	See data sheets					
	BrO_x Reactions						
*	$O + HBr \rightarrow HO + Br$	See previous evaluation					
*	$O + Br_2 \rightarrow BrO + Br$	See previous evaluation					
1523	$O + BrO \rightarrow O_2 + Br$	3×10^{-11}		± 0.5			
1523	$Br + HO_2 \rightarrow HBr + O_2$	2.0×10^{-12}		± 0.3	$1.4 \times 10^{-11}\exp(-590/T)$	260–390	± 200
1524	$Br + H_2O_2 \rightarrow HBr + HO_2$; $\rightarrow HOBr + HO$ }	$<5 \times 10^{-16}$					
1525	$Br + O_3 \rightarrow BrO + O_2$	1.2×10^{-12}		± 0.08	$1.7 \times 10^{-11}\exp(-800/T)$	195–392	± 200
1526	$Br + NO_2 + M \rightarrow BrNO_2 + M$	4.2×10^{-31} [N_2]	(k_0)	± 0.3	$4.2 \times 10^{-31}(T/300)^{-2.4}[N_2]$	200–300	$\Delta n = \pm 1$
		2.7×10^{-11}	(k_∞)	± 0.4	2.7×10^{-11}	200–300	$\Delta\log k = \pm 0.4$
		$F_c = 0.55$					
1527	$Br + OClO \rightarrow BrO + ClO$	3.4×10^{-13}		± 0.3	$2.6 \times 10^{-11}\exp(-1300/T)$	200–450	± 300
1528	$Br + Cl_2O \rightarrow BrCl + ClO$	3.8×10^{-12}		± 0.3	$2.1 \times 10^{-11}\exp(-520/T)$	220–298	± 300
1528	$Br + Cl_2O_2 \rightarrow BrCl + ClOO$	3.0×10^{-12}		± 0.3			
1529	$Br + HCHO \rightarrow HBr + HCO$	1.0×10^{-12}		± 0.15	$1.7 \times 10^{-11}\exp(-800/T)$	223–480	± 250
1529	$Br + CH_3CHO \rightarrow HBr + CH_3CO$	3.9×10^{-12}		± 0.2	$1.3 \times 10^{-11}\exp(-360/T)$	250–400	± 200
1530	$HO + HBr \rightarrow H_2O + Br$	1.1×10^{-11}		± 0.1	1.1×10^{-11}	249–416	± 250
1531	$HO + Br_2 \rightarrow HOBr + Br$	4.5×10^{-11}		± 0.15	$1.2 \times 10^{-11}\exp(400/T)$	260–360	± 400
1532	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	3.0×10^{-14}		± 0.10	$1.9 \times 10^{-12}\exp(-1240/T)$	240–300	± 200
1532	$HO + CHF_2Br \rightarrow H_2O + CF_2Br$	9.5×10^{-15}		± 0.2	$7.7 \times 10^{-13}\exp(-1310/T)$	240–300	± 200
1533	$HO + CF_3Br \rightarrow$ products	$<1 \times 10^{-16}$					
1534	$HO + CF_2ClBr \rightarrow$ products	$<1 \times 10^{-16}$					
1534	$HO + CF_2Br_2 \rightarrow$ products	$<5 \times 10^{-16}$					
1535	$HO + CF_3CHFBr \rightarrow H_2O + CF_3CFBr$	1.7×10^{-14}		± 0.3	$1.1 \times 10^{-12}\exp(-1250/T)$	270–430	± 500
1535	$HO + CF_3CHClBr \rightarrow H_2O + CF_3CClBr$	5.8×10^{-14}		± 0.3			
1536	$HO + CF_2BrCF_2Br \rightarrow$ products	$<1.3 \times 10^{-16}$					
1536	$BrO + HO_2 \rightarrow HOBr + O_2$; $\rightarrow HBr + O_3$ }	3.3×10^{-11}		± 0.5	$6.2 \times 10^{-12}\exp(500/T)$	200–300	± 500
1537	$BrO + O_3 \rightarrow Br + 2O_2$	$<5 \times 10^{-15}$					
1537	$BrO + NO \rightarrow Br + NO_2$	2.1×10^{-11}		± 0.1	$8.7 \times 10^{-12}\exp(260/T)$	224–425	± 100
1538	$BrO + NO_2 + M \rightarrow BrONO_2 + M$	4.7×10^{-31} [N_2]	(k_0)	± 0.1	$4.7 \times 10^{-31}(T/300)^{-3.1}[N_2]$	200–300	$\Delta n = \pm 1$
		1.7×10^{-11}	(k_∞)	± 0.1	$1.7 \times 10^{-11}(T/298)^{-0.6}$	200–300	$\Delta n = \pm 1$
		$F_c = 0.40$			$F_c = \exp(-T/327)$	200–300	
1540	$BrO + ClO \rightarrow Br + OClO$	6.8×10^{-12}		± 0.1	$1.6 \times 10^{-12}\exp(430/T)$	220–400	± 200
	$\rightarrow Br + ClOO$	6.1×10^{-12}		± 0.1	$2.9 \times 10^{-12}\exp(220/T)$	220–400	± 200
	$\rightarrow BrCl + O_2$	1.0×10^{-12}		± 0.1	$5.8 \times 10^{-13}\exp(170/T)$	220–400	± 200
1542	$BrO + BrO \rightarrow 2Br + O_2$	2.1×10^{-12}		± 0.1 }	$1.1 \times 10^{-12}\exp(250/T)$	223–400	± 200
	$\rightarrow Br_2 + O_2$	4.1×10^{-13}		± 0.2 }			
1543	$HOBr + h\nu \rightarrow$ products	See data sheets					
1543	$BrO + h\nu \rightarrow$ products	See data sheets					

2. Summary of Reactions and Preferred Rate Data — Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta \log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
1544	$BrONO_2 + h\nu \rightarrow$ products	See data sheets				
1545	$CH_3Br + h\nu \rightarrow$ products	See data sheets				
1545	$CF_3Br + h\nu \rightarrow$ products	See data sheets				
1546	$CF_2ClBr + h\nu \rightarrow$ products	See data sheets				
1547	$CF_2Br_2 + h\nu \rightarrow$ products	See data sheets				
1548	$CHBr_3 + h\nu \rightarrow$ products	See data sheets				
1550	$CF_2BrCF_2Br + h\nu \rightarrow$ products	See data sheets				
	IO_x Reactions					
1551	$O + I_2 \rightarrow IO + I$	1.4×10^{-10}	± 0.3	1.4×10^{-10}	200–400	± 250
1551	$O + IO \rightarrow O_2 + I$	3×10^{-11}	± 0.5			
1552	$I + HO_2 \rightarrow HI + O_2$	3.8×10^{-13}	± 0.3	$1.5 \times 10^{-11}\exp(-1090/T)$	250–350	± 500
1552	$I + O_3 \rightarrow IO + O_2$	1.0×10^{-12}	± 0.2	$2.0 \times 10^{-11}\exp(-890/T)$	200–350	± 300
1553	$I + NO + M \rightarrow INO + M$	1.8×10^{-32} [N_2] (k_0)	± 0.1	$1.8 \times 10^{-32}(T/300)^{-1.0}[N_2]$	200–400	$\Delta n = \pm 0.5$
		1.7×10^{-11} (k_∞)	± 0.3	1.7×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.75$		$F_c = [\exp(-T/1040) + \exp(-4160/T)]$	200–400	
1554	$I + NO_2 + M \rightarrow INO_2 + M$	3.0×10^{-31} [N_2] (k_0)	± 0.2	$3.0 \times 10^{-31}(T/300)^{-1}[N_2]$	200–400	$\Delta n = \pm 1$
		6.6×10^{-11} (k_∞)	± 0.3	6.6×10^{-11}	200–400	$\Delta \log k = \pm 0.3$
		$F_c = 0.63$		$F_c = [\exp(-T/650) + \exp(-2600/T)]$	200–400	
1555	$HO + HI \rightarrow H_2O + I$	3.0×10^{-11}	± 0.3			
1556	$HO + I_2 \rightarrow HOI + I$	1.8×10^{-10}	± 0.3			
1556	$HO + CH_3I \rightarrow H_2O + CH_2I$	7.2×10^{-14}	± 0.5	$3.1 \times 10^{-12}\exp(-1120/T)$	270–430	± 500
1557	$NO_3 + HI \rightarrow HNO_3 + I$	No recommendation (see data sheets)				
1557	$IO + HO_2 \rightarrow HOI + O_2$	6.4×10^{-11}	± 0.3			
1558	$IO + IO \rightarrow$ products	5.2×10^{-11}	± 0.3	$1.7 \times 10^{-12}\exp(1020/T)$	250–373	± 500
1558	$IO + NO \rightarrow I + NO_2$	2.2×10^{-11}	± 0.3	$7.3 \times 10^{-12}\exp(330/T)$	200–400	± 150
1559	$IO + NO_2 + M \rightarrow IONO_2 + M$	7.7×10^{-31} [N_2] (k_0)	± 0.3	$7.7 \times 10^{-31}(T/300)^{-5}[N_2]$	250–350	$\Delta n = \pm 2$
		1.6×10^{-11} (k_∞)	± 0.3	1.6×10^{-11}	250–350	$\Delta \log k = \pm 0.3$
		$F_c = 0.4$				
1560	$IO + CH_3SCH_3 \rightarrow$ products	1.2×10^{-14}	± 0.3			
1561	$INO + INO \rightarrow I_2 + 2\ NO$	1.3×10^{-14}	± 0.4	$8.4 \times 10^{-11}\exp(-2620/T)$	300–450	± 600
1562	$INO_2 + INO_2 \rightarrow I_2 + 2\ NO_2$	4.7×10^{-15}	± 0.5	$2.9 \times 10^{-11}\exp(-2600/T)$	298–400	± 1000
1562	$HOI + h\nu \rightarrow$ products	See data sheets				
1563	$IO + h\nu \rightarrow$ products	See data sheets				
1564	$INO + h\nu \rightarrow$ products	See data sheets				
1565	$INO_2 + h\nu \rightarrow$ products	See data sheets				
1565	$IONO_2 + h\nu \rightarrow$ products	See data sheets				

*No data sheet or recommendation presented in this article. See our earlier evaluation; J. Phys. Chem. Ref. Data **18**, 881 (1989) for our most recent recommendation.

3. Guide to the Data Sheets

The data sheets are of two types: (i) those for the thermal reactions and (ii) those for the photochemical reactions.

3.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in Appendix 1.

The available kinetic data on the reactions are summarized under three headings: (i) Absolute Rate Coefficients, (ii) Relative Rate Coefficients, and (iii) Reviews and Evaluations. Under headings (i) and (ii), we list either new data which have been published since the last IUPAC evaluation[4] or we reproduce the data sheet from a previous evaluation containing the most recent published data. Under heading (iii) are listed the preferred rate data from the most recent NASA evaluation and our own IUPAC evaluation, and from any new review or evaluation source. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated range of temperatures. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A\exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^{-n}$ or $CT^n\exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used mainly in the Comments section:

EPR-electron paramagnetic resonance
FTIR-Fourier transform infrared
GC-gas chromatography/gas chromatographic
IR-infrared
LIF-laser induced fluorescence
LMR-laser magnetic resonance
MS-mass spectrometry/mass spectrometric

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated range of temperatures.

This is followed by a statement of the error limits in $\log k$ at 298 K and the error limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of errors are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.,

$$A + A \rightarrow B + C$$

$$\frac{-\frac{1}{2}\,d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

Note that the stoichiometric coefficient for A, i.e., 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side.

3.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$A + B + M \rightleftharpoons AB + M$$

depend on the temperature T, and the nature and concentration of the third body [M]. The rate coefficients of these reactions have to be expressed in a form which is more complicated than those for simple bimolecular reactions. The combination reactions are described by a pseudo second-order rate law

$$\frac{d[AB]}{dt} = k\,[A]\,[B]$$

in which the second-order rate coefficient depends on [M]. The low-pressure third-order limit is characterized by k_o,

$$k_o = \lim_{[M] \to 0} k([M])$$

which is proportional to [M]. The high-pressure second-order limit is characterized by k_∞,

$$k_\infty = \lim_{[M] \to \infty} k([M])$$

which is independent of [M]. For a combination reaction in the low-pressure range, the summary table gives a second-order rate coefficient expressed as the product of a third-order rate coefficient and the third body concentration. The transition between the third-order and the second-order range is represented by a reduced falloff expression of k_o/k_∞ as a function of

$$k_o/k_\infty = [M]/[M]_c,$$

where the "center of the falloff curve" $[M]_c$ indicates the third-body concentration for which the extrapolated k_o would be equal to k_∞. The dependence of k on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

$$k = \frac{k_o k_\infty}{k_o + k_\infty} F = k_o \left(\frac{1}{1 + k_o/k_\infty}\right) F$$

$$= k_\infty \left(\frac{k_o/k_\infty}{1 + k_o/k_\infty}\right) F,$$

where the first factors at the right-hand side represent the Lindemann-Hinshelwood expression, and the additional broadening factor F, at not too high temperature, is approximately given by[6-8]

$$\log F \cong \frac{\log F_c}{1 + [\log(k_o/k_\infty)]^2} \quad .$$

In this way the three quantities k_o, k_∞, and F_c characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[M]_c$, and F_c (or k_o, $[M]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe.[6-8] The results can usually be represented[8] approximately by an equation

$$F_c = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^*) + \exp(-T^{**}/T).$$

The last term becomes relevant only at high temperatures. In Ref. 2, for simplicity $a = 1$ and $T^{**} = 4T^*$ was adopted. Often $F_c = \exp(-T/T^*)$ is sufficient for low temperature conditions. With molecules of increasing complexity, additional broadening of the falloff curves may have to be taken into account.[6-8] For simplicity these effects are neglected in the present evaluation. An even simpler policy was chosen in Ref. 5 where a temperature independent standard value of $F_c = 0.6$ was adopted.

Changes in F_c would require changes in the limiting k_o and k_∞ values. For the purpose of this evaluation, this will be irrelevant in most cases, if the preferred k_o and k_∞ are used consistently together with the preferred F_c values.

Theoretical predictions of F_c have been derived from rigid RRKM-type models including weak collision effects.[6-8]

The dependence of k_o and k_∞ on the temperature T is represented in the form:

$$k \propto T^{-n}$$

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it often gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_o on the nature of the third-body M generally is represented by the relative efficiencies of M_1 and M_2.

$$k_o(M_1)/[M_1]:k_o(M_2)/[M_2].$$

The few thermal dissociation reactions of interest in the present application are treated by analogy with combination reactions, with pseudo-first-order rate coefficients $k([M])$. The limiting low- and high-pressure rate coefficients expressed in units of s^{-1} are denoted in the tables by the symbols (k_o/s^{-1}) and (k_∞/s^{-1}). F_c is the same in combination and dissociation reactions.

3.4. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in Appendix 1. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed.

This is followed by tables summarizing the available experimental data on (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1, 5 or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates.

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

In this evaluation we have provided data sheets for all of the photochemical reactions listed in the Summary Table and not just those for which new data have become available since our last evaluation.

3.5. Conventions Concerning Absorption Cross-Sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e." They are defined according to the equations

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\}\ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), $[N]$ is the number concentration of absorber (expressed in cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition; it is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Naperian (base e) absorption coefficient of a gas at a pressure of one standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19}.

3.6. Assignment of Errors

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta\log k$, where $\Delta\log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D = \log_{10}F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta\log k\ (T) = \Delta\log k(298)\ \exp\left|\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right|$$

(note that the exponent in this equation is an absolute value).

The assignment of these absolute error limits in k and E/R is a subjective assessment of the evaluators. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic errors which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of errors made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations made and the number of different techniques used. On the whole, our assessment of error limits errs towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum error limits of a factor of 2 are appropriate.

In contrast with the usual situation for rate coefficients, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified now in assigning error limits to the parameters reported for the photochemical reactions.

3.7. Acknowledgments

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4. Data Sheets

4.1. Oxygen Species

$O + O_2 + M \rightarrow O_3 + M$

$\Delta H^\circ = -106.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
7.2×10^{-33} $(T/100)^{-3.7}$ [He]	100–200	Hippler, Rahn and Troe, 1990[1]	(a)
3.4×10^{-34} $(T/300)^{-1.2}$ [He]	200–1000		
8.0×10^{-33} $(T/100)^{-3.2}$ [Ar]	80–150		
4.5×10^{-34} $(T/300)^{-2.7}$ [Ar]	150–400		
4.0×10^{-35} $(T/1000)^{-1.0}$ [Ar]	700–3000		
5.5×10^{-34} $(T/300)^{-2.6}$ [N_2]	100–400		
5.2×10^{-35} $(T/1000)^{-1.3}$ [N_2]	700–900		
Reviews and Evaluations			
6.2×10^{-34} $(T/300)^{-2.0}$ [O_2]	200–300	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
5.7×10^{-34} $(T/300)^{-2.8}$ [N_2]	200–300		
6.0×10^{-34} $(T/300)^{-2.3}$ [air]	200–300	NASA, 1990[4]	(c)

Comments

(a) Oxygen atoms were generated by laser flash photolysis of O_2, N_2O or O_3. O_3 formation was studied by UV absorption measurements over the range 1–1000 bar and 90–370 K. The expressions given for k_0 at $T \leq 400$ K are from Ref. 1. They are consistent with less extensive earlier results from Refs. 5–9. The expressions for k_0 at $T >$ 400 K are based on dissociation experiments[10–12] converted to recombination data with the equilibrium constant. The reaction is suggested to follow the energy transfer mechanism at high temperatures. At low temperatures a radical-complex mechanism apparently dominates with contributions from metastable excited electronic states of O_3.

(b) Based on the data from Ref. 5–9.

(c) Average of the results from Ref. 7 and 8.

Preferred Values

$k_0 = 5.6 \times 10^{-34}(T/300)^{-2.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

$k_0 = 6.0 \times 10^{-34}(T/300)^{-2.8}$ [O_2] cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

Reliability

$\Delta \log k_0 = \pm 0.05$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new results obtained over extended temperature ranges[1] confirm the large negative values of n, and also confirm the earlier absolute values of k_0 at 298 K. The value of n is probably similar for N_2 and O_2, as for the reaction $Cl + O_2 + M \rightarrow ClOO + M$ also studied at low temperatures (see this evaluation) and governed by a radical-complex mechanism.

Comments on High-pressure Rate Coefficients and Falloff Range

The new experiments from Ref. 1 under low temperature and high pressure conditions indicate anomalous falloff behavior different from the formalism described in the Introduction. These effects are not relevant for atmospheric conditions, and they are not included in this evaluation.

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$O + O_3 \rightarrow 2O_2$

$\Delta H^\circ = -391.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-12} \exp(-1959/T)$	220–377	Wine *et al.*, 1983[1]	(a)
8.26×10^{-15}	297		
Reviews and Evaluations			
$8.0 \times 10^{-12} \exp(-2060/T)$	220–400	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$8.0 \times 10^{-12} \exp(-2060/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) $O(^3P)$ atoms produced by the laser photolysis of O_3 at 532 nm, and monitored by time-resolved resonance fluorescence.

(b) See Comments on Preferred Values.

(c) Obtained by Wine[1] from an unweighted linear least-squares fit of the data of Wine *et al.*,[1] McCrumb and Kaufman,[5] Davis *et al.*,[6] West *et al.*[7] and Arnold and Comes.[8]

Preferred Values

$k = 8.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.0 \times 10^{-12} \exp(-2060/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The study of Wine *et al.*[1] yields values of k in close agreement with those from other studies, over the whole temperature range covered. Our recommendations are based on the least-squares expression obtained by Wine *et al.*[1] from a fit of their data plus those of McCrumb and Kaufman,[5] Davis *et al.*,[6] West *et al.*[7] and Arnold and Comes.[8]

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$$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+) \quad (1)$$
$$\rightarrow O(^3P) + O_2(^1\Delta_g) \quad (2)$$
$$\rightarrow O(^3P) + O_2(^3\Sigma_g^-) \quad (3)$$

$\Delta H°(1) = -32.8$ kJ·mol^{-1}
$\Delta H°(2) = -95.4$ kJ·mol^{-1}
$\Delta H°(3) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 \pm 0.2) \times 10^{-11}$	295	Amimoto *et al.*, 1979[1]	(a)
$(4.0 \pm 0.6) \times 10^{-11}$	298	Brock and Watson, 1981[2]	(b)
Branching Ratios			
$k_1/k = 0.77 \pm 0.2$	300	Lee and Slanger, 1978[3]	(c)
$k_2/k \leq 0.05$	300	Gauthier and Snelling, 1971[4]	(d)
Reviews and Evaluations			
3.2×10^{-11} exp(67/T)	200–350	CODATA, 1982[5]; IUPAC, 1989[6]	(e)
3.2×10^{-11} exp(70/T)	200–300	NASA, 1990[7]	(f)

Comments

(a) $O(^1D)$ atoms produced by laser flash photolysis of O_3 at 248 nm, and $O(^3P)$ detected by resonance absorption at 130 nm.
(b) $O(^1D)$ atoms produced by laser flash photolysis of O_3 at 266 nm, and $O(^3P)$ detected by resonance fluorescence at 130 nm.
(c) $O(^1D)$ atoms detected by $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. $O_2(^1\Sigma_g^+)$ was monitored from the $O_2(^1\Sigma_g^+) \rightarrow O_2(^3\Sigma_g^-)$ (1–1) and (0–0) band emission. $O_2(^1\Sigma_g^+)$ is only formed in the $\nu = 0$ and 1 levels, with $k(1)/k(0) = 0.7$.
(d) $O(^1D)$ atom production by the photolysis of O_3.
(e) See Comments on Preferred Values.
(f) Based on the results of Amimoto *et al.*,[1] Brock and Watson,[2] and earlier references, excluding those measurements employing $O(^1D)$ atom absorption.

Preferred Values

$k = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-11}$ exp(67/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.
$k_1/k = 0.8$ at 298 K.
$k_2/k \leq 0.05$ at 298 K.

Reliability
$\Delta \log k = \pm 0.05$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta \log(k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[5] The earlier controversy between measurements using $O(^1D)$ emission at 630 nm and absorption at 115 nm now appears to be resolved, since $O(^3P)$ atom detection by absorption at 130 nm and fluorescence support the $O(^1D)$ emission results. Apparently the γ-value in the Lambert-Beer law used for the $O(^1D)$ absorption results was too small. The preferred 298 K rate coefficient is the average of the results from Amimoto *et al.*,[1] Brock and Watson,[2] Lee and Slanger[3] and Streit *et al.*[8] The branching ratios of Lee and Slanger[3] and Gauthier and Snelling[4] are recommended.

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$$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P) \quad (1)$$
$$\rightarrow O(^3P) + O_3 \quad (2)$$
$$\rightarrow 2O_2(^1\Delta_g) \quad (3)$$
$$\rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) \quad (4)$$
$$\rightarrow 2O_2(^3\Sigma_g^-) \quad (5)$$

$\Delta H°(1) = -83.2$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}
$\Delta H°(3) = -393.0$ kJ·mol^{-1}
$\Delta H°(4) = -424.7$ kJ·mol^{-1}
$\Delta H°(5) = -581.6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.2) \times 10^{-10}$	298	Greenblatt and Wiesenfeld, 1983[1]	(a)
Branching Ratios			
$k_1/k = 0.53$	298	Cobos, Castellano, and Schumacher, 1983[2]	(b)
$k_5/k = 0.47$			
Reviews and Evaluations			
2.4×10^{-10}	100–400	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$k_1/k = k_5/k = 0.5$	298		
2.4×10^{-10}	200–300	NASA, 1990[5]	(c)
$k_1/k = k_5/k = 0.5$	298		

(a) Laser photolysis of O_3 at 248 and 308 nm, using a flow system. $O(^3P)$ atoms were monitored by time-resolved resonance fluorescence.

(b) Steady-state photolysis of pure O_3 and O_3-inert gas mixtures. Ozone removal was monitored manometrically at high pressures and spectrophotometrically at lower pressures. The quantum yield of O_3 removal was interpreted in terms of a complex reaction scheme.

(c) Based on the data of Streit *et al.*,[6] Amimoto *et al.*,[7,8] Ravishankara and Wine[9] and Davenport *et al.*[10]

Preferred Values

$k = 2.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the temperature range 100–400 K.

$k_1/k = k_5/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.05$ over the temperature range 100–400 K.

$\Delta \log k_1/k = \Delta \log k_5/k = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The measurement of the rate coefficient k at 298 K by Greenblatt and Wiesenfeld[1] is in excellent agreement with our previous recommendation.[11] The determination of k_1/k_5 by Cobos *et al.*[2] is rather indirect, but provides further evidence that $k_1 \approx k_5$. Our previous recommendations[3,4,11] are unchanged.

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$O_2^* + O_3 \rightarrow O + 2O_2$

Comments

These Comments are reproduced from our previous evaluation, IUPAC, 1989.[1] Arnold and Comes[2,3] have studied this reaction of vibrationally excited oxygen molecules in the ground electronic state with ozone, and they report a rate coefficient value of 2.8×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K. The vibrationally excited oxygen molecules were produced in the reaction of $O(^1D)$ atoms with O_3 following the UV photolysis of ozone. This is the only reported study of this rate coefficient, and we prefer to make no recommendation. For further discussion the reader is referred to the review by Steinfeld *et al.*[4]

References

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$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$

$\Delta H° = -94.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(3.3 \pm 0.4) \times 10^{-19}$	O_2	298	Eisenberg *et al.*, 1984[1]	(a)
$(1.65 \pm 0.07) \times 10^{-18}$	O_2	298	Raja, Arora, and Chatha, 1986[2]	(b)
$3.15 \times 10^{-18} \exp(-205)/T$	O_2	100–450	Billington and Borrell, 1986[3]	(c)
1.57×10^{-18}	O_2	298		
5×10^{-19}	CO_2	298	Singh *et al.*, 1985[4]	(d)
Reviews and Evaluations				
$3.0 \times 10^{-18} \exp(-200/T)$	O_2	100–450	CODATA, 1984[5]; IUPAC, 1989[6]	(e)
$\leq 1.4 \times 10^{-19}$	N_2	298		(f)
5×10^{-18}	H_2O	298		(g)
$\leq 2 \times 10^{-20}$	CO_2	298		(h)

Comments

(a) Direct laser excitation of O_2 at 1065 nm to give $O_2(^1\Delta_g, v = 1)$. $O_2(^1\Delta_g)$ was observed in emission at 1270 nm. The pressure was 1 atm of O_2.
(b) Discharge flow system, with $O_2(^1\Delta_g)$ being monitored by its dimol emission at 635 nm. The total pressure was 5–12 Torr.
(c) Discharge flow system, with $O_2(^1\Delta_g)$ being monitored by its dimol emission at 635 nm and also by monitoring the emission from $O_2(^1\Sigma_g^+)$ at 762 nm. The total pressure was 3–12 Torr.
(d) Discharge flow system. $O_2(^1\Delta_g)$ was monitored in emission at 1270 nm. No quenching could be observed for M = CO_2.
(e) Based on the data of Borrell *et al.*,[7] Leiss *et al.*[8] and Findlay and Snelling.[9]
(f) Based on the data of Collings *et al.*[10]
(g) Based on the data of Findlay and Snelling[9] and Becker *et al.*[11]
(h) Based on the data of Leiss *et al.*[8] and Findlay and Snelling.[9]

Preferred Values

$k = 1.6 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for M = O_2 at 298 K.

$k = 3.0 \times 10^{-18} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} for M = O_2 over the temperature range 100–450 K.

$k \leq 1.4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} for M = N_2 at 298 K.

$k = 5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for M = H_2O at 298 K.

$k \leq 2 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} for M = CO_2 at 298 K.

Reliability

$\Delta\log k = \pm 0.2$ for M = O_2 at 298 K.
$\Delta(E/R) = \pm 200$ K for M = O_2.
$\Delta\log k = \pm 0.3$ for M = H_2O at 298 K.

Comments on Preferred Values

The preferred value of $k(M = O_2)$ is based on the results of Raja *et al.*,[2] Billington and Borrell,[3] Borrell *et al.*[7] and Leiss *et al.*[8] The temperature dependence of Billington and Borrell[3] is adopted in this evaluation. The much lower value of Eisenberg *et al.*[1] by a new technique is not used in derivation of the preferred value. The previous CODATA recommendations[5] for M = N_2, H_2O, and CO_2 are unchanged.

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$O_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions	ΔH_0°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	494	242
$\rightarrow O(^3P) + O(^1D)$	683	175
$\rightarrow O(^1D) + O(^1D)$	873	137
$\rightarrow O(^3P) + O(^1S)$	898	132

Absorption cross-section data

Wavelength range/nm	Reference	Comments
179–201	Yoshino *et al.*, 1983[1]	(a)
175–205	Yoshino, Freeman and Parkinson, 1984[2]	(b)
193–204	Cheung *et al.*, 1984[3]	(c)
205–225	Johnston, Paige and Yao, 1984[4]	(d)
205–241	Cheung *et al.*, 1986[5]	(e)
205–240	Jenouvrier, Coquart and Merienne, 1986[6]	(f)
175–247	WMO, 1986[7]	(g)
179–198	Yoshino *et al.*, 1987[8]	(h)
175–205	Nicolet, Cieslik and Kennes, 1987[9]	(i)

Comments

(a) Measured at 300 K with a spectral resolution of 0.0013 nm. Band oscillator strengths of S–R band (12,0) through (1,0) determined.

(b) Measured at 300 K at high resolution with a vacuum spectrograph. Includes an atlas of S–R absorption bands of O_2 at 300 K showing detailed rotation line assignments for 175–205 nm region.

(c) Measured at 300 K with a spectral resolution of 0.0013 nm. Absorption includes discrete line of S–R bands and two underlying dissociation continua – the weak Herzberg continuum of O_2 and a pressure dependent continuum involving two oxygen molecules.

(d) Measured at 206–327 K with a spectral resolution of 0.2 nm and O_2 pressures of 100–750 Torr.

(e) Measured at 296–300 K with a spectral resolution of 0.13 nm and O_2 pressures of 5–760 Torr. Observed attenuation was due to Rayleigh scattering and to absorption into two continua [see note (c)].

(f) Measured at 289–294 K at low spectral resolution and O_2 pressures of 5–100 Torr.

(g) Critical review of all published data. Recommended values given for standard spectral intervals from 175–247 nm. Transmission in the S–R system (bands + continuum) tabulated as a function of column O_2 for standard spectral intervals from 175–206 nm.

(h) Measured at 79 K with spectral resolution of 0.0013 nm. Band oscillator strengths of S–R bands (12,0) through (2,0) determined by numerical integration of cross-section data.

(i) Tables of calculated absorption cross-sections presented for the range of the (0,0) to (19,0) bands from 49000 to 57000 cm^{-1} and the temperature range 190–300 K in 32 intervals of 250 cm^{-1}.

Preferred Values

Absorption cross-sections of O_2 in the Herzberg continuum

λ/nm	10^{24} σ/cm^2
205	7.35
210	6.51
215	5.59
220	4.46
225	3.45
230	2.43
235	1.63
240	1.01

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989.[10] The recommended absorption cross-section values for the Herzberg continuum are taken from the recent study by Yoshino *et al.*,[11] where values are tabulated for every nm from 205–240 nm. These values were derived from an analysis and combination of the data of Cheung *et al.*[5] and those of Jenouvrier *et al.*[6] They are in agreement with the results of Johnston *et al.*[4] They are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,[12] by Herman and Mentall[13] and by Anderson and Hall,[14] but are in disagreement with the results derived by Pirre *et al.*[15] from a similar *in-situ* stratospheric study. An analysis of the photodissociation of oxygen in the Herzberg continuum has recently been published by Nicolet and Kennes.[16]

For the Schumann-Runge wavelength region the reader is referred to the review in WMO, 1986[7] and to the tables of absorption cross-sections in Nicolet *et al.*[9] In this spectral region a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0,0)–(12,0) S–R bands measured by the Harvard-Smithsonian group[1–3,8] are the first set of values which are independent of instrumental width. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. The results of more recent studies of the S–R bands for isotopic oxygen molecules are presented in references 17–21. The effect on ozone formation in the 214 nm photolysis of oxygen due to $O_2 - O_2$ collision pairs at high O_2 pressure and the effect of high N_2 pressure have been studied by Horowitz *et al.*[22] Greenblatt *et al.*[23] studied the absorption spectrum of O_2 and $O_2 - O_2$ collision pairs over the wavelength range 330–1140 nm for O_2 pressures from 1 to 55 bar at 298 K. Band centers, band widths, and absorption cross-sections were reported for the absorption features in this wavelength region.

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$O_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH°_0/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g)$	(1)	101	1180
$\rightarrow O(^3P) + O_2(^1\Delta_g)$	(2)	196	611
$\rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	(3)	258	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g)$	(4)	291	411
$\rightarrow O(^1D) + O_2(^1\Delta_g)$	(5)	386	310
$\rightarrow O(^1D) + O_2(^1\Sigma_g^+)$	(6)	448	267

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–350	Freeman *et al.*, 1984[1]	(a)
245–350	Bass and Paur, 1985[2]	(b)
310–350	Malicet, Brion and Daumont, 1985[3]	(c)
185–350	Molina and Molina, 1986[4]	(d)
254	Mauersberger *et al.*, 1986[5]	(e)
175–360	WMO, 1986[6]	(f)
238–335	Yoshino *et al.*, 1988[7]	(g)
590–610	Amoruso *et al.*, 1990[8]	(h)

Comments

(a) Measured at 195 K with a spectral resolution of 0.003 nm. Relative values normalized to values at five mercury lines.

(b) Measured at 200–300 K with a spectral resolution of 0.025 nm. Relative values normalized to value of 1147×10^{-20} cm^2 at the 253.65 nm mercury line.

(c) Measured at 228 K and 298 K at five mercury line wavelengths in the ultraviolet and in the continuous spectral range 320–330 nm with a spectral resolution of 0.02 nm.

(d) Measured at 226–298 K with a spectral resolution of 0.07 nm.

(e) Measured at 297 K at the 253.7 nm mercury line. Later measurements (Ref. 9) extended the measurements to the temperature range 195–351 K.

(f) Critical review of all published data. Recommended values given for standard spectral intervals from 175–360 nm for 203 K and 273 K. Recommended values were also tabulated for visible spectral region.

(g) Measured at 195 K, 228 K, and 295 K at thirteen wavelengths in this region. These absolute measurements were used to convert the relative values in Ref. 1 to absolute values.

(h) Measured at 230 K and 299 K. Results were tabulated at 0.5 nm intervals.

Ozone absorption cross-sections at 273 K averaged over spectral intervals

Int #	$\Delta\lambda$/nm	$10^{20}\ \sigma$/cm^2	Int #	$\Delta\lambda$/nm	$10^{20}\ \sigma$/cm^2
1	175.4–177.0	81.1	31	238.1–241.0	797
2	178.6	79.9	32	243.9	900
3	180.2	78.6	33	246.9	1000
4	181.8	76.3	34	250.1	1080
5	183.5	72.9	35	253.2	1130
6	185.2	68.8	36	256.4	1150
7	186.9	62.2	37	259.7	1120
8	188.7	57.6	38	263.2	1060
9	190.5	52.6	39	266.7	965
10	192.3	47.6	40	270.3	834
11	194.2	42.8	41	274.0	692
12	196.1	38.3	42	277.8	542

Ozone absorption cross-sections at 273 K averaged over spectral intervals – Continued

Int #	$\Delta\lambda$/nm	10^{20} σ/cm^2	Int #	$\Delta\lambda$/nm	10^{20} σ/cm^2
13	198.0	34.7	43	281.7	402
14	200.0	32.3	44	285.7	277
15	202.0	31.4	45	289.9	179
16	204.1	32.6	46	294.1	109
17	206.2	36.4	47	298.5	62.4
18	208.3	43.4	48	303.0	34.3
19	210.5	54.2	49	307.7	18.5
20	212.8	69.9	50	312.5	9.8
21	215.0	92	51	317.5	5.0
22	217.4	119	52	322.5	2.49
23	219.8	155	53	327.5	1.20
24	222.2	199	54	332.5	0.617
25	224.7	256	55	337.5	0.274
26	227.3	323	56	342.5	0.117
27	229.9	400	57	347.5	0.059
28	232.6	483	58	352.5	0.027
29	235.3	579	59	357.5	0.011
30	238.1	686	60	362.5	0.005

$\sigma = (1147 \pm 20) \times 10^{-20}$ cm^2 at 253.7 nm.

Ozone absorption cross-sections in the visible spectral region

λ/nm	10^{23} σ/cm^2	λ/nm	10^{23} σ/cm^2
410	2.9	560	388
420	4.0	580	455
440	12.5	600	489
460	35.7	620	390
480	71.1	640	274
500	122	660	202
520	178	680	142
540	288	700	92

Quantum yields for O_3 photolysis

λ/nm	Quantum yield	Temp./K
248–300	$\phi_5 = 0.9 \pm 0.1$	200–300
248–300	$\phi_1 + \phi_5 = 1.00$	200–300
302	$\phi_5 = 0.90$	298
304	0.90	298
306	0.85	298
308	0.74	298
310	0.56	298
312	0.34	298
314	0.18	298
316	0.08	298
318	0.02	298
320	0.00	298

Comments on Preferred Values

Absorption Cross-sections

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989.[10] The recommended absorption cross-section values for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in modeling calculations. These values have been adopted from the NASA 1990 review,[11] which accepted the values tabulated in the WMO 1986 review,[6] except for the region 185–225 nm where the values were taken from the recent study of Molina and Molina.[4] For the 245–350 nm region the results of Bass and Paur[2] are used, while for the remaining spectral regions the values were originally tabulated in Ackerman's review.[12] The value recommended for the mercury line at 253.7 nm is based on results reported by Hearn,[13] Molina and Molina[4] and Mauersberger *et al.*[5] The values for the wavelength range 400–700 nm are taken from the WMO 1986 review.[6] The spectroscopy of ozone has been reviewed very recently by Steinfeld, Adler-Golden and Gallagher.[14]

Quantum Yields

The recommended quantum yield values for the 248–300 nm region are based on absolute quantum yield measurements at 248–266 nm (see CODATA, 1984[15] and CODATA, 1982[16]). The quantum yield values for 300–320 nm have been calculated from the expression for $\phi_5(\lambda,T)$ given in the NASA, 1990 review.[11] That expression was derived from the expression of Moortgat and Kudszus[17] by using the scaling factor 0.9 to account for the absolute value of ϕ_5 at the shorter wavelengths. There is a need to confirm that the values of ϕ_5 determined at 248–266 nm applies throughout the wavelength region up to 300 nm (see review by Wayne[18]).

References

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4.2. Hydrogen Species

$$H + HO_2 \rightarrow H_2 + O_2 \quad (1)$$
$$\rightarrow 2HO \quad (2)$$
$$\rightarrow H_2O + O \quad (3)$$

$\Delta H^\circ(1) = -233$ kJ·mol^{-1}
$\Delta H^\circ(2) = -154$ kJ·mol^{-1}
$\Delta H^\circ(3) = -225$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.7 \pm 1.5) \times 10^{-11}$	245–300	Keyser, 1986[1]	(a)
Branching Ratios			
$k_1/k = 0.08 \pm 0.04$	245–300	Keyser, 1986[1]	(a)
$k_2/k = 0.90 \pm 0.04$			
$k_3/k = 0.02 \pm 0.04$			
Reviews and Evaluations			
8.0×10^{-11}	245–300	IUPAC, 1989[2]	(b)
8.1×10^{-11}	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with He as the carrier gas. HO_2 was produced by the F + H_2O_2 reaction and was present in large excess over H atoms. HO_2 was monitored by conversion to HO by reaction with NO, with resonance fluorescence detection of HO. The OH radical and $O(^3P)$ atom reaction products were also monitored by resonance fluorescence.

(b) See Comments on Preferred Values.

(c) Based on the data of Sridharan *et al.*[4] and Keyser.[1]

Preferred Values

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_1 = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_3 = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

Reliability

$\Delta \log k = \pm 0.1$ over the range 245–300 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_1 = \pm 0.5$ over the range 245–300 K.
$\Delta \log k_2 = \pm 0.1$ over the range 245–300 K.
$\Delta \log k_3 = \pm 0.5$ over the range 245–300 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The study of Keyser[1] is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with those obtained by Sridharan *et al.*,[4] who used a similar technique. The recommended rate coefficient k and the branching ratios are the averages from these two studies.[1,4] In both cases k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

The yield of $O_2(^1\Sigma_g^+)$ in this reaction has been measured by Hislop and Wayne,[5] Keyser *et al*[6] and Michelangeli *et al.*,[7] who report formation yields of $(2.8 \pm 1.3) \times 10^{-4}$, $<8 \times 10^{-3}$ and $<2.1 \times 10^{-2}$, respectively.

Keyser[1] observed no effect of temperature on the rate coefficient k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained by Pagsberg *et al.*[8] at 349 K is too low or that there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the range 245–300 K.

References

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$H + O_2 + M \rightarrow HO_2 + M$

$\Delta H° = -203.4$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.2 \times 10^{-32}(T/300)^{-1.66}$ [N_2]	298-639	Hsu *et al.*, 1989[1]	(a)
Reviews and Evaluations			
$5.9 \times 10^{-32}(T/300)^{-1.0}$ [N_2]	200-300	CODATA, 1980[2]; CODATA, 1984[3]; IUPAC, 1989[4]	(b)
$5.7 \times 10^{-32}(T/300)^{-1.6}$ [air]	200-300	NASA, 1990[5]	(c)

Comments

(a) Discharge flow study with resonance fluorescence detection of H, HO, and HO_2 (after chemical titration) using total pressures up to 70 Torr. Relative rate coefficients $k_0(M = H_2O) : k_0(He) : k(N_2) = 10.7 : 0.43 : 1$ were obtained at 298 K. The results are consistent with earlier recommendations from Ref. 3.

(b) Average of the data from Kurylo[6] and Wong and Davis.[7] The temperature coefficient was estimated on the basis of these experiments and calculations from Ref. 8.

(c) Based on data from Kurylo[6] and Wong and Davis.[7] The temperature coefficient estimated on the basis of Ref. 9.

Preferred Values

$k_0 = 6.2 \times 10^{-32}(T/300)^{-1.6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-600 K.

Reliability

$\Delta \log k_0 = \pm 0.05$ at 298 K.
$\Delta n = \pm 0.6$.

Comments on Preferred Values

The preferred values are from the recent study of Hsu *et al.*,[1] which appears to be most complete and accurate. The older data from Refs. 6–8 are in excellent agreement with the new results. Recent high temperature experiments by Pirraglia *et al.*[10] are consistent with the preferred values.

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$7.5 \times 10^{-11}(T/300)^{0.6}$	200-300	CODATA, 1984[3]; IUPAC, 1989[4]	(a)
7.5×10^{-11}	200-300	NASA, 1990[5]	(b)

Comments

(a) Based on measurements, as well as calculations, of the temperature coefficient by Cobos *et al.*[8]
(b) Based on measurements from Ref. 8. The temperature dependence was estimated.

Preferred Values

$k_\infty = 7.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-300 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.6$.

Comments on Preferred Values

Measurements in M = Ar, N_2 and CH_4 all extrapolate to the same limiting value. The results are from a single study.[8]

Intermediate Falloff Range

The measured broadening factor $F_c = 0.55 \pm 0.15$ for M = N_2 from reference 8 is in agreement with a calculated value of $F_c = 0.66$. Representation of the measured F_c by $F_c = \exp(-T/T^*)$ gives $T^* = 498$ K.

References

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$O + HO \rightarrow O_2 + H$

$\Delta H^\circ = -70.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.5) \times 10^{-11}$	300	Brune, Schwab and Anderson, 1983[1]	(a)
Relative Rate Coefficients			
3.4×10^{-11}	299	Keyser, 1983[2]	(b)
Reviews and Evaluations			
$2.3 \times 10^{-11} \exp(110/T)$	220–500	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$2.2 \times 10^{-11} \exp(117/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Fast flow discharge study with $O(^3P)$ atoms in excess. HO radicals were monitored by LMR and resonance fluorescence, $O(^3P)$ atoms were monitored by resonance fluorescence and absorption, and H atoms were monitored by resonance fluorescence.
(b) Fast flow discharge study. HO and HO_2 radicals were produced by the reactions of H with NO_2 and O_2, respectively. Steady-state concentrations of HO and HO_2 were established in the presence of excess $O(^3P)$ atoms by the reaction sequence $O + HO_2 \rightarrow HO + O_2$, $O + HO \rightarrow H + O_2$, and $H + O_2 + M \rightarrow HO_2 + M$. HO was monitored by resonance fluorescence. HO_2 was determined by titration with NO and detection of HO. The measured $[HO]/[HO_2]$ ratios gave a rate coefficient ratio of $k/k(O + HO_2) = 0.59 \pm 0.07$, which has been placed on an absolute basis by use of $k(O + HO_2) = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(c) See Comments on Preferred Values.
(d) Based on the data of Westenberg *et al.*,[6] Lewis and Watson[7] and Howard and Smith.[8]

Preferred Values

$k = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.3 \times 10^{-11} \exp(110/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–500 K.

Reliability
$\Delta\log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values
The most recent studies are those of Brune *et al.*[1] and Keyser.[2] Both are in excellent agreement with our previous recommendations,[3] which were based on a least squares fit to the data of Lewis and Watson[7] and Howard and Smith.[8] The reaction has been the subject of a number of theoretical studies; see Troe[9] and Miller.[10]

References

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$O + HO_2 \rightarrow HO + O_2$

$\Delta H° = -225$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.91 \times 10^{-11} \exp[(228 \pm 75)/T]$	266–391	Nicovich and Wine, 1987[1]	(a)
$(6.30 \pm 0.91) \times 10^{-11}$	298		
Reviews and Evaluations			
$2.9 \times 10^{-11} \exp(200/T)$	200–400	IUPAC, 1989[2]	(b)
$3.0 \times 10^{-11} \exp(200/T)$	200–300	NASA, 1990[3]	(b)

Comments

(a) Pulsed laser photolysis of H_2O_2-O_3-N_2 mixtures at 248.5 nm. Total pressure = 80 Torr. $O(^3P)$ atoms were monitored by resonance fluorescence.
(b) Based on the data of Keyser,[4] Sridharan *et al.*,[5] Ravishankara *et al.*,[6] Brune *et al.*[7] and Nicovich and Wine.[1]

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-11} \exp(224/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta\log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values
This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989.[2] The study of Nicovich and Wine[1] is in excellent agreement with the earlier data of Keyser,[4] Sridharan *et al.*,[5] Ravishankara *et al.*[6] and Brune *et al.*[7] The recommended 298 K rate coefficient is the mean of the values obtained in these studies.[1,4-7] The temperature coefficient is the mean of the values obtained by Nicovich and Wine[1] and Keyser,[4] with a pre-exponential

factor based on this value of E/R and the recommended value of k at 298 K.

Keyser *et al.*[8] have shown that the yield of $O_2(b^1\Sigma_g^+)$ from this reaction is $<1 \times 10^{-2}$ per HO_2 removed. Sridharan *et al.*[9] have shown, in an ^{18}O labelling experiment, that the reaction proceeds via formation of an $HO_2-{}^{18}O$ intermediate which dissociates to OH and ^{18}OO by rupture of an O–O bond rather than via a four centre intermediate yielding ^{18}OH + OO.

References

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[2]IUPAC, Supplement III, 1989 (see references in Introduction).
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$O + H_2O_2 \rightarrow HO + HO_2$

$\Delta H^\circ = -59.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
See comment (a)	302–349	Roscoe, 1982[1]	(a)
1.13×10^{-12} exp[-(2000 ± 160)/T]	298–386	Wine *et al.*, 1983[2]	(b)
(1.45 ± 0.29) × 10^{-15}	298		
Reviews and Evaluations			
1.4×10^{-12} exp(−2000/T)	250–390	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
1.4×10^{-12} exp(−2000/T)	200–300	NASA, 1990[5]	(d)

Comments

(a) Fast flow discharge system. $O(^3P)$ atoms were produced from the N + NO reaction and monitored by chemiluminescent reaction with NO. H_2O_2 was determined by trapping and titrating with $KMnO_4$. The rate coefficient k for $O(^3P)$ removal was found to vary with the initial $[H_2O_2]/[O_2]$ ratio in the range 5–220. The importance of secondary reactions was confirmed by computer modeling of the system. The author concluded that secondary reactions had affected all previous measurements except that of Davis *et al.*[6] Modeling confirmed the predominance of the channel leading to HO + HO_2 over the alternative giving $H_2O + O_2$.

(b) Laser flash photolysis of O_3 at 532 nm in the presence of excess H_2O_2. $O(^3P)$ atoms were monitored by time-resolved resonance fluorescence.

(c) See Comments on Preferred Values.

(d) Based on the data of Davis *et al.*[6] and Wine *et al.*[2]

Preferred Values

$k = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12}$ exp(−2000/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The results of Wine *et al.*[2] agree with those of Davis *et al.*[6] with regard to the temperature coefficient, but the absolute values of the rate coefficient k in the two studies[2,6] differ by approximately a factor of 2 throughout the range. In both cases[2,6] the observed pre-exponential factor is low compared with other atom-molecule reactions. The preferred values are derived from these[2,6] two sets of data.

References

[1]J. M. Roscoe, Int. J. Chem. Kinet. **14**, 471 (1982).
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[3]CODATA, Supplement II, 1984 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
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$$O(^1D) + H_2 \rightarrow HO + H \quad (1)$$
$$\rightarrow O(^3P) + H_2 \quad (2)$$

$\Delta H°(1) = -181.6$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-10}$	298	Force and Wiesenfeld, 1981[1]	(a)
Relative Rate Constants			
$(7.9 \pm 0.6) \times 10^{-11}$	298	Ogren *et al.*, 1982[2]	(b)
Branching Ratios			
$k_2/k < 0.049$	298	Wine and Ravishankara, 1982[3]	(c)
Reviews and Evaluations			
1.1×10^{-10}	200–350	CODATA, 1984[4]; IUPAC, 1989[5]	(d)
1.0×10^{-10}	200–300	NASA, 1990[6]	(e)

Comments

(a) Pulsed laser photolysis of O_3 at 248 nm. H and $O(^3P)$ atoms were monitored by time-resolved absorption spectroscopy.
(b) Photolysis of O_3-H_2 mixtures in the Hartley band. A rate coefficient ratio of $k/k[O(^1D) + O_2] = 1.97 \pm 0.15$ was obtained from measurements of O_2 depletion. The rate coefficient k was calculated using $k[O(^1D) + O_2] = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Reaction of $O(^1D)$ assumed to occur entirely via channel (1).
(c) Laser flash photolysis of O_3 at 248 nm. $O(^3P)$ atoms were monitored by time-resolved resonance fluorescence.
(d) See Comments on Preferred Values.
(e) Based on the data of Wine and Ravishankara,[3,7] Davidson *et al.*[8,9] and Force and Wiesenfeld.[1]

Preferred Values

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[4] The recommended value is the mean of the values of Wine and Ravishankara,[7] Davidson *et al.*[9] and Force and Wiesenfeld,[1] all of which are in excellent agreement. Channel (1) appears to be the dominant pathway (>95%)[3] for the reaction.

References

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[5]IUPAC, Supplement III, 1989 (see references in Introduction).
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[9]J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, J. Chem. Phys. **67**, 5021 (1977).

$$O(^1D) + H_2O \rightarrow 2HO \quad (1)$$
$$\rightarrow H_2 + O_2 \quad (2)$$
$$\rightarrow O(^3P) + H_2O \quad (3)$$

$\Delta H^\circ(1) = -118.5$ kJ·mol^{-1}
$\Delta H^\circ(2) = -197.1$ kJ·mol^{-1}
$\Delta H^\circ(3) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (2.02 \pm 0.41) \times 10^{-10}$	298	Gericke and Comes, 1981[1]	(a)
Branching Ratios			
$k_3/k < 0.049 \pm 0.032$	298	Wine and Ravishankara, 1982[2]	(b)
$k_2/k < 0.006 \pm 0.007$	298	Glinski and Birks, 1985[3]	(c)
Reviews and Evaluations			
2.2×10^{-10}	200–350	CODATA, 1984[4]; IUPAC, 1989[5]	(d)
2.2×10^{-10}	200–300	NASA, 1990[6]	(e)

Comments

(a) Laser flash photolysis of O_3-H_2O-Ar mixtures at 266 nm. HO radicals were monitored by light absorption using a tunable dye laser. The rate coefficient k_1 was shown to be independent of the translational energy of $O(^1D)$.

(b) Laser flash photolysis of O_3 at 248 nm. $O(^3P)$ atoms were monitored by time-resolved resonance fluorescence.

(c) Photolysis of O_3-H_2O mixtures at 253.7 nm. H_2 yield measured by GC.

(d) See Comments on Preferred Values.

(e) Based on the data of Gericke and Comes,[1] Amimoto *et al.*,[7] Lee and Slanger,[8] Wine and Ravishankara,[2,9] Streit *et al.*[10] and Glinski and Birks.[3]

Preferred Values

$k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

$k_1 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 < 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_3 < 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

$\Delta \log k_1 = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced largely from our previous evaluations, CODATA, 1984[4] with the comments from IUPAC, 1989[5] being included.

The preferred rate coefficient is a mean of the values of Gericke and Comes,[1] Amimoto *et al.*,[7] Lee and Slanger,[8] Wine and Ravishankara[9] and Streit *et al.*,[10] all of which are in good agreement. We make use of the work of Wine and Ravishankara[2] and the earlier work of Zellner *et al.*[11] in our recommendations for k_3/k, and the results of Glinski and Birks[3] and of Zellner *et al.*[11] for k_2/k.

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$HO + H_2 \rightarrow H_2O + H$

$\Delta H° = -63.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.1 \pm 1.0) \times 10^{-15}$	298	Zellner and Steinert, 1981[1]	(a)
Relative Rate Coefficients			
$(8.5 \pm 1.8) \times 10^{-15}$	296	Sworski, Hochanadel and Ogren, 1980[2]	(b)
Reviews and Evaluations			
$7.7 \times 10^{-12} \exp(-2100/T)$	200–450	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$5.5 \times 10^{-12} \exp(-2000/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Fast flow discharge study. The $H + NO_2$ reaction was used as the HO source. HO radicals were monitored by resonance fluorescence.

(b) Flash photolysis of H_2O-CH_4-H_2 mixtures at a total pressure of 760 Torr. CH_3 radicals were monitored by absorption at 216 nm. The rate coefficient k was derived by computer fit of CH_3 decay profile to an assumed reaction mechanism.

(c) See Comments on Preferred Values.

(d) Based on the data of Zellner and Steinert,[1] Greiner,[6] Tully and Ravishankara,[7] Ravishankara *et al.*,[8] Stuhl and Niki,[9] Westenberg and deHaas,[10] Smith and Zellner,[11] Overend *et al.*[12] and Atkinson *et al.*[13]

Preferred Values

$k = 6.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.7 \times 10^{-12} \exp(-2100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] There are several studies in good agreement on both the temperature coefficient and absolute values of the rate coefficient. The preferred 298 K rate coefficient is the mean of the results of Zellner and Steinert,[1] Greiner,[6] Tully and Ravishankara,[7] Stuhl and Niki,[9] Ravishankara *et al.*,[8] Westenberg and deHaas,[10] Smith and Zellner,[11] Overend *et al.*[12] and Atkinson *et al.*[13] The preferred value of E/R is the mean of the values of Smith and Zellner,[11] Atkinson *et al.*[13] and Ravishankara *et al.*[8] The pre-exponential factor in the rate expression is calculated to fit the preferred value of k at 298 K and of E/R.

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$HO + HO \rightarrow H_2O + O$

$\Delta H^\circ = -71.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.2) \times 10^{-12}$	298	Farquharson and Smith, 1980[1]	(a)
$4.2 \times 10^{-12} \exp(-242/T)$	250–580	Wagner and Zellner, 1981[2]	(b)
$(1.43 \pm 0.3) \times 10^{-12}$	298		
Reviews and Evaluations			
1.8×10^{-12}	298	CODATA, 1982[3]; IUPAC, 1989[4]	(c)
$4.2 \times 10^{-12} \exp(-240/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system used. HO radicals were generated by the $H + NO_2$ reaction and monitored by resonance fluorescence.
(b) Flash photolysis of N_2-H_2O mixtures. HO radicals were monitored by resonance absorption.
(c) Mean of results from Refs. 1 and 6–13.
(d) Based on average of the data from Refs. 1, 2 and 6–9 with the temperature dependence from Ref. 2.

Preferred Values

$k = 1.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.2 \times 10^{-12} \exp(-240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability
$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 240$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation[3] with the inclusion of the work of Wagner and Zellner.[2] There are a number of measurements[1,2,6-13] of the rate coefficient k at temperatures close to 298 K, with k being in the range $(1.4–2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We take the mean of the more recent studies[1,2,6-9] for our preferred value at 298 K and accept the temperature dependence determined by Wagner and Zellner[2] for the temperature coefficient of k.

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$HO + HO + M \rightarrow H_2O_2 + M$

$\Delta H^\circ = -214.9$ kJ·mol^{-1}

Low pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.9 \times 10^{-31}(T/300)^{-0.8}$ [N_2]	253-353	Zellner *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$8.0 \times 10^{-31}(T/300)^{-0.76}$ [N_2]	200-1500	Brouwer *et al.*, 1987[2]	(b)
$6.9 \times 10^{-31}(T/300)^{-0.8}$ [N_2]	200-300	CODATA, 1980;[3] IUPAC, 1989[4]	(c)
$6.9 \times 10^{-31}(T/300)^{-0.8}$ [air]	200-300	NASA, 1990[5]	(d)

Comments

(a) HO was generated by the flash photolysis of H_2O vapor in the pressure of 26–1100 mbar of N_2, and detected by resonance absorption. The reaction was found to be close to the low-pressure limit. Analysis of the falloff curves was made by estimating $F_c = 0.6$.
(b) Theoretical analysis of the collision-free dissociation of H_2O_2 after overtone excitation and the high pressure thermal recombination of HO radicals ($F_c = 0.5$). Limiting rate coefficients based on data from Ref. 6 in agreement with Ref. 1 at low temperatures and the data of Meyer *et al.*[7] at 1200 K (corrected according to Ref. 8).
(c) Based on the data from Ref. 6.
(d) Based on the data from Ref. 1.

Preferred Values

$k_0 = 8 \times 10^{-31}(T/300)^{-0.8}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values
Because of the discrepancy with the data from Trainor and von Rosenberg[9] (which were lower by a factor of 2.7), the low pressure rate coefficients of Ref. 1 need experimental verification. The recent high pressure measurements from Ref. 10 suggest a slight shift of the falloff curve which is more consistent with the k_0 value of the analysis of Ref. 2. The reported value of n is also consistent with this theoretical analysis.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.5×10^{-11}	253-353	Zellner *et al.*, 1988[1]	(a)
3.0×10^{-11}	295	Forster *et al.*, 1991[10]	(b)
Reviews and Evaluations			
$1.5 \times 10^{-11}(T/300)^{-0.37}$	200-1500	Brouwer *et al.*, 1987[2]	(c)
3.0×10^{-11}	200-300	CODATA, 1980[3]; IUPAC, 1989[4]	(d)
1.5×10^{-11}	200-300	NASA, 1990[5]	(e)

Comments

(a) See comment (a) for k_0. Only the lower part of the falloff curve was studied, with N_2 pressures ≤ 1 bar. The extrapolation to k_∞ was relatively uncertain.
(b) Laser flash photolysis in M = He at pressures up to 200 bar, with LIF detection of HO. The experiments approached the high pressure limit.
(c) See comment (b) for k_0.
(d) See comment (c) for k_0.
(e) See comment (d) for k_0.

Preferred Values

$k_\infty = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200-300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 208 K.
$\Delta n = \pm 0.5$.

Comments of Preferred Values
The new experiments from Ref. 10 are the first conducted close to the high pressure limit. Together with the analysis[2] of photolysis and thermal dissociation rates they provide a consistent picture of the falloff curve constructed with a theoretically determined value of $F_c = 0.5$ over the temperature range 200-300 K.

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$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H^\circ = -296$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2 \pm 1.2) \times 10^{-11}$	298	Rozenshtein *et al.*, 1984[1]	(a)
$1.7 \times 10^{-11} \exp[(416 \pm 86)/T]$	252–420	Sridharan, Qui and Kaufman, 1984[2]	(b)
$(6.9 \pm 1.1) \times 10^{-11}$	298		
$(1.1 \pm 0.28) \times 10^{-10}$	298	Dransfeld and Wagner, 1986[3]	(c)
$4.8 \times 10^{-11} \exp[(250 \pm 50)/T]$	254–383	Keyser, 1988[4]	(d)
$(1.1 \pm 0.3) \times 10^{-10}$	299		
$(8.0^{+3.0}_{-2.0}) \times 10^{-11}$	298	Schwab, Brune and Anderson, 1989[5]	(e)
Reviews and Evaluations			
$4.8 \times 10^{-11} \exp(250/T)$	250–400	IUPAC, 1989[6]	(f)
$4.8 \times 10^{-11} \exp(250/T)$	200–300	NASA, 1990[7]	(g)

Comments

(a) Discharge flow study with He as the carrier gas. HO_2 produced by the $F + H_2O_2$ reaction, and HO by the reaction sequence $H + O_2 \rightarrow HO_2 + M$ and $HO_2 + H \rightarrow HO + HO$. HO radicals were monitored by EPR and HO_2 by LMR.

(b) Discharge flow study with He as the carrier gas. HO produced by the reactions $H + F_2 \rightarrow HF + F$ and $F + H_2O \rightarrow HF + HO$. HO radicals were monitored by LIF at 308.6 nm. HO_2 produced by the reaction of $F + H_2O_2 \rightarrow HF + HO_2$. HO_2 was determined by rapid conversion to HO by reaction with NO and detection of HO by LIF. HO_2 was present in large excess over HO.

(c) Discharge flow study with He as the carrier gas. Isotopic labelling was used to study the reactions $^{18}OH + H^{16}O_2 \rightarrow H_2{}^{18}O + {}^{16}O_2$ and $^{18}OH + H^{16}O_2 \rightarrow {}^{16}OH + H^{18}O^{16}O$. HO_2 was prepared by $H + O_2 + M$ and OH by $F + H_2O$ reactions. ^{16}OH, ^{18}OH and $H^{16}O^{18}O$ were monitored by LMR. Results suggested that both reaction pathways are equally probable, but this result may have been affected by side reactions due to traces of H and $O(^3P)$ atoms. Kurylo *et al.*[8] found no evidence for isotopic scrambling.

(d) Discharge flow study with He as the carrier gas. HO_2 was produced by $F + H_2O_2$ and OH by $F + H_2O$. A large excess of HO_2 was used. HO was monitored by resonance fluorescence and HO_2 was determined by titration with NO. NO_2 was added to the system to scavenge small amounts of $O(^3P)$ and H atoms present.

(e) Discharge flow study using He and Ar as the carrier gases. HO and HO_2 radicals were monitored by LMR. Computer modeling was used to check on interference by reactions of traces of H and $O(^3P)$ atoms.

(f) See Comments on Preferred Values.

(g) Accepts the expression of Keyser.[4]

Preferred Values

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.8 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation[6] but with the inclusion of data from Dransfield and Wagner[3] which was overlooked previously and the new data of Schwab *et al.*,[5] both of which studies give a rate coefficient at 298 K in excellent agreement with our recommendations.[6]

There has been considerable controversy over the effects of pressure on the rate coefficient for this reaction. Discharge flow measurements at low total pressures (1–10 Torr) consistently gave values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge flow study of Keyser[4] appears to have resolved the problem. The results of Keyser[4] suggest that (a) the presence of small quantities of H and $O(^3P)$ atoms present in previous discharge flow studies could have led to erroneously low values of k, and (b) there is no evidence for any variation in k with pressure. These findings[4] are accepted and we take the expression of Keyser[4] for the rate coefficient k as our recommendation.

In another discharge-flow study, Keyser *et al.*[9] monitored the $O_2(b^1\Sigma_g^+) \rightarrow X(^3\Sigma_g^-)$ transition at 762 nm and showed that the yield of $O_2(b^1\Sigma_g^+)$ from the reaction is small ($<1 \times 10^{-3}$).

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H^\circ = -130.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.76 \times 10^{-12} \exp[-(110 \pm 60)/T]$	273–410	Vaghjiani, Ravishankara and Cohen, 1989[1]	(a)
$(1.86 \pm 0.18) \times 10^{-12}$	298		
Reviews and Evaluations			
$2.9 \times 10^{-12} \exp(-160/T)$	240–460	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$2.9 \times 10^{-12} \exp(-160/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) Pulsed laser photolysis of H_2O_2 or O_3-H_2O mixtures in a variety of buffer gases (He, N_2, SF_6) at total pressures of 50–500 Torr. $DO + D_2O_2$, $DO + H_2O_2$ and $HO + D_2O_2$ reactions were also studied in similar fashion.
(b) See Comments on Preferred Values.
(c) Based on the data of Wine *et al.*,[1] Kurylo *et al.*,[5] Sridharan *et al.*[6] and Keyser.[7]

Preferred Values

$k = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-12} \exp(-160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–460 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The most recent study[1] is in good agreement with previous work.[6–10] Our previous recommendations[2,3] are unchanged and are identical with the values derived by Kurylo *et al*[5] from a least-squares fit to the data in Refs. 6–10.

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$HO + O_3 \rightarrow HO_2 + O_2$

$\Delta H^\circ = -167.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.5 \pm 1.0) \times 10^{-14}$	300	Zahniser and Howard, 1980[1]	(a)
$1.52 \times 10^{-12} \exp[-(890 \pm 60)/T]$	240–295	Smith *et al.*, 1984[2]	(b)
$(7.46 \pm 0.16) \times 10^{-14}$	295		
Relative Rate Coefficients			
$(7.0 \pm 0.8) \times 10^{-14}$	300	Zahniser and Howard, 1980[1]	(c)
Reviews and Evaluations			
$1.9 \times 10^{-12} \exp(-1000/T)$	220–450	CODATA, 1982[3]; IUPAC, 1989[4]	(d)
$1.6 \times 10^{-12} \exp(-940/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system used. HO radicals were generated from $H + NO_2$ and monitored by LMR.

(b) Flash photolysis of O_3–H_2O mixtures in 1 atm He. HO radicals were monitored by resonance fluorescence.

(c) Discharge flow system used. HO radicals were generated from the $H + NO_2$ and $H + O_3$ reactions, and HO_2 radicals were generated from the reaction $H + O_2 + M$. HO_2 and HO radicals were monitored by LMR. A rate coefficient ratio of $k/k(HO_2 + O_3) = 35 \pm 4$ (average of three systems studied) was obtained and placed on an absolute basis by use of $k(HO_2 + O_3) = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K (this evaluation).

(d) See Comments on Preferred Values.

(e) Based on the work of Zahniser and Howard,[1] Smith *et al.*[2] Anderson and Kaufman,[6] Kurylo[7] and Ravishankara *et al.*[8]

Preferred Values

$k = 6.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-12} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

This data sheet is reproduced largely from our previous evaluation, CODATA, 1982,[3] with the addition of comments from IUPAC, 1989.[4] There is good agreement among the various studies for the rate coefficient k. The recommended value for E/R is the mean of the values of Smith *et al.*,[2] Anderson and Kaufman[6] and Ravishankara *et al.*[8] The recommended 298 K rate coefficient is the mean of the values from these studies[2,6,8] plus those of Zahniser and Howard[1] and Kurylo.[7] The pre-exponential factor is derived from the recommended values of E/R and the 298 K rate coefficient.

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$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (1)$$

$$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M \quad (2)$$

$\Delta H°(1) = \Delta H°(2) = -166$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.9) \times 10^{-12}$	298	Lightfoot, Veyret and Lesclaux, 1988[1]	(a)
$(1.5 \pm 0.5) \times 10^{-12}$	418		
$(8.8 \pm 1.2) \times 10^{-13}$	577		
$(8.2 \pm 2.0) \times 10^{-13}$	623		
$(8.1 \pm 1.5) \times 10^{-13}$	677		
$(7.6 \pm 1.4) \times 10^{-13}$	723		
$(9.1 \pm 2.5) \times 10^{-13}$	777		
$(2.44 \pm 0.20) \times 10^{-12}$ (760 Torr O_2)	298	Crowley *et al.*, 1991[2]	(b)
$(2.84 \pm 0.30) \times 10^{-12}$ (760 Torr N_2)	298		
Reviews and Evaluations			
$k_1 = 2.2 \times 10^{-13} \exp(600/T)$ $k_2 = 1.4 \times 10^{-33} [N_2] \exp(980/T)$	230–420	IUPAC, 1989[3]	(c)
$k_1 = 2.3 \times 10^{-13} \exp(590/T)$ $k_2 = 1.7 \times 10^{-33} [M] \exp(1000/T)$	200–300	NASA, 1990[4]	(d)

Comments

(a) Flash photolysis of Cl_2–O_2–CH_3OH mixtures. HO_2 radicals were monitored by UV absorption at 220–227.5 nm (2.0 nm band width). Values of k/σ given by authors were converted to the tabulated values of k using $\sigma(210 \text{ nm}) = 4.4 \times 10^{-18}$ cm^2 and the temperature dependence of σ of Kijewski and Troe,[5] as suggested by Lightfoot *et al.*[1]

(b) Molecular modulation technique used, with photolysis of Cl_2–H_2–O_2–N_2 mixtures. HO_2 radicals were monitored by UV absorption. Experiments were carried out independently in two laboratories (Mainz and Harwell). Rate coefficients k were calculated using values of σ determined in the same experiments.

(c) See Comments on Preferred Values.

(d) Expression for k_1 based on the results of Cox and Burrows,[6] Kircher and Sander,[7] Thrush and Tyndall,[8,9] Takacs and Howard[10] and Kurylo *et al.*[11] The expression for k_2 was based on the work of Sander *et al.*,[12] Simonaitis and Heicklen,[13] Kircher and Sander[7] and Kurylo *et al.*[11]

Preferred Values

$k_1 = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.2 \times 10^{-32} [N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 4.5 \times 10^{-32} [O_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 2.2 \times 10^{-13} \exp(600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.
$k_2 = 1.9 \times 10^{-33} \exp(980/T)[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

In the presence of H_2O, the expressions for k_1 and k_2 should be multiplied by the factor $\{1 + (1.4 \times 10^{-21} \exp(2200/T)[H_2O])\}$.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta(E_1/R) = \pm 200$ K.
$\Delta(E_2/R) = \pm 300$ K.

Comments on Preferred Values

The recommendations, which are unchanged from our previous evaluation,[3] are identical with the values derived by Kircher and Sander.[7] At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for k_1 are based on the work of Cox and Burrows,[6] Kircher and Sander,[7] Thrush and Tyndall,[8] Takacs and Howard,[10] Kurylo *et al.*[11] and Lightfoot *et al.*[1] The work of Kurylo *et al.*[11] and of Lightfoot *et al.*[1] has confirmed quantitatively the effects of pressure previously observed by Kircher and Sander[7] and Simonaitis and Heicklen.[13] The recommendations for k_2 are based on the work of these authors, the temperature coefficient of k_2 being taken from Lightfoot *et al.*[1] and Kircher and Sander.[7] At higher temperatures, $T > 600$ K, Hippler *et al.*[14] and Lightfoot *et al.*[1] observe a sharp change in the temperature dependence. The values of k obtained by Crowley *et al.*,[2] from experiments primarily aimed at characterizing the UV absorption spectrum, are in good agreement with the recommended expression for k.

There have been no recent experimental studies to check the marked effect of H_2O on the rate coefficient, but the work of Andersson *et al.*[15] shows that CH_3OH has a similar effect, suggesting that it is typical of strongly polar hydrogen bonding species. Mozurkewich and Benson[16] have considered the effect theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in terms of a cyclic hydrogen bonded, H_2OHO_2, intermediate in contrast to alternative structures suggested by others.

Sahetchian *et al.*[17] reported the formation of H_2 (10% at 500 K) in the system but this is contrary to earlier evidence of Baldwin *et al.*[18] and the more recent and careful study of Stephens *et al.*[19] who find less than 0.01% fractional contribution from the channel leading to H_2 + $2O_2$.

Keyser *et al.*[20] have measured a yield of $O_2(b^1\Sigma_g^+)$ of ~3 × 10^{-2} per HO_2 consumed.

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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H° = -118$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.3) \times 10^{-15}$	298	Manzanares *et al.*, 1986[1]	(a)
$3.2 \times 10^{-13} \exp[-(1730 \pm 740)/T]$ + $(1.2 \pm 0.5) \times 10^{-15}$	243–413	Sinha, Lovejoy and Howard, 1987[2]	(b)
$(2.14 \pm 0.14) \times 10^{-15}$	297		
$1.8 \times 10^{-14} \exp[-(680 \pm 148)/T]$	253–400	Wang, Suto and Lee, 1988[3]	(c)
$(1.3 \pm 0.3) \times 10^{-15}$	233–253		
$(1.9 \pm 0.3) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.4 \times 10^{-14} \exp(-600/T)$	250–350	IUPAC, 1989[4]	(d)
$1.1 \times 10^{-14} \exp(-500/T)$	240–300	NASA, 1990[5]	(e)

Comments

(a) Discharge flow study with He as the carrier gas. HO_2 was produced by the reaction sequence Cl + CH_3OH → CH_2OH + HCl and $CH_2OH + O_2 \rightarrow HO_2$ + CH_2O, and an excess of O_3 was used. O_3 was determined by absorption at 253.7 nm. HO_2 radicals were monitored by photodissociation at 147 nm and detection of HO(A–X) fluorescence at 310 nm. C_2F_3Cl and C_3H_8 were used as scavengers for HO radicals produced from the reaction.

(b) Discharge flow study with He as the carrier gas. HO_2 radicals were generated by the reaction sequence Cl + CH_3OH → CH_2OH + HCl and $CH_2OH + O_2$ → $HO_2 + CH_2O$, and ^{16}O and ^{18}O labelled species were used. $H^{16}O$, $H^{18}O$, $H^{16}O_2$ and $H^{18}O_2$ were monitored by LMR.

(c) Techniques as in (a), but only C_3H_8 used as an HO radical scavenger.

(d) See Comments on Preferred Values.

(e) Based on the work of Zahniser and Howard,[6] Manzanares *et al.*,[1] Sinha *et al.*[2] and Wang *et al.*[3]

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-14} \exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = {}^{+500}_{-100}$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] All of the recent studies are in excellent agreement on the rate coefficient k at 298 K. The studies of Sinha *et al.*[2] and Wang *et al.*[3] both agree that the rate coefficient exhibits non-Arrhenius behavior, apparently approaching a constant value of approximately 1×10^{-15} cm^3 molecule^{-1} s^{-1} at $T < 250$ K. There are experimental difficulties in working at these temperatures and this finding is not incorporated into our recommendations without further confirmation. At higher temperature, the results from these two studies diverge giving rate coefficients differing by nearly a factor of 2 at 400 K. We therefore limit the temperature of our recommendation to temperatures <350 K until this discrepancy is resolved.

For modeling at temperatures in the range 200–250 K a value of $k = 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} should be used.

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[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]M. S. Zahniser and C. J. Howard, J. Chem. Phys. **73**, 1620 (1980).

$H_2O + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H^\circ_{298}/kJ \cdot mol^{-1}$	$\lambda_{threshold}$/nm
$H_2O + h\nu \rightarrow H_2 + O(^3P)$	(1)	491.0	243
$\rightarrow H + HO$	(2)	499.1	239
$\rightarrow H_2 + O(^1D)$	(3)	680.7	176

Absorption cross-section data

Wavelength range/nm	Reference	Comments
176–185	Watanabe and Zelikoff, 1953[1]	(a)
185–198	Thompson, Harteck and Reeves, 1963[2]	(b)
175–185	Laufer and McNesby, 1965[3]	(c)
175–182	Schurgers and Welge, 1968[4]	(d)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 \leq 0.003$	174	Chou, Lo and Rowland, 1974[5]	(e)

Comments

(a) Static system. H_2O was determined by pressure measurement over the range 0.08–8 Torr. Resolution was approximately 0.1 nm. Only graphical presentation of data.

(b) Static system double beam Perkin-Elmer 350 spectrophotometer used with a 10 cm pathlength. H_2O pressure was 20 Torr. No details of pressure measurement or resolution were given. Only graphical presentation of data.

(c) Static system. H_2O was determined by pressure measurement. 0.5 m grating monochromator, with a 0.66 nm bandwidth. Only graphical presentation of data.

(d) Flowing system. H_2O was determined using a membrane manometer. 0.5 m grating monochromator, with 0.25 nm bandwidth. Only graphical presentation of data.

(e) Photolysis involved HTO. It was shown that the decomposition path is almost entirely via the reactions HTO + $h\nu \rightarrow$ H + OT and HTO + $h\nu \rightarrow$ T + HO, with $\leq$ 0.003 of molecules decomposing via the reaction HTO + $h\nu \rightarrow$ HT + O.

Preferred Values

λ/nm	10^{20} σ/cm²	ϕ_2
175.5	263	1.0
177.5	185	1.0
180.0	78	1.0
182.5	23	1.0
185.0	5.5	1.0
186.0	3.1	1.0
187.5	1.6	1.0
189.3	0.70	1.0

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[6] Water vapor has a continuous spectrum between 175 and 190 nm; the cross-section falls off rapidly towards longer wavelengths. The cross-section data from four studies[1–4] are in reasonable agreement. None of these studies report numerical data. The preferred values of the absorption cross-section are taken from the review of Hudson,[7] and were obtained by drawing a smooth curve through the data of Schurgers and Welge,[4] Watanabe and Zelikoff[1] and Thompson *et al.*[2]

On the basis of the nature of the spectrum and the results of Chou *et al.*[5] on the photolysis of HTO, it is assumed that over the wavelength region 175–190 nm reaction (2) is the only primary process and that ϕ_2 = 1.0.[8]

References

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H_2O_2 + $h\nu \rightarrow$ products

Primary photochemical processes

Reactions	$\Delta H^\circ_{298}/kJ\cdot mol^{-1}$	$\lambda_{threshold}$/nm
$H_2O_2 + h\nu \rightarrow HO + HO$ (1)	215	557
$\rightarrow H_2O + O(^1D)$ (2)	333	359
$\rightarrow H + HO_2$ (3)	368	324
$\rightarrow HO + HO(^2\Sigma)$ (4)	606	197

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190–254	Holt, McLane and Oldenberg, 1948[1]	(a)
195–350	Lin, Rohatgi and DeMore, 1978[2]	(b)
190–350	Molina and Molina, 1981[3]	(c)
193–350	Nicovich and Wine, 1988[5]	(d)
210–345	Vaghjiani and Ravishankara, 1989[6]	(e)

Quantum yield data

$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 1.0$	253.7	Volman, 1963[7]	(f)
$\phi_1 = 1.04 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[8]	(g)
$\phi_2 < 0.002$	248		
$\phi_3 < 0.0002$	248		

Comments

(a) Measured at 298 K. Intensity measurements used photographic plate densitometry. H_2O_2 was measured by titration with $KMnO_4$.

(b) Flowing mixtures of H_2O_2 in He. H_2O_2 was measured by reaction with Fe^{2+}. 10 cm path length for $\lambda < 275$ nm; White-optics (1 m path length) for $\lambda > 275$ nm.

(c) Measured at 298 K with a spectral resolution of 0.3–0.5 nm. These results supersede the earlier results of Molina *et al.*[4] which were slightly higher.

(d) Relative cross-sections measured over the temperature range 300–380 K and at 285 K for the wavelength range 230–295 nm. Room temperature literature values at 202.6 and at 228.8 nm were used for absolute calibration. A significant temperature dependence was observed for the wavelength range 310–350 nm, and a simple model was used to extrapolate the results to lower temperatures. Upper tropospheric photodissociation rates were calculated.

(e) Flowing mixture of H_2O_2 in He. H_2O_2 was measured by reaction with Fe^{2+} or with I^-. A diode array spectrometer was used for relative measurements (1.0 nm resolution) and the results placed on an absolute basis by absolute measurement of cross-sections at 213.9 (Zn lamp) and 253.7 nm (Hg lamp). Temperature was 297 K.

(f) Based on a measured overall quantum yield for H_2O_2 removal of $\phi(-H_2O_2) = 1.7 \pm 0.4$ and the assumed mechanism, $H_2O_2 + h\nu \rightarrow 2HO$, $HO + H_2O_2 \rightarrow H_2O + HO_2$, and $2HO_2 \rightarrow H_2O_2 + O_2$. This interpretation has been criticized by Greiner.[9]

(g) Photolysis of flowing mixtures of H_2O_2–H_2O–N_2 (or He) and of O_3–H_2O–N_2 (or He) at 298 K. H_2O_2 and O_3 were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO formation from H_2O_2–H_2O mixture was measured relative to that from O_3–H_2O mixture. These relative yields were placed on an absolute basis using the known quantum yield of OH radical production from the photolysis of O_3–H_2O mixtures at 248 nm, taken as $\phi(OH) = 1.73 \pm 0.09$.[8,10] O and H yields determined by resonance fluorescence.

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_1	λ/nm	$10^{19}\ \sigma/cm^2$	ϕ_1
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5	1.0	285	1.5	1.0
205	40.8	1.0	290	1.2	1.0
210	35.7	1.0	295	0.90	1.0
215	30.7	1.0	300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

Comments on Preferred Values

The measurements of the absorption cross-sections are in excellent agreement. The preferred values are the means of those determined by Lin *et al.*,[2] Molina and Molina,[3] Nicovich and Wine[5] and Vaghjiani and Ravishankara.[6] These agree with the earlier values of Holt *et al.*[1]

The absorption cross-section has also been measured at other temperatures by Troe[11] (220–290 nm at 600 K and 1100 K) and by Nicovich and Wine[5] (260–350 nm, 200–400 K). Both Nicovich and Wine[5] and Troe[11] have expressed their results in an analytical form.

It has long been assumed that channel (1) is the only significant primary photochemical process at $\lambda > 200$ nm, but until recently the only experimental evidence for that came from the measurements of Volman.[7] A careful study by Vaghjiani and Ravishankara[8] has now confirmed that this is the case at 248 nm and they conclude that it is safe to assume this value of $\phi_1 = 1$ for all wavelengths of interest in atmospheric modeling. However, it should be noted that H atom production with a quantum yield of 0.12 at $\lambda = 193$ nm has been observed by Gerlach-Meyer *et al.*[12] Thus at some wavelength close to 200 nm processes alternative to channel (1) may begin to become significant.

References

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4.3. Nitrogen Species

$O + NO + M \rightarrow NO_2 + M$

$\Delta H^\circ = -306.2$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$1.0 \times 10^{-31}(T/300)^{-1.6}$ [N_2]	200–300	CODATA, 1980[1]; CODATA, 1984[2]	(a)
$9.0 \times 10^{-32}(T/300)^{-1.5}$ [air]	200–300	NASA, 1990[3]	(b)

Comments

(a) Average of the data from Schieferstein *et al.*[4] and Whytock *et al.*[5]

(b) Based on the data of Ref. 4 and their reanalysis of the data of Ref. 5.

Preferred Values

$k_0 = 1.0 \times 10^{-31}(T/300)^{-1.6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 0.3$.

Comments on Preferred Values

Within the error limits, the preferred values from the most recent work[4] encompass most of the earlier measurements reviewed in Ref. 1.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$3.1 \times 10^{-11}(T/300)^{0.3}$	300–1500	CODATA, 1980[1]	(a)
3.0×10^{-11}	200–300	NASA, 1990[3]	(b)

Comments

(a) Based on the relative rate measurements of Hippler et al.,[6] slightly modified using the more recent value of $k(O + NO_2 \rightarrow O_2 + NO) = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The temperature coefficient was calculated theoretically in Ref. 7.
(b) Based on Ref. 1.

Preferred Values

$k_\infty = 3.0 \times 10^{-11}(T/300)^{0.3}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–1500 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.3$.

Comments on Preferred Values

A reconfirmation by an absolute rate measurement is required. A broadening factor $F_c = 0.85$ at 300 K was estimated, which would correspond to an estimated temperature dependence of $F_c = \exp(-T/1850)$.

References

[1]CODATA, 1980 (see references in Introduction).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
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[6]H. Hippler, C. Schippert, and J. Troe, Int. J. Chem. Kinet. Symp. **1**, 27 (1975).
[7]M. Quack and J. Troe, Ber. Bunsenges Phys. Chem. **78**, 240 (1974).

$O + NO_2 \rightarrow O_2 + NO$

$\Delta H° = -192$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.00 \pm 0.10) \times 10^{-11}$	298	Ongstad and Birks, 1984[1]	(a)
$6.58 \times 10^{-12} \exp[(142 \pm 23)/T]$	224–354	Ongstad and Birks, 1986[2]	(a)
$(1.03 \pm 0.09) \times 10^{-11}$	298		
$5.21 \times 10^{-12} \exp[(202 \pm 27)/T]$	233–357	Geers-Muller and Stuhl, 1987[3]	(b)
$(1.02 \pm 0.02) \times 10^{-11}$	301		
Reviews and Evaluations			
$6.5 \times 10^{-12} \exp(120/T)$	200–300	IUPAC, 1989[4]	(c)
$6.5 \times 10^{-12} \exp(120/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system at 2.3 Torr total pressure. Decay of oxygen atoms in excess NO_2 monitored by chemiluminescent reaction with NO.
(b) H_2-laser photolysis system at 6.0 Torr total pressure. Oxygen atoms generated by NO photolysis and their decay in excess NO_2 monitored by chemiluminescent reaction with NO. Values of rate coefficients for reactions of oxygen atoms with N_2O_4 and N_2O_5 at 199 K were estimated.
(c) See Comments on Preferred Values.
(d) Based on data of Davis et al.,[6] Bemand et al.,[7] Slanger et al.,[8] Ongstad and Birks[2] and Geers-Muller and Stuhl.[3]

Preferred Values

$k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.5 \times 10^{-12} \exp(120/T)$ cm^3 molecule^{-1} s^{-1} over the range 230–350 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 120$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred value at 298 K is the average of the values reported by Ongstad and Birks,[1] Geers-Muller and Stuhl,[2] Davis et al.,[6] Bemand et al.[7] and Slanger et al.[8] The recommended temperature dependence results from a least-squares fit to the data of Ongstad and Birks,[2] Geers-Muller and Stuhl[3] and Davis et al.,[6] and the pre-exponential factor has been adjusted to fit the preferred value of k(298 K).

References

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$O + NO_2 + M \rightarrow NO_3 + M$

$\Delta H° = -218$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$9.0 \times 10^{-32}(T/300)^{-2.0}$ [N_2]	200–400	CODATA, 1980[1]; IUPAC, 1989[2]	(a)
$9.0 \times 10^{-32}(T/300)^{-2.0}$ [air]	200–300	NASA, 1990[3]	(b)

Comments

(a) Based on the relative rate measurements by Harker and Johnston[4] and Hippler *et al.*[5] The temperature coefficient was calculated from a theoretical analysis.[6]
(b) Based on Ref. 1.

Preferred Values

$k_0 = 9.0 \times 10^{-32}(T/300)^{-2.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values
Since the preferred values are from relative rate data, absolute rate measurements are required. Changes of the reference rate constant for $k(O + NO_2 \rightarrow O_2 + NO)$ from the originally used value of 9.3×10^{-12} cm^3 molecule^{-1} s^{-1} to 9.7×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (this evaluation) does not influence the preferred value.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2.2×10^{-11}	200–400	CODATA, 1980[1]; IUPAC, 1989[2]	(a)
2.2×10^{-11}	200–300	NASA, 1990[3]	(b)

Comments

(a) Based on the relative rate measurements of Hippler *et al.*[5]
(b) Based on reference 1.

Preferred Values

$k_\infty = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_\infty = \pm 0.2$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values
See comments on k_0.

Intermediate Falloff Range
A broadening of the falloff curve, with $F_c(300\ K) = 0.8$ and an estimated temperature dependence of $F_c = \exp(-T/1300)$, has to be taken into account. The preferred k_0 and k_∞ values depend on the F_c value chosen.

References

[1]CODATA, 1980 (see references in Introduction).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
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$O + NO_3 \rightarrow O_2 + NO_2$

$\Delta H^\circ = -280$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.6) \times 10^{-11}$	297	Canosa-Mas, Carpenter and Wayne, 1989[1]	(a)
Reviews and Evaluations			
1.0×10^{-11}	298	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
1.0×10^{-11}	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection for $O(^3P)$ atoms; NO_3 detected by absorption at $\lambda = 662$ nm using $\sigma = 1.9 \times 10^{-17}$ cm^2 molecule^{-1}. NO_3 was in excess over $O(^3P)$ but not sufficient to give purely first order kinetics. Analysis was conducted to take account of the consequences of complex kinetics, secondary reactions and possible contribution of H atom reactions.

(b) Based on the results of Graham and Johnston.[5]

(c) As in comment (b); temperature independence based on analogy with the $O + NO_2$ reaction.

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is that reported by Canosa-Mas *et al.*,[1] which is the only direct measurement of this rate coefficient. The earlier relative rate value of Graham and Johnston[5] is consistent with the preferred value taking into account the experimental uncertainties. The temperature dependence is probably near zero by analogy with the reaction of $O(^3P)$ atoms with NO_2.

References

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$O(^1D) + N_2 \rightarrow O(^3P) + N_2$

$\Delta H^\circ = -189.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.1) \times 10^{-11}$	295	Amimoto *et al.*, 1979[1]	(a)
$(2.77 \pm 0.40) \times 10^{-11}$	298	Brock and Watson, 1980[2]	(b)
$(2.52 \pm 0.25) \times 10^{-11}$	297	Wine and Ravishankara, 1981[3]	(b)
Reviews and Evaluations			
$3.2 \times 10^{-11} \exp(107/T)$	200–350	CODATA, 1980[4]; IUPAC, 1989[5]	(c)
$1.8 \times 10^{-11} \exp(107/T)$	200–300	NASA, 1990[6]	(d)

Comments

(a) Pulsed photolysis of O_3 at 248 nm with a KrF excimer laser. The rate of appearance of the product $O(^3P)$ was monitored by resonance absorption at 130 nm.
(b) Laser flash photolysis of O_3 at 266 nm with a frequency quadrupled Nd:Yag laser. The rate of appearance of product $O(^3P)$ was monitored by resonance fluorescence at 130 nm.
(c) Based on averaging the room temperature results of Streit *et al.*,[7] Heidner *et al.*[8] and Cvetanovic's review of relative rate data.[9] The temperature dependence was from Streit *et al.*[7]
(d) Based on the room temperature results of Refs. 1–3 and 7. The temperature dependence was from Streit *et al.*[7]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-11} \exp(107/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability
$\Delta\log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values
This data sheet is reproduced in part from our previous evaluation, CODATA, 1982.[4] The preferred value at room temperature is the average of the results reported in Refs. 1–3 and 7, all of which are in close agreement. The weight of evidence from these studies lead us to reject the higher value reported by Heidner *et al.*[8] The temperature dependence of Ref. 7 is accepted, and the pre-exponential factor has been adjusted to fit the preferred room temperature value.

References

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[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
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[9]R. J. Cvetanovic, Can. J. Chem. **52**, 1452 (1974).

$O(^1D) + N_2O \rightarrow N_2 + O_2$ (1)
$\rightarrow 2NO$ (2)
$\rightarrow O(^3P) + N_2O$ (3)

$\Delta H°(1) = -521.0$ kJ·mol^{-1}
$\Delta H°(2) = -340.4$ kJ·mol^{-1}
$\Delta H°(3) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.20 \pm 0.1) \times 10^{-10}$	295	Amimoto *et al.*, 1979[1]	(a)
$(1.17 \pm 0.12) \times 10^{-10}$	298	Wine and Ravishankara, 1981[2]	(b)
Relative Rate Coefficients			
1.04×10^{-10}	298	Lam *et al.*, 1981[3]	(c)
Branching Ratios			
$k_2/k = 0.62 \pm 0.02$	298	Marx, Bahe and Schurath, 1979[4]	(d)
$k_2/k = 0.62 \pm 0.09$	177–296	Lam *et al.*, 1981[3]	(c)
$k_3/k = 0.12 \pm 0.04$	295	Amimoto *et al.*, 1979[1]	(a)
$k_3/k = 0$	295	Amimoto *et al.*, 1980[5]	(e)
Reviews and Evaluations			
$k_1 = 4.4 \times 10^{-11}$	200–350	CODATA, 1982[6]; IUPAC, 1989[7]	(f)
$k_2 = 7.2 \times 10^{-11}$			
$k_1 = 5.1 \times 10^{-11}$	200–300	NASA, 1990[8]	(g)
$k_2 = 6.6 \times 10^{-11}$			

(a) Pulsed photolysis of O_3 at 248 nm with a KrF excimer laser. The rate of appearance of the product $O(^3P)$ was monitored by resonance absorption at 130 nm.
(b) Laser flash photolysis of O_3 at 266 nm with a frequency quadrupled Nd: Yag laser. The rate of appearance of the product $O(^3P)$ was monitored by resonance fluoroscence at 130 nm.
(c) Steady state photolysis of N_2O–N_2–He mixtures with a Hg lamp (185 and 254 nm), a Zn lamp (214 nm), and a D_2 lamp (200–235 nm with a maximum output at 235 nm). The amount of NO produced was measured with a chemiluminescent NO analyzer. The rate coefficient ratio $k/k(O(^1D) + N_2) = 4.0 \pm 0.4$ was determined by measuring the ratio of the NO produced in the absence of N_2 to that in the presence of N_2. The rate coefficient k given here is based on this reported ratio and $k(O(^1D) + N_2) = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). The quantity k_2/k was determined by measuring the pressure rise in the cell and the amount of NO produced. No dependence of this quantity on the kinetic energy of the $O(^1D)$ atom was observed.
(d) Steady state photolysis of N_2O–He mixtures at 185 nm and 206 nm. Most determinations of the branching ratio were based on measurement of the ratio $[N_2]/[O_2]$ every three minutes by GC. Independent confirmation of the results was obtained by determining the ratio $[N_2]/[O_2]$ using GC and an NO chemiluminscent analyzer. The branching ratio value given here has been determined by a procedure of back extrapolation to zero conversion. No dependence of this quantity on the kinetic energy of the $O(^1D)$ atom was observed.
(e) Re-examination of results reported by Amimoto *et al.*[1] The use of improved high-speed detection electronics gave a value of 0.85 ± 0.2 for the quantum yield for $O(^1D)$ production in the primary photolysis of O_3 at 248 nm. As a result of this new measurement, the observation of $O(^3P)$ atoms in the presence of N_2O, CH_4, and H_2O, previously attributed to quenching components in reactions of these species with $O(^1D)$, is now attributed to its direct production in the primary photolysis of O_3.
(f) Based on averaging the room temperature results of Davidson *et al.*,[9] Heidner and Husain[10] and Cvetanovic's review of relative ratio data.[11] The zero temperature dependence is from Davidson *et al.*[9] The branching ratio is based on the results of Davidson *et al.*[12] and Volltrauer *et al.*[13]
(g) Based on the absolute values reported in Refs. 1, 2 and 9 and the branching ratio results reported in Refs. 4, 12 and 13.

Preferred Values

$k_1 = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},
$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},
$k_3 < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},
all independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta(E_1/R) = \Delta(E_2/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[6] The preferred value of k at room temperature is the average of the absolute values reported by Amimoto *et al.*,[1] Wine and Ravishankara[2] and Davidson *et al.*[9] The weight of evidence from these studies leads us to reject the higher value of Heidner and Husain.[10] The temperature independence reported by Davidson *et al.*[9] is accepted.

In the calculation of the individual values of k_1 and k_2, the value of $k_2/k = 0.62$ is used. This value is from the study of Marx *et al.*[4] and is confirmed by the work of Lam *et al.*[3] The procedure of back extrapolation to zero conversion used in reference[4] appears to provide a reasonable explanation for the difference between this value and the lower values reported in Refs. 12 and 13, (0.56 and 0.52, respectively). It may be noted that the quantity actually used in the calculation of the individual value of k_1 and k_2 is k_2/k and that the values of this ratio reported in Refs. 3, 4, 12 and 13 show much less spread (0.52 to 0.62) than do the corresponding values of the more sensitive ratio k_1/k_2 from these same studies (0.61 to 0.92). The lack of any significant quenching component is based on the results reported in Refs. 5 and 12.

References

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$HO + NH_3 \rightarrow H_2O + NH_2$

$\Delta H° = -50$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.29×10^{-12} exp[(−922 ± 100)/T]	273–433	Diau, Tso and Lee, 1990[1]	(a)
$(1.47 \pm 0.07) \times 10^{-13}$	297		
Reviews and Evaluations			
3.5×10^{-12} exp(−925/T)	230–450	IUPAC, 1989[2]	(b)
3.6×10^{-12} exp(−930/T)	200–300	NASA, 1990[3]	(c)

Comments

(a) HO produced by conventional flash photolysis and pulsed laser photolysis of H_2O and H_2O_2 with LIF detection of HO. Total pressure varied over the range 68–504 Torr.

(b) Based on the results of Stuhl,[4] Smith and Zellner[5], Perry *et al*.,[6] Silver and Kolb[7] and Stephens.[8]

(c) Based on the data cited in comment (b).

Preferred Values

$k = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.5 \times 10^{-12} \exp(-925/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The results of Diau *et al*.[1] are in excellent agreement with the previously recommended Arrhenius expression, which was based on the results of Stuhl,[4] Smith and Zellner,[5] Perry *et al*.,[6] Silver and Kolb[7] and Stephens.[8] There is no change in the preferred value resulting from the inclusion of the new data of Diau *et al*.[1] The many high temperature studies have been considered by Jeffries and Smith[9] to derive a modified Arrhenius expression over an extended temperature range of $k = 1.58 \times 10^{-17} T^{1.8} \exp(-250/T)$ cm^3 molecule^{-1} s^{-1} for the temperature range of 225–2350 K.

References

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$HO + HONO \rightarrow H_2O + NO_2$

$\Delta H° = -168$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.80×10^{-11} exp[−(390 ± 80)/T]	278–342	Jenkin and Cox, 1987[1]	(a)
4.50×10^{-12}	295		
Relative Rate Coefficient			
$(6.3 \pm 0.3) \times 10^{-12}$	296	Cox, Derwent and Holt, 1976[2]	(b)
Reviews and Evaluations			
1.8×10^{-11} exp(−390/T)	280–340	IUPAC, 1989[3]	(c)

Comments

(a) Modulated photolysis of O_3 at 254 nm in presence of H_2O and HONO in Ar at 11 Torr pressure. The time-resolved behavior of OH radicals intermittently generated in presence of excess HONO was monitored by resonance absorption at 308 nm.
(b) Photolysis of HONO in presence of added H_2, CH_4, CO_2, CO, and NO at room temperature and atmospheric pressure. A rate coefficient ratio of $k/k(HO + H_2) = 945 \pm 48$ was measured. Value of k given here calculated using $k(HO + H_2) = 6.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(c) See Comments on Preferred Values.

Preferred Values

$k = 4.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-11} \exp(-390/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–340 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred value is based on the recent results of Jenkin and Cox.[1] This is the only direct determination of this rate coefficient. The agreement between these results at low pressure and the earlier, indirect results of Cox *et al.*[2] at atmospheric pressure suggests that any pressure dependence of this rate is small.

References

[1]M. E. Jenkin and R. A. Cox, Chem. Phys. Lett. **137**, 548 (1987).
[2]R. A. Cox, R. G. Derwent, and P. M. Holt, J. Chem. Soc. Faraday Trans. 1, **72**, 2031 (1976).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).

$HO + HONO_2 \rightarrow H_2O + NO_3$ (1)
$\rightarrow [H_2NO_4] \rightarrow H_2O + NO_3$ (2)

$\Delta H° = -82$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.4 \times 10^{-15} \exp(843/T)$	253–295	Devolder *et al.*, 1984[1]	(a)
$(9.3 \pm 1.0) \times 10^{-14}$	295		
$(1.26 \pm 0.11) \times 10^{-13}$	298	Jolly, Paraskevopoulos and Singleton, 1985[2]	(b)
$(2.16 \pm 0.15) \times 10^{-13}$ (10 Torr N_2)	248	Stachnik, Molina and Molina, 1986[3]	(c)
$(1.28 \pm 0.10) \times 10^{-13}$ (10 Torr N_2)	297		
Reviews and Evaluations			
See comment	220–300	IUPAC, 1989[4]	(d)
See comment	220–300	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. Arrhenius expression quoted applies to results obtained below room temperature. The rate coefficient was measured up to 373 K and found to level off above room temperature.
(b) Laser flash photolysis system with resonance absorption detection of HO. HO radicals generated by photolysis of HNO_3 at 222 nm. Value given is for pressures of 1–16 Torr HNO_3. Experiments also done in presence of 500 Torr N_2 and 600 Torr SF_6. After corrections for contribution of reaction OH + NO_2+M were made, no significant effect of total pressure on the rate coefficient was observed.
(c) Laser flash photolysis system with resonance absorption detection of HO. HO radicals generated by photolysis of HNO_3 at 193 nm. Measurements made at 10, 60, and 730 Torr of He, N_2, and SF_6. The HNO_3 was determined to contain less than 0.1% NO_2 impurity. Data were fit to fall-off function given in Lamb *et al.*[13] Extrapolated zero-pressure rate constants correspond to $E/R = -710$ K.
(d) See Comments on Preferred Values.
(e) Based on data of Wine *et al.*,[6] Margitan and Watson,[7] Kurylo *et al.*,[8] Jourdain *et al.*,[9] Marinelli and Johnston,[10] Smith *et al.*,[11] Ravishankara *et al.*[12] and data in Refs. 1–3. Data was fit to fall-off expression given in Lamb *et al.*[13]

Preferred Values

$k = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 atm pressure.
See comments for expression to be used under other conditions of temperature and pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] There have been many studies of this reaction recently which have significantly improved our understanding of the kinetics and mechanism. From these studies there is general consensus on the following major features of the data: a strong negative temperature dependence below room temperature with a much weaker temperature dependence above room temperature which appears to level off near 500 K, and (b) a small but measurable pressure dependence at room temperature which increases at low temperatures. The pressure dependence from 20–100 Torr and 225–298 K was determined by Margitan and Watson,[7] and Stachnik *et al.*[3] measured rate coefficients over the range 10–730 Torr at 297 K and 248 K. These studies agree on a 50% increase in the rate constant at the highest pressure studied at room temperature and a doubling of the low pressure limit at 240 K.

Lamb *et al.*[13] have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex. This mechanism gives a rate coefficient expression which combines a low pressure limiting rate constant (k_1) and a Lindemann-Hinshelwood expression for the pressure dependence. This mechanism has been used in the NASA evaluation,[5] and the expression derived in the NASA panel's analysis[5] has been adopted for the evaluation. The overall rate constant can be expressed as:

$$k = k_1(T) + k_2(M,T)$$

where

$$k_2(M,T) = k_3[M]/(1 + k_3[M]/k_4).$$

The expressions for the elementary rate constants are:

$k_1 = 7.2 \times 10^{-15} \exp(785/T)$ cm^3 molecule^{-1} s^{-1},
$k_3 = 1.9 \times 10^{-33} \exp(725/T)$ cm^6 molecule^{-2} s^{-1}, and
$k_4 = 4.1 \times 10^{-16} \exp(1440/T)$ cm^3 molecule^{-1} s^{-1};

all expressions are valid over the temperature range 220–300 K. This expression has been evaluated for the conditions of 298 K and 1 atm pressure to yield the preferred value given here. The reader is referred to Ref. 5 for a more detailed discussion of this reaction. Bossard *et al.*[14] and Singleton *et al.*[15] have reported a pressure and temperature dependence, respectively, of the rate constant for the related reaction $OD + DNO_3$.

References

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[4] IUPAC, Supplement III, 1989 (see references in Introduction).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).
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[13] J. J. Lamb, M. Mozurkewich, and S. W. Benson, J. Phys. Chem. **88**, 6441 (1984).
[14] A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, Chem. Phys. Lett. **134**, 583 (1987).
[15] D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Phys. Chem. **95**, 694 (1991).

$HO + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$ (1)
$\rightarrow H_2O_2 + NO_3$ (2)

$\Delta H°(1) = -191$ kJ·mol^{-1}
$\Delta H°(2) = -54$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.5 \pm 1.4) \times 10^{-12}$	268–295	Barnes *et al.*, 1986[1]	(a)
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(380/T)$	240–340	IUPAC, 1989[2]	(b)
$1.3 \times 10^{-12} \exp(380/T)$	240–340	NASA, 1990[3]	(c)

Comments

(a) Relative rate study over the pressure range 1–300 Torr (M=He, N_2) in a 420 L static reaction vessel. HO_2NO_2 monitored by FTIR spectroscopy; reference hydrocarbons (propene, *n*-butane) monitored by gas chromatography. Rate coefficients k(OH + propene) as a function of temperature and pressure were taken from Klein *et al.*[4] and Zellner and Lorenz.[5] The rate coefficient k(OH + butane) was taken as 2.5×10^{-12} cm^3 molecule^{-1} s^{-1} with an activation energy of 4.6 kJ·mol^{-1}. Rate coefficient was reported to be independent of temperature and pressure over the ranges studied.
(b) See Comments on Preferred Values.
(c) Based on data of Trevor *et al.*,[6] Smith *et al.*[7] and Barnes *et al.*[1,8]

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-12} \exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–340 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = {}^{+300\text{ K}}_{-600\text{ K}}$.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is based on a least-squares fit to the data of Trevor *et al.*,[6] Smith *et al.*,[7] and Barnes *et al.*[1] Trevor *et al.*[6] studied this reaction from 246–324 K at low pressure (3–15 Torr) and recommended a temperature independent value, but also reported an Arrhenius expression with $E/R = (193 \pm 194)$ K. In contrast, Smith *et al.*[7] report data from 240–340 K at one atmosphere pressure and report a negative temperature dependence with $E/R = -(650 \pm 30)$ K. It is possible that the difference may be due to the reaction being complex with different temperature dependences at low and at high pressure. The error limits on the recommended E/R value encompass the results of both studies. At 220 K the values deduced from these studies differ by a factor of three. The recent study of Barnes *et al.*,[1] the first study over an extended pressure range, found the rate coefficient to be independent of pressure from 5–300 Torr at 278 K and also report the same value at 295 K (low pressure) and at 268 K (100 Torr He). They also report no change with synthetic air as buffer gas. A TST calculation by Lamb *et al.*[9] suggests that the pressure dependence for this rate coefficient will be much less than that for the corresponding reaction of HO with HNO_3.

References

[1] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, Chem. Phys. Lett. **123**, 28 (1986).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] NASA Evaluation No. 9, 1990 (see references in Introduction).
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HO + NO + M → HONO + M

$\Delta H° = -209.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$7.4 \times 10^{-31}(T/300)^{-2.4}$ [N_2]	200–440	CODATA, 1980[1]; CODATA, 1984[2]	(a)
$7.0 \times 10^{-31}(T/300)^{-2.6}$ [air]	200–300	NASA, 1990[3]	(a)

Comments

(a) Average of a large series of consistent data published during the period 1972– 1983.

Preferred Values

$k_0 = 7.4 \times 10^{-31}(T/300)^{-2.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values have not been changed since 1984, because the data base appears fairly complete and consistency with theoretical analysis was obtained. The new high pressure measurements put the falloff contributions on a sounder basis.

High-pressure rate coefficients

Rate coefficient data

[illegible] cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
[illegible] Rate Coefficients			
[illegible] $\times 10^{-11}$	295	Forster *et al.*, 1991[4]	(a)
[illegible] and Evaluations			
1.0 $\times 10^{-11}$	220–400	CODATA, 1980[1]	(b)
[illegible] $\times 10^{-11}$	200–300	NASA, 1990[3]	(b)

Comments

(a) Laser flash photolysis in M = He at pressures up to 200 bar, with LIF detection of HO. The experiments approach the high pressure limit.
(b) Based on falloff extrapolations from pressures ≤ 1 bar.

Preferred Values

$k_\infty = 3.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values
The new high pressure experiments allow for the construction of complete falloff curves with $F_c = 0.8$. They supersede earlier estimates which were based on limited parts of the falloff curve near to the low pressure limit.

References

[1]CODATA, 1980 (see references in Introduction).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]R. Forster, M. J. Frost, H. Hippler, and J. Troe, to be published (1991); R. Forster, Ph.D. Thesis, Göttingen, 1991.

$HO + NO_2 + M \rightarrow HNO_3 + M$

$\Delta H° = -207.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$2.6 \times 10^{-30}(T/300)^{-2.9}$ [N_2]	200–400	CODATA, 1980[1]; CODATA, 1984[2]	(a)
$2.6 \times 10^{-30}(T/300)^{-3.2}$ [air]	200–300	NASA, 1990[3]	(b)

Comments

(a) Average of the data from Anastasi and Smith[4] and Burrows *et al.*,[5] which are in agreement with a series of other, older, experiments reviewed in Ref. 1.
(b) Average of a series of studies conducted prior to 1980.

Preferred Values

$k_0 = 2.6 \times 10^{-30}(T/300)^{-2.9}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$.

Comments of Preferred Values
The data base for this reaction is large. Because measurements have most often been made in the falloff region, different k_0 and k_∞ values are obtained if different F_c values are used. Different from the standard value $F_c = 0.6$ of the NASA evaluation,[3] this evaluation is based on a calculated value of $F_c = 0.43$ at 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.5×10^{-11}	298	Forster *et al.*, 1991[6]	(a)
Reviews and Evaluations			
5.2×10^{-11}	200–400	CODATA, 1980[1]; CODATA, 1984[2]	(b)
$2.4 \times 10^{-11}(T/300)^{-1.3}$	200–300	NASA, 1990[3]	(c)

Comments

(a) Laser flash photolysis in M = He at pressures up to 200 bar, with LIF detection of HO. The experiments approach the high pressure limit.
(b) Reevaluation of medium pressure experiments by Robertshaw and Smith,[7] which indicated that k_∞ is higher than 3×10^{-11} cm^3 molecule^{-1} s^{-1}.
(c) Essentially based on falloff extrapolations of measurements below 1 bar. The temperature dependence was from an RRKM model of Smith and Golden.[8]

Preferred Values

$k_\infty = 6.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new direct measurements at pressures up to 200 bar[6] allow for a more accurate extrapolation to the high pressure limit than did earlier attempts based on measurements below 1 bar.

Intermediate Falloff Range

The calculated[2] value of $F_c = 0.43$ at 300 K is consistent with the experimental measurements from Ref. 6.

References

[1]CODATA, 1980 (see references in Introduction).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]C. Anastasi and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **72**, 1459 (1976).
[5]J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **79**, 111 (1983).
[6]R. Forster, H. Hippler, A. Schlepegrell, and J. Troe, to be published (1991); R. Forster, Ph.D. Thesis, Göttingen, 1991.
[7]J. S. Robertshaw and I. W. M. Smith, J. Phys. Chem. **86**, 785 (1982).
[8]G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).

$HO + NO_3 \rightarrow HO_2 + NO_2$

$\Delta H^\circ = -56$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.6) \times 10^{-11}$	298	Mellouki, Le Bras and Poulet, 1988[1]	(a)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Boodaghians *et al.*, 1988[2]	(b)
Reviews and Evaluations			
2.3×10^{-11}	298	IUPAC, 1989[3]	(c)
2.3×10^{-11}	298	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with EPR monitoring of HO and HO_2 (after conversion to HO) in the presence of excess NO_3, which was measured by titration with NO or 2,3-dimethyl-2-butene. Complex kinetic behavior to extract k values.
(b) Discharge flow system with resonance fluorescence detection of HO. NO_3 was monitored by longpath absorption at 662 nm. H + NO_2 reaction used to generate HO and F + HNO_3 to produce NO_3, which was in excess over HO. The measured rate coefficient was corrected for secondary reactions which accelerate the HO decay.
(c) See Comments on Preferred Values.
(d) Average of data from Ref. 1 and 2.

Preferred Values

$k = 2.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The two measurements of this rate constant using the discharge flow technique[1,2] are in good agreement, although in both systems corrections for secondary reactions were required. The preferred value is a simple average of the two reported values. In the absence of experimental data a temperature dependence cannot be recommended. In line with other radical + radical reactions, a small negative temperature coefficient is expected.

References

[1]A. Mellouki, G. Le Bras and G. Poulet, J. Phys. Chem. **92**, 2229 (1988).
[2]R. B. Boodaghians, C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 931 (1988).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO_2 + NO \rightarrow HO + NO_2$

$\Delta H° = -32$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5 \pm 1.3) \times 10^{-12}$	297	Jemi-Alade and Thrush, 1990[1]	(a)
Reviews and Evaluations			
$3.7 \times 10^{-12} \exp(240/T)$	230–500	CODATA, 1982; IUPAC, 1989[2]	(b)
$3.7 \times 10^{-12} \exp(240/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with mid-infrared LMR monitoring of HO_2 in the presence of excess NO. HO_2 radicals were produced from the $F + H_2O_2$ reaction and the OH product was scavenged by reaction with C_2F_3Cl. The rate coefficient k was independent of pressure in the range 0.8–13 Torr.

(b) Based on the data of Hack *et al.*,[4] Howard,[5] Leu,[6] Margitan and Anderson[7] and Kaufman and Reimann,[8] using the temperature dependence of Howard.[9]

(c) Based on measurements near room temperature of Howard and Evenson,[10] Glaschick-Schimpf *et al.*,[11] Thrush and Wilkinson[12] and the data of Refs. 4–6, with the temperature dependence of Howard.[9]

Preferred Values

$k = 8.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.7 \times 10^{-12} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–500 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The new measurement of Jemi-Alade and Thrush[1] is in excellent agreement with the previously recommended value at room temperature and extends the range over which the pressure independence of the rate is demonstrated. Therefore there is no change in the recommendation. The preferred value at 298 K is a mean of the five determinations of Hack *et al.*,[4] Howard,[5] Leu,[6] Howard and Evenson[10] and Jemi-Alade and Thrush.[1] The data of Margitan and Anderson[7] and Kaufman and Reimann[8] were not included because they have not been published. The value reported by Glaschick-Schimpf *et al.*[11] of 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} is high, but in ageement within the stated uncertainty. The temperature dependence is that reported by Howard[9] for the combined temperature range 232–1271 K, based on high temperature data[9] and the low temperature data of Howard.[5] This temperature dependence measured over a very large temperature range is preferred to that reported by Leu[6] (E/R = 130 K) obtained over a much smaller temperature range.

References

[1]A. A. Jemi-Alade and B. A. Thrush, J. Chem. Soc. Faraday Trans. **86**, 3355 (1990).
[2]CODATA, Supplement I, 1982; IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

[4]W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner, and K. Hoyermann, Int. J. Chem. Kinet. **12**, 851 (1980).
[5]C. J. Howard, J. Chem. Phys. **71**, 2352 (1979).
[6]M.-T. Leu, J. Chem. Phys. **70**, 1662 (1979).
[7]J. J. Margitan and J. G. Anderson, results presented at the 13th Informal Conference on Photochemistry, Clearwater Beach, FL, January 1978.
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[9]C. J. Howard, J. Am. Chem. Soc. **102**, 6937 (1980).
[10]C. J. Howard and K. M. Evenson, Geophys. Res. Lett. **4**, 437 (1977).
[11]I. Glaschick-Schimpf, A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker, and E. H. Fink, Chem. Phys. Lett. **67**, 318 (1979).
[12]B. A. Thrush and J. P. T. Wilkinson, Chem. Phys. Lett. **81**, 1 (1981).

$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$

$\Delta H° = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.2 \times 10^{-31}(T/300)^{-2.4}$ [Ar]	275–326	Jemi-Alade and Thrush, 1990[1]	(a)
Reviews and Evaluations			
$1.8 \times 10^{-31}(T/300)^{-3.2}$ [N_2]	220–360	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
$1.8 \times 10^{-31}(T/300)^{-3.2}$ [air]	200–300	NASA, 1990[4]	(b)

Comments

(a) Discharge flow study in the range 0.8–13 Torr, with HO_2 radicals being monitored by LMR.
(b) Based on the data by Kurylo and Ouelette,[5] which are consistent with a series of earlier studies. Evaluation using a fixed standard value of $F_c = 0.6$, independent of temperature.

Preferred Values

$k_0 = 1.8 \times 10^{-31}(T/300)^{-3.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The new data are consistent with the series of earlier measurements reviewed in Refs. 1–3, which are now in excellent agreement. Refinement of F_c by calculations will lead to minor modifications of k_0.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
4.7×10^{-12}	200–300	CODATA, 1980[2]; IUPAC, 1989[3]	(a)
$4.7 \times 10^{-12}(T/300)^{-1.4}$	200–300	NASA, 1990[4]	(b)

Comments

(a) From falloff extrapolation of the data from Ref. 5 at pressures below 1 bar. A temperature independent value of k_∞ was chosen in agreement with other reaction systems.
(b) From falloff extrapolations of data from Ref. 5.

Preferred Values

$k_\infty = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See comment (a) for k_∞. Improved falloff extrapolations would require measurements above 1 bar and the use of a calculated value of F_c different from a fixed value of $F_c = 0.6$.

References

[1]A. A. Jemi-Alade and B. A. Thrush, J. Chem. Soc. Faraday Trans. **86**, 3355 (1990).
[2]CODATA, 1980 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]M. J. Kurylo and P. A Ouelette, J. Phys. Chem. **91**, 3365 (1987).

$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$

$\Delta H^\circ = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$5 \times 10^{-6} \exp(-10000/T)$ [N_2]	260–300	CODATA, 1982[1]	(a)

Comments

(a) Based on the experiments of Graham *et al.*,[2] conducted in the falloff range near to the low pressure limit.

Preferred Values

$k_0 = 1.3 \times 10^{-20}$ [N_2] s^{-1} at 298 K.
$k_0 = 5 \times 10^{-6} \exp(-10000/T)$ [N_2] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

More studies of the dissociation reaction appear desirable. By combining these preferred values with the corresponding recombination results, an equilibrium constant of $K_c = 1.8 \times 10^{-27} \exp(10900/T)$ cm^3 molecule^{-1} is obtained, in close agreement with the evaluation of Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$3.5 \times 10^{14} \exp(-10420/T)$	250–300	CODATA, 1982[1]	(a)
0.23	298		

Comments

(a) Based on the falloff data of Graham *et al.*[2] using, however, a broader falloff extrapolation.

Preferred Values

$k_\infty = 0.34$ s^{-1} at 298 K.
$k_\infty = 2.6 \times 10^{15} \exp(-10900/T)$ s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

Because the falloff curves for recombination have been determined more systematically, we have combined the corresponding high pressure limit for the recombination reaction with the equilibrium constant K_c (see comment to preferred values of k_0) to obtain k_∞. Since $F_c = 0.6$ was used for the falloff extrapolation of the recombination, an even larger value of k_∞ is expected if $F_c = 0.4$ is used.[1]

References

[1]CODATA, Supplement I, 1982 (see references in Introduction).
[2]R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., J. Chem. Phys. **68**, 4505 (1978).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$$HO_2 + NO_3 \rightarrow O_2 + HNO_3 \quad (1)$$
$$\rightarrow HO + NO_2 + O_2 \quad (2)$$

$\Delta H°(1) = -214$ kJ·mol^{-1}
$\Delta H°(2) = -6.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (9.2 \pm 4.8) \times 10^{-13}$	298	Mellouki, Le Bras and Poulet, 1988[1]	(a)
$k_2 = (3.6 \pm 0.9) \times 10^{-12}$			
$2.3 \times 10^{-12} \exp[(170 \pm 270)/T]$	263–338	Hall *et al.*, 1988[2]	(b)
4.06×10^{-12}	298		
Branching Ratios			
$k_2/k < 0.6$	298	Hall *et al.*, 1988[2]	(b)
Reviews and Evaluations			
4.3×10^{-12}	298	IUPAC, 1989[3]	(c)
4.1×10^{-12}	298	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with EPR monitoring of HO and HO_2 (after conversion to HO) in the presence of excess NO_3, which was measured by titration with NO or 2,3-dimethyl-2-butene. Complex kinetic behavior of HO and HO_2 modeled to extract $k(HO_2 + NO_3)$ and $k(HO + NO_3)$ for which a value of $(2.6 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained (see HO + NO_3 data sheet).
(b) Molecular modulation system with detection by UV (for HO_2) and visible (for NO_3) absorption spectroscopy. Used photolysis of Cl_2 in the presence of $ClONO_2$, H_2 and O_2 to produce the radicals. Rate coefficients obtained by computer fitting of complex kinetics. The upper limit of k_2/k was obtained from measurement of HO by modulated resonance absorption.
(c) See Comments on Preferred Values.
(d) Based on 298 K rate coefficient of Mellouki *et al.*[1] and the 263–333 K rate coefficients of Hall *et al.*[2]

Preferred Values

$k = 4.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC 1989.[3] The two recent direct studies[1,2] provide the only kinetic information on this reaction. The values obtained for the overall rate coefficient are in good agreement, despite the need in both cases to analyze complex kinetics to extract the k values. There is a discrepancy in the reported values for the branching ratio, although Hall *et al.*[2] accept that their measurements are not definitive. The preferred value at 298 K is a mean from the two studies.[1,2] No recommendation is made for the branching ratio or the temperature dependence because of the experimental uncertainties. For stratospheric modeling, a temperature independent rate with the branching ratio given by Mellouki *et al.*[1] is probably the best available choice.

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$NH_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1.5 \times 10^{-36}[N_2]$	295	Patrick and Golden, 1984[1]	(a)
$< 3 \times 10^{-18}$	298	Lozovsky, Ioffe and Sarkisov, 1984[2]	(b)
$< 7.7 \times 10^{-18}$	298	Michael *et al.*, 1985[3]	(c)
Reviews and Evaluations			
$< 3 \times 10^{-18}$	298	IUPAC, 1989[4]	(d)
$< 3 \times 10^{-18}$	298	NASA, 1990[5]	(e)

Comments

(a) Laser flash photolysis of O_3 at 248 nm in presence of NH_3. Decay of NH_2 monitored by laser resonance absorption spectroscopy at 598 nm. NH_2 decayed by reaction with O_3 and with NH_2. Up to 15 Torr O_2 added to system at total pressure of 230 Torr but no increase in decay rate was observed. Equivalent to a bimolecular rate constant $<1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.

(b) Flash photolysis of NH_3–O_2–N_2 mixtures at total pressures less than 30 Torr. NH_2 radical decay monitored by intracavity laser absorption spectroscopy at 598 nm. Decay rate observed to be independent of O_2 partial pressures above 1 Torr. Observed decay attributed to reaction $NH_2 + HO_2$.

(c) Flash photolysis – laser induced fluorescence study. NH_2 radicals produced by flash photolysis of NH_3 and observed in fluorescence at 578 nm after excitation by pumped dye laser. Total pressure of 25 Torr He. No increase in decay rate with increasing O_2 concentration observed at low flash energy. Additional experiments done in presence of sufficient C_2H_4 to scavenge H atoms formed in NH_3 photolysis.

(d) See Comments on Preferred Values.

(e) Based on the data of Lesclaux and Demissy,[6] Cheskis and Sarkisov,[7] Patrick and Golden,[1] Lozovsky *et al.*[2] and Michael *et al.*[3]

Preferred Values

$k < 3 \times 10^{-18}$ cm^3 molecule^{-1} s^1 at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred value is based on the upper limits reported by Lesclaux and Demissy,[6] Cheskis and Sarkisov,[7] Patrick and Golden,[1] Lozovsky *et al.*[2] and Michael *et al.*[3] In most systems HO_2 radicals were produced from the H atoms formed in the initial photolysis of NH_3, and NH_2 decay by reaction with HO_2 was observed. Patrick and Golden[1] produced NH_2 radicals in the absence of H atoms and observed no reaction with O_2. Hack *et al.*[8] produced NH_2 radicals in the absence of H atoms by the reaction of F atoms with NH_3 in a discharge flow reactor at low pressures and reported a third order reaction with O_2. However the weight of evidence from the other studies indicates that there is no observable reaction. It is possible that heterogeneous processes were important in their system. Hack and Kurzke[9] have studied the reaction of NH_2 with electronically excited $O_2(^1\Delta_g)$ and reported a rate coefficient of 1×10^{-14} cm^3 molecule^{-1} s^{-1} for this reaction.

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$NH_2 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.57 \times 10^{-11} \exp[-(1151 \pm 123)/T]$	272–348	Patrick and Golden, 1984[1]	(a)
$(3.25 \pm 0.27) \times 10^{-13}$	298		
$(1.5 \pm 0.3) \times 10^{-13}$	298	Cheskis *et al.*, 1985[2]	(b)
Reviews and Evaluations			
$4.9 \times 10^{-12} \exp(-1000/T)$	250–380	IUPAC, 1989[3]	(c)
$4.3 \times 10^{-12} \exp(-930/T)$	250–360	NASA, 1990[4]	(d)

Comments

(a) Laser flash photolysis of O_3 at 248 nm in presence of NH_3. Decay of NH_2 monitored by laser resonance absorption spectroscopy at 598 nm.

(b) Laser flash photolysis of O_3 at 266 nm in presence of NH_3. Decay of NH_2 monitored by laser induced fluorescence at 598 nm. Also measured rate coefficient for reaction of vibrationally excited NH_2 with O_3 and found it to be a factor of ten higher.

(c) See Comments on Preferred Values.

(d) Based on data of Bulatov *et al.*,[6] Hack *et al.*,[7] Patrick and Golden[1] and Cheskis *et al.*[2]

Preferred Values

$k = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.9 \times 10^{-12} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The reported rate coefficients at room temperature vary by a factor of five, ranging from 6×10^{-14} cm^3 molecule^{-1} s^{-1} in reference 5 to 3×10^{-13} in Ref. 1. There is no convincing argument for rejecting any of these results and therefore, as before,[3] the 298 K preferred value is taken as the average of the results reported by Kurasawa and Lesclaux,[5] Bulatov *et al.*,[6] Hack *et al.*,[7] Patrick and Golden[1] and Cheskis *et al.*[2] The temperature dependence averages the values reported by Kurasawa and Lesclaux,[5] Hack *et al.*[7] and Patrick and Golden.[1] Although the products of this reaction have not been determined, the most likely process is abstraction of an oxygen atom by NH_2 to give $NH_2O + O_2$. While it has been suggested[6,7] that NH_2 may be regenerated by reaction of NH_2O with O_3, recent work[1] indicates that this reaction must be slow.

References

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$$NH_2 + NO \rightarrow N_2 + H_2O \quad (1)$$
$$\rightarrow N_2H + HO \quad (2)$$
$$\rightarrow N_2 + H + HO \quad (3)$$

$\Delta H^\circ(1) = -517$ kJ·mol^{-1}
$\Delta H^\circ(3) = -18$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.31 \times 10^{-8}\ T^{-(1.17 \pm 0.25)}$	294–1027	Atakan *et al.*, 1989[1]	(a)
$(1.67 \pm 0.25) \times 10^{-11}$	298		
$2.0 \times 10^{-11}\ (T/298)^{-2.2}$	295–620	Bulatov *et al.*, 1989[2]	(b)
Branching Ratios			
$(k_2 + k_3)/k = 0.1 \pm 0.025$	300	Atakan *et al.*, 1989[1]	(c)
$(k_2 + k_3)/k = 0.12 \pm 0.03$	520		
$(k_2 + k_3)/k = 0.19 \pm 0.05$	1000		
$(k_2 + k_3)/k = 0.1 \pm 0.02$	295	Bulatov *et al.*, 1989[2]	(d)
$(k_2 + k_3)/k = 0.14 \pm 0.03$	470		
$(k_2 + k_3)/k = 0.2 \pm 0.04$	620		
Reviews and Evaluations			
$1.6 \times 10^{-11}\ (T/298)^{-1.5}$	230–450	IUPAC, 1989[3]	(e)
$3.8 \times 10^{-12} \exp(450/T)$	200–300	NASA, 1990[4]	(e)

Comments

(a) Pulsed laser photolysis of NH_3 at 193 nm and the time resolved HO formation monitored using LIF. NO in excess over NH_2 with $[NO]/[NH_2] \sim 10^3$. Pressure = 10 Torr N_2.

(b) Flash photolysis of NH_3 with NH_2 being measured by intracavity laser absorption spectroscopy. Psuedo-first order decays of NH_2 in the presence of excess NO measured. No tabulated rate coefficients given.

(c) HO yield measured directly with the HO calibration being based on HO production in laser photolysis of H_2O_2. Temperature dependence of NH_3 cross-section taken into account in determination of temperature dependence of the branching ratio.

(d) Branching ratio determined indirectly from the decrease in the decay rate for NH_2 at high NH_3 concentrations, assumed to be due to the reaction of product HO radicals with NH_3.

(e) Based on the data of Whyte and Phillips,[5] Dreier and Wolfrum,[6] Silver and Kolb,[7] Stief *et al.*,[8] Andresen *et al.*,[9] Gordon *et al.*,[10] Gehring *et al.*,[11] Hancock *et al.*,[12] Sarkisov *et al.*,[13] Lesclaux *et al.*[14] and Hack *et al.*[15]

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11}\ (T/298)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the range 210–500 K.
$(k_2 + k_3)/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.5$.
$\Delta (k_2 + k_3)/k = \pm 0.03$ at 298 K.

Comments on Preferred Values

The results of Atakan *et al.*[1] and of Bulatov *et al.*[2] at 298 K are in good agreement with the previous data from flash and laser photolysis studies but are significantly higher than rate coefficients obtained using the discharge flow technique. This apparent discrepancy has been noted before[3,4] and cannot be easily accounted for. The temperature dependence reported by Atakan *et al.*[1] is slightly lower than the majority of the earlier results, which were mainly obtained at $T < 500$ K, while the results of Bulatov *et al.*,[2] which also covered a smaller temperature range, give a significantly higher temperature dependence.

The preferred value at 298 K is the average of the two new determinations of Atakan *et al.*[1] and of Bulatov *et al.*[2] together with the values reported in references 5–15. The temperature dependence is based on the data below 500 K in the six temperature dependence studies of Silver and Kolb,[7] Stief *et al.*,[8] Lesclaux *et al.*,[14] Hack *et al.*,[15] Atakan *et al.*[1] and Bulatov *et al.*[2]

The direct measurements of the branching ratio reported by Atakan *et al.*[1] are the basis for the recommendation for $(k_2 + k_3)/k$. Other, less direct, rate coefficient ratio determinations are consistent with the value recommended, with the exception of the results of Andresen *et al.*[8] who report that the production of HO dominates; this discrepancy has not been explained.

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$NH_2 + NO_2 \rightarrow N_2O + H_2O$ (1)
$\rightarrow N_2 + H_2O_2$ (2)

$\Delta H^\circ(1) = -378$ kJ·mol^{-1}
$\Delta H^\circ(2) = -355$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.4) \times 10^{-11} (T/298)^{-1.7}$	295–620	Bulatov *et al.*, 1989[1]	(a)
Reviews and Evaluations			
$1.9 \times 10^{-11} (T/298)^{-2.2}$	250–500	IUPAC, 1989[2]	(b)
$2.1 \times 10^{-12} \exp(650/T)$	200–300	NASA, 1990[3]	(b)

Comments

(a) Flash photolysis of NH_3 with NH_2 radicals being measured by intracavity laser absorption spectroscopy. Psuedo-first order decay of NH_2 monitored in the presence of excess NO_2. Pressure range = 10–650 Torr.

(b) Based on the data of Whyte and Phillips,[4] Kurasawa and Lesclaux,[5] Xiang *et al.*[6] and Hack *et al.*[7]

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-11} (T/298)^{-2.0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta n = \pm 0.7$.

Comments on Preferred Values

The result of Bulatov *et al.*[1] at 298 K is in very good agreement with the previous results from flash and laser photolysis studies, but is significantly higher than the measurement of Hack *et al.*,[7] obtained using the discharge flow technique. This apparent discrepancy has been noted before[3,4] for this reaction and also for the reaction of NH_2 with NO, and cannot be easily accounted for. The temperature dependence reported by Bulatov *et al.*[1] lies midway between the earlier data of Hack *et al.*[7] and Kurasawa and Lesclaux,[5] and is close to the previously recommended value for n. The preferred value at 298 K is the average of the values from Refs. 1, 4, 5, 6 and 7. The temperature dependence is the average from Refs. 1, 5 and 7. Hack *et al.*,[7] using mass spectrometric analysis, determined that the predominant reaction channel is channel (1) to give $N_2O + H_2O$, with at least 95% of the reaction proceeding by this channel.

References

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$2\ NO + O_2 \rightarrow 2\ NO_2$

$\Delta H = -114$ kJ·mol^{-1}

Rate coefficient data

k/cm^6 molecule^{-2} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.1) \times 10^{-38}$	298	Stedman and Niki, 1973[1]	(a)
$(2.4 \pm 0.4) \times 10^{-38}$	298	Brobst and Allen, 1989[2]	(b)
$1.8 \times 10^{-47}\ T^{2.7} \exp(1600/T)$	226–758	Olbregts, 1985[3]	(c)
2.1×10^{-38}	298		
Reviews and Evaluations			
$3.3 \times 10^{-39} \exp(530/T)$	273–660	IUPAC, 1989[4]	(d)

Comments

(a) Photolysis of NO_2 (1–100 part-per-million mixing ratio) in air using NO/O_3 chemiluminescence detectors.

(b) Intracavity dye laser absorption spectroscopy system. Total pressure ranged from 3.9 to 7.4 Torr. $[NO]/[O_2] > 1000$. Production of NO_2 monitored at 610 nm.

(c) Static one liter reactor. Total pressure measured with differential micromanometer. Partial pressure of NO_2 measured in absorption at 436 nm. Pressure of O_2 and NO range up to 26 Torr. Non-Arrhenius behavior observed with k first decreasing with increasing temperature, reaching a minimum value at 600 K and then increasing with increasing temperature.

(d) See Comments on Preferred Values.

Preferred Values

$k = 2.0 \times 10^{-38}$ cm^6 molecule^{-2} s^{-1} at 298 K.

$k = 3.3 \times 10^{-39} \exp(530/T)$ cm^6 molecule^{-2} s^{-1} over the temperature range 273–600 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] This evaluation accepts the recommendation given in the evaluation by Baulch *et al.*[5] The room temperature value has been confirmed by the newer studies. Olbregts[2] observed non-Arrhenius behavior over the entire temperature range studied and expressed k by the modified Arrhenius expression given here and also as the sum of two Arrhenius expressions. However, from 250 K to about 600 K the total rate coefficient of Olbregts[2] is in good agreement with the value calculated from the expression recommended here. Olbregts[2] interpreted his results in terms of a multi-step mechanism involving NO_3 or the dimer $(NO)_2$ as intermediates. For atmospheric modeling papers, the expression recommended here is adequate.

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$NO + O_3 \rightarrow NO_2 + O_2$

$\Delta H^\circ = -200\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.6 \times 10^{-12} \exp[-(1435 \pm 64)/T]$	195–369	Michael, Allen and Brobst, 1981[1]	(a)
$(2.0 \pm 0.2) \times 10^{-14}$	298		
$8.9 \times 10^{-19} T^{2.2} \exp(-765/T)$	204–353	Borders and Birks, 1982[2]	(b)
$(1.72 \pm 0.04) \times 10^{-14}$	298		
Reviews and Evaluations			
$1.8 \times 10^{-12} \exp(-1370/T)$	195–304	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$2.0 \times 10^{-12} \exp(-1400/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Three independent low-pressure fast flow studies under pseudo-first-order conditions. Extent of reaction was monitored by NO_2 chemiluminescence under conditions of excess NO or excess O_3. In other experiments, the decay of NO in excess O_3 was monitored by resonance fluorescence. The data from each study were in good agreement. The data showed significant curvature on an Arrhenius plot, and the value of E/R varied from 1258 K (195–260 K) to 1656 K (260–369 K).

(b) Dual flow tube technique with NO_2 chemiluminescence detection under pseudo-first-order conditions of the decay of NO in the presence of excess O_3. Authors claim this technique gives accurate value of E/R over temperature intervals as small as 10 K. Nonlinear Arrhenius behavior was observed with value of E/R increasing from a value of 1200 K at the lowest temperature to 1470 K at the highest temperatures.

(c) See Comments on Preferred Values.

(d) Based on least-squares analysis of the data from 195–304 K reported by Michael *et al.*,[1] Borders and Birks,[2] Lippmann *et al.*,[6] Ray and Watson[7] and Birks *et al.*[8]

Preferred Values

$k = 1.8 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.8 \times 10^{-12} \exp(-1370/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 195–304 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The preferred Arrhenius expression is based on least-squares analysis of the data at and below room temperature reported by Michael *et al.*,[1] Borders and Birks,[2] Lippmann *et al.*,[6] Ray and Watson[7] and Birks *et al.*,[8] with data at closely spaced temperatures reported by Borders and Birks[2] and Lippmann *et al.*[6] being grouped to give equal weight to each of the five studies. The expression fits these data to within 20%. Only data between 195 and 304 K were used due to the nonlinear Arrhenius behavior observed by Michael *et al.*,[1] Borders and Birks,[2] Birks *et al.*,[8] Clyne *et al.*[9] and Clough and Thrush.[10] Michael *et al.*,[1] Birks *et al.*,[8] Clyne *et al.*[9] and Schurath *et al.*[11] have reported individual Arrhenius parameters for each of two primary reaction channels (one to produce NO_2 in the ground electronic state and the other to produce electronically excited NO_2). Earlier room-temperature results of Stedman and Niki[12] and Bemand *et al.*[13] are in good agreement with the preferred value.

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$NO + NO_3 \rightarrow 2\ NO_2$

$\Delta H^\circ = -88$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.55 \times 10^{-11} \exp(195/T)$	209–299	Hammer, Dlugokencky, and Howard, 1986[1]	(a)
$(2.95 \pm 0.16) \times 10^{-11}$	299–414		
$1.59 \times 10^{-11} \exp(122/T)$	224–328	Sander and Kircher, 1986[2]	(b)
$(2.41 \pm 0.48) \times 10^{-11}$	298		
$1.68 \times 10^{-11} \exp(103/T)$	223–400	Tyndall *et al.*, 1991[3]	(c)
$(2.34 \pm 0.24) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(2 \pm 1) \times 10^{-11}$	298	Croce de Cobos, Hippler and Troe, 1984[4]	(d)
Reviews and Evaluations			
$1.6 \times 10^{-11} \exp(150/T)$	200–300	IUPAC, 1989[5]	(e)
$1.7 \times 10^{-11} \exp(150/T)$	200–300	NASA, 1990[6]	(f)

Comments

(a) Flow tube reactor. NO_3 radicals were produced by the reaction $F + HNO_3$ and by thermal decomposition of N_2O_5, and detected by LIF in the presence of excess NO. Non-linear Arrhenius behavior was observed over the temperature range 209–414 K, with a constant value of the rate coefficient above room temperature.

(b) Flash photolysis system with NO_3 decay in excess NO monitored by optical absorption at 661.8 nm. NO_3 was produced by photolysis of Cl_2–$ClONO_2$ mixtures at wavelengths longer than 300 nm. The total pressure was varied from 50–700 Torr He, N_2.

(c) Discharge flow system with the NO_3 decay in excess NO being monitored by LIF. NO_3 was produced by the reaction $F + HNO_3$ and by the thermal reaction of NO_2 with O_3. In other experiments, the decay of NO in excess NO_3 (from $F + HNO_3$) was monitored by chemiluminescence. The room temperature value given is the mean of the results from the three experimental systems.

(d) Derived from numerical simulation of study of the recombination reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ at high pressures.

(e) Based on the data of Hammer *et al.*[1] and Sander and Kircher.[2]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(110/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature values reported by Hammer *et al.*,[1] Sander and Kircher[2] and Tyndall *et al.*,[3] which are in excellent agreement. The preferred temperature dependence is the average of the temperature dependences reported by Sander and Kircher[2] and by Tyndall *et al.*,[3] which are in excellent agreement.

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[6] NASA Evaluation No. 9, 1990 (see references in Introduction).

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H° = -112$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.45 \pm 0.12) \times 10^{-17}$	296	Cox and Coker, 1983[1]	(a)
$2.97 \times 10^{-13} \exp[-(2620 \pm 90)/T]$	277–325	Verhees and Adema, 1985[2]	(b)
Reviews and Evaluations			
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	IUPAC, 1989[3]	(c)
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	NASA, 1990[4]	(d)

Comments

(a) Static system. Experiments done both with NO_2 and O_3 in excess. Time-resolved absorption spectroscopy used to monitor N_2O_5 with a diode laser infrared source. NO_2 and O_3 also monitored at 350 and 255 nm, respectively, using conventional UV techniques. Total pressure was 10 Torr N_2. N_2O_5 was shown to be the only stable nitrogen-containing product. The overall stoichiometry for reactant decay, defined as $\Delta NO_3/\Delta O_3$, was determined to be 1.85 ± 0.09. A minor role for unsymmetrical NO_3 species was suggested to account for the stoichiometric factor having a value less than 2.

(b) Continuous stirred tank reactor flow system. NO_2 and O_3 were present at sub-part-per-million concentrations. Chemiluminescent analysis. Wall reactions were found to be very important. Relative humidity levels up to 80% did not affect the value of the rate constant.

(c) See Comments on Preferred Values.

(d) Based on data of Davis *et al.*,[5] Graham and Johnston[6] and Huie and Herron.[7]

Preferred Values

$k = 3.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-13} \exp(-2450/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred value is unchanged from the previous IUPAC evaluation,[3] which was based on the data in the three temperature-dependent studies of Davis *et al.*,[5] Graham and Johnston[6] and Huie and Herron.[7] The recent results of Cox and Coker[1] are in excellent agreement with this recommendation. The recent results of Verhees and Adema[2] show a similar temperature dependence but a higher pre-exponential factor. It was shown that wall reactions play an important role in this study.[2] These results have not been included in the derivation of the preferred value, but may be considered to be in reasonable agreement with the recommendation.

References

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$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$\Delta H° = -92.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-30}(T/300)^{-3.5}$ [N_2]	236–358	Orlando *et al*., 1991[1]	(a)
Reviews and Evaluations			
3.0×10^{-30} [N_2]	298	Croce de Cobos, Hipper and Troe, 1984[2]	(b)
$2.7 \times 10^{-30}(T/300)^{-3.4}$ [N_2]	200–300	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$2.2 \times 10^{-30}(T/300)^{-4.3}$ [air]	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow study with LIF detection of NO_3. Experiments were conducted over the pressure range 0.5–8 Torr and the data evaluated using

$$F_c = \{2.5 \exp(-1950/T) + 0.9 \exp(-T/430)\} \ (F_c(298\ K) = 0.45).$$

(b) Analysis of high pressure recombination experiments and low pressure dissociation results[6,7] converted with equilibrium constants[8] using $F_c(298\ K) = 0.34$ from Ref. 9.

(c) Based on the recombination measurements of Croce de Cobos *et al*.,[2] Kircher *et al*.,[10] Smith *et al*.,[11] Burrows *et al*.[12] and Wallington *et al*.,[13] all of which give a consistent set of falloff curves.

$$F_c = [\exp(-T/250) + \exp(-1050/T)]$$

from Ref. 9 was employed for falloff extrapolation.

(d) See comment (c). In contrast, however, a value of $F_c = 0.6$ was used.

Preferred Values

$k_0 = 2.7 \times 10^{-30}(T/300)^{-3.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new measurements are in excellent agreement with the preferred values from the analyses of Refs. 2–4. The slightly different k_0 values of Ref. 5 arise from a falloff analysis with a larger fixed value of $F_c = 0.6$. The analysis with a theoretical F_c, such as from Ref. 9, is preferred.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-12}(T/300)^{-0.2}$	236–358	Orlando *et al*., 1991[1]	(a)
Reviews and Evaluations			
$2.0 \times 10^{-12}(T/300)^{0.2}$	200–500	CODATA, 1980[3]; IUPAC, 1989[4]	(b)
$1.5 \times 10^{-12}(T/300)^{-0.5}$	200–300	NASA, 1990[5]	(c)

Comments

(a) – (c) See comments (a) – (c) for k_0.

Preferred Values

$k_\infty = 2.0 \times 10^{-12}(T/300)^{0.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta\log k_\infty = \pm 0.2$ at 300 K.
$\Delta n = \pm 0.6$.

Comments of Preferred Values

The new experiments from Ref. 1 were performed at too low a total pressure to contribute to the falloff extrapolation to k_∞. The discrepancy between the IUPAC[4] and NASA[5] evaluations is due to the different values of F_c used.

Intermediate Falloff Range

Before more detailed falloff calculations are made, the expression $F_c = \{\exp(-T/250) + \exp(-1050/T)\}$ from Refs. 9 and 12 is recommended, which gives $F_c = 0.42$ at 220 K, 0.34 at 295 K, and 0.26 at 520 K. Expressions for increased width of the falloff curve should also be employed (see Introduction).

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$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

$\Delta H° = 92.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.0 \times 10^{-6} \exp(-9500/T)$ [N_2]		Cantrell *et al.*, 1990[1]	(a)
8.6×10^{-20} [N_2]	298		
Reviews and Evaluations			
$2.2 \times 10^{-3}(T/300)^{-4.4} \times \exp(-11080/T)$ [N_2]	220–300	CODATA, 1980[2]; CODATA, 1982[3]	(b)
1.6×10^{-19} [N_2]	298		

Comments

(a) N_2O_5 concentrations were monitored by FTIR in a temperature regulated long-path cell. An excess of NO was added to N_2O_5–N_2 mixtures in order to scavenge NO_3 and minimize the reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$. Preliminary data.

(b) Based on measurements by Connell and Johnston[4] and Viggiano *et al.*,[5] using the falloff extrapolation of Malko and Troe.[6]

Preferred Values

$k_0 = 1.6 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 2.2 \times 10^{-3}(T/300)^{-4.4} \exp(-11080/T)$ [N_2] s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta\log k_0 = \pm 0.2$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

Since more detailed data from Ref. 1 are not available, the preferred values from reference 3 remain unchanged. The discrepancies between the direct dissociation rate measurements, the direct recombination rate measurements (this evaluation), and some of the recent direct measurements of the equilibrium constant (Refs. 7–12) have not been resolved to date. When this is the case, recombination data will become convertible and improve the data base for the dissociation rates.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.4 \times 10^{14} \exp(-10980/T)$		Cantrell *et al.*, 1990[1]	(a)
5.3×10^{-2}	298		
Reviews and Evaluations			
$9.7 \times 10^{14}(T/300)^{0.1} \times \exp(-11080/T)$	200–300	CODATA, 1980[2]; CODATA, 1982[3]	(b)
6.9×10^{-2}	298		

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 6.9 \times 10^{-2}$ s^{-1} at 298 K.
$k_\infty = 9.7 \times 10^{14}(T/300)^{0.1} \exp(-11080/T)$ s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.
$\Delta n = \pm 0.2$.

Comments on Preferred Values
See Comments on Preferred Values for k_0.

Intermediate Falloff Range
The falloff expressions for dissociation and recombination are identical. Therefore, the same expression of

$$F_c = \{\exp(-T/250) + \exp(-1050/T)\}$$

is used as for the recombination reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (see this evaluation).

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[13]NASA Evaluation No. 9, 1990 (see references in Introduction).

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$\Delta H = -33$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1.3 \times 10^{-21}$	298	Tuazon *et al.*, 1983[1]	(a)
$<1.5 \times 10^{-21}$	298	Atkinson *et al.*, 1986[2]	(b)
$<1.1 \times 10^{-21}$	296	Hjorth *et al.*, 1987[3]	(c)
$<3 \times 10^{-22}$	298	Sverdrup, Spicer and Ward, 1987[4]	(d)
$<2.8 \times 10^{-21}$	296	Hatakeyama and Leu, 1989[5]	(e)
Reviews and Evaluations			
$<2 \times 10^{-21}$	298	IUPAC, 1989[6]	(f)
$<2 \times 10^{-21}$	298	NASA, 1990[7]	(f)

Comments

(a) N_2O_5 decay rates in two large volume (3800 and 5800 L) Teflon or Teflon-coated environmental chambers observed by FTIR absorption.
(b) Same as (a) except that a 2500–L Teflon chamber replaced the 3800–L Teflon chamber. Authors suggest that observed decay proceeded only by heterogeneous processes.
(c) N_2O_5 decay rates in a 1500–L FEP-Teflon bag observed by FTIR absorption.
(d) Large volume (17300–L) Teflon-lined chamber. Concentration profiles for O_3, total nitrogen oxides and NO_2 were measured and were calculated for N_2O_5 and HNO_3. Results modeled with kinetic mechanism of eleven gas phase reactions and five heterogeneous reactions.
(e) N_2O_5 decays monitored in a 320–L Pyrex chamber by FTIR absorption spectroscopy.
(f) Based on data of Tuazon *et al.*,[1] Atkinson *et al.*[2] and Hjorth *et al.*[3]

Preferred Values

$k < 2 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is based on data of Tuazon *et al.*,[1] Atkinson *et al.*,[2] Hjorth *et al.*[3] and Hatakeyama and Leu.[5] It is possible that the observed decays proceed only by heterogenous processes. While the lower value of Sverdrup *et al.*[4] may in fact be closer to the value of the rate coefficient for the homogeneous gas phase reaction, because it is less direct we prefer the more conservative recommendation given here.

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[6]IUPAC, Supplement III, 1989 (see references in Introduction).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).

HONO + $h\nu$ → products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HONO + $h\nu$ → HO + NO	(1)	202	591
→ H + NO_2	(2)	326	367
→ HNO + O(^{3}P)	(3)	423	283

Absorption cross-section data

Wavelength range/nm	Reference	Comments
185–270	Kenner, Rohrer and Stuhl, 1986[1]	(a)
310–393	Vasudev, 1990[2]	(b)
300–400	Bongartz *et al.*, 1991[3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
Φ(OH*)	193	Kenner, Rohrer and Stuhl, 1986[1]	(d)

Comments

(a) Relative absorption spectrum measured in the range 185–270 nm with absolute determinations at 193 and 215 nm; $\sigma = 1.6 \times 10^{-18}$ cm^2 molecule^{-1} at 193 nm. Two different methods used to prepare HONO gave similar results. The σ values agreed with results of Cox and Derwent[4] in the wavelength region 220–270, but the peak at 215 nm seen in the earlier study,[3] which could have been due to NO absorption, was not observed.

(b) Relative absorption cross-sections determined by tunable laser photolysis with LIF detection of the HO product. Absolute values based on $\sigma = 4.97 \times 10^{-19}$ cm^2 molecule^{-1} at 354 nm reported by Stockwell and Calvert.[5] Measurements actually provide the product of the HONO cross-section and the quantum yield, ϕ_1.

(c) Absolute absorption cross-sections determined by conventional absorption spectroscopy, using low, non-equilibrium concentrations of HONO determined by a combination of gas phase and wet chemical analysis. Spectral resolution 0.1 nm; cross-sections averaged over 0.5 nm given in a table.

(d) Laser photolysis of nitrous acid at 193 nm. HO$^\bullet$ measured by emission spectroscopy. A low quantum yield of about 10^{-5} was determined.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	127	260	8.0	330	10.9
195	172	265	5.2	335	7.7
200	197	270	3.4	340	19.7
205	220	275	2.5	345	11.2
210	214	280	–	350	13.4
215	179	285	–	355	27.6
220	146	290	–	360	9.4
225	120	295	–	365	18.8
230	86	300	0.0	370	24.0
235	60	305	0.8	375	5.7
240	42	310	1.9	380	10.8
245	30	315	2.9	385	16.9
250	18.5	320	5.2	390	2.8
255	12.4	325	5.8	395	0.7

Quantum Yields

$\phi_1 = 1$ throughout this wavelength range.

Comments on Preferred Values

The new measurements of Bongartz *et al.*[3] were made under conditions less likely to lead to systematic error than those of Stockwell and Calvert,[4] on which the previous CODATA[6] evaluation was based. Thus, corrections for N_2O_3 and N_2O_4 were unnecessary,[3] and estimated errors were a factor of at least 3 less. The absolute cross-sections of the prominent bands at wavelengths >331 nm were 20% larger than the values of Stockwell and Calvert.[5] At <330 nm spectral features of the two studies were inconsistent.

The new relative data from Vasudev[2] in the 310–393 nm region have the advantage that the technique was insensitive to interference from absorption due to NO_2, which is unavoidably present in samples of HONO, and which requires correction in conventional absorption measurements. The relative cross sections are in good agreement with those of Bongartz *et al.*[3] and Stockwell and Calvert[5] (on which the previous CODATA[5] evaluation was based), except in the bands at shorter wavelengths (339, 331 and 318 nm) where the relative measurements are more than 20% lower.

The preferred values in the 300–395 nm range are obtained from the data of Bongartz *et al.*[3] by averaging their 0.5 nm average values over 5 nm intervals centered on the wavelengths specified in the table.

In the second absorption band, which lies at wavelengths <275 nm, the new data from Kenner *et al.*[1] quantitatively confirm the earlier data from Cox and Derwent,[4] except at wavelengths <220 nm where interference due to NO in the latter studies is suspected. Cross-sections over the range 185–275 nm can now be recommended; the values given are obtained from the graph given by Kenner *et al.*,[1] which cover a wider range than those in Ref. 4.

The two recent photofragment studies[1,2] confirm that reaction (1) is the main photodissociation channel.

References

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$HONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	405	286
$\rightarrow HONO + O(^1D)$	(4)	488	245

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–340	Rattigan *et al.*, 1992[1]	(a)

Comments

(a) Absorption cross-sections measured using a dual-beam diode array spectrometer, with a resolution of 0.3 nm, over the temperature range 239–294 K. The room temperature results are in good agreement with earlier data. Cross-sections were observed to decline with decreasing temperature, especially in the long wavelength tail. An expression for the temperature dependence was given.

Preferred Values

Absorption cross-sections at 298 K[a]

λ/nm	$10^{20}\ \sigma$/cm^2	$10^3\ B$/K^{-1}	λ/nm	$10^{20}\ \sigma$/cm^2	$10^3\ B$/K^{-1}
190	1560	0	260	1.86	3.5
195	1150	0	265	1.71	3.5
200	661	0	270	1.59	3.5
205	293	0	275	1.35	3.5
210	105	2.5	280	1.10	3.5
215	35.6	2.5	285	0.85	4.0
220	15.1	2.5	290	0.61	4.5
225	8.62	3.0	295	0.41	5.2
230	5.62	3.5	300	0.243	6.0
235	3.67	3.5	305	0.155	7.5
240	2.44	3.5	310	0.081	9.0
245	2.06	3.5	315	0.037	13.0
250	1.92	3.5	320	0.017	18.0
255	1.90	3.5	325	0.006	>18
			330	0.003	>18

[a]Temperature dependence given by the expression: $\log_e\sigma = \log_e\sigma(298) + B(T-298)$ where T is temperature (K).

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 220$ nm.

Comments on Preferred Values

The preferred values at 298 K are averaged values from the work of Rattigan *et al.*,[1] Biaume,[2] Molina and Molina[3] and Johnson and Graham.[4] The temperature dependence is based on the data of Rattigan *et al.*[1] The room temperature data differ only slightly from those recommended in our previous evaluation (IUPAC, 1989[5]), which were based on the data of Molina and Molina.[3]

The preferred values of the quantum yield are based on the results of Johnston *et al.*,[6] the direct observations of Jolly *et al.*[7] at 222 nm, and the direct observations by Turnipseed *et al.*[8] of OH, $O(^3P)$, $O(^1D)$ and $H(^2S)$ at 248, 222, and 193 nm. The absence of the competing processes (2) and (3) at 266 nm is shown by the direct observation of Margitan and Watson[9]. The very recent study of Turnipseed *et al.*[8] reported a quantum yield near unity for OH radical production at 248 nm and 222 nm, but a significantly lower value (0.33 ± 0.06) at 193 nm. In this same study[8] the quantum yield for O-atom production at 193 nm was reported to be ~0.8, indicating that HONO is a major photolysis product at 193 nm.

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$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH^0/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	105	1141
$\rightarrow HO + NO_3$ (2)	161	743

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210–330	Singer *et al.*, 1989[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_2	248	Mac Leod, Smith and Golden, 1988[2]	(b)

Comments

(a) Cross-sections measured at 298, 273 and 253 K. Pernitric acid produced *in situ* by photolysis of Cl_2–H_2–NO_2–air mixtures with averaged absorption measurements at small extents of reaction. Relative spectrum over the range 210–230 nm determined in flowing mixture of pernitric acid vapor obtained from the reaction of BF_4NO_2 and H_2O_2, after correction for impurity of NO_2, H_2O_2 and HNO_3, which was determined by IR spectroscopy. Resolution = 1 nm.

(b) Laser photolysis of pernitric acid at 248 nm. HO measured by LIF and the yield determined relative to the yield from H_2O_2, assuming the rotational distribution of HO from photolysis of HO_2NO_2 and H_2O_2 was the same under the conditions of the experiment. A value of $\phi_2 = 0.34 \pm 0.16$ was obtained after correction for impurity in the pernitric acid sample. Fluorescence from NO_2^* was also observed after photolysis which was assigned to production via channel (1). The upper limit for NO_2^* production was 30%. It was concluded that under atmospheric conditions $\phi_1 \approx 0.65$ and $\phi_2 \approx 0.35$.

Preferred Values

Absorption cross-sections at 296 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
190	1010	260	28.4
195	816	265	22.9
200	563	270	18.0
205	367	275	13.3
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.2	295	2.4
230	78.8	300	1.4
235	68.0	305	0.85
240	57.9	310	0.53
245	49.7	315	0.39
250	41.1	320	0.24
255	34.9	325	0.15
		330	0.09

Quantum Yields

$\phi_1 = 0.61$.

$\phi_2 = 0.39$.

Comments on Preferred Values

The preferred absorption cross section values are based on the data of Singer *et al.*[1] and Molina and Molina,[3] which are in excellent agreement at wavelengths between 210–300 nm. Between 300 and 320 nm the cross sections of Singer *et al.*[1] are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole range.

For the quantum yield we recommend values based on the measurements of Mac Leod *et al.*,[2] with a small upward revision to take into account the present recommendation for the absorption cross section for H_2O_2. The uncertainties on the quantum yields are large and it should be noted that they are based on data at a single wavelength.

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$NO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$NO_2 + h\nu \rightarrow NO + O(^3P)$	(1)	300	398
$\rightarrow NO + O(^1D)$	(2)	490	244

Absorption cross-section data

Wavelength range/nm	Reference	Comments
264–649	Davidson *et al.*, 1988[1]	(a)

Comments

(a) Cross-sections measured over a wide range of temperature (233–397 K) and with low NO_2 concentrations $(3.4-73) \times 10^{13}$ molecule cm^{-3}, so that absorption due to N_2O_4 was minimized. Low resolution (1.5 nm) spectra were recorded using a diode array, and high resolution spectra (0.3 to 2.5 cm^{-1}) by FTIR.

Preferred Values

Absorption cross-sections[a]

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
205	43.06	230	27.39	255	1.95
210	47.20	235	16.69	260	2.24
215	49.54	240	9.31	265	2.73
220	45.61	245	4.74	270	4.12
225	37.88	250	2.48	275	4.92

[a]Absorption cross-sections in the range 200–275 nm are independent of temperature.

Absorption cross-sections, σ, at 273 K and their temperature-dependence

λ/nm	10^{20} σ/cm^2	10^{22} a *	λ/nm	10^{20} σ/cm^2	10^{22} a *
265	2.73	0.000	345	40.65	−1.890
270	4.11	0.048	350	43.13	−1.219
275	4.90	0.061	355	47.17	−1.921
280	5.92	0.068	360	48.33	−1.095
285	7.39	−0.045	365	51.66	−1.322
290	9.00	−0.060	370	53.15	−1.102
295	10.91	−0.139	375	55.08	−0.806
300	13.07	−0.216	380	56.44	−0.867
305	15.73	−0.361	385	57.57	−0.945
310	18.61	−0.531	390	59.27	−0.923
315	21.53	−0.686	395	58.45	−0.738
320	24.77	−0.786	400	60.21	−0.599
325	28.07	−1.105	405	57.81	−0.545
330	31.33	−1.355	410	59.99	−1.129
335	34.25	−1.277	415	56.51	0.001
340	37.98	−1.612	420	58.12	−1.208

*The quantity a is the temperature coefficient of σ, as defined in the equation $\sigma(T) = [\sigma(273) + a(T - 273)]$, where T is in kelvins; a has units of cm^2 molecule^{-1} K^{-1}.

Quantum yields

λ/nm	φ	λ/nm	φ	λ/nm	φ
<310	1.00	370	0.98	404	0.42
315	0.99	375	0.98	406	0.29
320	0.99	380	0.97	408	0.18
325	0.99	385	0.97	410	0.13
330	0.99	390	0.96	412	0.09
335	0.99			414	0.07
340	0.99	392	0.96	416	0.05
345	0.99	394	0.95	418	0.03
350	0.99	396	0.92	420	0.02
355	0.99	398	0.82	422	0.01
360	0.98	400	0.82	424	0.00
365	0.98	402	0.69		

Comments on Preferred Values

The new absorption cross-sections of Davidson *et al.*[1] are in very good ageement with the earlier data of Bass *et al.*[2] and Schneider *et al.*.[3] at room temperature. The agreement is within ±5% for the three studies over the range 305–345 nm; for <285 nm and >340 nm the differences are more significant but lie within the quoted uncertainty limits. The agreement with previous measurements at low temperature is poor. The most significant deviations occur in the 320–360 nm region and below 295 nm, which correspond to regions of absorption by N_2O_4, and errors from this source are least likely at the low NO_2 concentrations employed by Davidson *et al.*.[1]

The simultaneous spectral acquisition afforded by the diode array technique used by Davidson *et al.*[1] should in principle give more accurate data, and these provide the basis of the preferred temperature dependent values over the range 270–410 nm, which are averaged over 5 nm wavelength intervals. The preferred values for the wavelength range 205–265 nm, also averaged over 5 nm wavelength intervals, are taken from Schneider *et al.*,[2] Table 4 of their paper; there is no significant temperature dependence in this region.

The preferred quantum yields are those recommended by Gardner *et al.*[4] (see previous IUPAC evaluation[8]). They are based on a best fit to the data of Gardner *et al.*[4] from 334–404 nm, Jones and Bayes[5] for 297–412 nm, Davenport[6] for 400–420 nm and Harker *et al.*[7] (corrected for cross-sections) for 397–420 nm. The results of Gardner *et al.*[4] support the results of Jones and Bayes[5] showing that the primary quantum yield is nearly unity throughout the entire wavelength region from 290–390 nm, and that the low values reported by Harker *et al.*[7] for the 375–396 nm region must be in error. Possible reasons for these low values are discussed in Ref. 4.

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$NO_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$NO_3 + h\nu \rightarrow NO + O_2(^3\Sigma)$	(1)	26	4600
$\rightarrow NO_2 + O(^3P)$	(2)	218	550

Absorption cross-section data

Wavelength range/nm	Reference	Comments
652–672	Ravishankara and Mauldin, 1986[1]	(a)
400–700	Sander, 1986[2]	(b)
600–700	Cantrell *et al.*, 1987[3]	(c)
662	Canosa-Mas *et al.*, 1987[4]	(d)

Comments

(a) NO_3 generated from the F + HNO_3 reaction in a discharge flow apparatus. Measurements were made at 220, 240 and 298 K. For the 662 nm band at 298 K, an integrated absorption of 1.94×10^{-15} cm and a peak cross-section value of 1.90×10^{-17} cm^2 molecule^{-1} were reported. The absorption cross-section at 662 nm was found to increase with decreasing temperature while the shape of the band did not change.

(b) Two methods were used to produce NO_3. In one, NO_3 radicals were generated from the flash photolysis of Cl_2–$ClONO_2$ mixtures, with NO_3 formation and $ClONO_2$ loss being monitored by UV absorption. Measurements were made at 230, 250 and 298 K. The value of $\sigma(NO_3)$ at 662 nm determined by this method (2.28×10^{-17} cm^2 molecule^{-1}) was preferred by the author. The cross-section was observed to increase by a factor of 1.18 at 230 K. NO_3 was also produced in a discharge flow system by the F + HNO_3 reaction. The value of $\sigma(NO_3)$ at 662 nm determined by this method was 1.83×10^{-17} cm^2 molecule^{-1}. Values of σ were tabulated for 1 nm intervals from 400–700 nm for 298 and 230 K.

(c) NO_3 radicals generated from the $NO_x + O_3$ reaction. Fourier transform spectroscopy in the visible and UV regions over the temperature range from 215–348 K was used for the 662 nm band; an integrated absorption of 2.05×10^{-15} cm and a peak cross-section of 2.09×10^{-17} cm^2 molecule^{-1} were reported. No dependence on temperature was observed.

(d) NO_3 radicals were generated from the F + HNO_3 reaction in a discharge flow apparatus. The NO_3 radical concentration was determined by titration with NO, and a stoichiometric factor determined. The absorption cross-section of NO_3 at 662 nm was determined to be 2.23×10^{-17} cm^2 molecule^{-1}.

Preferred Values

Absorption cross-sections at 298 K and 220 K

λ/nm	$10^{19}\sigma$/cm^2	
	298 K	220 K
400	0.0	0.4
401	0.0	0.5
402	0.0	0.5
403	0.2	0.5
404	0.0	0.3
405	0.3	0.7
406	0.2	0.6
407	0.1	0.5
408	0.3	0.5
409	0.0	0.7
410	0.1	0.5
411	0.2	0.7
412	0.5	0.4

Absorption cross-sections at 298 K and 220 K – Continued

λ/nm	10^{19} σ/cm²	
	298 K	220 K
413	0.5	0.7
414	0.2	1.1
415	0.6	0.7
416	0.6	0.7
417	0.7	1.0
418	0.5	1.0
419	0.8	1.0
420	0.8	1.3
421	0.8	1.2
422	0.9	1.2
423	1.1	1.2
424	0.9	1.3
425	0.7	1.6
426	1.4	1.5
427	1.4	1.2
428	1.2	1.5
429	1.1	1.3
430	1.7	1.6
431	1.3	1.7
432	1.5	1.7
433	1.8	1.9
434	1.8	2.1
435	1.6	2.2
436	1.5	2.2
437	1.8	1.9
438	2.1	2.1
439	2.0	2.6
440	1.9	2.2
441	1.8	2.3
442	2.1	2.2
443	1.8	2.2
444	1.9	2.2
445	2.0	2.7
446	2.4	2.7
447	2.9	3.1
448	2.4	3.4
449	2.8	3.1
450	2.9	3.1
451	3.0	3.5
452	3.3	3.7
453	3.1	3.5
454	3.6	3.7
455	3.6	3.8
456	3.6	3.4
457	4.0	3.9
458	3.7	4.4
459	4.2	4.2
460	4.0	4.3
461	3.9	4.0
462	4.0	3.7
463	4.1	4.5
464	4.8	4.8
465	5.1	5.1
466	5.4	5.3
467	5.7	5.6
468	5.6	5.5
469	5.8	5.6
470	5.9	5.3
471	6.2	5.8
472	6.4	6.1
473	6.2	6.1
474	6.2	6.0
475	6.8	6.9
476	7.8	7.8

Absorption cross-sections at 298 K and 220 K – Continued

λ/nm	10^{19} σ/cm²	
	298 K	220 K
477	7.7	7.7
478	7.3	6.9
479	7.3	6.9
480	7.0	7.0
481	7.1	6.9
482	7.1	6.8
483	7.2	6.7
484	7.7	6.9
485	8.2	7.7
486	9.1	8.9
487	9.2	8.8
488	9.5	8.6
489	9.6	9.9
490	10.3	10.5
491	9.9	9.6
492	9.9	9.9
493	10.1	10.2
494	10.1	9.5
495	10.6	10.4
496	12.1	12.1
497	12.2	13.1
498	12.0	12.4
499	11.7	11.8
500	11.3	11.5
501	11.1	10.7
502	11.1	10.4
503	11.1	11.1
504	12.6	12.5
505	12.8	13.1
506	13.4	14.1
507	12.8	13.1
508	12.7	12.2
509	13.5	13.2
510	15.1	15.5
511	17.3	18.7
512	17.7	19.8
513	16.0	18.0
514	15.8	16.2
515	15.8	15.9
516	15.6	16.4
517	14.9	14.4
518	14.4	14.0
519	15.4	14.9
520	16.8	16.2
521	18.3	17.7
522	19.3	19.3
523	17.7	17.9
524	16.4	15.7
525	15.8	15.0
526	16.3	15.7
527	18.1	18.1
528	21.0	22.3
529	23.9	25.6
530	22.3	23.1
531	20.9	21.3
532	20.2	20.6
533	19.5	19.8
534	20.4	21.3
535	23.0	24.9
536	25.7	28.7
537	25.8	28.6
538	23.4	24.4
539	20.4	21.0
540	21.0	21.2

Absorption cross-sections at 298 K and 220 K – Continued

λ/nm	10^{19} σ/cm²	
	298 K	220 K
541	20.4	20.4
542	18.8	18.5
543	16.8	16.4
544	17.0	16.2
545	19.6	20.0
546	24.2	24.8
547	29.1	30.9
548	29.8	31.3
549	27.1	27.8
550	24.8	26.0
551	24.3	25.9
552	24.7	26.7
553	25.3	27.5
554	27.8	31.0
555	31.1	35.6
556	32.6	36.7
557	32.9	36.8
558	35.1	39.5
559	37.2	42.4
560	33.2	36.1
561	29.8	31.7
562	29.0	30.6
563	28.0	30.1
564	27.2	28.8
565	27.3	29.0
566	28.5	30.9
567	28.1	29.4
568	28.5	30.0
569	28.9	30.5
570	27.9	29.1
571	27.6	28.9
572	27.4	28.6
573	27.8	28.9
574	28.6	29.9
575	30.8	33.7
576	32.7	36.2
577	33.8	37.0
578	33.1	36.1
579	32.4	35.9
580	33.4	37.4
581	35.5	41.1
582	32.8	37.0
583	29.3	32.4
584	28.2	30.7
585	28.9	31.8
586	33.2	37.2
587	41.6	48.5
588	50.4	59.8
589	61.3	72.4
590	59.6	67.3
591	54.4	60.5
592	51.1	56.4
593	45.8	49.8
594	41.9	47.0
595	42.9	49.5
596	46.2	54.4
597	43.6	50.6
598	36.7	40.9
599	31.0	34.2
600	27.6	27.8
601	28.6	28.5
602	33.2	33.4
603	38.0	40.3
604	43.7	48.1

Absorption cross-sections at 298 K and 220 K – Continued

λ/nm	10^{19} σ/cm²	
	298 K	220 K
605	43.6	49.8
606	33.2	37.1
607	24.0	24.8
608	18.5	17.9
609	17.1	16.6
610	17.7	17.3
611	19.1	19.4
612	22.3	23.6
613	26.3	30.0
614	25.5	28.6
615	22.6	24.2
616	20.9	21.1
617	21.1	20.6
618	23.9	22.9
619	25.6	25.4
620	32.7	33.5
621	52.4	58.9
622	101.8	113.6
623	147.3	163.5
624	120.5	129.9
625	83.8	94.3
626	73.0	82.6
627	75.3	90.0
628	73.7	88.3
629	69.8	84.6
630	67.6	84.0
631	48.4	57.1
632	32.7	37.3
633	21.7	23.5
634	16.4	16.2
635	14.4	13.1
636	16.9	15.2
637	20.7	18.8
638	20.3	17.7
639	15.8	13.3
640	12.3	10.6
641	10.0	8.9
642	9.2	7.9
643	9.7	7.6
644	9.5	7.9
645	8.6	7.5
646	7.5	6.5
647	7.0	6.4
648	6.2	5.9
649	5.4	5.0
650	5.0	4.7
651	5.5	5.2
652	6.1	6.2
653	7.1	7.4
654	8.2	8.6
655	9.8	10.3
656	13.3	13.5
657	17.1	17.3
658	24.2	24.3
659	40.7	40.0
660	74.5	74.0
661	144.8	156.9
662	210.0	250.0
663	174.4	215.2
664	112.9	136.3
665	74.1	87.0
666	49.6	58.9
667	30.4	35.0
668	19.0	21.8

Absorption cross-sections at 298 K and 220 K – Continued

λ/nm	10^{19} σ/cm²	
	298 K	220 K
669	12.5	13.6
670	9.5	10.5
671	7.9	8.8
672	7.6	9.1
673	6.4	7.6
674	5.2	5.9
675	4.8	5.2
676	4.9	4.9
677	5.9	5.8
678	7.5	6.7
679	7.8	6.8
680	6.9	6.0
681	5.3	5.0
682	4.0	4.1
683	3.0	3.0
684	2.6	2.6
685	1.8	2.2
686	1.6	1.4
687	1.2	2.2
688	1.2	1.9
689	1.2	1.8
690	1.0	2.0
691	0.7	1.6

Quantum Yields

No recommendation.

Comments on Preferred Values

No new data have been reported on either the cross-sections or the quantum yields for NO_3 photolysis since our previous evaluation, IUPAC, 1989.[5] However, a re-evaluation appears in the most recent NASA evaluation,[6] and a detailed critical evaluation has been reported by Wayne *et al.*[7] The preferred values are based on the peak value of the cross-section at 662 nm of 2.10×10^{-17} cm² molecule^{-1}, adopted from the evaluation of Wayne *et al.*,[7] which was obtained by averaging the data from the four most recent studies cited above.[1-4] The slightly lower peak value recommended by NASA,[6] of $\sigma = 2.00 \times 10^{-17}$ cm² molecule^{-1}, averages in additional earlier data which has larger experimental errors and a higher probability of systematic errors due to secondary chemistry. The values of σ in the wavelength range 400–691 nm are calculated from the data of Sander,[2] normalized to the preferred peak value. The shape of the 662 nm absorption band reported by Sander[2] is in good agreement with the higher resolution study of Marinelli *et al.*[8] The shape and position of the other features in the spectrum match those reported in other studies.[9-11]

Conflicting results have been reported for the effect of temperature on the cross-section. Ravishankara and Mauldin[1] and Sander[2] observed a significant increase in the value of $\sigma(NO_3)$ at 662 nm at lower temperatures, while Cantrell *et al.*[3] reported no temperature dependence over the range 215–348 K. This discrepancy has not been resolved. We adopt the average cross-section at 220 K and 662 nm suggested by Wayne *et al.*[2] of 2.50×10^{-17} cm² molecule^{-1}, obtained by averaging the data from all three of these experimental studies. If this value is combined with the preferred value at 298 K, the following expression is obtained,

$$\sigma(T) = 3.63 \times 10^{-17} - (5.13 \times 10^{-20}\ T)\ \text{cm}^2\ \text{molecule}^{-1} \text{ at 662 nm}$$

with T in K. The absorption cross-section obtained by Sander[2] at 230 K over the wavelength range 400–700 nm were normalized to the value of 2.50×10^{-17} cm² molecule^{-1} at 662 nm to provide the preferred values given in the table for 230 K, following the recommendation of Wayne *et al.*[7]

No recommendation for absolute quantum yields is given. As disussed in an earlier CODATA evaluation[12] and in the review of Wayne *et al.*,[7] the primary quantum yield determined by Magnotta and Johnston[13] was the product of the absorption cross-section and the quantum yield. However, even with the upward revision of the cross-section, these data[13] give quantum yields greater than unity for <610 nm, indicating some systematic error. The current recommendation is to use the photodissociation rates suggested by Magnotta and Johnston[13] for an overhead sun at the earth's surface and the wavelength range 470–700 nm: $J_1(NO + O_2) = 0.022 \pm 0.007\ s^{-1}$ and $J_2(NO_2 + O) = 0.18 \pm 0.06\ s^{-1}$.

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$N_2O + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$N_2O + h\nu \rightarrow N_2 + O(^3P)$	(1)	161	742
$\rightarrow N_2 + O(^1D)$	(2)	351	341
$\rightarrow N + NO$	(3)	475	252
$\rightarrow N_2 + O(^1S)$	(4)	565	212

Absorption cross-section data

Wavelength range/nm	Reference	Comments
160–250	Hubrich and Stuhl, 1980[1]	(a)

Comments

(a) Measured at 298 K and 208 K. In very good agreement with results of Selwyn *et al.*[2]

Preferred Values

Absorption cross-sections

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

$$\ln \sigma(\lambda,T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 + (T - 300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$A_1 = 68.21023$
$A_2 = -4.071805$
$A_3 = 4.301146 \times 10^{-2}$
$A_4 = -1.777846 \times 10^{-4}$
$A_5 = 2.520672 \times 10^{-7}$

$B_1 = 123.4014$
$B_2 = -2.116255$
$B_3 = 1.111572 \times 10^{-2}$
$B_4 = -1.881058 \times 10^{-5}$

Quantum Yields

$\phi_2 = 1.0$ for $\lambda = 185$–230 nm.

Comments on Preferred Values

The preferred absorption cross-section values and the expression for $\ln \sigma(\lambda,T)$ are from Selwyn *et al.*[2] These cross-section values have been confirmed both at room temperature and at 208 K by the recent results of Hubrich and Stuhl.[1]

The preferred value of the quantum yield (ϕ_2 equal to unity) is based on the results reported in Paraskevopoulos and Cvetanovic,[3] Preston and Barr[4] and Greiner.[5]

These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980[6] where a detailed discussion can be found.

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$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	(1)	93	1290
$\rightarrow NO_3 + NO + O(^3P)$	(2)	399	300
$\rightarrow NO_3 + NO_2^* \rightarrow NO_3 + NO_2 + h\nu$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–380	Yao, Wilson and Johnston, 1982[1]	(a)

Quantum yield data

Measurement	Wavelength nm	Reference	Comments
$\phi(NO_3)$	249–350	Swanson, Kan and Johnston, 1984[2]	(b)
$\phi(NO_3)$, $\phi[O(^3P)]$	290	Barker *et al.*, 1985[3]	(c)
$\phi(NO_3)$, $\phi[O(^3P)]$	248–289	Ravishankara *et al.*, 1986[4]	(d)
ϕ_3	266–305	Oh *et al.*, 1986[5]	(e)

Comments

(a) Measured over the temperature range 223–300 K. For the wavelength range 200–280 nm, no temperature dependence was observed, and values were tabulated at 5 nm intervals. For 285–380 nm a pronounced temperature dependence was observed and the results were presented by an equation expressing σ as a function of λ and T.

(b) Laser flash photolysis, mostly at 249 nm with a few experiments at 350 nm. The NO_3 quantum yield was measured to be 0.89 ± 0.15. At low reactant concentration, the quantum yield approached a value of 1.0 ± 0.1.

(c) Pulsed laser photolysis. Quantum yield for production of $O(^3P)$ atoms was determined to be <0.1 in experiments with resonance fluorescence detection of oxygen atoms. Optoacoustic techniques with added NO were used to determine $\phi(NO_3)$ to be 0.8 ± 0.2.

(d) Pulsed laser photolysis. Quantum yield for NO_3 production at 248 nm was determined to be unity in experiments with detection of NO_3 by absorption at 662 nm. Quantum yield for $O(^3P)$ production was determined by resonance fluorescence and observed to decrease from 0.27 ± 0.17 at 248 nm to 0.15 ± 0.05 at 289 nm.

(e) Pulsed laser photolysis. The photolysis induced fluorescence, PIF, of NO_2 was compared with the laser induced fluorescence, LIF, of NO_2 excited by a pulsed visible laser. Analysis of results indicated that electronically excited NO_2 in the $^2B_1$ state was produced in the UV photolysis of N_2O_5.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	920	245	52
205	820	250	40
210	560	255	32
215	370	260	26
220	220	265	20
225	144	270	16
230	99	275	13
235	77	280	12
240	62		

For the wavelength interval 285–380 nm: $10^{20}\ \sigma(\text{cm}^2) = \exp[2.735 + (4728 - 17.13\ \lambda)/T]$ for temperatures, T, in the range 225–300 K.

Quantum yields

$\phi_1 + \phi_2 + \phi_3 = 1.0$ for λ = 248–350 nm

λ/nm	ϕ_2
248	0.72 ± 0.17
266	0.38 ± 0.10
287	0.21 ± 0.05
289	0.15 ± 0.05

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The preferred absorption cross-section values are those of Yao *et al.*[1] For wavelengths less than 280 nm no significant temperature dependence was observed, and for this region the preferred values are tabulated. For the region 285–380 nm there is a significant temperature dependence, and the preferred values must be calculated from the expression given. These results agree well with the room temperature values for 210–310 nm reported by Graham and Johnston.[7] The preferred quantum yield of unity for NO_3 production is based on the results of Swanson *et al.*[2] at 249 and 350 nm, those of Ravishankara *et al.*[4] at 248 nm, and those of Barker *et al.*[3] at 290 nm. The preferred quantum yield values for $O(^3P)$ atom production are those reported by Ravishankara *et al.*[4] The recent study of Oh *et al.*[5] indicates that electronically excited NO_2 in the $^2B_1$ state is produced and photolysis induced flourescence (PIF) quantum yield values are reported. For calculation of photodissociation rates in the atmosphere, pathway (3) is equivalent to pathway (1). In summary, it appears that NO_3 is produced with unit quantum yield throughout the region 248–350 nm, and that the quantum yield for oxygen atom production decreases at longer wavelengths and appears to be approaching zero in the neighborhood of the thermodynamic threshold for $O(^3P)$ atom production at 300 nm.

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4.4. Organic Species

$O + CH_3 \rightarrow HCHO + H$

$\Delta H° = -285.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987[1]	(a)
Reviews and Evaluations			
1.4×10^{-10}	200–900	IUPAC, 1989[2]	(b)
1.1×10^{-10}	200–300	NASA, 1990[3]	(c)

Comments

(a) Flow system with generation of CH_3 and $O(^3P)$ from simultaneous in situ photolysis of CH_3COCH_3 and SO_2, and determination of $[CH_3]$ and [O] by photoionization MS. Experiments were performed under conditions such that $[O]/[CH_3] > 20$, and rate coefficients were determined from the decay of CH_3. The rate coefficient k was found to be independent of pressure over the range 1–11 Torr, and its value was confirmed by measurement of the rate of formation of HCHO, the sole observable product.

(b) See Comments on Preferred Values.

(c) Weighted average of the measurements of Washida and Bayes,[5] Washida[6] and Plumb and Ryan.[4]

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–900 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The recommended rate coefficient is taken from the extensive study of Slagle *et al.*[1] which is in good agreement with previous recommendations.[3,7]

References

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$O(^1D) + CH_4 \rightarrow HO + CH_3$ (1)
$\rightarrow O(^3P) + CH_4$ (2)
$\rightarrow HCHO + H_2$ (3)

$\Delta H^\circ(1) = -179.8$ kJ·mol^{-1}
$\Delta H^\circ(2) = -189.7$ kJ·mol^{-1}
$\Delta H^\circ(3) = -472.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
k_2/k = <0.040	298	Wine and Ravishankara, 1982[1]	(a)
Reviews and Evaluations			
$k_1 = 1.4 \times 10^{-10}$	200–300	NASA, 1990[2]	(b)
$k_3 = 1.4 \times 10^{-11}$	200–300		
$k = 1.5 \times 10^{-10}$	200–300	CODATA, 1982[3]; IUPAC, 1989[4]	(b,c)
$k_1/k = 0.9$	200–300		
$k_3/k = 0.1$	200–300		
$k_2/k = 0$	200–300		

Comments

(a) $O(^1D)$ atoms generated from the 248 nm laser flash photolysis of O_3 in CH_4–He mixtures. Time-resolved measurement of $O(^3P)$ by resonance fluorescence detection.
(b) Based on data of Davidson *et al.*[5] and Amimoto *et al.*[6]
(c) See Comments on Preferred Values.

Preferred Values

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

$k_1/k = 0.9$; $k_3/k = 0.1$; $k_2/k = 0$ over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta k_1/k = \Delta k_3/k = \pm 0.1$.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation,[3] but includes additional comments from a later evaluation.[4] The most recent data[1] on this reaction are in excellent agreement with the previous recommendation[3] which is unaltered. Casavecchia *et al.*[7] have carried out a molecular beam study which indicates an alternative reaction channel yielding CH_3O (or CH_2OH) + H. Further work is needed to confirm this observation.

A recent study[8] of the 248 nm laser flash photolysis of O_3–CH_4 mixtures, with low-pressure FTIR emission spectroscopy to monitor the HO* product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to $n = 4$, the maximum allowable according to the energetics of the reaction) is non-statistical.

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$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H^\circ = -60.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3 \pm 0.9) \times 10^{-12}$	1234 ± 15	Bott and Cohen, 1989[1]	(a)
$1.59 \times 10^{-20}\, T^{2.84} \exp(-978/T)$	223–420	Vaghjiani and Ravishankara, 1991[2]	(b)
6.35×10^{-15}	298		
Reviews and Evaluations			
$3.7 \times 10^{-12} \exp(-1820/T)$	240–300	IUPAC, 1989[3]	(c)
$6.95 \times 10^{-18}\, T^2 \exp(-1282/T)$	240–1512	Atkinson, 1989[4]	(d)
$2.3 \times 10^{-12} \exp(-1700/T)$	240–373	NASA, 1990[5]	(e)

Comments

(a) HO radicals were generated from the thermal decomposition of *t*-butyl hydroperoxide in a shock tube and monitored by UV absorption at 309 nm.

(b) HO radicals generated from the pulsed photolysis of H_2O, H_2O_2 and O_3–H_2O or O_3–CH_4 reactants, and detected by LIF. The CH_4–HO concentration ratios were sufficiently high that secondary reactions of HO radicals were calculated to be negligible. Using the Arrhenius expression, $k = A \exp(-B/T)$, the rate coefficient data measured yielded the expression $k = 2.94 \times 10^{-12} \exp[-(1815 \pm 30)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–420 K.

(c) Derived from the absolute rate coefficient data of Greiner,[6] Davis *et al.*,[7] Margitan *et al.*,[8] Overend *et al.*,[9] Howard and Evenson,[10] Tully and Ravishankara,[11] Husain *et al.*,[12] Jeong and Kaufman[13,14] and Madronich and Felder.[15] The three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to these data, resulting in $k = 7.04 \times 10^{-18}\, T^2 \exp(-1286/T)$ cm^3 molecule^{-1} s^{-1} over the range 240–1512 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C\, e^2\, T^2$ and $B = D + 2T$.

(d) Derived from the absolute rate coefficient data of Dixon-Lewis and Williams,[16] Greiner,[6] Davis *et al.*,[7] Margitan *et al.*,[8] Overend *et al.*,[9] Howard and Evenson,[10] Ernst *et al.*,[17] Tully and Ravishankara,[11] Husain *et al.*,[12] Jeong and Kaufman,[13,14] Madronich and Felder,[15] Cohen and Bott[18] and Smith *et al.*,[19] using the three parameter expression $k = CT^2 \exp(-D/T)$.

(e) Derived from the absolute rate coefficient data of Davis *et al.*,[7] which are in agreement with other temperature dependent studies.[6,8,11,12,15,20,21]

Preferred Values

$k = 7.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.9 \times 10^{-12} \exp(-1885/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients measured by Vaghjiani and Ravishankara[2] over the temperature range 223–420 K are ~20% lower than the majority of the previously measured absolute rate coefficients. In particular, the data of Vaghjiani and Ravishankara[2] at room temperature and below are significantly lower than the rate coefficients of Davis *et al.*[7] and Jeong and Kaufman,[13,14] probably because of the occurrence of secondary reactions of HO radicals with CH_3 radicals in these earlier studies.[2] The CH_4/HO concentration ratios used in the studies of Greiner,[6] Davis *et al.*,[7] Overend *et al.*[9] and Jeong and Kaufman[13] were significantly lower than those used by Vaghjiani and Ravishankara,[2] and all of these earlier rate coefficient studies may have been subject to the occurrence of secondary reactions, leading to measured rate coefficients higher than that for the elementary HO + CH_4 reaction, especially at the lowest temperatures studied.

At around room temperature, the absolute rate coefficients of Greiner,[6] Davis *et al.*,[7] Margitan *et al.*,[8] Overend *et al.*,[9] Howard and Evenson,[10] Zellner and Steinert,[20] Tully and Ravishankara,[11] Husain *et al.*,[12] Jeong and Kaufman,[13] Jonah *et al.*[21] Madronich and Felder[15] and Vaghjiani and Ravishankara[2] are in reasonable agreement, ranging from 6.35×10^{-15} to 1.06×10^{-14} cm^3 molecule^{-1} s^{-1} at ~298 K. At higher temperatures there are discrepancies between the rate coefficients determined by Zellner and Steinert[20] (above ~625 K) and Jonah *et al.*[21] (400–600 K) and those of Greiner,[6] Margitan *et al.*,[8] Tully and Ravishankara,[11] Jeong and Kaufman,[13] Madronich and Felder,[15] Baulch *et al.*[22] and Vaghjiani and Ravishankara[2] (see also Ref. 4).

The preferred values are derived from the absolute rate coefficient data of Refs. 1, 2, 8, 10, 11, 15–17 and 19. The three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to these data, resulting in $k = 7.44 \times 10^{-18}\, T^2 \exp(-1355/T)$ cm^3 molecule^{-1} s^{-1} over the range 223–1512 K. The preferred Arrhenius expression, $k = A$

exp($-B/T$), is centered at 265 K and is derived from the three parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$. The preferred 298 K rate coefficient is 17% lower than that recommended by the previous IUPAC evaluation[3] and 10% lower than the most recent NASA evaluation.[5]

At 270 K, the preferred rate coefficient is 6% higher than that calculated from the three parameter expression of Vaghjiani and Ravishankara[2] (and 2% higher than calculated from the Arrhenius expression cited[2]). This preferred 270 K rate coefficient is 17% lower than the NASA, 1990[5] recommendation and 21% lower than that recommended by the previous IUPAC[3] evaluation.

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$HO + C_2H_2 + M \rightarrow C_2H_2OH + M$

$\Delta H° = -152$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6 \pm 3) \times 10^{-30}$ [He]	298	Hack *et al.*, 1983[1]	(a)
$(2.5 \pm 0.3) \times 10^{-30}$ [Ar]	295	Schmidt *et al.*, 1985[2]	(b)
5×10^{-30} [N_2]	298	Wahner and Zetzsch, 1985[3]	(c)
Reviews and Evaluations			
5.6×10^{-30} [Ar]	228–300	Smith, Fairchild and Crosley, 1984[4]	(d)
5×10^{-30} [N_2]	220–300	CODATA, 1982[5]; IUPAC, 1989[6]	(e)
$5 \times 10^{-30}(T/298)^{-1.5}$ [N_2]	230–500	Atkinson, 1989[7]	(f)
5.5×10^{-30} [air]	200–300	NASA, 1990[8]	(g)

Comments

(a) Discharge flow system with EPR detection of HO radicals and MS identification of products.

(b) Flash photolysis of H_2O_2 (or HNO_3)–C_2H_2 mixtures, with HO radicals being detected by LIF near 300 nm. Experiments were conducted in He, Ar, and N_2 diluents at pressures between 1 and 1000 mbar (in Ar). Construction of falloff curve used a value of $F_c = 0.6$ to derive $k_\infty = (8.3 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. In the presence of O_2, glyoxal and vinoxy radicals were detected while HO radicals were regenerated. The following mechanism was postulated

$$HO + C_2H_2 \xrightarrow{M} C_2H_2OH \xrightarrow{O_2} (CHO)_2 + HO$$
$$\downarrow$$
$$CH_2CHO \xrightarrow{O_2} (CHO)_2 + HO$$

(c) Flash photolysis of H_2O_2 (or H_2O) mixtures in the presence of C_2H_2, with long path absorption detection of HO radicals. Experiments were carried out in N_2 diluent over the pressure range 10–1000 mbar. Falloff curve constructed with $F_c = 0.6$ to derive $k_\infty = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(d) Theoretical evaluation of the data of references 9 and 10 using $F_c = 0.6$ and $k_\infty(300\ K) = 8.3 \times 10^{-13}$

cm³ molecule⁻¹ s⁻¹. Simulation of k_0 up to a temperature of 1400 K.

(e) Based on the data of Refs. 2 and 3 together with earlier results. This preferred value is in agreement with simulations of the falloff curve, such as those in Ref. 4.

(f) Temperature dependence based on data from Refs. 9–11 in accord with evaluation from Ref. 4. Absolute value at 298 K based on data from Refs. 2 and 3.

(g) Based on the evaluation of Ref. 4 and earlier data.

Preferred Values

$k_0 = 5 \times 10^{-30}(T/300)^{-1.5}[N_2]$ cm³ molecule⁻¹ s⁻¹ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

Experimental data from Refs. 2 and 3 in the falloff range together with the theoretical analysis from Ref. 4 lead to a fairly reliable falloff extrapolation. The preferred temperature dependence follows the analysis of the data of Refs. 9–11 given in Ref. 7. At temperatures above ~500 K another component of the rate coefficient with much stronger temperature dependence has also to be taken into account (see Ref. 7).

High-pressure rate coefficients

Rate coefficient data

k_∞/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.8 \pm 1.4) \times 10^{-13}$	298	Atkinson and Aschmann, 1984[12]	(a)
$(8.3 \pm 0.8) \times 10^{-13}$	295	Schmidt *et al.*, 1985[2]	(b)
9×10^{-13}	298	Wahner and Zetzsch, 1985[3]	(c)
$(8.8 \pm 2.0) \times 10^{-13}$	297	Hatakeyama, Washida, and Akimoto, 1986[13]	(d)
$8.5 \times 10^{-12} \exp(-705/T)$	333–1273	Liu, Mulac and Jonah, 1988[14]	(e)
8.0×10^{-13}	298*		
Reviews and Evaluations			
$8.3 \times 10^{-13}(T/300)^2$	220–300	CODATA, 1982[5]; IUPAC, 1989[6]	(f)
$9.4 \times 10^{-12} \exp(-700/T)$	230–500	Atkinson, 1989[7]	(g)
9.0×10^{-13}	298		
$8.3 \times 10^{-13}(T/300)^2$	200–300	NASA, 1990[8]	(h)

Comments

(a) HO radicals generated in the photolysis of CH_3ONO–NO–C_2H_2–cyclohexane-air mixtures at 1 atm total pressure. Rates measured relative to the HO + cyclohexane reaction, and the data were evaluated using k(HO + cyclohexane) = 7.57×10^{-12} cm³ molecule⁻¹ s⁻¹.

(b) See comment (b) for k_0.

(c) See comment (c) for k_0.

(d) Generation of HO radicals by photolysis of H_2O_2 or ethyl nitrite. Reactant and product concentrations monitored by long path FTIR spectrometry. Measurements were carried out at 1 atm pressure in air. The reaction mechanism in the presence of O_2 was in accord with Ref. 2.

(e) Pulsed radiolysis technique with resonance absorption measurement of HO radicals. Measurements were conducted at 1 atm of Ar.

(f) See comment (e) for k_0. The temperature coefficient corresponds to a small barrier for the addition reaction.

(g) Based on data from Refs. 3, 9, and 14.

(h) See Comment (g) for k_0.

Preferred Values

$k_\infty = 9.0 \times 10^{-13}(T/300)^2$ cm³ molecule⁻¹ s⁻¹ over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the evaluation of Ref. 7. Falloff curves are constructed with $F_c = 0.69$ at 228 K and 0.62 at 298 K such as modeled in Ref. 4.

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$HO + C_2H_4 + M \rightarrow C_2H_4OH + M$

$\Delta H^\circ = -126$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.1 \pm 1.2) \times 10^{-29}$ [N_2]	300	Kuo and Lee, 1991[1]	(a)
$(5.2 \pm 1.1) \times 10^{-29}$ [O_2]	300		
$(2.7 \pm 0.5) \times 10^{-29}(T/300)^{-4.8}$ [He]	251–430		
Reviews and Evaluations			
$9.5 \times 10^{-29}(T/300)^{-3.1}$ [N_2]	200–300	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$1.0 \times 10^{-28}(T/298)^{-3}$ [N_2]	295–420	Atkinson, 1989[4]	(c)
$1.5 \times 10^{-28}(T/300)^{-0.8}$ [air]	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals, carried out at total pressure of 0.3–5 Torr. HO radicals were generated by reacting H with excess NO_2. Data extrapolated using $F_c = 0.7$. The temperature dependence was obtained assuming $k_\infty = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with $E/R = -400$ K. If $E/K = -1000$ K was assumed, a value of $n = 4.0$ was derived.

(b) Based on a series of earlier data, in particular on the data of Ref. 6. Falloff extrapolation with a calculated $F_c = 0.7$.

(c) Detailed review of all available earlier data. Based on experiments from Refs. 6–8. Falloff extrapolation with $F_c = 0.7$.

(d) See comment (b). Temperature dependence from theoretical calculations. Falloff extrapolation with $F_c = 0.6$. The reaction may have a small activation barrier.

Preferred Values

$k_0 = 7 \times 10^{-29}(T/300)^{-3.1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

Because of the smaller scatter of the new data from reference 1, as well as of the lower data from earlier studies, an average of the available results was preferred with heavier weight given at the smaller values of k_0. Falloff curves are constructed with the calculated $F_c = 0.7$ from Ref. 6. The temperature dependence remains uncertain, being possibly influenced by a small activation barrier.

Lee and Tang,[23] Leu,[10] Tully *et al.*,[12,13] Jeong *et al.*[14] and Nielsen *et al.*,[24] using a temperature dependence of $E/R = 1100$ K to recalculate the reported room temperature data to 298 K. The temperature depen-

... is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The room temperature (the temperature not being specified) absolute rate coefficient of Schiffman *et al.*[3] is in good agreement with the preferred

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High-presure rate coefficients

Rate coefficient data

298 K rate coefficient, as are the relative rate coefficients of Baulch *et al.*[26] and Edney *et al.*[27]

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$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$

$\Delta H^\circ = -134$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$8 \times 10^{-27}(T/300)^{-3.5}$ [N_2]	200–300	CODATA, 1984[1]; IUPAC, 1989[2]	(a)
$3 \times 10^{-27}(T/298)^{-3}$ [air]	298–400	Atkinson, 1989[3]	(b)

Comments

(a) In the pressure range 1–760 Torr at 298 K, the reaction is close to its high-pressure limit. The falloff extrapolation, therefore, is very uncertain. The k_0 value was based on the data from Klein *et al.*[4] which show little scatter. $F_c = 0.5$ at 300 K was used such as in Refs. 4 and 5. The temperature dependence was estimated by analogy to the reaction $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

(b) Extensive evaluation of earlier data. Chosen value of k_0 was the geometrical mean of the data from Refs. 4 and 5. The temperature dependence was estimated by analogy to $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

Preferred Values

$k_0 = 8 \times 10^{-27}(T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at pressures of 1 bar. The preferred values follow the falloff extrapolations from Refs. 4 and 5 which show the smallest scatter. Falloff extrapolations are made using $F_c = 0.5$ at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

$HO + C_2H_6 \rightarrow H_2O + C_2H_5$

$\Delta H^\circ = -78.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.70×10^{-13}	294	Lafage *et al.*, 1987[1]	(a)
1.12×10^{-12}	413		
$(2.38 \pm 0.16) \times 10^{-13}$	297 ± 2	Abbatt, Demerjian, and Anderson, 1990[2]	(b)
$(2.43 \pm 0.12) \times 10^{-13}$	Room temp.	Schiffman *et al.*, 1991[3]	(c)
Reviews and Evaluations			
$7.4 \times 10^{-12} \exp(-990/T)$	230–300	IUPAC, 1989[4]	(d)
$1.42 \times 10^{-17}\ T^2 \exp(-462)/T$	226–800	Atkinson, 1989[5]	(e)
$1.1 \times 10^{-11} \exp(-1100/T)$	248–800	NASA, 1990[6]	(f)

Comments

(a) Discharge flow system with resonance fluorescence and LIF detection of the HO radical.

(b) Discharge flow system with LIF detection of HO radicals. The total pressure was varied over the range 7–381 Torr. Flow velocity and HO radical concentration radial/axial profiles were measured, allowing the full continuity equation to be solved and hence eliminating the need to use the "plug flow" approximation.

(c) Pulsed laser photolysis system with laser infrared absorption detection of the HO radical. HO radicals generated by laser photolysis of HNO_3 at 193 nm. Total pressure, with argon diluent, was 9 Torr.

(d) Derived using the absolute rate coefficient data of Greiner,[7] Overend *et al.*,[8] Howard and Evenson,[9] Leu,[10] Margitan and Watson,[11] Tully *et al.*,[12,13] Jeong *et al.*,[14] Smith *et al.*,[15] Baulch *et al.*,[16] Schmidt *et al.*,[17] Devolder *et al.*,[18] Stachnick *et al.*,[19] Wallington *et al.*,[20] Bourmada *et al.*[21] and Zabarnick *et al.*[22] The absolute rate coefficient data used in the evaluation[7-22] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.42 \times 10^{-17}\ T^2 \exp(-461/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 226–800 K. The Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$.

(e) Derived from the absolute rate coefficient data of Greiner,[7] Overend *et al.*,[8] Howard and Evenson,[9] Leu,[10] Margitan and Watson,[11] Tully *et al.*,[12,13] Jeong *et al.*,[14] Smith *et al.*,[15] Baulch *et al.*,[16] Devolder *et al.*,[18] Stachnik *et al.*,[19] Wallington *et al.*,[20] Bourmada *et al.*[21] and Zabarnick *et al.*[22] These data were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$.

(f) The 298 K rate coefficient was derived from the data of Greiner,[7] Overend *et al.*,[8] Howard and Evenson,[9] Lee and Tang,[23] Leu,[10] Tully *et al.*,[12,13] Jeong *et al.*[14] and Nielsen *et al.*,[24] using a temperature dependence of $E/R = 1100$ K to recalculate the reported room temperature data to 298 K. The temperature dependence was derived from the data of Greiner,[7] Tully *et al.*[12] and Jeong *et al.*[14]

Preferred Values

$k = 2.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.8 \times 10^{-12} \exp(-1020/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values were obtained by using the absolute rate coefficient data of Howard and Evenson,[9] Leu,[10] Margitan and Watson,[11] Tully *et al.*,[12,13] Smith *et al.*,[15] Baulch *et al.*,[16] Devolder *et al.*,[18] Stachnick *et al.*,[19] Wallington *et al.*,[20] Bourmada *et al.*,[21] Zabarnick *et al.*[22] and Abbatt *et al.*[2] The rate coefficient data of Greiner,[7] Overend *et al.*[8] and Jeong *et al.*[14] were not used in the evaluation since, analogous to the situation for the reaction of the HO radical with methane (see $HO + CH_4$ data sheet), the C_2H_6/HO concentration ratios were such that the possibility of secondary reactions existed, leading to erroneously high measured rate coefficients. The data of Gordon and Mulac,[25] Lee and Tang,[23] and Nielsen *et al.*[24] were also not included in the evaluation since, while their data are in good agreement with the other rate coefficients for C_2H_6, these studies exhibit significant discrepancies with the consensus literature data for other organic compounds studied.

The absolute rate coefficient data used in the evaluation[2,9-13,15,16,18-22] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.51 \times 10^{-17}\ T^2 \exp(-492/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 226–800 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$. The room temperature (the temperature not being specified) absolute rate coefficient of Schiffman *et al.*[3] is in good agreement with the preferred

298 K rate coefficient, as are the relative rate coefficients of Baulch *et al.*[26] and Edney *et al.*[27]

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$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$

$\Delta H° = -134$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$8 \times 10^{-27}(T/300)^{-3.5}$ [N$_2$]	200–300	CODATA, 1984[1]; IUPAC, 1989[2]	(a)
$3 \times 10^{-27}(T/298)^{-3}$ [air]	298–400	Atkinson, 1989[3]	(b)

Comments

(a) In the pressure range 1–760 Torr at 298 K, the reaction is close to its high-pressure limit. The falloff extrapolation, therefore, is very uncertain. The k_0 value was based on the data from Klein *et al.*[4] which show little scatter. $F_c = 0.5$ at 300 K was used such as in Refs. 4 and 5. The temperature dependence was estimated by analogy to the reaction $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

(b) Extensive evaluation of earlier data. Chosen value of k_0 was the geometrical mean of the data from Refs. 4 and 5. The temperature dependence was estimated by analogy to $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

Preferred Values

$k_0 = 8 \times 10^{-27}(T/300)^{-3.5}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, becaus the reaction is close to the high-pressure limit at pres sures of 1 bar. The preferred values follow the falloff ex trapolations from Refs. 4 and 5 which show the smalles scatter. Falloff extrapolations are made using $F_c = 0.5$ a 300 K. The temperature coefficient of k_0 is estimated b analogy to the reaction $HO + C_2H_4 + M \rightarrow C_2H_4OH + M$.

High-pressure rate coefficients

Rate coefficients data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.01 \pm 0.42) \times 10^{-11}$	298	Nielsen *et al.*, 1990[6]	(a)
Reviews and Evaluations			
3.0×10^{-11}	200–300	CODATA, 1984[1]; IUPAC, 1989[2]	(b)
[illegible]$.8 \times 10^{-11}(T/298)^{-1.3}$	290–470	Atkinson, 1989[3]	(c)

Comments

(a) Pulsed radiolysis of H_2O–Ar mixtures at a total pressure of 1 bar. The generated HO was determined by absorption spectroscopy at 309 nm.

(b) Based on a variety of experimental data at pressures below 1 bar. Falloff extrapolations of the experiments of references 4, 5, and 7 showed consistency.

(c) Extensive evaluation of earlier data. The temperature coefficient was from the data of Refs. 5 and 7. Falloff extrapolation using $F_c = 0.5$ at 300 K.

Preferred Values

$k_\infty = 3.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ over the temperature range 200–300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on Refs. 1–7. Because there is uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, as in the reaction HO + C_2H_2 + M → C_2H_2OH + M, we prefer a temperature independent value of k_∞ in contrast to the recommendation of Ref. 3.

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$HO + C_3H_8 \rightarrow H_2O + n\text{-}C_3H_7$ (1)
$\rightarrow H_2O + i\text{-}C_3H_7$ (2)

$\Delta H°(1) = -75.9$ kJ·mol⁻¹
$\Delta H°(2) = -87.6$ kJ·mol⁻¹

Rate coefficient data ($k = k_1 + k_2$)

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.27 \pm 0.11) \times 10^{-12}$	295 ± 2	Nielsen *et al.*, 1988[1]	(a)
$(1.21 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt, Demerjian, and Anderson, 1990[2]	(b)
$(1.22 \pm 0.08) \times 10^{-12}$	298	Mac Leod *et al.*, 1990[3]	(c)
$(1.02 \pm 0.05) \times 10^{-12}$	Room temperature	Schiffman *et al.*, 1991[4]	(d)
Relative Rate Coefficients			
1.38×10^{-12}	300 ± 3	Behnke, Nolting and Zetzsch, 1987[5]	(e)
Reviews and Evaluations			
$8.6 \times 10^{-12} \exp(-610/T)$	~270–340	IUPAC, 1989[6]	(f)
$1.50 \times 10^{-17} T^2 \exp(-44/T)$	293–1220	Atkinson, 1989[7]	(g)
$1.4 \times 10^{-11} \exp(-750/T)$	293–500	NASA, 1990[8]	(h)

Comments

(a) HO radicals generated by pulsed radiolysis of Ar–H_2O mixtures at 750 Torr total pressure and detected by UV absorption at 309 nm.
(b) Discharge flow system with LIF detection of HO radicals. The total pressure was 51 ± 2 Torr (N_2). Flow velocity and HO radical concentration radial/axial profiles were measured, allowing the full continuity equation to be solved and hence eliminating the need to use the "plug flow" approximation.
(c) HO radicals generated by the pulsed laser photolysis of HNO_3, and detected by LIF.
(d) HO radicals generated by the pulsed laser photolysis of HNO_3 at 193 nm, and detected by laser infrared absorption. Total pressure, with argon as the diluent, was 9 Torr.
(e) Relative rate method. HO radicals generated by photolysis of NO_x-organic-air mixtures at atmospheric pressure, and the relative decay rates of propane and n-butane measured. The cited rate coefficient was obtained relative to a rate coefficient of k(HO + n-butane) = 2.56×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[7]
(f) Derived from the absolute rate coefficient data of Greiner,[9] Schmidt *et al.*,[10] Baulch *et al.*[11] and Droege and Tully[12] and the relative rate coefficient of Atkinson *et al.*[13] (these studies of Droege and Tully[12] and Atkinson *et al.*[13] superseding the previous studies of Tully *et al.*[14] and Darnall *et al.*,[15] respectively). These data[9–13] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.29 \times 10^{-17}$ $T^2 \exp(6/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 293–854 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 300 K, and was derived from the three parameter equation with

$$A = C\,e^2\,T^2 \text{ and } B = D + 2T.$$

(g) Derived from the absolute rate coefficient data of Greiner,[9] Baulch *et al.*,[11] Droege and Tully,[12] Bott and Cohen[16] and Smith *et al.*[17] and the relative rate coefficients of Baker *et al.*[18,19] and Atkinson *et al.*[13] (the studies of Droege and Tully[12] and Atkinson *et al.*[13] superseding the previous studies of Tully *et al.*[14] and Darnall *et al.*,[15] respectively). These data[9,11–13,16–19] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$.
(h) The room temperature rate coefficients of Greiner,[9] Bradley *et al.*,[20] Tully *et al.*,[14] Baulch *et al.*,[21] Schmidt *et al.*[10] and Droege and Tully[12] were used to derive the 298 K value. The temperature dependence was derived from a least-squares analysis of the rate coefficients of Greiner,[9] Tully *et al.*[14] and Tully and Droege[12] at <500 K, with the A factor being adjusted to fit the 298 K value.

Preferred Values

$k = 1.14 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 9.8 \times 10^{-12} \exp(-640/T)$ cm^3 $molecule^{-1}$ s^{-1} over a small temperature range around 300 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values
The available rate coefficient data exhibit a large amount of scatter, especially at 350 K and below. The absolute rate coefficient data of Greiner,[9] Bott and Cohen,[16] Smith *et al.*,[17] Baulch *et al.*,[11] Droege and Tully,[12] Abbatt *et al.*[2] and Mac Leod *et al.*[3] and the relative rate coefficients of Baker *et al.*[18,19] and Atkinson *et al.*[13] were used to derive the preferred value. These data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.48 \times 10^{-17}$ $T^2 \exp(-39/T)$ cm^3 $molecule^{-1}$ s^{-1} over the range 293–1220 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K, and is derived from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$. Note that the data upon which this expression is derived do not extend below 293 K. The relative rate coefficients of Baulch *et al.*[21] and Edney *et al.*[22] are in good agreement with the recommended expression, as is the absolute rate coefficient of Schiffman *et al.*[4] at room temperature (which was not specified).

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$HO + CO \rightarrow H + CO_2$

$\Delta H^\circ = -104.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}		Temp./K	Reference	Comments
Absolute Rate Coefficients				
1.72×10^{-13}	(P = 0.6 bar)	295	Forster *et al.*, 1992[1]	(a)
2.67×10^{-13}	(P = 1.1 bar)	295		
6.19×10^{-13}	(P = 130 bar)	295		
Reviews and Evaluations				
1.5×10^{-13} [1 + (0.6 P/bar)]		200–300	IUPAC, 1989[2]	(b)
1.5×10^{-13} [1 + (0.6 P/bar)]		200–300	NASA, 1990[3]	(b)

Comments

(a) Laser flash photolysis of N_2O at 193 nm in the presence of H_2O–CO–He mixtures at total pressures between 0.6 and 130 bar. HO radicals were detected by saturated LIF near 308 nm. Pseudo-first order conditions used with excess CO. Analysis of the pressure dependence in terms of a complex mechanism involving addition of HO gave a value of $k_\infty = 6.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(b) Weighted non-linear least-squares fit of pressure dependent data in N_2 and air from Paraskevopoulos and Irwin,[4] DeMore,[5] Hofzumahaus and Stuhl,[6] Niki *et al.*,[7] Hynes *et al.*,[8] Wahner and Zetzsch[9] and unpublished data of Fritz and Zellner, Stachnik and Molina, and Wine and co-workers. The zero temperature dependence was recommended on the basis of the data of Hynes *et al.*[8] and Stachnik and Molina.

Preferred Values

$k = 1.5 \times 10^{-13}$ [1 + 0.6 P/bar)] over the temperature range 200–300 K and the pressure range 0 – 1 bar N_2 or air.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) - \pm 300$ K.

Comments on Preferred Values

The preferred values are unchanged from our previous evaluation[2] and are recommended on the same basis [see comment (b)]. The recent investigation of the pressure dependence up to very high pressures confirms the complex addition mechanism, and increases the confidence in the recommended pressure dependence for atmospheric conditions. There is little or no temperature dependence under conditions relevant for atmospheric chemistry. At higher temperatures, the rate coefficient k increases in a strongly non-Arrhenius fashion (see the review by Tsang and Hampson[10]).

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$$HO + HCHO \rightarrow H_2O + HCO \quad (1)$$
$$\rightarrow H + HCOOH \quad (2)$$

$\Delta H°(1) = -135.3$ kJ·mol^{-1}
$\Delta H°(2) = -91.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.95^{+2.04}_{-1.44}) \times 10^{-12}$	298	Yetter *et al.*, 1989[1]	(a)
Branching Ratios			
$k_1/k = 0.97^{+0.03}_{-0.10}$	298	Yetter *et al.*, 1989[1]	(a)
Reviews and Evaluations			
$1.6 \times 10^{-11} \exp(-110/T)$	230–580	IUPAC. 1989[2]	(b)
$1.25 \times 10^{-17} T^2 \exp(648/T)$	228–426	Atkinson, 1989[3]	(c)
1.0×10^{-11}	228–426	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals. HO radicals generated by reaction of H atoms with NO_2. Branching ratio derived from modeling of HO radical decays obtained in the presence of HCHO in the presence and absence of O_2.

(b) Derived from the absolute rate coefficients determined by Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner[7] and Zabarnick *et al.*,[8] which are in reasonably good agreement at room temperature. The rate coefficients of Morris and Niki[9] and Niki *et al.*[10,11] are consistent with the 298 K value.

(c) Derived from the absolute rate coefficients of Atkinson and Pitts[5] and Stief *et al.*,[6] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(d) The 298 K rate coefficient was the average of the absolute rate coefficients determined by Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner[7] and Zabarnick *et al.*[8] The combined data set yielded no evidence for any temperature dependence of the rate coefficient.

Preferred Values

$k = 9.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.8 \times 10^{-12} \exp(25/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

$k_1/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts,[5] Stief *et al.*,[6] Temps and Wagner,[7] Zabarnick *et al.*[8] (averaging the 296–301 K and 567–574 K values to yield rate coefficients of 1.25×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and 1.45×10^{-11} cm^3 molecule^{-1} s^{-1} at 572 K) and Yetter *et al.*[1] and the relative rate coefficient of Niki *et al.*[11] (for formaldehyde-^{13}C) were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in

$$k = 1.69 \times 10^{-17} T^2 \exp(557/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 228–572 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A = C e^2T^2$ and $B = D + 2T$.

The product data of Temps and Wagner[7] and Niki *et al.*[11] and the kinetic/modeling results of Yetter *et al.*[1] show that at 298 K this reaction proceeds essentially totally via pathway (1) to yield H_2O + HCO.

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$HO + CH_3CHO \rightarrow H_2O + CH_3CO$

$\Delta H^\circ = -139.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.6 \times 10^{-12} \exp[(200 \pm 60)/T]$	297–517	Dóbé, Khachatryan and Bérces, 1989[1]	(a)
$(1.69 \pm 0.34) \times 10^{-11}$	298 ± 2		
$(1.7 \pm 0.3) \times 10^{-11}$	298	Balestra-Garcia *et al.*, 1992[2]	(b)
Reviews and Evaluations			
$5.6 \times 10^{-12} \exp(310/T)$	240–530	IUPAC, 1989[3]	(c)
$5.55 \times 10^{-12} \exp(311/T)$	244–528	Atkinson, 1989[4]	(c)
$6.0 \times 10^{-12} \exp(250/T)$	244–528	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with resonance fluorescence or LIF detection of HO radicals. HO radicals generated from the reactions $H + NO_2$ and $F + H_2O$.

(b) Laser photolysis system with resonance fluorescence detection of HO radicals.

(c) Derived from the absolute rate coefficient data of Atkinson and Pitts[6] and Michael *et al.*,[7] and the relative rate coefficient of Niki *et al.*[8] at 298 K. The data of Semmes *et al.*[9] were not used in the evaluation because of their reported difficulties in determining the acetaldehyde concentration.

(d) The 298 K rate coefficient was based upon the rate coefficient data of Morris *et al.*,[10] Niki *et al.*,[8] Atkinson and Pitts,[6] Kerr and Sheppard,[11] Semmes *et al.*[9] and Michael *et al.*[7] The temperature dependence was the average of those measured by Atkinson and Pitts,[6] Semmes *et al.*[9] and Michael *et al.*[7]

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.6 \times 10^{-12} \exp(310/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–530 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values were obtained from a least-squares analysis of the absolute rate coefficient data of Atkinson and Pitts[6] and Michael *et al.*,[7] and the relative rate coefficient of Niki *et al.*[8] at 298 K. The absolute and relative rate data of Morris *et al.*,[10] Cox *et al.*,[12] Kerr and Sheppard[11] and Balestra-Garcia *et al.*[2] are in agreement with the preferred 298 K value. The data of Semmes *et al.*,[9] which are lower than the preferred values by up to ~25%, were not used in the evaluation because of their reported difficulties in accurately determining the acetaldehyde concentrations.

While the absolute rate coefficients measured by Dóbé *et al.*[1] for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(CH_3)_2CHCHO$ and $(CH_3)_3CCHO$ are significantly higher, by factors of ~1.5–2.3, than the rate coefficients of Kerr and Sheppard[11] and Semmes *et al.*[9] (which are in good agreement). Accordingly, the rate coefficient data of Dóbé *et al.*[1] have not been used in the evaluation.

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HO + C_2H_5CHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.71 \pm 0.24) \times 10^{-11}$	298	Semmes *et al.*, 1985[1]	(a)
Relative Rate Coefficients			
3.06×10^{-11}	298	Morris and Niki, 1971[2]	(b)
$(2.22 \pm 0.09) \times 10^{-11}$	298 ± 2	Niki *et al.*, 1978[3]	(c)
$(1.94 \pm 0.15) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981[4]	(c)
$(1.83 \pm 0.21) \times 10^{-11}$	298	Audley, Baulch and Campbell, 1981[5]	(d)
$<3.0 \times 10^{-11}$	296	Kerr and Stocker, 1985[6]	(e)
Reviews and Evaluations			
2.0×10^{-11}	298	IUPAC, 1989[7]	(f)
1.96×10^{-11}	298	Atkinson, 1989[8]	(g)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Discharge flow system with MS detection of 1-propanal and propene in the presence of excess HO radicals. Rate coefficient determined relative to that for propene, and placed on an absolute basis using k(HO + propene) = 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} under the experimental conditions used.[9]

(c) Relative rate method. HO radicals generated by photolysis of HONO in air at atmospheric pressure. Decay of 1-propanal monitored relative to that for ethene, and placed on an absolute basis using k(HO + ethene) = 8.52×10^{-12} cm^3 molecule^{-1} s^{-1}.[8]

(d) Relative rate method. HO radicals generated from the heterogeneous reaction of H_2O_2 with NO_2. Rate coefficient measured relative to that for acetaldehyde, and placed on an absolute basis by use of k(HO + CH_3CHO) = 1.6×10^{-11} cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Relative rate method. Rate coefficient determined relative to that for HO + HONO from the observed dependence of the rate of change of NO on the NO_x/C_2H_5CHO concentration ratio, and placed on an absolute basis by use of k(HO + HONO) = 4.8×10^{-12} cm^3 molecule^{-1} s^{-1} (this evaluation).

(f) See Comments on Preferred Values.

(g) Derived from the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[3] and Kerr and Sheppard.[4]

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[7] The preferred rate coefficient is derived from the mean of the absolute rate coefficient of Semmes *et al.*[1] and the relative rate coefficients of Niki *et al.*[3] and Kerr and Sheppard.[4] The upper limit to the rate coefficient obtained by Kerr and Stocker[6] is consistent with the preferred value. The relative rate coefficient of Audley *et al.*[5] was not used in the evaluation, due to questions concerning the applicability of the experimental technique used.[1,8] The rate coefficient derived by Kaiser[10] at 553 K relative to those for ethene, propene and *trans*-2-butene of $\leq 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, though of only semi-quantitative value, suggests a zero or close to zero temperature dependence, as expected by analogy with HCHO and CH_3CHO. The major reaction channel is expected[8] to be H-atom abstraction from the –CHO group to form H_2O + C_2H_5CO.

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$HO + (CHO)_2 \rightarrow H_2O + CHOCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.14 \pm 0.04) \times 10^{-11}$	298 ± 2	Plum *et al.*, 1983[1]	(a)
Reviews and Evaluations			
1.1×10^{-11}	298	IUPAC, 1989[2]	(b)
1.14×10^{-11}	298	Atkinson, 1989[3]	(c)

Comments

(a) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Relative decay rates of glyoxal and cyclohexane monitored in the presence of varying concentrations of HO radicals. Relative rate coefficient placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 molecule^{-1} s^{-1}.[3]

(b) See Comments on Preferred Values.

(c) Based on the study of Plum *et al.*[1]

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred rate coefficient is based on the study of Plum *et al.*,[1] with increased uncertainty limits. The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield H_2O + HC(O)CO.

References

[1]C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

[2]IUPAC, Supplement III, 1989 (see references in Introduction).

[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).

$HO + HOCH_2CHO \rightarrow H_2O + HOCH_2CO$ (1)
$\rightarrow H_2O + HOCHCHO$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.0 \pm 0.1) \times 10^{-11}$	298 ± 2	Niki *et al.*, 1987[1]	(a)
Branching Ratios			
$k_2/k = 0.20$	298	Niki *et al.*, 1987[1]	(a)
$k_1/k = 0.80$			
Reviews and Evaluations			
1.0×10^{-11}	298	IUPAC, 1989[2]	(b)

Comments

(a) HO radicals generated by photolysis of CH_3ONO–NO–air and C_2H_5ONO–NO–air mixtures at 700 Torr total pressure. Rate coefficient measured relative to that for reaction of HO radicals with CH_3CHO, and placed on an absolute basis by use of $k(HO + CH_3CHO) = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Branching ratio determined by measuring the formation of the $(CHO)_2$, CO_2 and HCHO products, with $(CHO)_2$ being produced by reaction of O_2 with the $HO\dot{C}HCHO$ radical formed in step (2), and CO_2 + HCHO being produced from the $HOCH_2\dot{C}O$ radical formed in step (1).
(b) See Comments on Preferred Values.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.80$ at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred 298 K rate coefficient is taken from the study of Niki *et al.*,[1] with the error limits increased accordingly.

References

[1]H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley, J. Phys. Chem. **91**, 2174 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$HO + CH_3COCHO \rightarrow H_2O + CH_3COCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.1 \pm 1.6) \times 10^{-12}$	297	Kleindienst, Harris and Pitts, 1982[1]	(a)
Relative Rate Coefficients			
$(1.72 \pm 0.12) \times 10^{-11}$	298 ± 2	Plum *et al.*, 1983[2]	(b)
Reviews and Evaluations			
1.7×10^{-11}	298	IUPAC, 1989[3]	(c)
1.72×10^{-11}	298	Atkinson, 1989[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.
(b) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Relative decay rates of methylglyoxal and cyclohexane monitored in the presence of varying concentrations of HO radicals. Relative rate coefficient placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 molecule^{-1} s^{-1}.[4]
(c) See Comments on Preferred Values.
(d) Based upon the relative rate coefficient of Plum *et al.*[2]

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred 298 K rate coefficient is based upon the data obtained by Plum *et al.*[2] The absolute rate coefficient measured by Kleindienst *et al.*[1] may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal. A close to zero temperature dependence is expected at around room temperature. The reaction is assumed to proceed via H-atom abstraction to form H_2O + CH_3COCO.

References

[1]T. E. Kleindienst, G. W. Harris, and J. N. Pitts, Jr., Environ. Sci. Technol. **16**, 844 (1982).
[2]C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).

$HO + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2$

$\Delta H^\circ = -87.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-12} \exp[-(600 \pm 75)/T]$	240–440	Wallington and Kurylo, 1987[1]	(a)
$(2.16 \pm 0.16) \times 10^{-13}$	296		
Relative Rate Coefficients			
$\leq 5 \times 10^{-13}$	300	Cox, Derwent and Williams, 1980[2]	(b)
$(6.3 \pm 0.9) \times 10^{-13}$	298	Chiorboli *et al.*, 1983[3]	(c)
$(2.7 \pm 0.8) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986[4]	(d)
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(-600/T)$	240–440	IUPAC, 1989[5]	(e)
$2.13 \times 10^{-18} T^2 \exp(53/T)$	240–440	Atkinson, 1989[6]	(f)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

(b) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. Relative decay rate of CH_3COCH_3 measured relative to those for ethene and toluene. Due to photolysis of CH_3COCH_3, the measured decay rate is an upper limit to that due to HO radical reaction.

(c) Relative rate method. HO radicals generated by photolysis of organic–NO–air mixtures at atmospheric pressure. Relative decay rates of CH_3COCH_3 and n-hexane measured, and rate coefficient placed on an absolute basis by use of k(HO + n-hexane) = 5.61×10^{-12} cm^3 molecule^{-1} s^{-1}.[6]

(d) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. Decay rate of CH_3COCH_3 measured relative to that for ethene, with account being taken of the concurrent photolysis of CH_3COCH_3. Rate coefficient placed on an absolute basis by use of k(HO + ethene) = 8.32×10^{-12} cm^3 molecule^{-1} s^{-1}.[6]

(e) See Comments on Preferred Values.

(f) Derived from the absolute rate coefficients of Wallington and Kurylo[1] and Zetzsch (unpublished data, 1982) and the relative rate coefficient of Kerr and Stocker,[4] using the expression

$$k = CT^2 \exp(-D/T).$$

Preferred Values

$k = 2.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-12} \exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–440 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The preferred rate coefficient is based on the absolute study of Wallington and Kurylo,[1] which is in good agreement with the relative rate coefficient of Kerr and Stocker[4] and consistent with that of Cox *et al.*[2] The higher rate coefficient reported by Chiorboli *et al.*[3] could be due to photolysis of CH_3COCH_3, which was not taken into account.

References

[1] T. J. Wallington and M. J. Kurylo, J. Phys. Chem. **91**, 5050 (1987).
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[4] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).

$$HO + CH_3OH \rightarrow H_2O + CH_2OH \quad (1)$$
$$\rightarrow H_2O + CH_3O \quad (2)$$

$\Delta H°(1) = -105.4$ kJ·mol^{-1}
$\Delta H°(2) = -61.9$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.8 \pm 1.8) \times 10^{-13}$	298	Pagsberg *et al.*, 1988[1]	(a)
$(1.01 \pm 0.10) \times 10^{-12}$	298 ± 2	McCaulley *et al.*, 1989[2]	(b)
$5.89 \times 10^{-20}\ T^{2.65} \exp(444/T)$	294–866	Hess and Tully, 1989[3]	(c)
9.42×10^{-13}	298		
$(9.0 \pm 0.9) \times 10^{-13}$	298 ± 2	Nelson *et al.*, 1990[4]	(d)
Relative Rate Coefficients			
$(1.00 \pm 0.23) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[4]	(e)
Branching Ratios			
$k_2/k = 0.15 \pm 0.08$	298 ± 2	McCaulley *et al.*, 1989[2]	(f)
Reviews and Evaluations			
$9.1 \times 10^{-12} \exp(-690/T)$	240–1000	IUPAC, 1989[5]	(g)
$6.39 \times 10^{-18}\ T^2 \exp(148/T)$	240–866	Atkinson, 1989[6]	(h)
$6.7 \times 10^{-12} \exp(-600/T)$	240–400	NASA, 1990[7]	(i)

Comments

(a) HO radicals generated by pulsed radiolysis of Ar–CH_3OH mixtures at 750 Torr total pressure. HO radicals monitored by UV absorption at 309 nm and HO radical decay rates measured in the presence of excess CH_3OH.

(b) Determined using a discharge flow system with LIF detection of HO radicals.

(c) HO radicals produced by the reaction of O(^{1}D) atoms, generated from the pulsed laser photolysis of N_2O, with H_2O. HO radicals monitored by LIF detection.

(d) HO radicals generated by pulsed radiolysis of Ar–H_2O mixtures at 1 atmosphere total pressure. HO radicals monitored by UV absorption at 309 nm.

(e) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures, and methanol and cyclohexane concentrations monitored by gas chromatography. Rate constant ratio placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 molecule^{-1} s^{-1}.[6]

(f) Derived from measurements at 298 ± 2 K of the rate coefficients for the reactions of the HO radical with CH_3OH, CD_3OH and CD_3OH and of the DO radical with CH_3OH, CH_3OD, CD_3OH and CD_3OD, assuming that secondary kinetic isotope effects are negligible.

(g) The 298 K rate coefficient was based upon the room temperature absolute rate coefficients of Overend and Paraskevopoulos,[8] Ravishankara and Davis,[9] Hägele *et al.*,[10] Meier *et al.*,[11] Greenhill and O'Grady[12] and Wallington and Kurylo[13] and the relative rate coefficients of Barnes *et al.*[14] and Tuazon *et al.*[15] The temperature dependence was the average of those reported from the absolute rate coefficient studies,[10–13] with the A factor being adjusted to yield the 298 K value.

(h) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,[8] Ravishankara and Davis,[9] Wallington and Kurylo[13] and Hess and Tully[3] and the relative rate coefficient of Tuazon *et al.*,[15] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(i) The 298 K rate coefficient was the average of the absolute rate coefficients of Overend and Paraskevopoulos,[8] Ravishankara and Davis,[9] Hägele *et al.*,[10] Meier *et al.*,[11] Greenhill and O'Grady,[12] Wallington and Kurylo[13] and Hess and Tully.[3] The temperature dependence was derived from those reported by Greenhill and O'Grady[12] and Wallington and Kurylo.[13]

Preferred Values

$k = 9.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.3 \times 10^{-12} \exp(-380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta\log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta k_2/k = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Overend and Paraskevopoulos,[8] Ravishankara and Davis,[9] Wallington and Kurylo,[13] McCaully *et al.*,[2] Hess and Tully[3] and Nelson *et al.*[4] and the relative rate coefficient of Tuazon *et al.*[15] to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.37 \times 10^{-18}\ T^2 \exp(150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–866 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 365 K, and is derived from the three parameter equation with $A = C\, e^2 T^2$ and $B = D + 2T$. The kinetic[2] and product[10,11] studies show that the reaction proceeds mainly by step (1) at room temperature, as expected from the thermochemistry of the reaction steps (1) and (2).

References

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$HO + C_2H_5OH \rightarrow H_2O + CH_2CH_2OH$ (1)
$\rightarrow H_2O + CH_3CHOH$ (2)
$\rightarrow H_2O + CH_3CH_2O$ (3)

$\Delta H°(1) = -80$ kJ·mol^{-1}
$\Delta H°(2) = -109.9$ kJ·mol^{-1}
$\Delta H°(3) = -63.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.26 \pm 0.14) \times 10^{-12}$	293	Hess and Tully, 1988[1]	(a,b)
$(3.33 \pm 0.14) \times 10^{-12}$	326.5		
$(3.63 \pm 0.15) \times 10^{-12}$	380		
$(3.94 \pm 0.16) \times 10^{-12}$	441		
$(3.32 \pm 0.16) \times 10^{-12}$	295	Hess and Tully, 1988[1]	(b,c)
$(5.47 \pm 0.34) \times 10^{-12}$	599		
$(3.04 \pm 0.25) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[2]	(d)
Relative Rate Coefficients			
$(3.46 \pm 0.52) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[2]	(e)
Reviews and Evaluations			
$9.3 \times 10^{-12} \exp(-300/T)$	250–450	IUPAC, 1989[3]	(f)
$6.18 \times 10^{-18}\ T^2 \exp(532/T)$	293–599	Atkinson, 1989[4]	(g)
$6.8 \times 10^{-12} \exp(-225/T)$	240–600	NASA, 1990[5]	(h)

Comments

(a) HO radicals generated by pulsed laser photolysis of N_2O to form $O(^1D)$ atoms, with the $O(^1D)$ atoms reacting with H_2O. HO radicals detected by LIF.

(b) Thermal decomposition of the $HO^{16}CH_2CH_2$ radical formed by H-atom abstraction from the $-CH_3$ group to regenerate HO^{16} radicals occurs at temperatures >500 K, and hence the HO^{16} rate coefficient data do not yield the rate coefficient $k = k_1 + k_2 + k_3$ above ~500 K. Since thermal decomposition of the $HO^{16}CH_2\dot{C}H_2$ radical does not lead to regeneration of the HO^{18} radical, the HO^{18} rate coefficient data yield the overall reaction rate coefficient, $k = k_1 + k_2 + k_3$.

(c) Rate coefficients for reaction of the HO^{18} radical. HO^{18} radicals generated from pulsed laser photolysis of $H_2{}^{18}O$, with HO^{18} being detected by LIF.

(d) HO radicals generated from pulsed radiolysis of

that of Hess and Tully[1] [see comments (a–c)]. The pre-

Comments

(a) HO radicals generated from the pulsed radiolysis of Ar–H_2O mixtures at atmospheric pressure and detected by UV absorption at 309 nm.

(b) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decay rate of *i*-propanol measured relative to that for cyclohexane. The rate coefficient ratio measured was placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3]

(c) The 298 K rate coefficient was derived from the average of those of Overend and Paraskevopoulos[4] and Wallington and Kurylo,[5] combined with a zero temperature dependence.[5]

(d) The absolute rate coefficients of Overend and Paraskevopoulos[4] and Wallington and Kurylo[5] were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 5.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 240–440 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature absolute rate coefficients of Overend and Paraskevopoulos,[4] Wallington and Kurylo[5] and Nelson *et al.*[1] and the relative rate coefficient of Nelson *et al.*[1] The preferred rate coefficient is in agreement with the relative rate coefficients reported by Lloyd *et al.*[6] and Klöpffer *et al.*[7] A zero temperature dependence is used, consistent with the data of Wallington and Kurylo.[5]

References

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HO + CH_3COCH_2OH → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.3) \times 10^{-12}$	298	Dagaut *et al.*, 1989[1]	(a)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Dagaut *et al.*,[1] with expanded uncertainty limits.

References

[1] P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem. **93**, 7838 (1989).

HO + n-C_3H_7OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.64 \pm 0.48) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[1]	(a)
Relative Rate Coefficients			
$(5.50 \pm 0.44) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[1]	(b)
Reviews and Evaluations			
5.3×10^{-12}	298	IUPAC, 1989[2]	(c)
5.34×10^{-12}	298	Atkinson, 1989[3]	(c)

Comments

(a) HO radicals generated by pulsed radiolysis of Ar–H_2O mixtures at 1 atmosphere total pressure and detected by UV absorption at 309 nm.

(b) Relative rate method. HO radicals generated from the photolysis of CH_3ONO–NO–air mixtures. Rate coefficient measured relative to that for cyclohexane, and placed on an absolute basis by use of k(HO + cyclohexane) $= 7.49 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[3]

(c) Average of the room temperature absolute rate coefficients of Overend and Paraskevopoulos[4] and Wallington and Kurylo.[5]

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The experimental technique of Campbell *et al.*[6] was possibly prone to unrecognized problems,[3] and hence this rate coefficient was not used in deriving the preferred values. The 298 K value is the mean of the absolute rate coefficients of Overend and Paraskevopoulos,[4] Wallington and Kurylo[5] and Nelson *et al.*[1] and the relative rate coefficient of Nelson *et al.*[1]

References

[1] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).
[4] R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (1976).
[5] T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (1987).
[6] I. M. Campbell, D. F. McLaughlin, and B. J. Handy, Chem. Phys. Lett. **38**, 362 (1976).

HO + i-C_3H_7OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.69 \pm 1.09) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[1]	(a)
Relative Rate Coefficients			
$(5.78 \pm 0.75) \times 10^{-12}$	298 ± 2	Nelson *et al.*, 1990[1]	(b)
Reviews and Evaluations			
5.6×10^{-12}	240–440	IUPAC, 1989[2]	(c)
$7.32 \times 10^{-18}\ T^2 \exp(620/T)$	240–440	Atkinson, 1989[3]	(d)

Comments

(a) HO radicals generated from the pulsed radiolysis of Ar–H_2O mixtures at atmospheric pressure and detected by UV absorption at 309 nm.
(b) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decay rate of *i*-propanol measured relative to that for cyclohexane. The rate coefficient ratio measured was placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3]
(c) The 298 K rate coefficient was derived from the average of those of Overend and Paraskevopoulos[4] and Wallington and Kurylo,[5] combined with a zero temperature dependence.[5]
(d) The absolute rate coefficients of Overend and Paraskevopoulos[4] and Wallington and Kurylo[5] were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 5.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the range 240–440 K.

Reliability
$\Delta\log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The preferred 298 K rate coefficient is the average the room temperature absolute rate coefficients Overend and Paraskevopoulos,[4] Wallington and Kury and Nelson *et al.*[1] and the relative rate coefficient of N son *et al.*[1] The preferred rate coefficient is in agreeme with the relative rate coefficients reported by Lloyd *et a* and Klöpffer *et al.*[7] A zero temperature dependence used, consistent with the data of Wallington and Kuryl

References

[1]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[4]R. Overend and G. Paraskevopoulos, J. Phys. Chem. **82**, 1329 (197
[5]T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet. **19**, 1015 (198
[6]A. C. Lloyd, K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., Che Phys. Lett. **42**, 205 (1976).
[7]W. Klöpffer, R. Frank, E.-G. Kohl, and F. Haag, Chemiker-Zeitun **110**, 57 (1986).

HO + CH_3COCH_2OH → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.3) \times 10^{-12}$	298	Dagaut *et al.*, 1989[1]	(a)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO radicals.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability
$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
Based on the sole study of Dagaut *et al.*,[1] with expanded uncertainty limits.

References

[1]P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, J. Phys. Chem **93**, 7838 (1989)

$HO + CH_3OOH \rightarrow H_2O + CH_2OOH$ (1)
$\rightarrow H_2O + CH_3OO$ (2)

$\Delta H(2) = -140$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.93 \times 10^{-12} \exp[(190 \pm 14)/T]$	223–423	Vaghjiani and Ravishankara, 1989[1]	(a)
5.54×10^{-12}	298		
$k_2 = 1.78 \times 10^{-12} \exp[(220 \pm 21)/T]$	203–348	Vaghjiani and Ravishankara, 1989[1]	(a)
$k_2 = (3.85 \pm 0.23) \times 10^{-12}$	298		
Reviews and Evaluations			
1.1×10^{-11}	298	IUPAC, 1989[2]	(b)
$2.93 \times 10^{-12} \exp(190/T)$	223–423	Atkinson, 1989[3]	(c)
$3.8 \times 10^{-12} \exp(200/T)$	203–423	NASA, 1990[4]	(d)

Comments

(a) HO^{16}, HO^{18} and DO radicals generated by flash or pulsed laser photolysis of the precursors: for HO^{16}; CH_3OOH, H_2O^{16}, O_3/H_2O^{16}; for HO^{18}; H_2O^{18}, O_3/H_2O^{18}; and for DO; D_2O, O_3/D_2O, O_3/D_2, and were monitored by LIF. Rate coefficients $k_1 + k_2$ obtained from measurements of the decay rates of HO^{18} and DO radicals in the presence of excess CH_3OOH. Rate coefficients k_2 were obtained from the decay rates of HO^{16} radicals in the presence of CH_3OOH. The CH_2OOH radical formed in reaction channel (1) rapidly decomposes to HO + HCHO, and hence the use of HO^{16} allows only the rate coefficient k_2 to be measured.

(b) Based on the relative rate coefficient measured by Niki *et al.*[5]

(c) Based on the absolute rate coefficient study of Vaghjiani and Ravishankara.[1]

(d) The 298 K rate coefficient was the average of those of Niki *et al.*[5] and Vaghjiani and Ravishankara.[1] The temperature dependence was that measured by Vaghjiani and Ravishankara.[1]

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-12} \exp(190/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–430 K.
$k_1/k = 0.35$ over the temperature range 220–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.
$\Delta(k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara.[1] The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara,[1] is in good agreement with the earlier measurement of Niki *et al.*[5]

References

[1]G. L. Vaghjiani and A. R. Ravishankara, J. Phys. Chem. **93**, 1948 (1989).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 2190 (1983).

HO + HCOOH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.91 \times 10^{-13} \exp[(102 \pm 194)/T]$	297–445	Singleton *et al.*, 1988[1]	(a)
$(4.47 \pm 0.28) \times 10^{-13}$	297		
Reviews and Evaluations			
4.8×10^{-13}	290–430	IUPAC, 1989[2]	(b)
4.5×10^{-13}	296–445	Atkinson, 1989[3]	(c)

Comments

(a) HO radicals generated by pulsed laser photolysis of HCOOH at 222 nm, and detected by UV absorption at 308.2 nm.

(b) The average of the room temperature data of Wine *et al.*[4] and Jolly *et al.*[5] was used to derive the preferred 298 K value. The temperature dependence of the rate coefficient was taken to be zero, in agreement with the data of Wine *et al.*[4]

(c) Derived from a unit-weighted average of the absolute rate coefficients of Wine *et al.*,[4] Jolly *et al.*[5] and Singleton *et al.*[1] The data of Wine *et al.*[4] and Singleton *et al.*[1] show no evidence for a temperature dependence of the rate coefficient, within the experimental uncertainties.

Preferred Values

$k = 4.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HCOOH. The studies of Wine *et al.*,[4] Jolly *et al.*[5] and Singleton *et al.*[1] monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies[1,4,5] agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut *et al.*[6] The data of Wine *et al.*[4] and Singleton *et al.*[1] show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficient data of Wine *et al.*,[4] Jolly *et al.*[5] and Singleton *et al.*[1] has been used to derive the preferred rate coefficient.

Recent studies of Wine *et al.*[4] and Jolly *et al.*[5] showed that H atoms are produced in this reaction, with a yield of 0.75 ± 0.25.[4] Furthermore, Wine *et al.*[4] and Singleton *et al.*[1] showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DCOOH is identical to that for HCOOH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radical with HCOOD and DCOOD are significantly lower than those for the reactions of the HO radical with HCOOH and DCOOH.[1] This reaction then appears to proceed by

$$OH + HC(O)OH \rightarrow H_2O + HCO_2 \qquad HCO_2 \rightarrow H + CO_2$$

with abstraction of the H (or D) atom from the –OH (or –OD) group being the major pathway at room temperature.

References

[1]D. L. Singleton, G. Paraskevopoulos, R. S. Irwin, G. S. Jolly, and D. J. McKenney, J. Am. Chem. Soc. **110**, 7786 (1988).

[2]IUPAC, Supplement III (see references in Introduction).

[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

[4]P. H. Wine, R. J. Astalos, and R. L. Mauldin, III, J. Phys. Chem. **89**, 2620 (1985).

[5]G. S. Jolly, D. J. McKenney, D. L. Singleton, G. Paraskevopoulos, and A. R. Bossard, J. Phys. Chem. **90**, 6557 (1986).

[6]P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).

HO + $CH_3COOH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.67 \pm 0.65) \times 10^{-13}$	296.8	Singleton, Paraskevopoulos, and Irwin, 1989[1]	(a)
$(5.63 \pm 0.44) \times 10^{-13}$	326.2		
$(4.88 \pm 0.17) \times 10^{-13}$	356.4		
$(4.09 \pm 0.14) \times 10^{-13}$	396.8		
$(3.95 \pm 0.07) \times 10^{-13}$	446.2		
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(-170/T)$	290–440	IUPAC, 1989[2]	(b)

Comments

(a) HO radicals generated by the pulsed laser photolysis of CH_3COOH at 222 nm, and detected by UV absorption at 308.2 nm.

(b) Based on the absolute rate coefficient study of Dagaut *et al.*[3]

Preferred Values

$k = 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

At 298 K, the rate coefficients of Dagaut *et al.*[3] and Singleton *et al.*[1] are in reasonable agreement. However, at temperatures above 298 K, Dagaut *et al.*[3] observed the rate coefficient to increase with increasing temperature, while Singleton *et al.*[1] observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. At 400–440 K, the rate coefficients of Dagaut *et al.*[3] and Singleton *et al.*[1] disagree by a factor of 2.2.

The preferred 298 K rate coefficient is an average of the data of Dagaut *et al.*[3] and Singleton *et al.*[1] No recommendation is made regarding the temperature dependence. The rate coefficient data of Singleton *et al.*[1] for the reactions of the HO radical with CH_3COOH, CD_3COOH and CD_3COOD indicate that at room temperature the major reaction channel involves H atom abstraction from the –OH bond:

$$HO + CH_3COOH \rightarrow H_2O + CH_3CO_2$$

References

[1]D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Am. Chem. Soc. **111**, 5248 (1989).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, Int. J. Chem. Kinet. **20**, 331 (1988).

HO + $CH_3ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.4 \pm 0.4) \times 10^{-14}$	298	Gaffney *et al.*, 1986[1]	(a)
$8.8 \times 10^{-15} \exp[(1050 \pm 180)/T]$	298–393	Nielsen *et al.*, 1991[2]	(b)
$(3.2 \pm 0.5) \times 10^{-13}$	298 ± 2		
Relative Rate Coefficients			
$(3.8 \pm 1.0) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986[3]	(c)
$(3.4 \pm 0.7) \times 10^{-13}$	298 ± 2	Nielsen *et al.*, 1991[2]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals.
(b) HO radicals generated by pulsed radiolysis of H_2O–Ar mixtures at 1 bar total pressure, and detected by UV absorption at 309 nm.
(c) Relative rate method. HO radicals generated from the photolysis of HONO–air mixtures at atmospheric pressure. Relative decay rates of methyl nitrate and ethene measured, and the rate coefficient ratio placed on an absolute basis by use of k(HO + ethene) = 8.32×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[4]
(d) Relative rate method. HO radicals generated by the photolysis of CH_3ONO–NO–air mixtures at 730–750 Torr total pressure. The decays of CH_3ONO_2 and $(CH_3)_3CH$ measured by GC. The rate coefficient ratio was placed on an absolute basis by use of k(HO + $(CH_3)_3CH$) = 2.34×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[4]

Preferred Values

$k = 3.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 bar.
$k = 1.0 \times 10^{-14} \exp(1060/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290–400 K at 1 bar.

Reliability
$\Delta\log k = \pm 0.10$ at 298 K (1 bar).
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
At room temperature, the absolute and relative rate coefficients of Nielsen *et al.*[2] and Kerr and Stocker[3] measured at 1 bar pressure are in good agreement, but are an order of magnitude higher than the rate coefficient measured by Gaffney *et al.*[1] at 0.003–0.004 bar pressure. This may indicate that the rate coefficient is pressure dependent and hence that the reaction proceeds by H-atom abstraction and OH radical addition (and by ~90% OH radical addition at 298 K and 1 bar). This conclusion is supported by the negative temperature dependence.[2] The preferred 298 K rate coefficient at 1 bar pressure is the average of the rate coefficients of Nielsen *et al.*[2] and Kerr and Stocker[3] (note that formation of CH_3ONO_2 in the photolysis of CH_3ONO–NO–air mixtures could have lead to a low measured rate coefficient in the relative rate coefficient study of Nielsen *et al.*,[2] although the agreement of this relative rate coefficient[2] with the absolute rate coefficient of Nielsen *et al.*[2] and the relative rate coefficient of Kerr and Stocker[3] suggests that any such formation of CH_3ONO_2 was small). The temperature dependence is derived from the absolute rate coefficient data of Nielsen *et al.*,[2] and is applicable only at 1 bar pressure.

References

[1] J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, Int. J. Chem. Kinet. **18**, 399 (1986).
[2] O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[3] J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

HO + $C_2H_5ONO_2$ → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.7 \times 10^{-14} \exp[(716 \pm 138)/T]$	298–373	Nielsen *et al.*, 1991[1]	(a)
$(5.3 \pm 0.6) \times 10^{-13}$	298 ± 2		
Relative Rate Coefficients			
$(4.9 \pm 2.1) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986[2]	(b)
$(4.6 \pm 0.3) \times 10^{-13}$	298 ± 2	Nielsen *et al.*, 1991[1]	(c)

Comments

(a) HO radicals generated by pulsed radiolysis of H_2O–Ar mixtures at atmospheric pressure, and detected by UV absorption at 309 nm.
(b) Relative rate method. HO radicals generated by photolysis of HONO–air mixtures at atmospheric pressure. Decay rates of ethyl nitrate and ethene measured and the rate coefficient ratio placed on an absolute basis by use of k(HO + ethene) = 8.32×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3]
(c) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decays of ethyl nitrate and 2-methylpropane measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(HO + 2-methylpropane) = 2.34×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3]

Preferred Values

$k = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

$k = 4.4 \times 10^{-14} \exp(720/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–380 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K (1 bar).

$\Delta(E/R) = \pm 500$ K (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker[2] and Nielsen *et al.*[1] are in good agreement at room temperature. All three rate coefficients have been determined at ~1 bar pressure, and it is possible that the rate coefficient is pressure dependent at low total pressures. The preferred 298 K rate coefficient is the average of those determined by Kerr and Stocker[2] and Nelson *et al.*[1] The preferred temperature dependence is that of Nielsen *et al.*[1] The preferred values are applicable to 1 bar pressure.

References

[1]O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

[2]J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).

[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989)

$HO + n\text{-}C_3H_7ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.0 \times 10^{-13} \exp[(140 \pm 144)/T]$	298–368	Nielsen *et al.*, 1991[1]	(a)
$(8.2 \pm 0.8) \times 10^{-13}$	298 ± 2		
Relative Rate Coefficients			
$(7.2 \pm 2.3) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986[2]	(b)
$(6.2 \pm 1.0) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989[3]	(c)
$(7.7 \pm 0.8) \times 10^{-13}$	298 ± 2	Nielsen *et al.*, 1991[1]	(d)

Comments

(a) HO radicals generated by the pulsed radiolysis of H_2O–Ar mixtures at atmospheric pressure, and detected by UV absorption at 309 nm.

(b) Relative rate method. HO radicals generated by the photolysis of HONO–air mixtures at atmospheric pressure. Decay rates of *n*-propyl nitrate and ethene measured, and rate coefficient ratio placed on an absolute basis by use of k(HO + ethene) $= 8.32 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

(c) Relative rate method. HO radicals generated by the photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decays of *n*-propyl nitrate and cyclohexane measured, and rate coefficient ratio placed on an absolute basis by use of k(HO + cyclohexane) $= 7.49 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

(d) Relative rate method. HO radicals generated by the photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decays of *n*-propyl nitrate and 2-methylpropane measured by GC and the rate coefficient ratio placed on an absolute basis by use of k(HO + 2-methylpropane) $= 2.34 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

Preferred Values

$k = 7.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–370 K (1 bar).

Reliability

$\Delta \log k = \pm 0.15$ at 298 K (1 bar).

$\Delta(E/R) = \pm 500$ K (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker,[2] Atkinson and Aschmann[3] and Nielsen *et al.*[1] are in reasonable agreement at room temperature. All studies have been carried out at ~1 bar pressure. The reaction may proceed by H-atom abstraction and OH radical addition, and the rate coefficient may be pressure dependent at low total pressures. The preferred 298 K rate coefficient is the average of those measured by Kerr and Stocker,[2] Atkinson and Aschmann[3] and Nielsen *et al.*[1] A zero temperature dependence is assumed, consistent with the data of Nielsen *et al.*[1] The preferred rate coefficients are applicable to 1 bar pressure.

References

[1]O. J. Nielsen, H. W. Sidebottom, M. Donlan, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).
[2]J. A. Kerr and D. W. Stocker, J. Atmos. Chem. **4**, 253 (1986).
[3]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **21**, 1123 (1989).
[4]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

HO + *i*-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.8 \pm 0.5) \times 10^{-13}$	299 ± 2	Atkinson *et al*., 1982[1]	(a)
$(5.7 \pm 2.3) \times 10^{-13}$	295 ± 2	Becker and Wirtz, 1989[2]	(b)
$(4.1 \pm 0.6) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989[3]	(c)

Comments

(a) Relative rate method. HO radicals generated from the photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decay rates of isopropyl nitrate and cyclohexane measured, and rate coefficient ratio placed on an absolute basis by use of k(HO + cyclohexane) = 7.51×10^{-12} cm^3 molecule^{-1} s^{-1}.[4]

(b) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at 1 bar. Decay rates of isopropyl nitrate and n-butane measured, and the rate coefficient ratio placed on an absolute basis by use of k(HO + n-butane) = 2.48×10^{-12} cm^3 molecule^{-1} s^{-1}.[4]

(c) Relative rate method. HO radicals generated by photolysis of CH_3ONO–NO–air mixtures at atmospheric pressure. Decays of isopropyl nitrate and cyclohexane measured, and the rate coefficient ratio placed on an absolute basis by use of k(HO + cyclohexane) = 7.49×10^{-12} cm^3 molecule^{-1} s^{-1}.[4]

Preferred Values

$k = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K (1 bar).

Comments on Preferred Values

The study of Atkinson and Aschmann,[3] carried out in a 6400 liter reaction chamber, supersedes the earlier study of Atkinson *et al*.[1] carried out in a 50 liter chamber and in which wall losses were concluded (probably erroneously) to have occurred. The relative rate coefficients of Becker and Wirtz[2] and Atkinson and Aschmann[3] are in reasonable agreement. The preferred 298 K rate coefficient is the average of those of Becker and Wirtz[2] and Atkinson and Aschmann.[3] As for the other alkyl nitrates, this reaction may proceed by H-atom abstraction and OH radical addition, and the preferred rate coefficient is applicable to 1 bar pressure.

References

[1]R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, Int. J. Chem. Kinet. **14**, 919 (1982).
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HO + $CH_3CO_3NO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.5 \pm 1.4) \times 10^{-14}$	298	Tsalkani *et al*., 1988[1]	(a)
Reviews and Evaluations			
$1.2 \times 10^{-12} \exp(-650)/T$	270–300	IUPAC, 1989[2]	(b)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO radicals.
(b) Based upon the absolute rate coefficient study of Wallington *et al.*[3]

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.5 \times 10^{-13} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–300 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values
The 298 K preferred value is the average of the room temperature rate coefficients of Wallington *et al.*[3] and Tsalkani *et al.*,[1] both of which are consistent with the upper limit to the rate coefficient previously determined by Winer *et al.*[4] The temperature dependence is that reported by Wallington *et al.*[3] The reaction is expected to proceed via H-atom abstraction from the C–H bonds to yield H_2O + $CH_2CO_3NO_2$.

References

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HO + HCN → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
See comment (b)	373	Phillips, 1978[1]	(a,b)
$1.6 \times 10^{-11} T^{-1} \exp(-1860/T)$	298–563	Phillips, 1979[2]	(a,c)
1.0×10^{-16}	298		
$1.2 \times 10^{-13} \exp(-400/T)$	296–433	Fritz *et al.*, 1984[3]	(d)
$(3 \pm 1) \times 10^{-14}$	298		
Reviews and Evaluations			
$1.2 \times 10^{-13} \exp(-400/T)$	296–433	CODATA, 1984[4]; IUPAC, 1989[5]	(e)
$1.2 \times 10^{-13} \exp(-400/T)$	296–433	NASA, 1990[6]	(f)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) The rate coefficient was observed to be pressure dependent below 15 Torr, with the rate coefficient increasing with increasing pressure. These data indicate an addition reaction in the fall-off region.
(c) Carried out at total pressures of 10–15 Torr. Data were probably still in the fall-off region.
(d) Flash photolysis system with UV absorption detection of HO radicals. The rate coefficients were observed to be pressure dependent over the range ~10–450 Torr of N_2 diluent, with the measured rate coefficients increasing with increasing pressure. The cited rate coefficient is that extrapolated to the high-pressure limit (k_∞).
(e) See Comments on Preferred Values.
(f) Uses the extrapolated high pressure rate coefficient data of Fritz *et al.*[3]

Preferred Values

$k = 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.
$k = 1.2 \times 10^{-13} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–440 K at 1 bar.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1984.[4] The preferred values are those of Fritz *et al.*[3] with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients cited are those extrapolated by Fritz *et al.*[3] to the high-pressure limit.

The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction.[7]

References

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$HO + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.1 \times 10^{-12} \exp[-(1130 \pm 90)/T]$	256–388	Hynes and Wine, 1991[1]	(a)
$(2.48 \pm 0.38) \times 10^{-14}$	298		
Reviews and Evaluations			
$6.3 \times 10^{-13} \exp(-1030/T)$	250–420	IUPAC, 1989[2]	(b)
$6.77 \times 10^{-13} \exp(-1030/T)$	250–363	Atkinson, 1989[3]	(c)
$4.5 \times 10^{-13} \exp(-900/T)$	250–391	NASA, 1990[4]	(d)

Comments

(a) HO radicals were generated by pulsed laser photolysis of H_2O_2 or HNO_3 and detected by LIF. No definitive evidence for a pressure dependence of the rate coefficient for the $HO + CH_3CN$ reaction was observed in N_2 or He diluent over the pressure range 46–700 Torr (N_2 diluent) or 30–630 Torr (He diluent). In the presence of O_2, the HO radical decays were non-exponential, indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD_3CN (for which the rate coefficient was pressure dependent over the pressure range 40–692 Torr of N_2 diluent) and of DO radicals with CH_3CN and CD_3CN, these data suggest that the initial HO radical reaction proceeds by H atom abstraction from the $-CH_3$ group and HO radical addition to the $-CN$ group.[1]

$$HO + CH_3CN \rightarrow H_2O + {}^{\cdot}CH_2CN$$
$$HO + CH_3CN \rightarrow [CH_3CNOH]^{\ddagger}$$

Subsequent reactions of the addition adduct in the presence of O_2 then lead to the regeneration of HO radicals.

(b) The 298 K value was derived from the average of the rate coefficients reported by Kurylo and Knable[5] and Poulet *et al.*[6] The temperature dependence was that determined by Kurylo and Knable,[5] with the A factor being adjusted to fit the 298 K value.

(c) Derived from a unit-weighted average of the room temperature rate constants of Fritz *et al.*,[7] Poulet *et al.*,[6] Zetzsch (unpublished data, 1983) and Kurylo and Knable,[5] combined with the temperature dependence of Kurylo and Knable.[5]

(d) The 298 K value was derived from the average of the absolute rate coefficients of Kurylo and Knable,[5] Zetzsch (unpublished data, 1983), Rhäsa and Zellner (unpublished data, 1984) and Poulet *et al.*[6] The temperature dependence was obtained from the 295–391 K data of Rhäsa and Zellner (unpublished data, 1984) and those of Kurylo and Knable.[5]

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (1 bar).
$k = 8.1 \times 10^{-13} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet *et al.*,[6] Kurylo and Knable[5] and Hynes and Wine.[1] The temperature dependence is the mean of those determined by Kurylo and Knable[5] and Hynes and Wine.[1] The mechanism and products of this reaction are not understood at present [see comment (a) above]. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures[1] (≤ 0.1 bar), the preferred values are applicable to atmospheric conditions.

References

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$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H$

$\Delta H° = -156$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.8 \pm 0.2) \times 10^{-12}$	298	Moortgat *et al.*, 1989[1]	(a)
4.4×10^{-13} exp[(780 ± 55)/*T*]	248–573	Lightfoot, Lesclaux, and Veyret, 1990[2]	(b)
$(6.2 \pm 1.0) \times 10^{-12}$	298		
Reviews and Evaluations			
1.7×10^{-13} exp(1000/*T*)	250–380	IUPAC, 1989[3]	(c)
3.3×10^{-13} exp(800/*T*)	200–300	NASA, 1990[4]	(d)

Comments

(a) Study of the photooxidation of CH_3CHO at 700 Torr, with double multipath spectrometer, combining both IR and UV absorption spectrometry for monitoring reactants and products, together with modulated photolysis for transient detection. Transient absorptions were assigned to peroxy radicals and the rate coefficient was obtained from kinetic analysis by computer simulation.

(b) Flash photolysis-UV absorption study of Cl_2–CH_3OH–CH_4–O_2–N_2 mixtures at pressures of 120 or 760 Torr. Revised cross section data were used, $\sigma(HO_2) = 5.3 \times 10^{-18}$ cm^2 molecule^{-1} at 210 nm and $\sigma(CH_3O_2) = 3.6 \times 10^{-18}$ cm^2 molecule^{-1} at 260 nm.

(c) Derived from the data of Dagaut *et al.*,[5] Jenkin *et al.*[6] and Cox and Tyndall.[7]

(d) The 298 K rate coefficient was the average of the data of Dagaut *et al.*,[5] Jenkin *et al.*,[6] Moortgat *et al.*,[1] Lightfoot *et al.*[2] and Cox and Tyndall.[7] The recommended value of *E/R* was obtained from an analysis of the temperature dependences of Dagaut *et al.*,[5] Lightfoot *et al.*[2] and Cox and Tyndall,[7] with the *A*-factor being adjusted to yield the preferred 298 K rate coefficient.

Preferred Values

$k = 5.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.8 \times 10^{-13}$ exp(780/*T*) cm^3 molecule^{-1} s^{-1} over the temperature range 225–580 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The discrepancies in the data for this reaction, due in part to the different values of the UV absorption cross sections used in the various studies,[3,4] remain unresolved. The preferred rate coefficient at 298 K is the mean of the values of Dagaut *et al.*,[5] Jenkin *et al.*,[6] Moortgat *et al.*,[1] Lightfoot *et al.*[2] and Cox and Tyndall.[7] The recommended temperature coefficient is that reported by Lightfoot *et al.*,[2] selected on the basis of their wider range of temperatures than the previous studies.[5,7] The *A*-factor was then adjusted to fit the preferred value of k_{298}. The preferred rate parameters are in agreement with the most recent NASA recommendation.[4]

The studies of Kurylo *et al.*[8] Jenkin *et al.*[6] and Lightfoot *et al.*,[2] show that the rate coefficient is independent of pressure over the range 10–760 Torr.

The possibility of a second reaction channel, yielding $HCHO + H_2O + O_2$, discussed by Jenkin *et al.*,[6] receives some indirect support from the study of Moortgat *et al.*[1] They calculated a rate coefficient of $k(HO_2 + CH_3O_2 \rightarrow O_2 + CH_3O_2H) = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at room temperature, from the computer simulation of the rate of formation of CH_3O_2H. Since this is lower than their value based on the rate of decay of the peroxy radicals, they concluded that there could be an additional product channel. More direct information concerning the possible second channel comes from the report of Wallington and Japar,[9] on the products of the $HO_2 + CH_3O_2$ reaction studied by FTIR spectroscopy. On the basis of their analyses of CH_3OOH and only trace quantities of HCHO (attributed to secondary reactions), Wallington and Japar[9] concluded that the reaction involves only the one channel yielding CH_3O_2H and O_2.

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$$HO_2 + HOCH_2O_2 \rightarrow O_2 + HOCH_2O_2H \quad (1)$$
$$\rightarrow O_2 + HCO_2H + H_2O \quad (2)$$

$\Delta H°(2) = -473.1$ kJ·mol−1

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T]$	275–333	Veyret *et al.*, 1989[1]	(a)
$(1.2 \pm 0.4) \times 10^{-11}$	295		
$(1.2 \pm 0.3) \times 10^{-11}$	298	Burrows *et al.*, 1989[2]	(b)
Branching Ratios			
$k_2/k = 0.40 \pm 0.15$	298	Burrows *et al.*, 1989[2]	(c)

Comments

(a) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with time-resolved absorption spectroscopy for HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of nine elementary reactions.

(b) Molecular modulation study of Cl_2–HCHO–O_2 mixture with diode laser IR spectroscopy for HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k was obtained from a computer simulation of HO_2 absorption profiles based on a mechanism of eight elementary reactions.

(c) Same experimental system as for comment (b). The branching ratio was determined from a computer simulation of the quantum yields of HCOOH formation.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.6 \times 10^{-15} \exp(2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–335 K.

$k_2/k = 0.4$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 1500$ K.

$\Delta(k_1/k) = \pm 0.4$ at 298 K.

Comments on Preferred Values

The two studies[1,2] of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO_2 radical reactions with CH_3O_2 and $C_2H_5O_2$ radicals. The product channel yielding HCOOH is presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO, CH_3OH and O_2 from the interaction of CH_3O_2 radicals.[3] Both the temperature dependence and the branching ratio require independent confirmation.

References

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$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5O_2H$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.3 \pm 0.9) \times 10^{-12}$	295	Cattell *et al.*, 1986[1]	(a)
$5.6 \times 10^{-13} \exp[(650 \pm 125)/T]$	248–380	Dagaut, Wallington and Kurylo, 1988[2]	(b)
$(5.3 \pm 1.0) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.5 \pm 0.5) \times 10^{-12}$	298	Niki *et al.*, 1982[3]	(c)
Reviews and Evaluations			
$6.5 \times 10^{-13} \exp(650/T)$	240–380	IUPAC, 1989[4]	(d)
$6.5 \times 10^{-13} \exp(650/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) Molecular modulation spectrometry system used, with HO_2 and $C_2H_5O_2$ radicals being generated simultaneously by photolysis of Cl_2 in the presence of C_2H_6–CH_3OH–O_2–N_2 mixtures at pressures of 2.4 Torr. HO_2 monitored by IR absorption with a tunable diode laser and $C_2H_5O_2$ monitored by UV absorption at 260 nm. The rate coefficient k was determined from the observed perturbation of the second-order kinetics of the HO_2 self-reaction when $C_2H_5O_2$ was present in large excess, and shown to be essentially independent of pressure over the range 2.4–760 Torr.

(b) Flash photolysis of Cl_2 in the presence of C_2H_6–CH_3OH–O_2–N_2 mixtures at total pressures of 25–400 Torr. Composite transient absorption decay curves for HO_2 and $C_2H_5O_2$ were measured at 230, 250 and 280 nm. Kinetic analysis derived from computer modeling of experimental data.

(c) FTIR spectroscopic study of product formation in the photolysis of Cl–C_2H_6–O_2 and $(C_2H_5)_2N_2$–O_2 mixtures at 700 Torr total pressure. The rate coefficient k was derived from computer simulation of the proposed mechanism.

(d) See Comments on Preferred Values.

(e) Derived on the same basis as in the IUPAC, 1989[4] evaluation.

Preferred Values

$k = 5.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5 \times 10^{-13} \exp(650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989.[4] The two direct studies of this rate coefficient are in good agreement at 298 K, and the preferred value is the mean of these data. The rate coefficient reported by Niki *et al.*[3] is considerably lower than the preferred value but it is derived on the basis of a much less direct technique. The preferred temperature dependence of the rate coefficient is based on the data of Dagaut *et al.*,[2] but requires further experimental confirmation. The experiments of Cattell *et al.*[1] indicate that the rate coefficient is independent of total pressure based on measurements at 2.4 and 760 Torr.

Wallington and Japar[6] have carried out a study of the products of the $HO_2 + C_2H_5O_2$ reaction, using FTIR spectroscopy. From the analyses of C_2H_5OOH, they concluded that the reaction involves only the one channel yielding C_2H_5OOH and O_2.

References

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$$HO_2 + CH_3CO_3 \rightarrow O_2 + CH_3CO_3H \quad (1)$$
$$\rightarrow O_3 + CH_3CO_2H \quad (2)$$

$\Delta H°(2) = -132$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$	253–368	Moortgat, Veyret and Lesclaux, 1989[1]	(a)
$(1.3 \pm 0.3) \times 10^{-11}$	298		
Branching Ratios			
$k_1/k = 0.23$	298	Niki *et al.*, 1985[2]	(b)
$k_1/k = 0.33 \pm 0.07$	253–368	Moortgat, Veyret and Lesclaux, 1989[1]	(c)

Comments

(a) Flash photolysis of Cl_2 in the presence of $CH_3CHO-CH_3OH-O_2-N_2$ mixtures at total pressures of 600–650 Torr. $[CH_3CO_3]$ was monitored by UV absorption over the wavelength range 195–280 nm and the absorption cross section measured relative to $\sigma(HO_2) = 5.3 \times 10^{-18}$ cm^2 molecule^{-1} at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of CH_3CO_3.

(b) FTIR study of irradiated $Cl_2-HCHO-CH_3CHO-O_2$ mixtures. The branching ratio was based on analysis of the products, CH_3CO_3H, CH_3CO_2H, and O_3.

(c) Derived from same experiments as in comment (a) by making allowance for absorption by the O_3 product.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.3 \times 10^{-13} \exp(1040/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

$k_1/k = 0.3$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

$\Delta(k_1/k) = \pm 0.1$ over the range 250–370 K.

Comments on Preferred Values

The data of Moortgat *et al.*[1] are in line with their results for the reactions of HO_2 radicals with CH_3O_2 and $HOCH_2O_2$ radicals.[3,4] While the results appear reasonable and we recommend their value of k, this requires independent confirmation before the error limits can be reduced.

Channel (2) leading to O_3 formation is well supported by the studies of Niki *et al.*[2] and of Moortgat *et al.*[1] Such a pathway does not take place in the $HO_2 + RO_2$ interactions and may be unique to the $HO_2 + RCO_3$ systems. The recommended branching ratio is a rounded-off mean from both studies.[1,2]

References

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$HO_2 + HOCH_2CH_2O_2 \rightarrow$ products

Rate coefficient data

[illegible]m^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
[illegible]lute Rate Coefficients			
([illegible]8 ± 1.5) × 10^{-12}	298	Jenkin and Cox, 1991[1]	(a)
[illegible]0 × 10^{-11}	298	Anastasi *et al.*, 1991[2]	(b)
([illegible] ± 0.3) × 10^{-11}	296	Murrells *et al.*, 1991[3]	(c)

Comments

(a) Molecular modulation study with $HOCH_2CH_2O_2$ radicals being generated from the photolysis of $HOCH_2CH_2I$ in the presence of O_2 and N_2 at total pressures of 10, 100 and 760 Torr in a slow flow system. Evidence from the modulated absorption spectrum in the range 205–310 nm showed additional transient species were absorbing, and these were ascribed to $HOCH_2CH_2OOI$ and HO_2. The rate coefficient was obtained from computer simulations of the time-resolved absorption waveforms at 220–310 nm for experiments at 10 Torr pressure.

(b) Pulse radiolysis study, with the $HOCH_2CH_2O_2$ radical being generated from C_2H_4–O_2–H_2O–SF_6 and CH_3CH_2OH–O_2–SF_6 mixtures at a total pressure of 760 Torr. [$HOCH_2CH_2O_2$] was monitored by absorption at 230 nm and k derived from kinetic modeling of absorption profiles.

(c) Laser flash photolysis study, with $HOCH_2CH_2O_2$ radicals being generated from photolysis of $HOCH_2CH_2Cl$ in the presence of O_2 and N_2 at total pressures of 710 Torr. The rate coefficient was obtained by modeling the observed absorption profiles on the basis of a simplified mechanism of four reactions.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The studies of Murrells *et al.*[3] by laser flash photolysis and by molecular modulation of the absorption spectrum of the $HOCH_2CH_2O_2$ radical have shown that the absorption cross sections reported earlier by Jenkin and Cox[1] from molecular modulation studies of the photolysis of $HOCH_2CH_2I$ are approximately a factor of two low. Jenkin and Cox[1] made the assumption that the photolysis of $HOCH_2CH_2I$ in their system yields entirely $HOCH_2CH_2O_2$ radicals, which is apparently not the case. Increasing σ_{230} ($HOCH_2CH_2O_2$) by a factor of two in the interpretation[3] of the data of Jenkin and Cox[1] yields the revised value of $k = (8.4 \pm 3.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

The recommended rate coefficient is the mean of this revised value together with the value of Murrells *et al.*[3] The approximate value derived by Anastasi *et al.*[2] in the pulse radiolysis experiments is a factor of two higher than our recommended value, and we have not taken this value of Anastasi *et al.*[2] into account, owing to the differences in the absorption spectrum of the radical observed by Anastasi *et al.*[2] compared with the consistent spectra reported by Jenkin and Cox[1] and Murrells *et al.*[2] (see data for the reaction $2HOCH_2CH_2O_2 \rightarrow$ products).

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$HO_2 + HCHO \rightarrow HOCH_2OO$

$\Delta H° = -68.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.4) \times 10^{-13}$	273	Barnes *et al.*, 1985[1]	(a)
$7.7 \times 10^{-15} \exp[(625 \pm 550)/T)]$	275–333	Veyret *et al.*, 1989[2]	(b)
$(6.0 \pm 0.7) \times 10^{-14}$	295		
Reviews and Evaluations			
$9.7 \times 10^{-15} \exp(625/T)$	275–333	IUPAC, 1989[3]	(c)
$6.7 \times 10^{-15} \exp(600/T)$	200–300	NASA, 1990[4]	(d)

Comments

(a) FTIR spectroscopic study in a 420 ℓ reaction chamber. HO_2 radicals were generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2 and synthetic air at a total pressure of 400 Torr. The rate coefficient k was obtained from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $HOCH_2O_2NO_2$, based on a reaction scheme consisting of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long path absorption measurements of HO_2 and $HOCH_2O_2$ radicals at total pressures of 85–170 Torr. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

(c) See Comments on Preferred Values.

(d) k_{298} obtained from average of values obtained by Su *et al.*,[5] Veyret *et al.*[2] and Veyret *et al.*[6] Temperature dependence taken from Veyret *et al.*[2]

Preferred Values

$k = 7.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.7 \times 10^{-15} \exp(625/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The most recent studies of Barnes *et al.*[1] and of Veyret *et al.*[2] are in excellent agreement regarding this rate coefficient and both are in good agreement with the earlier data of Veyret *et al.*[6] The preferred rate equation is derived by taking an average value of the rate coefficients of Barnes *et al.*[1] [$k(273\ K) = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}] and of Veyret *et al.*[2] [$k(275\ K) = 8.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] together with the value of E/R determined by Veyret *et al.*[2]

This reaction is believed to proceed via the initial formation of the adduct radical, HO_2CH_2O, which rapidly isomerizes to the product radical, $HOCH_2OO$, via H-atom transfer.

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$HOCH_2OO \rightarrow HO_2 + HCHO$

$\Delta H^\circ = 68.1$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.5	298	Su, Calvert, and Shaw, 1979[1]	(a)
30	298	Veyret, Rayez and Lesclaux, 1982[2]	(b)
20^{+20}_{-10}	273	Barnes *et al.*, 1985[3]	(c)
$2.0 \times 10^{12} \exp[(-7000 \pm 2000)/T]$	275–333	Veyret *et al.*, 1989[4]	(d)
100 ± 50	295		
Reviews and Evaluations			
$2.4 \times 10^{12} \exp(-7000/T)$	275–333	IUPAC, 1989[5]	(e)

Comments

(a) Photooxidation of $HCHO-Cl_2$ mixtures in H_2, O_2 and N_2 diluent or in synthetic air (total pressure $\sim$700 Torr) studied by FTIR spectroscopy. The rate coefficient k was derived from a computer simulation of a complex system.

(b) Flash photolysis of $HCHO-O_2-NO$ mixtures at total pressures of 62–230 Torr. Kinetic analysis based solely on measured $+d[NO_2]/dt$. The rate coefficient k was derived from a computer simulation of a complex system.

(c) FTIR spectroscopic study in a 420 ℓ reaction chamber. HO_2 radicals were generated from the thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2 and synthetic air at total pressures of 400 Torr. The rate coefficient k was derived from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $HOCH_2O_2NO_2$ based on a reaction scheme consisting of nine elementary reactions.

(d) Flash photolysis of Cl_2 in presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of $[HO_2]$ and $[HOCH_2O_2]$ at total pressures of 85–170 Torr. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

(e) See Comments on Preferred Values.

Preferred Values

$k = 1.5 \times 10^2$ s^{-1} at 298 K.

$k = 2.4 \times 10^{12} \exp(-7000/T)$ s^{-1} over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 2000$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The studies of Barnes *et al.*[3] and of Veyret *et al.*[4] are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K from these studies together with the E/R determined by Veyret *et al.*[4]

It should be pointed out that the equilibrium constant for the reactions $HO_2 + HCHO \rightleftharpoons HOCH_2O_2$ (1,–1), $K_1 = 5.2 \times 10^{-16}$ cm^3 molecule^{-1} at 298 K, derived from the kinetic study of Veyret *et al.*[4] (which is identical to the value obtained from our recommended data for k_1 and k_{-1}), is in excellent agreement with the value $K_1 = 4.0 \times 10^{-16}$ cm^3 molecule^{-1} at 298 K obtained independently by Burrows *et al.*[6] from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1 = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} at 298 K reported by Zabel *et al.*[7] from ESR spectroscopic measurements of the ratio of concentrations of HO_2 and $HOCH_2OO$ radicals in the photolysis of $HCHO-O_2$ mixtures.

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$NO_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.9 \times 10^{-13} \exp[-(2742 \pm 542)/T]$	296–523	Canosa-Mas *et al.*, 1988[1,2]	(a)
$(5.1 \pm 3.5) \times 10^{-17}$	295		
Relative Rate Coefficients			
$\leq 3.0 \times 10^{-17}$	298	Atkinson, Aschmann and Goodman, 1987[3]	(b)
Reviews and Evaluations			
$<1 \times 10^{-16}$	298	IUPAC, 1989[4]	(c)
$<5 \times 10^{-17}$	298	Atkinson, 1991[5]	(d)

Comments

(a) Discharge flow system with optical absorption detection of NO_3.

(b) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 in NO_2–air mixtures at atmospheric pressure. Relative decay rates of C_2H_2 and C_2H_4 monitored, leading to $k(NO_3 + C_2H_2)/k(NO_3 + C_2H_4) \leq 0.14$. Placed on an absolute basis by use of $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) See Comments on Preferred Values.

(d) Derived from the room temperature rate coefficients of Canosa-Mas *et al.*[1] and Atkinson *et al.*[3]

Preferred Values

$$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements[3] show C_2H_2 to be significantly less reactive than C_2H_4. The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas *et al.*[1] Until there are confirmatory data for the reported temperature dependence[2] of this rate coefficient, no temperature dependence is recommended.

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$NO_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.43 \pm 0.54) \times 10^{-16}$	296 ± 1	Andersson and Ljungström, 1989[1]	(a)
$(1.85 \pm 0.39) \times 10^{-16}$	298 ± 2	Barnes *et al.*, 1990[2]	(b)
Reviews and Evaluations			
2.1×10^{-16}	298	IUPAC, 1989[3]	(c)
$4.88 \times 10^{-18} T^2 \exp(-2282/T)$	295–523	Atkinson, 1991[4]	(d)

Comments

(a) Relative rate study, with the rate coefficient being determined relative to the equilibrium constant K for the $NO_3 + NO_2 \rightleftharpoons N_2O_5$ reactions. Placed on an absolute basis by use of $K = 4.40 \times 10^{-11}$ cm^3 $molecule^{-1}$ at 296 K.[4]

(b) Relative rate study with the rate coefficient being determined relative to the rate coefficient for the reaction of the NO_3 radical with 2-methylpropane. Placed on an absolute basis by use of $k(NO_3$ + 2-methylpropane) $= 1.04 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}.[4,5]

(c) Based upon the relative rate coefficient of Atkinson *et al.*,[6] which is in agreement with the absolute rate coefficient data of Canosa-Mas *et al.*[7,8]

(d) Derived from the absolute rate coefficients of Canosa-Mas *et al.*[7,8] and the relative rate coefficient of Atkinson *et al.*,[6] using the three parameter expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 2.1 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 3.3 \times 10^{-12} \exp(-2880/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 270–330 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas *et al.*[7,8] and the relative rate coefficient of Atkinson *et al.*[6] These data were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.88 \times 10^{-18}$ $T^2 \exp(-2282/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 295–523 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A = C\,e^2\,T^2$ and $B = D + 2T$.

The preferred rate coefficient is in reasonable agreement with the relative rate coefficient data of Atkinson *et al.*[9] (which is superseded by the more recent study of Atkinson *et al.*[6]), Andersson and Ljungström[1] and Barnes *et al.*,[2] all of which have significant uncertainties due to the uncertainties in the equilibrium constant for the $NO_3 + NO_2 \rightleftharpoons N_2O_5$ reactions or in the reference reaction rate coefficient.

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$NO_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(6.4 \pm 1.6) \times 10^{-15}$	300	Morris and Niki, 1974[1]	(a)
$(1.08 \pm 0.07) \times 10^{-14}$	300	Japar and Niki, 1975[2]	(a)
$(7.57 \pm 1.54) \times 10^{-15}$	298 ± 1	Atkinson *et al.*, 1984[3]	(a)
$(7.41 \pm 1.95) \times 10^{-15}$	298 ± 1	Atkinson *et al.*, 1984[3]	(b)
$(9.45 \pm 0.47) \times 10^{-15}$	296 ± 2	Atkinson, Aschmann, and Pitts, 1988[4]	(c)
Reviews and Evaluations			
9.4×10^{-15}	298	IUPAC, 1989[5]	(d)
9.45×10^{-15}	298	Atkinson, 1991[6]	(e)

Comments

(a) Relative rate method. Decay of N_2O_5 monitored by infrared absorption spectroscopy in N_2O_5–NO_2–NO_3–C_3H_6–O_2–Ar (or N_2) mixtures at ~750 Torr total pressure. The rate coefficient derived for C_3H_6 is dependent on the equilibrium constant K for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$. The cited values in the table use an equilibrium constant of $K = 1.26 \times 10^{-27} \exp(11275/T)$ cm³ molecule^{-1}.[6]

(b) Relative rate method in which the decay rate of C_3H_6 was monitored relative to that of *trans*-2-butene in N_2O_5–NO_2–NO_3–air mixtures by GC. The measured rate coefficient ratio of $k(NO_3$ + propene)/$k(NO_3$ + *trans*-2-butene) of 0.019 ± 0.005 has been placed on an absolute basis by use of $k(NO_3$ + *trans*-2-butene) $= 3.90 \times 10^{-13}$ cm³ molecule^{-1} s^{-1}.[6]

(c) Relative rate method. The relative decay rates of several sets of organics were monitored by GC in N_2O_5–NO_2–air mixtures at atmospheric pressure. By combining the rate coefficient ratios for *trans*-2-butene and bicyclo[2.2.2]-2-octene, bicyclo[2.2.2]-2-octene and thiophene, and thiophene and propene, a rate coefficient ratio of $k(NO_3$ + propene)/$k(NO_3$ + *trans*-2-butene) = 0.0243 ± 0.0012 was obtained. Placed on an absolute basis by use of $k(NO_3$ + *trans*-2-butene) $= 3.89 \times 10^{-13}$ cm³ molecule^{-1} s^{-1}.[6]

(d) See Comments on Preferred Values.

(e) Based on the most recent and precise relative rate coefficient study of Atkinson *et al.*[4]

Preferred Values

$k = 9.4 \times 10^{-15}$ cm³ molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The preferred 298 K rate coefficient is based on the most recent relative rate study of Atkinson *et al.*,[4] which supersedes the earlier work from this group[3] and which is in reasonable agreement with the earlier studies of Niki and co-workers[1,2] when the differing equilibrium constants used for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reactions are taken into account (see cited values in table). The reaction proceeds by NO_3 radical addition to the carbon-carbon double bond.[1-3,6-10]

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$NO_3 + HCHO \rightarrow HNO_3 + HCO$

$\Delta H° = -53.7$ kJ·mol^{-1}

Rate coefficient data

k/cm³ molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.9 \pm 0.5) \times 10^{-16}$	298 ± 1	Atkinson *et al.*, 1984[1]	(a)
5.6×10^{-16}	298	Cantrell *et al.*, 1985[2]	(b)
$(8.7 \pm 0.6) \times 10^{-16}$	298	Cantrell *et al.*, 1985[2]	(c)
$(7.9 \pm 1.6) \times 10^{-16}$	295	Hjorth, Ottobrini and Restelli, 1988[3]	(d)
Reviews and Evaluations			
6×10^{-16}	298	IUPAC, 1989[4]	(e)
5.8×10^{-16}	298	NASA, 1990[5]	(f)
5.8×10^{-16}	298	Atkinson, 1991[6]	(e)

Comments

(a) Relative rate method. N_2O_5 decay rates monitored in N_2O_5–NO_2–HCHO–air mixtures as a function of the HCHO/NO_2 concentration ratio. The rate coefficient derived is dependent on the value of the equilibrium constant K for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$. An equilibrium constant of $K = 3.41 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K[6] has been used to place the rate coefficient on an absolute basis.

(b) Derived from computer fits of time-concentration data for reactants and products, monitored by FTIR absorption spectroscopy, in O_3–NO_2–HCHO–O_2–N_2 mixtures. For four experiments in which the NO_3 radical was monitored, the rate coefficient was not dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$, and a rate coefficient of 5.6×10^{-16} cm^3 molecule^{-1} s^{-1} was obtained.

(c) Derived from computer fits of time-concentration data for reactants and products, monitored by FTIR absorption spectroscopy, in O_3–NO_2–HCHO–O_2–N_2 mixtures. For five of the nine experiments the rate coefficient derived was dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$. An equilibrium constant of 3.41×10^{-11} cm^3 molecule^{-1} [6] has been used to place the data on an absolute basis.

(d) Derived from computer fits of time-concentration data for reactants and products, monitored by FTIR absorption spectroscopy, in O_3–NO_2–HCHO–O_2–N_2 and N_2O_5–NO_2–HCHO–O_2–N_2 mixtures. The rate coefficient derived is dependent on the equilibrium constant for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$. An equilibrium constant of 4.00×10^{-11} cm^3 molecule^{-1} [6] has been used to place the data on an absolute basis, although the equilibrium constant cited by Hjorth *et al.*[3] is not consistent with the temperature employed. Hence reevaluation of the Hjorth *et al.*[3] data is subject to large uncertainties.

(e) Based upon the relative rate coefficient of Atkinson *et al.*[1] and the absolute rate coefficient of Cantrell *et al.*[2]

(f) Based on the absolute and relative rate coefficient data of Atkinson *et al.*,[1] Cantrell *et al.*[2] and Hjorth *et al.*[3]

Preferred Values

$k = 5.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The data of Atkinson *et al.*,[1] Cantrell *et al.*[2] and Hjorth *et al.*[3] disagree by a factor of ~1.5 when the same equilibrium constant for the reactions $NO_2 + NO_3 \rightleftharpoons N_2O_5$ is used to place the rate coefficients on an absolute basis. However, the rate coefficient obtained by Cantrell *et al.*[2] from experiments which were independent of this equilibrium constant agree well with that derived from the Atkinson *et al.*[1] data.

Accordingly, a rate coefficient of 5.8×10^{-16} cm^3 molecule^{-1} s^{-1} is recommended, with the uncertainty limits reflecting the need for an absolute measurement. While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO, a preexponential factor of $\sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is expected, and hence $k(NO_3 + HCHO) \sim 2 \times 10^{-12} \exp(-2430/T)$ cm^3 molecule^{-1} s^{-1}.

This reaction proceeds by H atom abstraction

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$

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$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO$

$\Delta H° = -58.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.44×10^{-12} exp[$-(1860 \pm 300)/T$]	264–374	Dlugokencky and Howard, 1989[1]	(a)
$(2.74 \pm 0.33) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(2.54 \pm 0.64) \times 10^{-15}$	300	Morris and Niki, 1974[2]	(b)
$(2.44 \pm 0.52) \times 10^{-15}$	298 ± 1	Atkinson *et al.*, 1984[3]	(c)
$(3.15 \pm 0.60) \times 10^{-15}$	299	Cantrell *et al.*, 1986[4]	(d)
Reviews and Evaluations			
1.4×10^{-12} exp($-1860/T$)	260–370	IUPAC, 1989[5]	(e)
1.4×10^{-12} exp($-1900/T$)	264–374	NASA, 1990[6]	(f)
1.44×10^{-12} exp($-1862/T$)	264–374	Atkinson, 1991[7]	(g)

Comments

(a) Flow system with LIF detection of NO_3.

(b) Relative rate method. NO_3 radicals generated from the thermal decomposition of N_2O_5 in O_2/Ar mixtures at 750 Torr total pressure. Decays of N_2O_5 monitored by IR absorption spectroscopy in the presence of excess CH_3CHO. Placed on an absolute basis by use of an equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reactions of 2.65×10^{-11} cm^3 molecule^{-1}.[7]

(c) Relative rate method. NO_3 radicals generated from the thermal decomposition of N_2O_5 in air at 740 Torr total pressure, and the decays of N_2O_5 in the presence of excess CH_3CHO monitored by FTIR absorption spectroscopy. Placed on an absolute basis by use of an equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reactions of 3.41×10^{-11} cm^3 molecule^{-1}.[7]

(d) NO_3 radicals generated from the thermal decomposition of N_2O_5 in synthetic air at 700 Torr total pressure. Reactants and products monitored by FTIR absorption spectroscopy, and their time-concentration profiles fitted by computer modeling, using an equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reactions of 3.00×10^{-11} cm^3 molecule^{-1} at 299 K.[7]

(e) See Comments on Preferred Values.

(f) The 298 K value was derived from the rate coefficient data of Atkinson *et al.*[3] (as reevaluated), Cantrell *et al.*[4] and Dlugokencky and Howard.[1] The temperature dependence of Dlugokencky and Howard[1] was utilized with the A-factor being adjusted to yield the preferred 298 K value.

(g) Based on the absolute rate coefficient study of Dlugokencky and Howard.[1] The reevaluated relative rate coefficients of Morris and Niki,[2] Atkinson *et al.*[3] and Cantrell *et al.*[4] are in good agreement with the recommended value.

Preferred Values

$k = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-12}$ exp($-1860/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 260–370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The preferred values are based upon the sole absolute rate coefficient study of Dlugokencky and Howard.[1] The rate coefficients reported by Morris and Niki,[2] Atkinson *et al.*[3] and Cantrell *et al.*[4] (when reevaluated[7] to be consistent with recent values of the equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reactions) are in good agreement with this preferred value. However, because of the significant uncertainties in this equilibrium constant,[7] these relative rate coefficient data were not used in the evaluation of the preferred rate coefficient.

References

[1]E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **93**, 1091 (1989).
[2]E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **78**, 1337 (1974).
[3]R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **88**, 1210 (1984).
[4]C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, J. Geophys. Res. **91**, 5347 (1986).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
[7]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CH_3OH \rightarrow$ products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.25 \times 10^{-12} \exp[-(2562 \pm 241)/T]$	294–473	Canosa-Mas *et al.*, 1989[1]	(a)
$(2.1 \pm 1.1) \times 10^{-16}$	294		
Reviews and Evaluations			
$<1 \times 10^{-15}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Discharge flow system with optical absorption detection of NO_3.

(b) Based on the upper limit to the absolute rate coefficient determined by Wallington *et al.*[3] using a flash photolysis system with optical absorption detection of NO_3.

Preferred Values

$k = 2.4 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 1.3 \times 10^{-12} \exp(-2560/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 290–480 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 700$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient study of Canosa-Mas *et al.*[1] The 298 K preferred rate coefficient is consistent with the upper limit to the rate coefficient determined by Wallington *et al.*[3]

References

[1]C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, **85**, 709 (1989).

[2]IUPAC, Supplement III, 1989 (see references in Introduction).

[3]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).

$NO_3 + C_2H_5OH \rightarrow$ products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 9 \times 10^{-16}$	298	Wallington *et al.*, 1987[1]	(a)
Reviews and Evaluations			
$<2 \times 10^{-15}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Flash photolysis system with optical absorption detection of NO_3.

(b) See Comments on Preferred Values.

Preferred Values

$k < 2 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is based on the only study carried out to date.[1] A somewhat higher upper limit is recommended than cited by Wallington *et al.*[1]

References

[1]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **19**, 243 (1987).

[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$NO_3 + i\text{-}C_3H_7OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2.3 \times 10^{-15}$	298	Wallington *et al.*, 1987[1]	(a)
Reviews and Evaluations			
$< 5 \times 10^{-15}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Flash photolysis system with optical absorption detection of NO_3.
(b) See Comments on Preferred Values.

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is based on the only study carried out to date.[1] A somewhat higher upper limit is recommended than cited by Wallington *et al.*[1]

References

[1]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. 19, 243 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$\Delta H° = -135.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.3) \times 10^{-30}(T/300)^{-3.3}$ [Ar]	300–850	Keiffer and Pilling, 1991[1]	(a)
Reviews and Evaluations			
$8 \times 10^{-31}(T/300)^{-3.3}$ [N_2]	200–600	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
$4.5 \times 10^{-31}(T/300)^{-3.0}$ [air]	200–300	NASA, 1990[4]	(c)

Comments

(a) CH_3 radicals were produced by laser flash photolysis of acetone at 193 nm and detected by UV absorption at 216 nm. At the temperatures employed (775–850 K) the reaction is in the equilibrium regime. The pressure of Ar was varied between 54 and 560 Torr. The rate data were fitted, together with previous values at lower temperatures,[5,6] using $F_c = 0.46 - 0.039(T/300)$ which corresponds to $F_c = 0.43$ at 300 K.
(b) Based on earlier data, in particular from Refs. 6 and 7, using $F_c = 0.27$ at 300 K.
(c) Based on the low-pressure data of Selzer and Bayes,[8] using $F_c = 0.6$ at 300 K.

Preferred Values

$k_0 = 1.0 \times 10^{-30}(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The evaluation uses the new results of Ref. 1 which are in good agreement with the previously preferred values of Ref. 3, although different values of F_c were employed. The temperature dependence of F_c applied in Ref. 1 does not extend to temperatures below 300 K. The calculated values of F_c used in Ref. 3 are preferred, i.e., $F_c = 0.27$ at 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-12}(T/300)^{1\ 2}$	300–850	Keiffer and Pilling, 1991[1]	(a)
Reviews and Evaluations			
$2.2 \times 10^{-12}(T/300)^{1}$	200–400	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
$1.8 \times 10^{-12}(T/300)^{-1\ 7}$	200–300	NASA, 1990[4]	(c)

Comments

(a) See comment (a) for k_0. Falloff extrapolation with a fitted value of $F_c = 0.43$ at 300 K.

(b) Based on data from Ref. 7. The temperature dependence was from the measured dependence from Ref. 6 and that theoretically predicted in Ref. 7. Falloff extrapolation conducted with a calculated value of $F_c = 0.27$ at 300 K.

(c) Based on the rate data from Ref. 3. The temperature dependence was an estimate. The standard value of $F_c = 0.6$ was used.

Preferred Values

$k_\infty = 2.2 \times 10^{-12}(T/300)^{1\ 0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.

$\Delta n = \pm 1$.

Comments on Preferred Values

Most of the discrepancies between Refs. 1, 3, and 4 are due to the choice of different F_c values. The preferred values correspond to $F_c = 0.27$ at 300 K. At pressures below 1 bar all recommended falloff experiments give similarly good fits to the data. The present preferred values follow Refs. 3 and 7.

References

[1] M. Keiffer and M. J. Pilling, J. Chem. Soc. Faraday Trans. **87**, in press (1991).

[2] CODATA, 1980 (see references in Introduction).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

[5] M. J. Pilling and M. J. C. Smith, J. Phys. Chem. **89**, 4713 (1985).

[6] M. Keiffer, M. J. Pilling and M. J. C. Smith, J. Phys. Chem. **91**, 6028 (1987).

[7] C. J. Cobos, H. Hippler, K. Luther, A. R. Ravishankara, and J. Troe, J. Phys. Chem. **89**, 4334 (1985).

[8] E. A. Selzer and K. D. Bayes, J. Phys. Chem. **87**, 392 (1983).

$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$

$\Delta H^\circ = -51.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<10^{-13}$	1000	Wagner *et al.*, 1990[1]	(a)
Relative Rate Coefficients			
1.9×10^{-14} (100 Torr, air)	298	Kaiser, Lorkovic, and Wallington, 1990[2]	(b)
3.8×10^{-15} (760 Torr, air)	298		
9.8×10^{-16} (6000 Torr, air)	298		
Reviews and Evaluations			
$1.4 \times 10^{-12} \exp(-1950/T)$	300–2500	IUPAC, 1989[3]	(c)
$1.7 \times 10^{-14} \exp(1100/T)$	600–1200	Baulch *et al.*, 1992[4]	(d)

Comments

(a) Experimental and theoretical study of the $C_2H_5 + O_2$ reaction. Experiments were carried out in tubular flow reaction; C_2H_5 formed from the laser photolysis of C_2H_5Br or CCl_4–C_2H_6 mixtures; [C_2H_5] decay and [C_2H_4] growth monitored by photoionization MS.

(b) Study of the yields of C_2H_4 produced relative to the C_2H_6 consumed (GC analysis) in a system in which C_2H_5 radicals were generated from UV irradiation of Cl_2–C_2H_6–O_2–N_2 (or air) mixtures. Over the pressure range 1–6000 Torr the percentage of C_2H_4 produced, relative to the C_2H_6 consumed, decreased from 12% to 0.02%, following a $P^{(-0\ 8 \pm 0\ 1)}$ pressure dependence in air. The listed pressure-dependent k values are relative to values of $k(C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M)$ calculated from the recommended data of this evaluation.

(c) Based on previous evaluations of Tsang and Hampson.[5]

(d) Based on data of McAdam and Walker[6] and of Slagle *et al.*[7]

Preferred Values

$k = 3.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

$k = 1.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K and 0.133 bar.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended pressure-dependent values of k_{298} are from the product study of Kaiser *et al.*[2] The temperature dependence of the rate coefficient has yet to be established, but at a given pressure, increasing the temperature leads to an increased yield of C_2H_4.

For a full discussion on the mechanism of the $C_2H_5 + O_2$ reaction see the paper of Wagner *et al.*[1] It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $C_2H_5O_2$ radicals is by far the dominant pathway.

References

[1]A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **94**, 1853 (1990).

[2]E. W. Kaiser, I. M. Lorkovic, and T. J. Wallington, J. Phys. Chem. **94**, 3352 (1990).

[3]IUPAC, Supplement III, 1989 (see references in Introduction).

[4]D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).

[5]W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1987 (1986).

[6]K. G. McAdam and R. W. Walker, J. Chem. Soc. Faraday Trans. 2, **83**, 1509 (1987).

[7]I. R. Slagle, Q. Feng, and D. Gutman, J. Phys. Chem. **88**, 3648 (1984).

$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$

$\Delta H° = -147.2$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.96 \times 10^{-5} T^{-8\ 24} \times \exp(-2150/T)$ [He]	296–805	Wagner *et al.*, 1990[1]	(a)
5.9×10^{-29} [He]	298		
Relative Rate Coefficients			
$(6.5 \pm 2.0) \times 10^{-29}$ [He]	298	Kaiser, Wallington and Andino, 1990[2]	(b)
Reviews and Evaluations			
$2.0 \times 10^{-28}(T/300)^{-3\ 8}$ [N_2]	200–300	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$2.0 \times 10^{-28}(T/300)^{-3\ 8}$ [air]	200–300	NASA, 1990[5]	(d)

Comments

(a) C_2H_5 radicals were generated by photolysis of C_2H_5Br at 248 nm or photolysis of CCl_4–C_2H_6 mixtures at 193 nm. The experiments were carried out in a heatable tubular reactor coupled to a photoionization MS. C_2H_5 and C_2H_4 were detected in real time. He pressures from 0.5 to 15 Torr were used.
(b) Mixtures of Cl_2–C_2H_6–O_2 and diluent gases were irradiated using the output from UV blacklights to produce C_2H_5 radicals. The C_2H_6 consumed was determined by either FTIR or GC with flame ionization detection (which also allowed the amount of C_2H_5Cl formed to be measured). Rate coefficients were measured as a function of pressure (3–1500 Torr) relative to that of $C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl$, and have been placed on an absolute basis by use of $k(C_2H_5 + Cl_2) = 2.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 5 Torr.
(c) Based on rate constants from Plumb and Ryan,[6] using $F_c = 0.7$ and assuming collision efficiencies β_c for N_2 and O_2 of 0.3 and $\Delta H° = -133$ kJ·mol^{-1}.
(d) From IUPAC, 1989.[4]

Preferred Values

$k_0 = 5.9 \times 10^{-29}(T/300)^{-3.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Experiments so far have mainly been conducted using the bath gas He, with the previously recommended rate coefficients[4] for M = N_2 and O_2 being estimated relative to the He data. The new study of Ref. 2 reports identical rate coefficients for M = He and N_2 in the upper half of the falloff curve. For this reason, we revise the preferred values by using identical k_0 values for M = He and N_2. We prefer the most extensive results from Ref. 1 because the long falloff extrapolation to k_0 was done with a careful theoretical analysis. However, we retain the temperature coefficient from Ref. 6 which was determined theoretically. Falloff extrapolations were made with theoretically derived[1] values of $F_c = 0.64$ at 200 K and 0.54 at 300 K.

High-pressure rate coefficient

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.3×10^{-12} exp(420/T)	298–400	Munk *et al.*, 1986[7]	(a)
5.3×10^{-12}	298		
$3.67 \times 10^{-14}T^{0.772}$ exp(287/T)	296–805	Wagner *et al.*, 1990[1]	(b)
Relative Rate Coefficients			
$(9.2 \pm 0.9) \times 10^{-12}$	298	Kaiser, Wallington and Andino, 1990[2]	(c)
Reviews and Evaluations			
5×10^{-12}	200–300	CODATA, 1984[3]; IUPAC, 1989[4]	(d)
5×10^{-12}	200–300	NASA, 1990[5]	(e)

Comments

(a) Pulsed radiolysis in H_2 at 1 atm. C_2H_5 radicals generated from the reaction H + C_2H_4, and $C_2H_5O_2$ radicals were monitored by absorption at 240 nm.
(b) See comment (a) for k_0.
(c) See comment (b) for k_0.
(d) Based on the analysis of data of Plumb and Ryan,[6] assuming that $F_c = 0.7$.
(e) From IUPAC, 1989.[4]

Preferred Values

$k_\infty = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

As for k_0, we prefer the more extensive data from Ref. 1 because of their combination with a careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted[1] with an expression $F_c = \{0.58 \exp(-T/1250) + 0.42 \exp(-T/183)\}$ which leads to $F_c = 0.64$ at 200 K and 0.54 at 300 K. Within the stated error limits, the available data all agree with the preferred values based on Ref. 1. QRRK calculations[8] of the reaction are less realistic than the RRKM calculations of Ref. 1. The analysis of the reaction system is complicated, because there is a coupling of the addition reaction with the reaction forming C_2H_4, $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (see the analysis in Ref. 1).

References

[1]A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **94**, 1853 (1990).
[2]E. W. Kaiser, T. J. Wallington, and J. M. Andino, Chem. Phys. Lett. **168**, 309 (1990).
[3]CODATA, Supplement II, 1984 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet. **13**, 1011 (1981).
[7]J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, J. Phys. Chem. **90**, 2752 (1986).
[8]J. W. Boselli and A. M. Dean, J. Phys. Chem. **94**, 3313 (1990).

$n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6×10^{-12}	297	Slagle *et al.*, 1985[1]	(a)
Reviews and Evaluations			
6×10^{-12}	200–300	CODATA, 1984[2]; IUPAC, 1989[3]	(b)

Comments

(a) Flow system study using photoionization MS for the detection of $n\text{-}C_3H_7$ radicals, which were produced by CO_2 laser photolysis of $C_6F_7C_4H_9$. Only weak pressure dependences were observed over the range of He or N_2 pressures from 0.4 to 6.8 Torr. The rate coefficient decreased from 6×10^{-12} to 2.8×10^{-13} cm^3 molecule^{-1} s^{-1} over the temperature range 297–635 K.

(b) Based on Ref. 1 and earlier data by Ruiz and Bayes.[4] The observed negative temperature coefficient was attributed to falloff effects, and experiments conducted near 300 K were assumed to be close to the high pressure limit.

Preferred Values

$k = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1–10 Torr and 298 K.

$k_\infty = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

The available experimental data are consistent with each other. Because they were obtained at total pressures below 100 Torr, we estimate that some falloff corrections have to be applied, which is taken into account in the preferred values. These values are consistent with experiments for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$ (see this evaluation).

References

[1]I. R. Slagle, J.-Y. Park, and D. Gutman, 20th International Symposium on Combustion, 1984 (Combustion Institute, Pittsburgh, PA, 1985), pp. 733–741.
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).

$i\text{-}C_3H_7 + O_2 + M \rightarrow i\text{-}C_3H_7O_2 + M$

$\Delta H^\circ = -157.9$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.41×10^{-11}	300	Ruiz and Bayes, 1984[1]	(a)
8.3×10^{-12}	300	Munk *et al.*, 1986[2]	(b)
Reviews and Evaluations			
1.5×10^{-11}	200–300	CODATA, 1984[3]; IUPAC, 1989[4]	(c)

Comments

(a) Flash photolysis system with detection of radicals by photoionization MS. No pressure dependence detected for He or N_2 pressures from 1 to 4 Torr.

(b) Pulsed radiolysis study in H_2 at 1 atm. i-C_3H_7 generated by the addition of H to C_3H_6 and detected by UV absorption at 253 nm. Absorption spectrum of i-$C_3H_7O_2$ also detected.

(c) Based on the data from reference 1.

Preferred Values

$k_\infty = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are taken as the average of the results from Ref. 1 and 2. Falloff corrections are probably within the uncertainties of the average. This rate coefficient k_∞ appears consistent with those for the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $n\text{-}C_3H_7 + O_2 + M \rightarrow n\text{-}C_3H_7O_2 + M$ (see this evaluation).

References

[1]R. P. Ruiz and K. D. Bayes, J. Phys. Chem. **88**, 2592 (1984).
[2]J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, Chem. Phys. Lett.**132**, 417 (1986).
[3]CODATA, Supplement II, 1984 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3COCH_2 + O_2 + M \rightarrow CH_3COCH_2O_2 + M$

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.45×10^{-12}	298	Cox *et al.*, 1990[1]	(a)

Comments

(a) Pulsed radiolysis of CH_3COCH_3–O_2–SF_6 mixtures at 1 bar of SF_6. CH_3COCH_2 radicals were formed by the reaction of F atoms with CH_3COCH_3. At the monitoring wavelength of 310 nm both CH_3COCH_2 and $CH_3COCH_2O_2$ radicals absorb, with the absorption cross-section of the peroxy radical being a factor of 1.7 greater than that of the CH_3COCH_2 radical. The rate coefficient was evaluated by simulations of the above reaction together with the reaction $CH_3COCH_2 + CH_3COCH_2O_2 \rightarrow 2CH_3COCH_2O$.

Preferred Values

$k_\infty = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability

$\Delta\log k_\infty = \pm 0.5$ at 300 K.

Comments on Preferred Values

Because this is the only study of this reaction, we recommend large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit.

References

[1]R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

$HCO + O_2 \rightarrow CO + HO_2$

$\Delta H^\circ = -133.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-11} \exp[-(204 \pm 180)/T]$	295–713	Timonen, Ratajczak, and Gutman, 1988[1]	(a)
6.2×10^{-12}	295		
$3.2 \times 10^{-12} \exp(87/T)$	200–398	Stief, Nesbitt, and Gleason, 1990[2]	(b)
4.3×10^{-12}	298		
Reviews and Evaluations			
$3.5 \times 10^{-12} \exp(140/T)$	300–500	CODATA, 1984; IUPAC, 1989[3]	(c)
$3.5 \times 10^{-12} \exp(140/T)$	200–300	NASA, 1990[4]	(d)
5.0×10^{-12}	300–2500	Baulch *et al*, 1992[5]	(e)

Comments

(a) Laser pulsed photolysis of CH_3CHO; [HCO] monitored by photoionization MS.
(b) Discharge-flow system; HCO generated from Cl + HCHO and monitored by photoionization MS.
(c) Based on data of Veyret and Lesclaux,[6] Washida *et al.*[7] and Shibuya *et al.*[8]
(d) As for comment (c) with addition of data of Langford and Moore.[9]
(e) Based on data of Veyret and Lesclaux[6] and Timonen *et al.*[1]

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

omments on Preferred Values

The most recent measurements of the room temperature rate coefficient[1,2] are in good agreement with our previous recommendation.[3] The above temperature-independent rate coefficient is the averaged room-temperature rate coefficient of the results of Washida *et al.*,[7] Shibuya *et al.*,[8] Veyret and Lesclaux,[6] Timonen *et al.*[1] and Stief *et al.*[2] Taken together, the temperature dependent studies of Veyret and Lesclaux,[6] Timonen *et al.*[1] and Stief *et al.*[2] show that the rate coefficient of this reaction is essentially independent of temperature over the temperature range 200–400 K, within the error limits of the measurements.

References

[1]R. S. Timonen, E. Ratajczak, and D. Gutman, J. Phys. Chem. **92**, 651 (1988).
[2]L. J. Stief, F. L. Nesbitt, and J. F. Gleason, Abstracts of papers presented at the International Symposium of Gas Kinetics, Assisi, Italy, Sept. 1990.
[3]CODATA, Supplement II, 1984; IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data **21**, 411 (1992).
[6]B. Veyret and R. Lesclaux, J. Phys. Chem. **85**, 1918 (1981).
[7]N. Washida, R. I. Martinez, and K. D. Bayes, Z. Naturforsch. **29a**, 251 (1974).
[8]K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, J. Phys. Chem. **81**, 2292 (1977).
[9]A. O. Langford and C. B. Moore, J. Chem. Phys. **80**, 4211 (1984).

$CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$

$\Delta H^\circ = -148$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficients data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
5×10^{-12}	200–300	CODATA, 1984[1]	(a)

Comments

(a) Based on a direct measurement from Ref. 2 at total pressures of 1–4 Torr, where a rate coefficient of $k = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was measured near 298 K. This rate coefficient is consistent with a series of earlier relative rate measurements.

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1–4 Torr.

$k_\infty = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred value is based on Ref. 2, with some falloff correction estimated by comparison with the reaction $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ (this evaluation).

References

[1]CODATA, Supplement II, 1984 (see references in Introduction).
[2]C. E. McDade, T. M. Lenhardt, and K. D. Bayes, J. Photochem. **20**, 1 (1982).

$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -68.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\{2.5 \times 10^{-9}\, T^{-1.0} + 4.0 \times 10^{-10} \exp(-2525/T)\}$	298–682	Grotheer *et al.*, 1988[1]	(a)
$(8.0 \pm 1.5) \times 10^{-12}$	298		
$5.6 \times 10^{-9} \exp(-1700/T)$	215–250	Nesbitt, Payne and Stief, 1988[2]	(b)
$(8.61 \pm 1.14) \times 10^{-12}$	300		
$(8.8 \pm 0.2) \times 10^{-12}$	298	Pagsberg *et al.*, 1989[3]	(c)
$(1.17 \pm 0.12) \times 10^{-11}$	296	Miyoshi *et al.*, 1990[4]	(d)
Reviews and Evaluations			
$1.7 \times 10^{-11} \exp(-3600/T)$	300–2000	Warnatz, 1984[5]	(e)
9.8×10^{-12}	298	IUPAC, 1989[6]	(f)
9.1×10^{-12}	298	NASA, 1990[7]	(g)

Comments

(a) Discharge flow system in which CH_2OH was generated from the reaction $Cl + CH_3OH$ in the presence of a large excess of O_2 at total pressures of ~0.8 Torr. The rate coefficient k was derived from the disappearance of CH_2OH, as monitored by low electron energy MS.

(b) Similar system to comment (a), with total pressures of ~1 Torr and CH_2OH monitored by MS.

(c) Pulsed radiolysis generation of CH_2OH from $F + CH_3OH$, with the decay of CH_2OH monitored by absorption at 285.5 nm.

(d) Laser flash photolysis of CH_3COCH_2OH with the decay of CH_2OH monitored by photoionization MS.

(e) Includes high-temperature data from shock-tube and other studies.

(f) Average of the data of Grotheer *et al.*,[8] Dóbé *et al.*[9] and Payne *et al.*[10]

(g) Average of the data of Grotheer *et al.*,[8] Dóbé *et al.*,[9] Payne *et al.*,[10] Grotheer *et al.*[1] and Nesbitt *et al.*[2]

Preferred Values

$k = 9.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta\log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction and our recommendation is the average of the results of Grotheer *et al.*,[1] Nesbitt *et al.*,[2] Pagsberg *et al.*,[3] Miyoshi *et al.*,[4] Grotheer *et al.*,[8] Dóbé *et al.*[9] and Payne *et al.*[10] The earlier data of Wang *et al.*[11] and Radford *et al.*[12] are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications.[6] The two recent studies[1,2] of the temperature dependence of this reaction indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200–700 K. The existing data are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

Grotheer *et al.*[1] have carried out experiments replacing CH_3OH by CH_3OD and have observed no kinetic effect for the $CH_2OH/CH_2OD + O_2$ reactions.

References

[1]H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, J. Phys. Chem., **92**, 4028 (1988); idem, 22nd International Symposium on Combustion, 1988 (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.
[2]F. L. Nesbitt, W. A. Payne, and L. J. Stief, J. Phys. Chem. **92**, 4030 (1988).
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[6]IUPAC, Supplement III, 1989 (see references in Introduction).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).
[8]H.-H. Grotheer, G. Riekert, U. Meier, and Th. Just, Ber. Bunsenges Phys. Chem. **89**, 187 (1985).
[9]S. Dóbé, F. Temps, T. Bohland, and H. Gg. Wagner, Z. Naturforsch. **40A**, 1289 (1985).
[10]W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).
[11]W. C. Wang, M. Suto, and L. C. Lee, J. Chem. Phys. **81**, 3122 (1984).
[12]H. E. Radford, Chem. Phys. Lett. **71**, 195 (1980).

$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = -87.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\{1.4 \times 10^{-8} T^{-1.2} + 8.0 \times 10^{-10} \exp(-2525/T)\}$	300–682	Grotheer *et al.*, 1988[1]	(a)
1.56×10^{-11}	300		
$(1.3 \pm 0.2) \times 10^{-11}$	300	Anastasi *et al.*, 1989[2]	(b)
$(2.8 \pm 0.2) \times 10^{-11}$	293	Miyoshi, Matsui and Washida, 1989[3]	(c)

Comments

(a) Discharge flow system in which CH_3CHOH was generated from $Cl + C_2H_5OH$ in the presence of a large excess of O_2 at total pressures of ~0.8 Torr. The rate coefficient k was derived from the disappearance of CH_3CHOH, as monitored by low electron energy MS.

(b) Pulsed radiolysis of $Ar-SF_6-HCl-C_2H_5OH-O_2$ mixtures at total pressures of 760 Torr and with $[SF_6] >> [HCl] >> [C_2H_5OH] >> [O_2]$. CH_3CHOH was generated from $Cl + C_2H_5OH$ and monitored by UV absorption at 260 nm.

(c) Laser flash photolysis of $CH_3COCHOHCH_3$ in a large excess of He at total pressures of 2–7 Torr. CH_3CHOH was monitored by photoionization MS in the presence of excess O_2.

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results of Grotheer *et al.*,[1] Anastasi *et al.*[2] and Miyoshi *et al.*[3] The rather large discrepancy between the data of Miyoshi *et al.*[3] and the other two studies[1,2] could be due to the different sources of generation of the CH_3CHOH radical. The radical generation[1,2] involving Cl attack on C_2H_5OH may not be as clean a source as is the photolysis[3] of $CH_3COCHOHCH_3$.

The temperature dependence of the rate coefficient determined by Grotheer *et al.*[1] shows a marked non-Arrhenius behavior, but this needs to be confirmed before a recommendation can be made.

Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product studies of the photooxidations of ethanol.[4]

References

[1]H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, 22nd International Symposium on Combustion, 1988 (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.

[2]C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, Chem. Phys. Lett. **164**, 18 (1989).

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$CH_2CH_2OH + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.4) \times 10^{-12}$	293	Miyoshi, Matsui and Washida, 1989[1]	(a)

Comments

(a) Laser flash photolysis of $ClCH_2CH_2OH$ and $BrCH_2CH_2OH$ in a large excess of He at total pressures of 2–7 Torr. CH_2CH_2OH was monitored by photoionization MS in the presence of excess O_2.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The direct measurements[1] of this rate coefficient, from the pulsed laser photolysis of either $ClCH_2CH_2OH$ or $BrCH_2CH_2OH$ as the radical source, showed a good level of consistency. By analogy with the reactions $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ and $CH_3CO + O_2 + M \rightarrow CH_3CO_3 + M$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $HOCH_2CH_2O_2$ radical has recently been observed[2,3] by pulsed radiolysis of SF_6–H_2O mixtures[2] and laser flash photolysis of H_2O_2[3] in the presence of C_2H_4 and O_2. These observations indicate that the reaction between CH_2CH_2OH radicals and O_2 leads significantly to the adduct peroxy radical.

References

[1]A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 291 (1989).

[2]C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).

[3]T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -111.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.5 \times 10^{-14} \exp(-1000/T)$	298–450	Lorenz *et al.*, 1985[1]	(a)
1.9×10^{-15}	298		
$2.3 \times 10^{-14}(1000/T)^{-9.5} \exp(2768/T)$	298–973	Wantuck *et al.*, 1987[2]	(b)
2.1×10^{-15}	298		
Reviews and Evaluations			
$1.7 \times 10^{-11} \exp(-3610/T)$	300–2000	Warnatz, 1984[3]	(c)
$7.2 \times 10^{-14} \exp(-1080/T)$	298–610	IUPAC, 1989[4]	(d)
$3.9 \times 10^{-14} \exp(-900/T)$	200–300	NASA, 1990[5]	(e)
$6.7 \times 10^{-14} \exp(-1070/T)$	300–1000	Baulch *et al.*, 1992[6]	(f)

Comments

(a) Laser photolysis of CH_3ONO with monitoring of CH_3O by LIF, at pressures of 75 Torr of He. At 298 K the rate coefficient was shown to be independent of pressure over the range 7.5–150 Torr of He.
(b) Laser photolysis of CH_3OH or CH_3ONO at 193 nm in presence of O_2 plus 25 Torr of Ar. CH_3O radicals were monitored by LIF. Non-Arrhenius behavior observed over entire temperature range and rate coefficients were found to obey a double exponential expression, with $k = 1.5 \times 10^{-10} \exp(-6028/T) + 3.6 \times 10^{-14} \exp(-880/T)$ cm^3 molecule^{-1} s^{-1}.
(c) Includes high-temperature data from shock-tube and other studies.
(d) See Comments on Preferred Values.
(e) Based on the data of Gutman *et al.*[7] and Lorenz *et al.*[1]
(f) Obtained by a least square fit to the data of Gutman *et al.*[7] and Lorenz *et al.*[1]

Preferred Values

$k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.2 \times 10^{-14} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–610 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The direct measurements of the rate coefficients by Lorenz *et al.*[1] (298–450 K) and Wantuck *et al.*[2] (298–973 K) are in good agreement with the similar measurements of Gutman *et al.*[6] (413–608 K), where the temperature ranges overlap. The preferred temperature dependence of the rate coefficient was derived from a least-mean-squares analysis of the three sets of data over the temperature range 298–608 K and is essentially in agreement with the most recent NASA recommendation.[5] The higher temperature measurements of Wantuck *et al.*[2] give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low *A*-factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted.[5]

References

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[3]J. Warnatz, "Rate Coefficients in the C/H/O System", in *Combustion Chemistry*, edited by W. C. Gardiner, (Springer, New York, 1984), p. 197.
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data, **21**, 411 (1992).
[7]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = -134.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$7.1 \times 10^{-14} \exp[(-552 \pm 64)/T]$	295–411	Hartmann *et al.*, 1990[1]	(a)
$(1.08 \pm 0.20) \times 10^{-14}$	295		
Reviews and Evaluations			
8.0×10^{-15}	298	IUPAC, 1989[2]	(b)
$1.0 \times 10^{-13} \exp(-830/T)$	300–1000	Baulch *et al.*, 1992[3]	(c)

Comments

(a) Laser photolysis of C_2H_5ONO in C_2H_5ONO–O_2–He mixtures, with LIF monitoring of C_2H_5O in the wavelength range 310–330 nm. Studies carried out at a total pressure of 26 Torr.
(b) Based on the data of Gutman *et al.*[4]
(c) Based on the mean values of k_{298} of Gutman *et al.*[4] and Zabarnick and Heicklen,[5] assuming that the *A*-factor is the same as that of the reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$.

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.0 \times 10^{-14} \exp(-550/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295–425 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient and the temperature dependence were obtained from the mean of the room temperature rate coefficients of Gutman *et al.*[4] (296 K) and of Hartmann *et al.*[1] (295 K) and by taking the rounded-off value of E/R of Hartmann *et al.*[1] The rate coefficients of Gutman *et al.*[4] and of Hartmann *et al.*[1] differ by between 30 and 50%, which although within the range of the individual error limits, is somewhat higher than might be expected from two direct studies.

The relative rate measurements of Zabarnick and Heicklen[5] are within the error limits which we recommend for our preferred values. We have not taken these results into account, however, owing to the uncertainty concerned with the rate coefficient of the reference reaction of $CH_3O + NO \rightarrow$ products.

It should be noted that the A-factor for the above reaction is very low, but in keeping with that for the analogous reaction $CH_3O + O_2 \rightarrow HCHO + HO_2$.

References

[1]D. Hartmann, J. Karthäuser, J. P. Sawerysyn, and R. Zellner, Ber. Bunsenges Phys. Chem. **94**, 639 (1990).

[2]IUPAC, Supplement III, 1989 (see references in Introduction).

[3]D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Franck, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, J. Phys. Chem. Ref. Data, **21**, 411 (1992).

[4]D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

[5]S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 455 (1985).

$n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$

$\Delta H° = -131.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$1.3 \times 10^{-13} \exp[-(879 \pm 117)/T]$	247–393	Zabarnick and Heicklen, 1985[1]	(a)
6.8×10^{-15}	298		
Reviews and Evaluations			
4.2×10^{-13}	298	Demerjian, Kerr and Calvert, 1974[2]	(b)
8×10^{-15}	298	IUPAC, 1989[3]	(c)

Comments

(a) Photolysis with 366 nm radiation of $n\text{-}C_3H_7ONO$ in a static system in the presence of NO, O_2, and N_2 at total pressures of >150 Torr. Rate data based on measured quantum yields of C_2H_5CHO product. The rate coefficient k was measured relative to $n\text{-}C_3H_7O + NO \rightarrow$ products with $k(n\text{-}C_3H_7O + O_2)/k(n\text{-}C_3H_7O + NO) = 6.8 \times 10^{-3} \exp(-879/T)$, and placed on an absolute basis by use of $k(n\text{-}C_3H_7O + NO) = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature. This value of $k(n\text{-}C_3H_7O + NO)$ is estimated on the assumptions (i) that the rate coefficient for the reaction $n\text{-}C_3H_7O + NO + M \rightarrow n\text{-}C_3H_7ONO + M$ is approximately equal to that[4] for the reaction $CH_3O + NO + M \rightarrow CH_3ONO + M$ ($k_\infty = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K) (CODATA value), and (ii) that[5] $k_d/k_c = 0.35$ for the reactions $n\text{-}C_3H_5O + NO \rightarrow C_2H_5CHO + HNO$ (d) and $n\text{-}C_3H_7O + NO\ (+M) \rightarrow n\text{-}C_3H_7ONO\ (+M)$ (c).

(b) Estimate based on an assumed A-factor for $RO + O_2$ reactions and E calculated empirically from $\Delta H°$ for the reaction.

(c) See Comments on Preferred Values.

Preferred Values

$k = 8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The rate coefficient at 298 K derived from the Zabarnick and Heicklen[1] study, though heavily dependent upon the choice of data for the reference reaction, $n\text{-}C_3H_7O + NO \rightarrow$ products, is consistent with data for other $RO_2 + O_2$ reactions obtained from direct studies. Here we have selected k_{298} to be equal to that for the $C_2H_5O + O_2$ reaction.

The temperature coefficient determined by Zabarnick and Heicklen[1] from their relative rate system is considerably greater than those for the $C_2H_5O + O_2$ reaction (E/R = 650 K) or the i-$C_3H_7 + O_2$ reaction (E/R = 200 K), both of which were obtained from direct studies. This aspect of the reaction requires further experimental work.

References

[1]S. Zabarnick and J. Heicklen, Int. J. Chem Kinet. 17, 477 (1985).
[2]K. L. Demerjian, J. A. Kerr, and J. G. Calvert, Adv. Environ. Sci Technol. 4, 1 (1974).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]R. Zellner, J. Chim. Phys.-Chim. Biol. 84, 403 (1987).
[5]P. Morabito and J. Heicklen, J. Phys. Chem. 89, 2914 (1985).

i-$C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$

$\Delta H° = -150.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.51 \times 10^{-14} \exp[-(200 \pm 140/T)]$	294–384	Balla, Nelson, and McDonald, 1985[1]	(a)
7.72×10^{-15}	298		
Reviews and Evaluations			
$1.5 \times 10^{-14} \exp(-200/T)$	290–390	IUPAC, 1989[2]	(b)

Comments

(a) Pulsed laser photolysis of isopropyl nitrite at 355 nm, with LIF detection of i-C_3H_7O. Pressure range 1–50 Torr.
(b) See Comments on Preferred Values.

Preferred Values

$k = 8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-14} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–390 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The results of Balla *et al.*[1] on the rate coefficient of this reaction appear reasonable in relation to data for other reactions of this type. Both the rate coefficient and temperature coefficient require confirmation.

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. 99, 323 (1985).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.1 \times 10^{-12} \exp[-(210 \pm 84)/T]$	243–384	Paltenghi, Ogryzlo and Bayes, 1984[1]	(a)
$(2.53 \pm 0.54) \times 10^{-12}$	298		
Reviews and Evaluations			
$5.1 \times 10^{-12} \exp(-210/T)$	240–400	IUPAC, 1989[2]	(b)
$5.4 \times 10^{-12} \exp(-220/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Revised calculations of the measurements of Ogryzlo *et al.*[4]
(b) See Comments on Preferred Values.
(c) Based on the data of Ogryzlo *et al.*[4]

Preferred Values

$k = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.1 \times 10^{-12} \exp(-210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The slight change from the earlier evaluation[5] takes account of the revised calculations on the data of Ogryzlo *et al.*,[4] which result from a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.

References

[1]R. Paltenghi, E. A. Ogryzlo, and K. D. Bayes, J. Phys. Chem. **88**, 2595 (1984).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]E. A. Ogryzlo, R. Paltenghi, and K. D. Bayes, Int. J. Chem. Kinet. **13**, 667 (1981).
[5]CODATA, Supplement II, 1984 (see references in Introduction).

$CH_3O + NO + M \rightarrow CH_3ONO + M$ (1)
$CH_3O + NO \rightarrow HCHO + HNO$ (2)

$\Delta H°(1) = -173.2$ kJ·mol^{-1}
$\Delta H°(2) = -116.9$ kJ·mol^{-1}

Low pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-28} [He]	298	Zellner, 1987[1]	(a)
$1.35 \times 10^{-29}(T/298)^{-3.8}$ [Ar]	296–573	Frost and Smith, 1990[2]	(b)
$1.8 \times 10^{-29}(T/300)^{-3.2}$ [Ar]	220–473	McCaulley *et al.*, 1990[3]	(c)
Reviews and Evaluations			
6×10^{-28} [N_2]	298	IUPAC, 1989[4]	(d)

Comments

(a) Laser photolysis of CH_3ONO at 248 or 351 nm in the presence of NO. The rate coefficient k was determined from the rate of recovery of CH_3ONO by time-resolved laser absorption at 257 nm. Falloff curve measured over the range 3.8–375 Torr. k_0 extrapolated using $F_c = 0.6$.
(b) Laser pulsed photolysis of CH_3ONO at 260 nm in the presence of NO. The CH_3O radical decay was monitored by laser-induced fluorescence at 298.5 nm. Rate coefficients were measured up to 125 Torr of Ar or CF_4 diluent. Evaluation of the chemical activation system $CH_3O + NO \rightarrow CH_3ONO^*$, $CH_3ONO^* + M \rightarrow CH_3ONO + M$, and $CH_3ONO^* \rightarrow HCHO + HNO$ using an extended Lindemann-Hinshelwood mechanism. At low pressures the disproportionation reaction $CH_3O + NO \rightarrow HCHO + HNO$ dominated ($k_2 = 5.0 \times 10^{-12}(T/298)^{-0.6}$ cm^3 molecule^{-1} s^{-1}).
(c) Discharge flow study with LIF detection of CH_3O near 320 nm. Measurements were made over the pressure range 0.75–5.0 Torr in He or Ar. The disproportionation reaction $CH_3O + NO \rightarrow HCHO + HNO$ was measured by molecular beam MS ($k_2 = 1.3 \times 10^{-12} \exp(250/T)$ cm^3 molecule^{-1} s^{-1}).
(d) Based on the data from Ref. 1.

Preferred Values

$k_{01} = 1.6 \times 10^{-29}(T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
$k_2 = 4 \times 10^{-12}(T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_{01} = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$

Comments of Preferred Values

The new experiments from Refs. 2 and 3, on which the preferred values for k_{o1} are based, allow for a separation of the combination and disproportionation reactions. A broadening factor $F_c = 0.6$ was used for the combination part of the reaction. The disproportionation/combination ratio $k_2/(k_1 + k_2)$ from Refs. 2 and 3 at 8 Torr total pressure is in excellent agreement with the result of 0.45 from Jenkin *et al.*[5] Apparently the distinction between reactions (1) and (2) was not possible in Refs. 2 and 3.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×10^{-11}	298	Zellner, 1987[1]	(a)
$3.6 \times 10^{-11}(T/298)^{0.6}$	296–573	Frost and Smith, 1990[2]	(b)
Review and Evaluations			
3×10^{-11}	300–400	Atkinson and Lloyd, 1984[6]	(c)
2×10^{-11}	200–400	CODATA, 1982[7]; IUPAC, 1989[4]	(d)

Comments

(a) See comment (a) for k_{o1}.
(b) See comment (b) for k_{o1}.
(c) Comparison of RONO + M → RO + NO + M dissociation data. Calculations via the equilibrium constants led to a constant value of k for RO + NO + M → RONO + M which was independent of R up to C_5.
(d) Based on reference 1 and earlier results from methyl nitrite photolysis.

Preferred Values

$k_{\infty 1} = 3.6 \times 10^{-11}(T/300)^{-0.6}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.5$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are those from Ref. 2. Because these have been evaluated with $F_c = 1$, an increase of $k_{\infty 1}$ is expected when an analysis with a smaller value of F_c is done.

References

[1]R. Zellner, J. Chim. Physique **84**, 403 (1987).
[2]M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).
[3]J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson, and F. Kaufman, J. Chem. Soc. Faraday Trans. **86**, 4001 (1990).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]M. E. Jenkin, G. D. Hayman, and R. A. Cox, J. Photochem. A, **42**, 187 (1988).
[6]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[7]CODATA, Supplement I, 1982 (see references in Introduction).

$$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M \quad (1)$$
$$C_2H_5O + NO \rightarrow CH_3CHO + HNO \quad (2)$$

$\Delta H°(1) = -176.9$ kJ·mol^{-1}
$\Delta H°(2) = -139.3$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.4 \pm 0.4) \times 10^{-11}$	298	Frost and Smith, 1990[1]	(a)

Comments

(a) Laser photolysis of C_2H_5ONO at 266 nm in the presence of NO. The reaction was followed by monitoring the decay of C_2H_5O radicals by LIF at 322.8 nm. The same rate coefficients were found in the presence of 15 or 100 Torr of Ar.

Preferred Values

$k_{\infty 1} = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.
$k_2 = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability
$\Delta\log k_{\infty 1} = \pm 0.3$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The value of $k_{\infty 1}$ appears consistent with values for related reactions such as $CH_3O + NO + M \rightarrow CH_3ONO + M$ and $i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$ (see this evaluation). The value of k_2 is estimated via the preferred value of $k_{\infty 1}$ and the ratio $k_2/k_{\infty 1} = 0.3$ such as measured in Ref. 2.

References

[1]M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).
[2]G. Baker and R. Shaw, J. Chem. Soc. A, 6965 (1965).

$i\text{-}C_3H_7O + NO + M \rightarrow i\text{-}C_3H_7ONO + M$ (1)
$i\text{-}C_3H_7O + NO \rightarrow (CH_3)_2CO + HNO$ (2)

$\Delta H°(2) = -155.6$ kJ·mol^{-1}

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.4×10^{-11}	298	Balla, Nelson and McDonald, 1985[1]	(a)
Reviews and Evaluations			
3×10^{-11}	300–400	Atkinson and Lloyd, 1984[2]	(b)

Comments

(a) Pulsed laser photolysis at 355 nm of $i\text{-}C_3H_7ONO$ in the presence of NO. $i\text{-}C_3H_7O$ was detected by LIF. No dependence of the rate coefficient was observed over the pressure range 1–50 Torr. The small negative temperature dependence ($k = 1.2 \times 10^{-11} \exp(310/T)$ cm^3 molecule^{-1} s^{-1}) observed over the range 298–383 K may be attributed to falloff effects.
(b) Results on the reverse dissociations of RONO were converted via the equilibrium constants.

Preferred Values

$k_{\infty 1} = 3.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.
$k_2 = 6.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Reliability
$\Delta\log k_{\infty 1} = \pm 0.3$ at 300 K.
$\Delta n = \pm 0.5$.
$\Delta\log k_2 = \pm 0.5$.

Comments on Preferred Values

The values for $k_{\infty 1}$ for related reactions such as $CH_3O + NO + M \rightarrow CH_3ONO + M$ and $C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$ (see this evaluation and Ref. 2) are consistent with the preferred values based on Ref. 1. The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1 = 0.19 \pm 0.03$, independent of temperature, measured in Ref. 3.

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).
[2]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[3]L. Batt and R. T. Milne, Int. J. Chem. Kinet. **9**, 141 (1977).

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M \quad (1)$$
$$CH_3O + NO_2 \rightarrow HCHO + HONO \quad (2)$$

$\Delta H°(1) = -170.5$ kJ·mol^{-1}
$\Delta H°(2) = -238.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.6 \times 10^{-29}(T/300)^{-4.5}$ [He]	220–473	McCaulley *et al.*, 1985[1]	(a)
$(1.6 \pm 0.6) \times 10^{-29}$ [He]	295	Frost and Smith, 1990[2]	(b)
$(2.8 \pm 0.6) \times 10^{-29}$ [Ar]	295		
$(3.4 \pm 1.0) \times 10^{-29}$ [CF_4]	295		
$(2.0 \pm 0.5) \times 10^{-29}$ [Ar]	390		
Reviews and Evaluations			
$2.6 \times 10^{-29}(T/300)^{-4.5}$ [He]	200–400	IUPAC, 1989[3]	(c)

Comments

(a) Studied using a discharge flow system over the pressure range 0.6–4 Torr of He. CH_3 produced by IR laser dissociation of $C_6F_6OCH_3$, followed by the reaction $CH_3 + NO_2 \rightarrow CH_3O + NO$, with CH_3O being monitored by LIF. Direct measurements of the branching ratio k_1/k_2 were not possible. A separation was performed by assuming that reaction (1) was in the low pressure limit which led to a value of $k_2 = 1 \times 10^{-11} \exp(-1150/T)$ cm^3 molecule^{-1} s^{-1}.

(b) Laser photolysis of CH_3ONO–NO mixtures at 266 nm with CH_3O being monitored by LIF at 298.5 nm. Rate coefficients were measured over the total pressure ranges 30–100 Torr of He, 6–100 Torr of Ar and 30–125 Torr of CF_4. Falloff curves were fitted to the experimental data using the F_c values of 0.41, 0.44, and 0.48 for He, Ar, and CF_4, respectively. The association reaction (1) appears to dominate over reaction (2).

(c) The derived values for k_0 and its temperature coefficient were in good agreement with theoretical simulations by Patrick and Golden.[4]

Preferred Values

$k_{01} = 2.8 \times 10^{-29}(T/300)^{-4.5}$ [N_2] over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The agreement between the two studies appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_0 for M = Ar and N_2. Falloff curves are constructed with $F_c = 0.44$ at 300 K such as chosen in Ref. 2. Reaction (2) appears to play only a minor role at pressures above 10 Torr [see k_2 value in comment (a)].

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-11}$	295	Frost and Smith, 1990[2]	(a)
Reviews and Evaluations			
1.5×10^{-11}	300–400	Atkinson and Lloyd, 1984[5]	(b)
1.5×10^{-11}	300–400	CODATA, 1982[6]; IUPAC, 1989[3]	(c)

Comments

(a) See comment (b) for k_{01}.
(b) Derived on the basis that $k_\infty(RO + NO + M)/k_\infty(RO + NO_2 + M) = 2$ independent of temperature and taking $k_\infty(RO + NO + M) = 3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, irrespective of R.
(c) This value of $k_{\infty 1}$ can only be a lower limit if falloff curves are broader than assumed.

Preferred Values

$k_{\infty 1} = 2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred $k_{\infty 1}$ value based on Ref. 2 appears consistent with the values for the related reactions RO + NO + M → RONO + M (with R = CH_3, C_2H_5, i-C_3H_7, see this evaluation). Falloff curves are constructed with $F_c = 0.44$ from Ref. 2. Reaction (2) appears to be only of minor importance [see comment (a) for k_{01})].

References

[1]J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. **115**, 180 (1985).
[2]M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).
[5]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[6]CODATA, Supplement I, 1982 (see references in Introduction).

$$C_2H_5O + NO_2 + M \rightarrow C_2H_5ONO_2 + M \quad (1)$$
$$C_2H_5O + NO_2 \rightarrow CH_3CHO + HONO \quad (2)$$

$\Delta H°(1) = -170.0$ $kJ \cdot mol^{-1}$
$\Delta H°(2) = -261.3$ $kJ \cdot mol^{-1}$

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.8 \pm 0.3) \times 10^{-11}$	295	Frost and Smith, 1990[1]	(a)

Comments

(a) Laser photolysis of $C_2H_5ONO_2$ at 266 nm in the presence of NO_2. The reaction was followed by monitoring the decay of C_2H_5O radicals by LIF at 322.8 nm. The same rate coefficients were found in the presence of 1.5 or 100 Torr of Ar.

Preferred Values

$k_{\infty 1} = 2.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The value of $k_{\infty 1}$ appears consistent with values for related reactions[2] such as RO + NO + M → RONO + M (with M = CH_3, C_2H_5, and i-C_3H_7) or $CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$ (see this evaluation). Reaction (2) appears to be of minor importance ($k_2/k_{\infty 1} < 0.2$) in the high-pressure range of the reaction[2] (see also the $CH_3O + NO_2$ reaction system; this evaluation).

References

[1]M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).
[2]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

$$i\text{-}C_3H_7O + NO_2 + M \rightarrow i\text{-}C_3H_7ONO_2 + M \quad (1)$$
$$i\text{-}C_3H_7O + NO_2 \rightarrow (CH_3)_2CO + HONO \quad (2)$$

$\Delta H°(1) = -171.7$ kJ·mol^{-1}
$\Delta H°(2) = -277.6$ kJ·mol^{-1}

High-pressure rate coefficient

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.5×10^{-11}	298	Balla, Nelson and McDonald, 1985[1]	(a)

Comments

(a) Pulsed laser photolysis of isopropyl nitrite at 355 nm in the presence of NO_2. i-C_3H_7O was detected by LIF. By extrapolation to zero laser power, a rate coefficient of $k_{\infty 1} = 1.5 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} was derived from measurements over the temperature range 295–384 K. No pressure dependence was observed between 1 and 10 Torr. Reaction (2) appears to be the minor channel ($k_2/k_{\infty 1} < 0.2$) in the high pressure range of reaction (1).

Preferred Values

$k_{\infty 1} = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

Δog $k_{\infty 1} = \pm 0.3$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

This recommendation is based on Ref. 1. The values of $k_{\infty 1}$ are consistent with other related reactions such as RO + NO + M → RONO + M and RO + NO_2 + M → $RONO_2$ + M (with R = CH_3, C_2H_5, i-C_3H_7; see this evaluation and reference 2). It is estimated that $k_2/k_{\infty 1} < 0.2$.

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).
[2]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$\Delta H° = -49.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-12} \exp[(380 \pm 250)/T]$	218–365	Simonaitis and Heicklen, 1981[1]	(a)
$(7.7 \pm 0.9) \times 10^{-12}$	296		
$(8.6 \pm 2.0) \times 10^{-12}$	295	Plumb *et al.*, 1981[2]	(b)
$(7 \pm 2) \times 10^{-12}$	298	Zellner, Fritz and Lorenz, 1986[3]	(c)
Reviews and Evaluations			
$4.2 \times 10^{-12} \exp(180/T)$	240–360	CODATA, 1984; IUPAC, 1989[4]	(d)
$4.2 \times 10^{-12} \exp(180/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) CH_3O_2 radicals were produced from the flash photolysis of Cl_2 in the presence of CH_4 and O_2, and monitored by UV absorption at 270 nm. The rate coefficient k was independent of pressure over the range 70–600 Torr.

(b) Discharge flow system with CH_3O_2 radicals being generated from Cl + CH_4–O_2 reactions and monitored by MS.

(c) Pulsed laser photolysis of $(CH_3)_2N_2$–O_2–NO mixtures, with CH_3O_2 radicals being monitored by UV absorption at 257 nm.

(d) See Comments on Preferred Values.

(c) The k_{298} rate coefficient was the average of the data of Sander and Watson,[6] Ravishankara *et al.*,[7] Cox and Tyndall,[8] Plumb *et al.*,[2] Simonaitis and Heicklen[1] and Zellner *et al.*[3]

Preferred Values

$k = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.2 \times 10^{-12} \exp(180/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–360 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 180$ K.

Comments on Preferred Values

There have been no new data on this reaction since 1986, and here we largely reproduce our previous data sheet, CODATA, 1984 combined with the subsequent Comments.[4] The recommended rate coefficient at 298 K is the average of the data of Sander and Watson,[6] Ravishankara *et al.*,[7] Cox and Tyndall,[8] Plumb *et al.*[2] and Zellner *et al.*[3] We recommend the slight negative temperature dependence of the rate coefficient obtained[5] by a least-squares analysis of the results of Ravishankara *et al.*[7] and Simonaitis and Heicklen.[1] Ravishankara *et al.*[7] have shown that the channel leading to NO_2 accounts for at least 80% of the reaction and Zellner *et al.*[3] and Zellner[9] have shown, from product studies, that $\phi/(CH_3O) = 1.0 \pm 0.2$. These results, along with the indirect evidence of Pate *et al.*,[10] confirm that the product channel to give CH_3O and NO_2 is the major, if not the only, reaction pathway.

References

[1]R. Simonaitis and J. Heicklen, J. Phys. Chem. **85**, 2946 (1981).
[2]I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, J. Phys. Chem. **85**, 3136 (1981).
[3]R. Zellner, B. Fritz, and K. Lorenz, J. Atmos. Chem. **4**, 241 (1986).
[4]CODATA, Supplement II, 1984; IUPAC, Supplement III, 1989 (see references in Introduction).
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[6]S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[7]A. R. Ravishankara, F. L. Eisele, N. M. Kreutter, and P. H. Wine, J. Chem. Phys. **74**, 2267 (1981).
[8]R. A. Cox and G. Tyndall, Chem. Phys. Lett. **65**, 357 (1979); J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[9]R. Zellner, J. Chim. Phys. Phys. Chim. Biol. **84**, 403 (1987).
[10]C. T. Pate, B. J. Finlayson, and J. N. Pitts, Jr., J. Am. Chem. Soc. **96**, 6554 (1974).

$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$ (1)
$C_2H_5O_2 + NO + M \rightarrow C_2H_5ONO_2 + M$ (2)

$\Delta H^\circ(1) = -45.6$ kJ·mol^{-1}
$\Delta H^\circ(2) = -215.6$ kJ·mol^{-1}

Rate coefficient data $k = (k_1 + k_2)$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.2) \times 10^{-12}$	298	Adachi and Basco, 1979[1]	(a)
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb *et al.*, 1982[2]	(b)
Branching Ratios			
$k_2/k \leq 0.014$ (735 Torr air)	299	Atkinson *et al.*, 1982[3]	(c)
Reviews and Evaluations			
8.9×10^{-12}	298	CODATA, 1984[4]; IUPAC, 1989[5]	(d)
$k_2/k \leq 0.014$	298		(d)

Comments

(a) $C_2H_5O_2$ radicals were generated from the flash photolysis of azoethane in the presence of O_2 and monitored by UV absorption at 250 nm. The rate coefficient k was obtained from the pseudo-first-order decay of $C_2H_5O_2$ in the presence of NO.

(b) Discharge flow system with MS analysis. $C_2H_5O_2$ radicals were generated from Cl + C_2H_6–O_2 reactions; $C_2H_5O_2^+$ ions could not be detected. The rate coefficient k was based on a complex analysis of rate of formation of NO_2, with account taken of the reaction $HO_2 + NO \rightarrow HO + NO_2$. The branching ratios were based on the amount of NO_2 produced.

(c) Product study of the OH radical-initiated or Cl atom-initiated photooxidation of C_2H_6 in NO_x-air mixtures at atmospheric pressure. HO radicals generated from photolysis of CH_3ONO and Cl atoms generated from photolysis of Cl_2. The branching ratio was determined from GC analysis of $C_2H_5ONO_2$ (presumed to be formed from the reactions $C_2H_5O_2 + NO \rightarrow C_2H_5O_2NO^* \xrightarrow{M} C_2H_5ONO_2$) relative to the rate of consumption of C_2H_6.

(d) See Comments on Preferred Values.

Preferred Values

$k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k \leq 0.014$ at 298 K and 1 bar pressure.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
This data sheet is largely reproduced from our previous evaluation, CODATA, 1984,[4] combined with the subsequent Comments.[5] The discrepancy between the data of Adachi and Basco[1] and Plumb *et al.*[2] remains unexplained. Since, however, the technique of Adachi and Basco[1] gave a low rate constant for the analogous reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$, it seems likely that the results of these authors are in error. It has been suggested[6] that for the CH_3O_2 + NO system of Adachi and Basco,[1] the formation of CH_3ONO could lead to interference at the wavelength used to measure the CH_3O_2 absorption and hence to a low value of measured rate coefficient. A similar argument can be applied to the data of Adachi and Basco[1] for the $C_2H_5O_2$ + NO reaction.

The preferred rate coefficient at 298 K is that of Plumb *et al.*,[2] and the preferred branching ratio is that of Atkinson *et al.*[3]

References

[1]H. Adachi and N. Basco, Chem. Phys. Lett. **64**, 431 (1979).
[2]I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Int. J. Chem. Kinet. **14**, 183 (1982).
[3]R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
[4]CODATA, Supplement II, 1984 (see references in Introduction).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).

$n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$ (1)
$n\text{-}C_3H_7O_2 + NO + M \rightarrow n\text{-}C_3H_7ONO_2 + M$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k = 0.020 \pm 0.009$ (735 Torr air)	299	Atkinson *et al.*, 1982[1]	(a)
Reviews and Evaluations			
8.9×10^{-12}	298	IUPAC, 1989[2]	(b)
$k_2/k = 0.020$	298		

Comments

(a) Photolysis of CH_3ONO–NO–C_3H_8 or Cl_2–NO–C_3H_8 mixtures at total pressures of 735 Torr in air. Branching ratio determined from yields of $n\text{-}C_3H_7ONO_2$ product together with consumption of C_3H_8.
(b) See Comments on Preferred Values.

Preferred Values

$k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.020$ at 298 K and 1 bar pressure.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.01$ at 298 K (1 bar).

Comments on Preferred Values
This data sheet is largely reproduced from our previous evaluation, CODATA, 1984,[3] combined with the subsequent Comments.[2] We have assumed that the rate coefficient at room temperature for the overall reaction has the same value as that of the reaction $C_2H_5O_2 + NO \rightarrow$ products. The preferred branching ratio is that determined by Atkinson *et al.*[1]

Carter and Atkinson[4] have recently described a revised method of calculating the effects of temperature and pressure upon the ratio k_2/k_1, based on the pressure fall-off treatment of Troe (see Introduction).

References

[1]R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]CODATA, Supplement II, 1984 (see references in Introduction).
[4]W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).

i-$C_3H_7O_2$ + NO → i-C_3H_7O + NO_2 (1)
i-$C_3H_7O_2$ + NO + M → i-$C_3H_7ONO_2$ + M (2)

$\Delta H°(1) = -40.5$ kJ·mol^{-1}
$\Delta H°(2) = -212.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.3) \times 10^{-12}$	298	Adachi and Basco, 1982[1]	(a)
Branching Ratios			
$k_2/k = 0.042 \pm 0.003$ (735 Torr air)	299	Atkinson *et al.*, 1982[2]; Carter and Atkinson, 1989[3]	(b)
Reviews and Evaluations			
8.9×10^{-12}	298	IUPAC, 1989[4]	(c)
$k_2/k = 0.043$	298		

Comments

(a) Flash photolysis of azoisopropane in the presence of O_2, NO and added He at total pressures of 55–401 Torr. i-$C_3H_7O_2$ radicals were monitored by absorption at 270 nm. The rate coefficient k was derived from modeling of the i-$C_3H_7O_2$ time-concentration profiles on the basis of a mechanism of 8 reactions including secondary reactions of i-C_3H_7O radicals.

(b) Photolysis of CH_3ONO–NO–C_3H_8 or Cl_2–NO–C_3H_8 mixtures at total pressures of 735 Torr of air. Branching ratio determined[2] from yields of i-$C_3H_7ONO_2$ product together with consumption of C_3H_8. Carter and Atkinson[3] have recalculated the branching ratio, listed above, from the original data[2] on the basis of revised data for the rate coefficients of the HO + alkane reactions.

(c) The value of k was assumed to be equal to that of the reaction $C_2H_5O_2$ + NO → products and the branching ratio was taken from Atkinson *et al.*[2]

Preferred Values

$k = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.042$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(k_2/k) = \pm 0.01$ at 298 K (1 bar).

Comments on Preferred Values

In keeping with the n-$C_3H_7O_2$ + NO reaction, we have assumed that the rate coefficient at room temperature for the overall reaction has the same value as that of the reaction $C_2H_5O_2$ + NO → products. Thus the preferred value is considerably larger than that reported by Adachi and Basco[1] (inadvertently omitted from previous IUPAC evaluations). This latter value is subject to the same criticism as for their data on the CH_3O_2 and $C_2H_5O_2$ radical reactions with NO (see data sheets for the CH_3O_2 + NO and $C_2H_5O_2$ + NO reactions). The preferred branching ratio is that recalculated by Carter and Atkinson.[3]

Carter and Atkinson[3] have recently described a revised method of calculating the effects of temperature and pressure upon the ratio k_2/k_1, based on the pressure fall-off treatment of Troe (see Introduction).

References

[1] H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1243 (1982).
[2] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
[3] W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$

$\Delta H° = -133$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.5) \times 10^{-11}$	304–321	Kirchner, Zabel and Becker, 1990[1]	(a)
1.85×10^{-11}	283–313	Tuazon, Carter and Atkinson, 1991[2]	(b)
Reviews and Evaluations			
1.4×10^{-11}	298	IUPAC, 1989[3]	(c)

Comments

(a) Thermal decomposition of PAN (synthesized *in situ*) in an environmental chamber in NO–NO_2–air mixtures. The rate coefficient ratio $k/k(CH_3CO_3 + NO_2)$ was determined from the effect of $[NO]/[NO_2]$ on the rate of the thermal decomposition of PAN. The cited value of k is the average calculated from the measured values of $k/k(CH_3CO_3 + NO_2)$ combined with the corresponding value[4] of $k(CH_3CO_3 + NO_2)$ at total pressures of 22, 75, 225, and 750 Torr.

(b) Similar experimental approach as in comment (a) but without *in situ* synthesis of PAN. A rate coefficient ratio of $k/k(CH_3CO_3 + NO_2) = 1.95 \pm 0.28$ was determined, independent of temperature, at a total pressure of 740 Torr. The cited value of k is calculated taking $k/k(CH_3CO_3 + NO_2) = 9.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at a total pressure of 740 Torr, independent of temperature.[4]

(c) Calculated from the average value of the ratio $k/k(CH_3CO_3 + NO_2)$ of Refs. 5–7, together with $k(CH_3CO_3 + NO_2) = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA, 1982[8]).

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 280–325 K.

Reliability

$\Delta \log k = \pm 0.2$ over the temperature range 280–325 K.
$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

The two recent studies[1,2] of the rate coefficient ratio $k/k(CH_3CO_3 + NO_2)$ are in good agreement and, together with revised data for the rate coefficient $k(CH_3CO_3 + NO_2)$, enable the error limits which were previously recommended[3] to be considerably reduced. Thus, the preferred value has been obtained from the mean value of $k/k(CH_3CO_3 + NO_2) = 2.1 \pm 0.3$ obtained from the data of Kirchner *et al.*[1] and Tuazon *et al.*,[2] at total pressures of 740 and 750 Torr of air. Over the temperature range 283–321 K these two sets of data indicate that this ratio is essentially temperature independent, within the error limits of the measurements ($E/R = 646 \pm 564$ K). The rate coefficient k was then obtained by taking $k(CH_3CO_3 + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 atm pressure (see data sheets for the reaction $CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$).

The experiments of Kirchner *et al.*[1] also show that the rate coefficient k shows no pressure dependence over the pressure range 22–750 Torr.

References

[1] F. Kirchner, F. Zabel, and K. H. Becker, Ber. Bunsenges Phys. Chem. **94**, 1379 (1990).
[2] E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. **95**, 2434 (1991).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).
[4] I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. **95**, 3594 (1991).
[5] R. A. Cox, R. G. Derwent, P. M. Holt, and J. A. Kerr, J. Chem. Soc. Faraday Trans 1, **72**, 2061 (1976).
[6] R. A. Cox and M. J. Roffey, Environ. Sci. Technol. **11**, 900 (1977).
[7] D. G. Hendry and R. A. Kenley, J. Am. Chem. Soc. **99**, 3198 (1977).
[8] CODATA, Supplement I, 1982 (see references in Introduction).

$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$

$\Delta H° = -88$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.33 \pm 0.08) \times 10^{-30}$ [N_2]	298	Sander and Watson, 1980[1]	(a)
$2.2 \times 10^{-30}(T/298)^{-2.5}$ [N_2]	253–353	Ravishankara, Eisele, and Wine, 1980[2]	(b)
Reviews and Evaluations			
$2.3 \times 10^{-30}(T/300)^{-4.0}$ [N_2]	200–300	CODATA, 1982[3]	(c)
$1.5 \times 10^{-30}(T/300)^{-4.0}$ [air]	200–300	NASA, 1990[4]	(d)
$2.5 \times 10^{-30}(T/298)^{-5.5}$ [N_2]	253–353	Destriau and Troe, 1990[5]	(e)

Comments

(a) Flash photolysis system with UV absorption detection of CH_3O_2 radicals. Pressure range was 50–700 Torr, with M = He, N_2 and SF_6. A complete analysis of the falloff curve was carried out with a theoretical F_c value of 0.39, in good agreement with the fitted value of $F_c = 0.40 \pm 0.10$.

(b) Laser flash photolysis system with long path absorption detection of CH_3O_2 radicals. Pressure range = 76–722 Torr, with the bath gas N_2. Complete analysis of the falloff curve for 253, 298, and 353 K was carried out with $F_c = 0.4$ independent of temperature.

(c) Based on the data from Refs. 1 and 2.

(d) Based on the data of Refs. 1 and 2, but using $F_c = 0.6$ and k_∞ with a negative temperature exponent. Satisfactory fit of data for atmospheric applications was also obtained.

(e) Detailed theoretical analysis based on recombination data from Refs. 1 and 2 and dissociation rate data from Ref. 6. In order to extrapolate k_0, a temperature-independent value of $k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $F_c = 0.36$ (at 300 K) were used. The comparison of dissociation and recombination experiments led to $\Delta H° = -88.5$ kJ·mol^{-1}.

Preferred Values

$k_0 = 2.5 \times 10^{-30}(T/300)^{-5.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the theoretical analysis of Ref. 5, which used the previous experimental determinations. These values are based on a theoretically determined value of $F_c = 0.36$ at 300 K. The difference between references 3 and 4 is due to the different values of F_c used, with the analysis of Ref. 4 being based on a standard value of $F_c = 0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.0 \pm 1.0) \times 10^{-12}$	298	Sander and Watson, 1980[1]	(a)
$7 \times 10^{-12}(T/298)^{-3.5}$	253–353	Ravishankara, Eisele, and Wine, 1980[2]	(b)
Reviews and Evaluations			
8×10^{-12}	200–300	CODATA, 1982[3]	(c)
$6.5 \times 10^{-12}(T/300)^{-2}$	200–300	NASA, 1990[4]	(d)
7.5×10^{-12}	253–353	Destriau and Troe, 1990[5]	(e)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0. We consider the large negative temperature coefficient to be an artifact of the interpretation. If a larger negative temperature exponent for k_0 and a smaller F_c value at higher temperature are used, the large negative temperature exponent of k_∞ will decrease considerably.
(c)–(e) See comments (c)–(e) for k_0.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0.

Intermediate Falloff Range

An experimental value of $F_c = 0.4$ at 298 K appears well established. A temperature dependence of F_c must be expected, probably similar to that for $NO_2 + NO_3 \rightarrow N_2O_5$ (see this evaluation). Less complete information on the falloff range arises from the experiments by Cox and Tyndall,[7] who measured $k = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 540 Torr of N_2 and 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 50 Torr of Ar at 275 K. The apparent observation of a pressure independent rate coefficient k over the range 50–580 Torr of Ar, reported by Adachi and Basco,[8] is not confirmed by Refs. 1 and 2.

References

[1]S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[2]A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **73**, 3743 (1980).
[3]CODATA, Supplement I, 1982 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[6]F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
[7]R. A. Cox and G. S. Tyndall, J. Chem. Soc. Faraday Trans. 2, **76**, 153 (1980).
[8]H. Adachi and N. Basco, Int. J. Chem. Kinet. **12**, 1 (1980).

$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$

$\Delta H° = 88$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.3 \times 10^{-4} \exp(-10140/T)$ [CH_4]	256–268	Bahta, Simonaitis, and Heicklen, 1982[1]	(a)
5.5×10^{-19} [CH_4]	298*		
$9.0 \times 10^{-5} \exp(-9694/T)$ [N_2]	248–273	Reimer *et al.*, 1989[2]	(b)
6.7×10^{-19} [N_2]	298*		
Reviews and Evaluations			
$9 \times 10^{-5} \exp(-9690/T)$ [N_2]	250–300	IUPAC, 1980[3]	(c)

Comments

(a) $CH_3O_2NO_2$ generated by photolysis of Cl_2 in the presence of NO_2, CH_4 and O_2. The kinetics were monitored in the presence of NO by UV absorption at 250 nm. At 350 Torr total pressure, $k = 6 \times 10^{15} \exp(-10620/T)$ s^{-1}. The given values of k_0 and k_∞ are derived with $F_c = 0.6$. The data depend to some extent on the rate coefficient for the reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$.
(b) Rate of decomposition of $CH_3O_2NO_2$ followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge CH_3O_2 radicals. Falloff curves were fitted with $F_c = 0.4$ and F_c-dependent broadening (see Ref. 4).
(c) Based on the data and analysis of Ref. 2.

Preferred Values

$k_0 = 6.8 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 9 \times 10^{-5} \exp(-9690/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values correspond to the data and analysis of Ref. 2. A theoretical analysis of these data and those of the reverse reaction in Ref. 5 gives an internally consistent picture (with $\Delta H^\circ = 88.5$ kJ·mol^{-1}). Slightly lower limiting rate coefficients are obtained in Ref. 1, where a value of $F_c = 0.6$ was used.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1 \times 10^{16} \exp(-10920/T)$	256–268	Bahta, Simonaitis, and Heicklen, 1982[1]	(a)
2.6	298*		
$1.1 \times 10^{16} \exp(-10560/T)$	248–273	Reimer *et al.*, 1989[2]	(b)
4.5	298*		
Reviews and Evaluations			
$1.1 \times 10^{16} \exp(-10560/T)$	250–300	IUPAC, 1989[3]	(c)
4.5	298		

Comments

(a)–(c) See comments (a)–(c) for k_0.

Preferred Values

$k_\infty = 1.1 \times 10^{16} \exp(-10560/T)$ s^{-1} over the temperature range 250–300 K.
$k_\infty = 4.5$ s^{-1} at 298 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on preferred values for k_0.

References

[1]A. Bahta, R. Simonaitis, and J. Heicklen, J. Phys. Chem. **86**, 1849 (1982).
[2]A. Reimer, K. H. Becker, E. H. Fink, and F. Zabel, J. Phys. Chem. **93**, 5500 (1989).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]J. Troe, Ber. Bunsenges Phys. Chem. **87**, 161 (1983); R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges Phys. Chem. **87**, 169 (1983).
[5]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

$C_2H_5O_2 + NO_2 + M \rightarrow C_2H_5O_2NO_2$

$\Delta H^\circ = -67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
4.8×10^{-29} [N_2]	254	Elfers, Zabel and Becker, 1990[1]	(a)
Reviews and Evaluations			
$7.9 \times 10^{-30}(T/298)^{-6.2}$ [N_2]	200–300	Destriau and Troe, 1990[2]	(b)
2.2×10^{-29} [N_2]	254		

Comments

(a) Thermal decomposition of $C_2H_5O_2NO_2$ in a glass reaction chamber in the presence of different initial $[NO_2]/[NO]$ ratios at total pressures of 10–1000 mbar. $C_2H_5O_2NO_2$ was prepared *in situ* by the photolysis of Cl_2–C_2H_6–O_2–NO_2–N_2 mixtures. $C_2H_5O_2NO_2$, NO_2 and NO concentrations were monitored by long-path IR absorption and rate coefficient ratios for the reaction of $C_2H_5O_2$ with NO and NO_2 were obtained. The reported rate coefficient for $C_2H_5O_2 + NO_2$ was derived using a rate coefficient of 8.9×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$. Falloff curves were constructed based on the theoretical analysis from Ref. 2.

(b) Rate coefficients for the $C_2H_5O_2NO_2$ dissociation[3] were converted, using modeled equilibrium constants, to recombination rate coefficients at 253 K. A theoretical analysis of the falloff curves using $F_c = 0.31$ and $k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} permitted extrapolation to the low-pressure rate coefficients. The slightly different k_0 value from that of Ref. 1 is due to the use of a different data base and the long and uncertain falloff extrapolation.

Preferred Values

$k_0 = 1.3 \times 10^{-29}(T/300)^{-6.2}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments to Preferred Values

The preferred values are an average of the data from Refs. 1 and 2. The temperature dependence is from the theoretical analysis of Ref. 2. Falloff extrapolations were made with $F_c = 0.31$ at 250–300 K such as given from the theoretical analysis of Ref. 2.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
1.0×10^{-11}	254	Elfers, Zabel and Becker, 1990[1]	(a)
Reviews and Evaluations			
7.5×10^{-12}	200–300	Destriau and Troe, 1990[2]	(b)
5×10^{-12}	200–300	CODATA, 1984[4]	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. k_∞ was estimated to be similar to the values of k_∞ for the recombination reactions $CCl_3O_2 + NO_2$ and $CCl_2FO_2 + NO_2$ (see this evaluation).

(c) Estimated to be similar to the values for the reactions $CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ and $C_3H_7O_2 + NO_2 \rightarrow C_3H_7O_2NO_2$.

Preferred Values

$k_\infty = 8.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comments on k_0.

References

[1] G. Elfers, F. Zabel, and K. H. Becker, Chem. Phys. Lett. **168**, 14 (1990).

[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

[3] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).

[4] CODATA, Supplement II, 1984 (see references in Introduction).

$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$

$\Delta H° = 67.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.8 \times 10^{-4} \exp(-9285/T)$ [N_2]	245–273	Zabel *et al.*, 1989[1]	(a)

Comments

(a) The unimolecular decay of $C_2H_5O_2NO_2$ was followed *in situ* by long-path FTIR spectroscopy at total pressures ranging from 10 to 800 mbar. A falloff extrapolation using $F_c = 0.3$ leads to the cited limiting rate coefficient.

Preferred Values

$k_0 = 1.4 \times 10^{-17}$ [N_2] s^{-1} at 298 K.
$k_0 = 4.8 \times 10^{-4} \exp(-9285/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_0 = \pm 0.5$ at 300 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values
The dissociation data are consistent with the experimental recombination data (see this evaluation) and with a theoretical analysis of the dissociation/recombination data from Ref. 2. Falloff curves are constructed with $F_c = 0.31$ (over the range 250–300 K).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.8 \times 10^{15} \exp(-10440/T)$	245–273	Zabel *et al.*, 1990[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 5.4$ s^{-1} at 298 K.
$k_\infty = 8.8 \times 10^{15} \exp(-10440/T)$ s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.5$ at 300 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values
See comment on k_0.

References

[1] F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
[2] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990)

$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$

$\Delta H° = -119$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.1×10^{-29} [N_2]	298	Basco and Parmar, 1987[1]	(a)
$(2.7 \pm 1.5) \times 10^{-28}(T/298)^{-7.1}$ [air]	248–393	Bridier *et al.*, 1991[2]	(b)
Reviews and Evaluations			
2×10^{-28} [N_2]	298	IUPAC, 1989[3]	(c)

Comments

(a) Flash photolysis system with detection of CH_3CO_3 radicals by absorption at 250 nm. Mixtures of Cl_2, CH_3CHO, O_2, N_2, and NO_2 were photolyzed at total pressures of 76–612 Torr. Extrapolation of falloff curves used a theoretically modeled value of F_c = 0.19.

(b) Flash photolysis of Cl_2–CH_3CHO–NO_2–air mixtures. The decay of CH_3CO_3 radicals was monitored by UV absorption. The falloff curves were fitted using F_c = 0.30. The discrepancy with the data of Ref. 1 is attributed to an oversimplified kinetic scheme used in Ref. 1.

(c) Based on the preliminary rate data from Ref. 2.

Preferred Values

$k_0 = 2.7 \times 10^{-28}(T/300)^{-7.1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 300 K.

$\Delta n = \pm 2$.

Comment on Preferred Values

The extensive and internally consistent study of $CH_3CO_3NO_2$ (PAN) formation and dissociation in Ref. 2 is preferred. Falloff extrapolations were performed with a modeled value of F_c = 0.3.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.1×10^{-12}	298	Basco and Parmar, 1987[1]	(a)
$(1.21 \pm 0.05) \times 10^{-11}(T/298)^{-0.9}$	248–393	Bridier *et al.*, 1991[2]	(b)
Reviews and Evaluations			
9.3×10^{-12} (1 atm air)	298	Atkinson and Lloyd, 1984[4]	(c)
8.4×10^{-12}	298	IUPAC, 1989[3]	(d)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) Evaluated from the rate coefficient ratio $k(CH_3CO_3 + NO)/k(CH_3CO_3 + NO_2) = 1.5$ at 1 atm, using a rate coefficient for the reaction $CH_3CO_3 + NO \rightarrow CH_3CO_2 + NO_2$ of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}.[3]

(d) Based on the data of Refs. 1 and 5, using a falloff correction from k(1 atm) to k_∞ of a factor of 1.4.

Preferred Values

$k_\infty = 1.2 \times 10^{-11}(T/300)^{-0.9}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0.

References

[1]N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **19**, 115 (1987).
[2]I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and R. Zabel, J. Phys. Chem. **95**, 3594 (1991).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[6]M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, Chem. Phys. Lett. **77**, 283 (1980).

$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$

$\Delta H^\circ = 119$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.9 \pm 0.3) \times 10^{-3} \times \exp(-12100/T)$ [N_2]	300–330	Bridier *et al.*, 1991[1]	(a)
Reviews and Evaluations			
$6.3 \times 10^{-2} \exp(-12785/T)$ [N_2]	300–320	IUPAC, 1989[2]	(b)
1.5×10^{-20} [N_2]	298		

Comments

(a) Rate of the thermal decomposition of PAN measured by FTIR absorption spectroscopy in the presence of an excess of NO to scavenge CH_3CO_3 radicals. Pressure range = 7.5–600 Torr of N_2. Falloff curves were analyzed with $F_c = 0.30$.

(b) Based on the preliminary data of Ref. 1.

Preferred Values

$k_0 = 1.1 \times 10^{-20}$ [N_2] s^{-1} at 298 K.

$k_0 = 4.9 \times 10^{-3} \exp(-12100/T)$ [N_2] s^{-1} over the temperature range 300–330 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 300 K.

$\Delta(E/R) = \pm 1000$ K.

Comment on Preferred Values

The data base of Ref. 1 is large enough to allow for a falloff extrapolation to k_0, in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of $F_c = 0.3$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.2) \times 10^{-4}$ (700 Torr N_2)	297	Niki *et al.*, 1985[3]	(a)
2.2×10^{-4} (12.4 Torr NO)	298	Senum, Fajer, and Gaffney, 1986[4]	(b)
$2.52 \times 10^{16} \exp(-13573/T)$	283–313	Tuazon, Carter, and Atkinson, 1991[5]	(c)
4.2×10^{-4} (740 Torr air or N_2)	298		
$(4.0 \pm 0.8) \times 10^{16} \exp(-13600/T)$	300–330	Bridier *et al.*, 1991[1]	(d)
6.1×10^{-4}	298		
Reviews and Evaluations			
$1.95 \times 10^{16} \exp(-13543/T)$	280–320	Atkinson and Lloyd, 1984[6]	(e)
3.6×10^{-4}	298		
$2.2 \times 10^{16} \exp(-13435/T)$	300–320	IUPAC, 1989[2]	(f)
5.8×10^{-4}	298		

Comments

(a) Decay of $CH_3CO_3{}^{15}NO_2$ in the presence of $^{14}NO_2$ monitored by FTIR spectroscopy in a long-path cell at a total pressure of 700 Torr of N_2.
(b) Decay of $CH_3CO_3NO_2$ (2 Torr) in the presence of NO (0.2–10.3 Torr) monitored by FTIR spectroscopy in a 10 cm cell. Second reaction channel, leading to $CH_3ONO_2 + CO_2$, was monitored by FTIR absorption in experiments with 2.4 to 27.5 Torr of pure PAN and no added gases. The rate coefficient derived [$k(298\text{ K}) = 1.3 \times 10^{-6}\text{ s}^{-1}$] and the evidence for this reaction channel need to be confirmed.
(c) Thermal decomposition of PAN was monitored in an environmental chamber in the presence of 740 Torr of synthetic air or N_2. The concentrations of PAN, NO, NO_2 and other reactions products were monitored by FTIR absorption spectroscopy.
(d) See comment (a) for k_0.
(e) Based on the data from Ref. 7.
(f) See comment (b) for k_0.

Preferred Values

$k_\infty = 6.1 \times 10^{-4}\text{ s}^{-1}$ at 298 K.
$k_\infty = 4.0 \times 10^{16} \exp(-13600/T)\text{ s}^{-1}$ over the temperature range 280–330 K.

Reliability
$\Delta\log k_\infty = \pm 0.2$ at 300 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
See comment on k_0. The actual rate data at 1 bar of Refs. 1 and 5 agree very well and are also consistent with a series of earlier results included in the evaluation of Ref. 2. The temperature dependence of $F_c = 0.3$, which was used[1] over the range 300–330 K, needs further theoretical investigation.

References

[1]I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, J. Phys. Chem. 95, 3594 (1991).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]H. Niki, P.D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. 17, 525 (1985).
[4]G. I. Senum, R. Fajer, and J. S. Gaffney, J. Phys. Chem. 90, 152 (1986).
[5]E. C. Tuazon, W. P. L. Carter, and R. Atkinson, J. Phys. Chem. 95, 2434 (1991).
[6]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data 13, 315 (1984).
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$CH_3O_2 + NO_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.3 \pm 0.7) \times 10^{-12}$	298	Crowley *et al.*, 1990[1]	(a)

Comments

(a) Molecular modulation study involving the 253.7 nm photolysis of HNO_3–CH_4–O_2 mixtures in a flow system. The rate coefficient k was derived from a computer fit of the NO_3 absorption profiles (623 nm) based on a mechanism of 33 reactions.

Preferred Values

No recommendation.

Comments on Preferred Values
The only reported study of this reaction by Crowley *et al.*[1] involves a complex system of chemical reactions and consequently leads to a very indirect determination of the rate coefficient. Until more work is carried out on this reaction, we make no recommendation.

References

[1]J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. 22, 673 (1990).

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \quad (1)$$
$$\rightarrow 2CH_3O + O_2 \quad (2)$$
$$\rightarrow CH_3OOCH_3 + O_2 \quad (3)$$

$\Delta H°(1) = -331.0$ kJ·mol^{-1}
$\Delta H°(2) = 14.4$ kJ·mol^{-1}
$\Delta H°(3) = -146.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6 \pm 0.55) \times 10^{-13}$	300	Simon, Schneider and Moortgat, 1990[1]	(a,b)
$1.3 \times 10^{-13} \exp(365/T)$	248–573	Lightfoot, Lesclaux and Veyret, 1990[2]	(a,c)
$(4.1 \pm 0.9) \times 10^{-13}$	300		
4.6×10^{-13}	298	Jenkin and Cox, 1991[3]	(a,d)
Branching Ratios			
$k_2/k = 0.29$	388	Lightfoot, Lesclaux and Veyret, 1990[2]	(c)
$k_2/k = 0.49$	423		
$k_2/k = 0.64$	473		
$k_2/k = 0.79$	523		
$k_2/k = 0.82$	573		
$k_2/k = 1/\{1 + [\exp(1131 \pm 30)/T]/(19 \pm 5)\}$	223–333	Horie, Crowley and Moortgat, 1990[4]	(e)
Reviews and Evaluations			
$1.7 \times 10^{-13} \exp(220/T)$	200–400	IUPAC, 1989[5]	(f)
$2.2 \times 10^{-13} \exp(220/T)$	200–300	NASA, 1990[6]	(g)

Comments

(a) k is defined by $-d[CH_3O_2]/dt = 2k[CH_3O_2]^2$ and has been derived from the measured overall second-order decay of CH_3O_2 (k_0) by correcting for secondary removal of CH_3O_2.

(b) Molecular modulation study, with CH_3O_2 being generated by photolysis of Cl_2 in the presence of CH_4–O_2 mixtures at pressures of ~240 Torr. CH_3O_2 radicals were monitored by absorption over the range 220–270 nm. $k_0/\sigma(250 \text{ nm}) = 1.16 \times 10^5$ cm s^{-1} and $\sigma(250 \text{ nm}) = 4.14 \times 10^{-18}$ cm^2 molecule^{-1}, leading to $k_0 = (4.8 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The cited value of k was obtained by taking $k_0/k = 1.35$ to allow for secondary removal of CH_3O_2.

(c) Flash photolysis of Cl_2 in the presence of CH_4–O_2–N_2 mixtures over the pressure range 200–700 Torr. CH_3O_2 radicals were monitored by UV absorption, with $k_0/\sigma(210\text{–}260 \text{ nm}) = 1.17 \times 10^5$ cm s^{-1} and $\sigma(250 \text{ nm}) = 4.8 \times 10^{-18}$ cm^2 molecule^{-1}. k_0/k taken to be 1.35. At temperatures >373 K, the second-order decays of CH_3O_2 were affected by HO_2 reactions. The branching ratio was obtained from the effect of HO_2 on the CH_3O_2 decays.

(d) Molecular modulation study, with CH_3O_2 being generated by photolysis of CH_3I in the presence of 10 Torr O_2 with added N_2 (total pressures 10–760 Torr). CH_3O_2 radicals were monitored by absorption over the range 210–320 nm. System generated absorption due to a second transient species, ascribed to CH_3OOI. $k_0/\sigma(230 \text{ nm})$ was determined as a function of temperature and pressure. At 298 K, $k_0/\sigma(230 \text{ nm}) = 1.01 \times 10^5$ cm s^{-1} over the pressure range 10–760 Torr. Over the temperature range 268–350 K, $k_0/\sigma(230 \text{ nm}) = 4.85 \times 10^4 \exp[(220 \pm 72)/T]$ cm s^{-1} at 760 Torr and $k_0/\sigma(230 \text{ nm}) = 7.45 \times 10^4 \exp[(92 \pm 53)/T]$ cm s^{-1} at 10.8 Torr. The cited value of k was obtained from the measured value of $k_0/\sigma(250 \text{ nm}) = 1.17 \times 10^5$ cm s^{-1} with $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1}.

(e) Study of the photooxidation of CH_4, initiated by Cl atoms generated from Cl_2, in a slow-flow system under steady-state illumination. Analysis of HCHO, CH_3OH and HCOOH products by FTIR spectroscopy.

(f) Calculated from the average value of $k_0/\sigma(250 \text{ nm}) = 1.24 \times 10^5$ cm s^{-1} from the results of Parkes,[7] Hochanadel *et al.*,[8] Anastasi *et al.*,[9] Kan *et al.*,[10] Adachi *et al.*,[11] Sander and Watson,[12] McAdam *et al.*,[13] Kurylo *et al.*[14] and Jenkin *et al.*,[15] and the value $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1} (average of the results of McAdam *et al.*,[13] Kurylo and Wallington,[14] Jenkin *et al.*,[15] Kan *et al.*,[10] Cox and Tyndall,[16] Sander and Watson,[12] Adachi *et al.*,[11] Hochanadel *et al.*,[8] Parkes,[7] Anastasi *et al.*,[9] Moortgat *et al.*[17] and Pilling and Smith[18]).

(g) Calculated from the average value of $k_0/\sigma(250 \text{ nm})$ from Cox and Tyndall,[16] Jenkin *et al.*,[15] Sander and Watson,[12] McAdam *et al.*,[13] Kurylo and Wallington[14] and Lightfoot *et al.*,[2] and the average value of $\sigma(250 \text{ nm}) = 3.7 \times 10^{-18}$ cm^2 molecule^{-1}.

Preferred Values

$k = 3.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-13} \exp(365/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
$k_2 = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.9 \times 10^{-13} \exp(-509/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–330 K.

Reliability
$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta(E_2/R) = \pm 300$ K.

Comments on Preferred Values

The recent room temperature measurements[1-3] of k_0/σ are in excellent agreement with our previously recommended value of $k_0/\sigma(250 \text{ nm}) = 1.24 \times 10^5$ cm s^{-1}, which is unaltered. In addition, the measurements of the absorption cross-section by Simon *et al.*[1] are also in agreement with our previous recommendation of $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1} which is also unaltered. Thus, our recommended[5] value of $k_0 = 4.8 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} at 298 K is confirmed.

Taking the revised branching ratio of $k_2/k = 0.30$ at 298 K (see below) yields the slightly revised value of k at 298 K listed above.

The temperature dependence of k reported by Lightfoot *et al.*[2] is in excellent agreement with the previous studies of Sander and Watson[12] and Kurylo and Wallington.[14] Here we have recommended the E/R value of Lightfoot *et al.*,[2] on the basis of their more extensive temperature range. This is larger than our previously recommended value of E/R, since the data have now been treated in terms of a temperature dependent branching ratio k_2/k (see below). The recommended Arrhenius equation follows from the recommended values of k_{298} and E/R.

The two recent studies[2,4] of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie *et al.*,[4] over the more atmospherically relevant temperature range 220–330 K, in calculating the recommended value of k_2. This is derived from the above[4] tabulated temperature dependent value of k_2/k and our recommended Arrhenius equation for k.

It should be noted that, from an analysis of their own data[4] together with the results of Lightfoot *et al.*,[2] Anastasi *et al.*,[9] Kan *et al.*,[19] Parkes,[7] Niki *et al.*[20] and Weaver *et al.*,[21] the equation $k_2/k = 1/\{1+[\exp(1330/T)]/33\}$ was obtained by Horie *et al.*[4] for the more extensive temperature range 223–573 K. This equation shows slight non-Arrhenius behavior.

Lightfoot *et al.*[2] observed no pressure dependence of the branching ratio, k_2/k, over the range 210–760 Torr.

References

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[17] G. K. Moortgat, J. P. Burrows, W. Schneider, G. S. Tyndall, and R. A. Cox, Proceedings of the 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, D. Reidel Pub. Co., Dordrecht, Holland, 1987, pp. 271–281.
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[21] J. Weaver, J. Meagher, R. Shortridge, and J. Heicklen, J. Photochem. **4**, 34 (1975).

$$CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2 \quad (1)$$
$$\rightarrow CH_3CO_2H + HCHO + O_2 \quad (2)$$

$\Delta H°(1) = -28$ kJ·mol^{-1}
$\Delta H°(2) = -379$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-12}	302	Addison *et al.*, 1980[1]	(a)
$(1.4 \pm 0.3) \times 10^{-11}$	253–368	Moortgat, Veyret, and Lesclaux, 1988[2]	(b)
$k_1 = 1.8 \times 10^{-9} \exp[-(1800 \pm 1100)/T]$	253–368		
$k_1 = (5.5 \pm 3) \times 10^{-12}$	298		
$k_2 = 4.1 \times 10^{-15} \exp[(2100 \pm 1200)/T]$	253–368		
$k_2 = (5.5 \pm 2) \times 10^{-12}$	298		
Reviews and Evaluations			
$k_1 = 5.5 \times 10^{-12}$	298	IUPAC, 1989[3]	(c)
$k_2 = 5.5 \times 10^{-12}$	298		

Comments

(a) Molecular modulation study involving UV absorption of CH_3CO_3 (210–280 nm) produced from the photolysis of Cl_2 in the presence of CH_3CHO–O_2 mixtures at a total pressure of 710 Torr. The rate coefficient k was obtained from a computer simulation of absorption curves, involving a mechanism of nine elementary reactions.

(b) Flash photolysis of Cl_2 in the presence of CH_3CHO–O_2 mixtures at a total pressure of 620 Torr. Rate coefficients were derived by fitting the experimental optical density traces at several wavelengths in the range 200–250 nm using a computer simulation model of CH_3O_2 and CH_3CO_3 reactions together with the absorption cross-sections of the radicals. Inclusion of channel (2) was necessary to account for the observed removal of CH_3O_2 in the first 100 μs after the flash.

(c) See Comments on Preferred Values.

Preferred Values

$k_1 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.5$ at 298 K.
$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The two reported studies of this reaction are not in good agreement. The discrepancy arises primarily from the different absorption cross-sections used for the CH_3CO_3 radical and the rate coefficient determined for its self-reaction in these studies. We have selected the more recent study of Moortgat *et al.*[2] as the basis for a recommendation, on the grounds that the CH_3CO_3 cross-section determination is more direct, and the complex kinetic behavior of the radicals appears to be better defined in the flash photolysis system. Further confirmation of the rate coefficient and the branching ratio of this reaction are required.

References

[1] M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, Chem. Phys. Lett. **73**, 283 (1980).
[2] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).

$$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH + CH_2(OH)_2 + O_2 \quad (1)$$
$$\rightarrow 2HOCH_2O + O_2 \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275–323	Veyret *et al.*, 1989[1]	(a,b)
$k_1 = (7.0 \pm 2.1) \times 10^{-13}$	295		
$k_1 = (5.6 \pm 2.8) \times 10^{-13}$	298	Burrows *et al.*, 1989[2]	(a,c)
Relative Rate Coefficients			
$k_2 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows *et al.*, 1989[2]	(a,c)

Comments

(a) k is defined by $-d[HOCH_2O_2]/dt = 2k[HOCH_2O_2]^2$.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2, with time-resolved absorption spectroscopy for the detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k_1 was obtained from a computer fit of the absorption profiles of $HOCH_2O_2$ radicals at 250 nm. Channel (2) leads to the re-generation of HO_2 radicals and is thus not observable in this system.

(c) Molecular modulation study of Cl_2–HCHO–O_2 mixture with diode laser infrared spectroscopy for the detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k_2 was obtained from a computer simulation of quantum yields for HCOOH formation.

Preferred Values

$k_1 = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 5.7 \times 10^{-14} \exp(750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 275–325 K.

$k_2 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \pm 750$ K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret *et al.*[1] and Burrows *et al.*[2] confirm that the interaction of $HOCHO_2$ radicals involves two channels. The two reports[1,2] of the rate coefficient k_1 at room temperature are in good agreement, and indicate that this channel is a factor of ~3–4 faster than the interaction of CH_3O_2 radicals. The rate coefficient k_2 is even faster than k_1, with a value of about 50 times that of the analogous reaction of CH_3O_2 radicals. Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2.

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5OH + CH_3CHO + O_2 \quad (1)$$
$$\rightarrow 2C_2H_5O + O_2 \quad (2)$$
$$\rightarrow C_2H_5OOC_2H_5 + O_2 \quad (3)$$

$\Delta H°(1) = -343.2$ kJ·mol^{-1}
$\Delta H°(2) = 23.0$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.1×10^{-14}	298	Bauer, Crowley and Moortgat, 1992[1]	(a,b)
Branching Ratios			
$k_2/k_1 = 2.1$	295	Wallington *et al.*, 1989[2]	(c)
$k_3/k \leq 0.06$	295		
Reviews and Evaluations			
$1.2 \times 10^{-13} \exp(-110/T)$	250–450	IUPAC, 1989[3]	(d)
$1.6 \times 10^{-13} \exp(-300/T)$	200–300	NASA, 1990[4]	(e)

Comments

(a) k is defined by $-\,d[C_2H_5O_2]/dt = 2k[C_2H_5O_2]^2$ and has been derived from the measured overall second-order decay of $C_2H_5O_2$ (k_0) by correcting for secondary removal of $C_2H_5O_2$.

(b) Molecular modulation study. $C_2H_5O_2$ radicals were generated from the photolysis of flowing mixtures of Cl_2–C_2H_6–O_2–N_2 at a total pressure of 100 Torr and monitored by absorption at 210 and 330 nm. Values of k/s were determined at 220, 250 and 280 nm, leading to $k_0 = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The cited value of k was calculated taking $k_2/k = 0.65$.

(c) $C_2H_5O_2$ radicals were generated from the steady-state photolysis of Cl_2–C_2H_6 mixtures at 700 Torr pressure of air. Products were monitored by FTIR spectroscopy.

(d) k_{298} was the mean of the data of Adachi *et al.*,[5] Anastasi *et al.*,[6] Cattell *et al.*[7] and Wallington *et al.*[8] E/R was from Wallington *et al.*[8] and the A-factor was adjusted to fit k_{298}. k_2/k at 298 K was the mean of the data of Niki *et al.*[9] and Anastasi *et al.*[6]

(e) The rate coefficient k_{298} was derived from the studies of Adachi *et al.*,[5] Anastasi *et al.*,[6] Munk *et al.*,[10] Cattell *et al.*,[7] Anastasi *et al.*[11] and Wallington *et al.*[8] The above Arrhenius equation was then obtained using an E/R value derived from the data of Adachi *et al.*,[5] Anastasi *et al.*[6] and Wallington *et al.*[8]

Preferred Values

$k = 6.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.8 \times 10^{-14} \exp(-110/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–450 K.
$k_2/k = 0.62$ at 298 K.

Reliability
$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta(E/R) = ^{+300}_{-100}$ K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} has been calculated from the mean value of $k_0 = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} obtained from the studies of Adachi *et al.*,[5] Anastasi *et al.*,[6] Cattell *et al.*,[7] Wallington *et al.*[8] and Bauer *et al.*,[1] all of which are in good agreement. This mean value of k_0 was converted to the above preferred value of k_{298} by use of the preferred branching ratio of $k_2/k = 0.62$ (see below).

Our recommended value of E/R is from the study of Wallington *et al.*,[8] and the A-factor has been adjusted to give the preferred value of k_{298}.

The recommended branching ratio has been calculated from the mean value of k_1/k_2 from the results of Niki *et al.*[9] ($k_1/k_2 = 0.76$ at 298 K), Anastasi *et al.*[6] ($k_1/k_2 = 0.59$ at 298 K), and Wallington *et al.*[2] ($k_1/k_2 = 0.48$ at 295 K). The temperature dependence of the branching ratio reported by Anastasi *et al.*[6] requires confirmation.

The product study of Wallington *et al.*[2] failed to reveal any $C_2H_5OOC_2H_5$ product, and while their reported branching ratio k_3/k is based on their detection limits for $C_2H_5OOC_2H_5$, it is recommended that channel (3) be discounted under atmospheric conditions.

References

[1]D. Bauer, J. N. Crowley, and G. K. Moortgat, J. Photochem. Photobiol., **A65**, 329 (1992).
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[4]NASA Evaluation No 9, 1990 (see references in Introduction).
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[6]C. Anastasi, D. J. Waddington, and A. Woolley, J. Chem. Soc. Faraday Trans. 1, **79**, 505 (1983).

[7]F. C. Cattell, J. Cavanagh, R. A. Cox, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. 2, **82**, 1999 (1986).
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[10]J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, J. Phys. Chem. **90**, 2752 (1986).
[11]C. Anastasi, M. J. Brown, D. B. Smith, and D. J. Waddington, Joint French and Italian sections of the Combustion Institute, Amalfi, Italy, June 1987.

$CH_3CO_3 + CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2$

$\Delta H° = -71$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5\,^{+2.5}_{-1.3}) \times 10^{-12}$	302	Addison *et al.*, 1980[1]	(a,b)
$(8.0 \pm 1.3) \times 10^{-12}$	298	Basco and Parmar, 1985[2]	(a,c)
$2.8 \times 10^{-12} \exp[(530 \pm 100)/T]$	253–368	Moortgat, Veyret and Lesclaux, 1989[3]	(a,d)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
Reviews and Evaluations			
$2.8 \times 10^{-12} \exp(530/T)$	250–370	IUPAC, 1989[4]	(e)

Comments

(a) k is defined by $-d[CH_3CO_3]/dt = 2k[CH_3CO_3]^2$ and has been derived from the measured overall second-order decay of CH_3CO_3 (k_0) by correcting for secondary removal of CH_3CO_3.

(b) Molecular modulation study involving UV absorption (210–280 nm) of CH_3CO_3 radicals produced from the photolysis of Cl_2 in the presence of CH_3CHO and O_2 at a total pressure of 710 Torr. A computer simulation of the absorption curves, involving a mechanism of nine elementary reactions with secondary removal of CH_3CO_3, yielded the cited rate coefficient k from the experimental value of $k_0 = (6.5 \pm 3.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Flash photolysis of Cl_2 in the presence of CH_3CHO and O_2 at a total pressure of 153 Torr. CH_3CO_3 was monitored by UV absorption (210–280 nm). The rate coefficient k was derived from a computer simulation of absorption profiles over the wavelength range 198–208 nm, where the contribution of CH_3O_2 radicals to the total absorbance was assumed to be negligible. The reported rate coefficient, which is listed above, is effectively k.

(d) Flash photolysis of Cl_2 in the presence of CH_3CHO–O_2 mixtures at a total pressure of 620 Torr. CH_3CO_3 radicals were monitored by absorption over the range 190–280 nm and the absorption cross-section was measured relative to $\sigma(HO_2) = 5.3 \times 10^{-18}$ cm^2 molecule^{-1} at 210 nm. The rate coefficient was derived from a computer simulation of the absorption traces at a range of wavelengths, from a mechanism including secondary removal of CH_3CO_3.

(e) See Comments on Preferred Values.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-12} \exp(530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta E/R = \pm 500$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The agreement among the three measurements[1-3] of this rate coefficient at room temperature is rather poor. We have selected the most recent study of Moortgat *et al.*[3] as the basis for a recommendation, on the grounds that it is based upon a more complete knowledge of the complicated chemistry involved than was available for the earlier studies.[1,2] At the same time, until more experimental data are available we have assigned considerable error limits, particularly with regard to the temperature coefficient.

References

[1]M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, Chem. Phys. Lett. **73**, 283 (1980).
[2]N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **17**, 891 (1985).
[3]G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).

$$HOCH_2CH_2O_2 + HOCH_2CH_2O_2 \rightarrow HOCH_2CH_2OH + HOCH_2CHO + O_2 \quad (1)$$
$$\rightarrow 2HOCH_2CH_2O + O_2 \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.36 \pm 0.21) \times 10^{-12}$	298	Jenkin and Cox, 1991[1]	(a,b)
$(7.7 \pm 1.2) \times 10^{-12}$	298	Anastasi *et al.*, 1991[2]	(a,c)
$(2.2 \pm 0.3) \times 10^{-12}$	296	Murrells *et al.*, 1991[3]	(a,d)
Branching Ratios			
$k_2/k = 0.18 \pm 0.02$	298	Jenkin and Cox, 1991[1]	(e)
$k_2/k = 0.25$	298	Anastasi *et al.*, 1991[2]	(f)
$k_2/k = 0.36 \pm 0.07$	298	Murrells *et al.*, 1991[3]	(g)

Comments

(a) k is defined as $-d[HOCH_2CH_2O_2]/dt = 2k[HOCH_2CH_2O_2]^2$ and has been derived from the measured overall second-order decay of $HOCH_2CH_2O_2$ (k_0) by correcting for secondary removal of $HOCH_2CH_2O_2$.

(b) Molecular modulation study, with radicals being generated from the photolysis of $HOCH_2CH_2I$ in the presence of O_2 and N_2 at a total pressure of 760 Torr in a slow flow system. $HOCH_2CH_2O_2$ radicals were monitored by absorption at 230 nm for which $\sigma(HOCH_2CH_2O_2) = 2.35 \times 10^{-18}$ cm^2 molecule^{-1}. The cited rate coefficient k was calculated from the experimental value of $k_0/\sigma_{230} = 6.8 \times 10^5$ cm s^{-1} and the estimated branching ratio, $k_2/k = 0.18$. The value $k_0/\sigma_{250} = 6.5 \times 10^5$ cm s^{-1} was also obtained.

(c) Pulsed radiolysis study, with radicals being generated from C_2H_4–O_2–H_2O–SF_6 and CH_3CH_2OH–O_2–SF_6 mixtures at a total pressure of 760 Torr. $HOCH_2CH_2O_2$ radicals were monitored by absorption at 230 nm, with $\sigma_{230} = 3.5 \times 10^{-18}$ cm^2 molecule^{-1}. The rate coefficient k_{298} listed above is the average from the studies of the two sources of the radical, obtained by computer simulation of the absorption traces of the radical.

(d) Separate laser flash photolysis and molecular modulation studies, with radicals being generated from the photolysis of H_2O_2 in the presence of C_2H_4 and O_2 at total pressures of 730 ± 30 Torr (N_2). $HOCH_2CH_2O_2$ radicals were monitored by time-resolved UV absorption spectroscopy. Values of $k_0/\sigma_{250} = 6.6 \times 10^5$ and 6.8×10^5 cm s^{-1} and $\sigma_{250} = 4.47 \times 10^{-18}$ and 4.90×10^{-18} cm^2 molecule^{-1} were obtained from the flash photolysis and modulation experiments, respectively. The above value of k is that from the flash photolysis experiments, taking $k_2/k = 0.36$.

(e) Determined in same experiments as for comment (b) from the measured yields of HCHO and the amount of $HOCH_2CH_2I$ reacted, assuming that photodissociation of $HOCH_2CH_2I$ yields exclusively $HOCH_2CH_2O_2$ radicals at 760 Torr.

(f) Derived from computer simulation of the absorption profile of the $HOCH_2CH_2O_2$ radical at 225 nm.

(g) Re-evaluation of the data of Jenkin and Cox,[1] in light of evidence that only ~50% of the $HOCH_2CH_2I$ photolyzed yields $HOCH_2CH_2O_2$.

Preferred Values

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.36$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} has been obtained from the average value of $k_0/\sigma_{250} = 6.6 \times 10^5$ cm s^{-1} obtained from the laser flash photolysis experiments[3] and the two molecular modulation studies.[1,3] Taking the average value of $\sigma_{250} = 4.7 \times 10^{-18}$ cm^2 molecule^{-1} from the two sets of experiments of Murrells *et al.*[3] yields $k_0 = 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which leads to the preferred value of k_{298} from the re-assessed branching ratio $k_2/k = 0.36$.

The absorption spectrum of the $HOCH_2CH_2O_2$ radical reported by Anastasi *et al.*[2] from pulsed radiolysis experiments shows several distinctly different features to that reported by Murrells *et al.*[3] The value of $k_0/\sigma_{250} = 3.3 \times 10^6$ cm s^{-1} which can be calculated[3] from the results of Anastasi *et al.*[2] is a factor of ~5 larger than the value from the other work.[1,3] These discrepancies are not easily explained, but the weight of evidence appears to support the consistent data from the flash photolysis[3] and molecular modulation[1,3] experiments.

The re-assessment of the data of Jenkin and Cox[1] by Murrells *et al.*[3] also leads to the higher value of the branching ratio, which we have recommended here. The approximate branching ratio reported by Anastasi *et al.*[2] is consistent with this value, within the suggested error limits.

References

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$$n\text{-}C_3H_7O_2 + n\text{-}C_3H_7O_2 \rightarrow n\text{-}C_3H_7OH + C_2H_5CHO + O_2 \quad (1)$$
$$\rightarrow 2n\text{-}C_3H_7O + O_2 \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.3) \times 10^{-13}$	298	Adachi and Basco, 1982[1]	(a,b)
Reviews and Evaluations			
3×10^{-13}	298	IUPAC, 1989[2]	(c)

Comments

(a) k is defined by $-\,d[n\text{-}C_3H_7O_2] = 2k[n\text{-}C_3H_7O_2]^2$ and has been derived from the measured overall second-order decay of n-$C_3H_7O_2$ (k_0) by correcting for secondary removal of n-$C_3H_7O_2$.
(b) Flash photolysis of 1,1'-azopropane in the presence of O_2 and added N_2 at total pressures up to 720 Torr. n-$C_3H_7O_2$ radicals were monitored by absorption at 260 nm, for which $\sigma(260\text{ nm}) = 3.15 \times 10^{-18}$ cm^2 molecule^{-1}. The rate coefficient k was calculated from the experimental value of $k_0 = (3.84 \pm 0.33) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} on the basis of a mechanism of 12 elementary reactions, including secondary removal of n-C_3H_7O radicals.
(c) See Comments on Preferred Values.

Preferred Values

$k = 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta\log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The recommended rate coefficient, which is the rounded-off value from the study of Adachi and Basco,[1] requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $C_2H_5O_2$ radicals. On the other hand, the recommended rate coefficient for the interaction of the i-$C_3H_7O_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) and that reported[3] for the t-$C_4H_9O_2$ radical is even lower still ($k_{298} = 2.3 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}). This trend is in keeping with that observed in the liquid phase for the RO_2 interactions,[4] i.e., k(primary RO_2) > k(secondary RO_2) > k(tertiary RO_2).

References

[1]H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).
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[3]C. Anastasi, I. W. M. Smith, and D. A. Parks, J. Chem. Soc. Faraday Trans. 1, **74**, 1693 (1978).
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$$i\text{-}C_3H_7O_2 + i\text{-}C_3H_7O_2 \rightarrow i\text{-}C_3H_7OH + (CH_3)_2CO + O_2 \quad (1)$$
$$\rightarrow 2i\text{-}C_3H_7O + O_2 \quad (2)$$

$\Delta H^\circ(1) = -351.9$ kJ·mol^{-1}
$\Delta H^\circ(2) = 33.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.43 \times 10^{-12} \exp[-(2243 \pm 69)/T]$	300–373	Kirsch *et al.*, 1978[1]	(a,b)
8.10×10^{-16}	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1989[2]	(a,c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk *et al.*, 1986[3]	(a,d)
Branching Ratios			
$k_2/k_1 = 1.39 \pm 0.04$	302	Kirsch *et al.*, 1979[4]	(e)
$k_2/k_1 = 56.3 \exp(-1130/T)$	302–372	Cowley, Waddington, and Woolley, 1982[5]	(f)
Reviews and Evaluations			
$1.6 \times 10^{-12} \exp(-2200/T)$	300–400	IUPAC, 1989[6]	(g)

Comments

(a) k is defined by $-d[i\text{-}C_3H_7O_2]/dt = 2k[i\text{-}C_3H_7O_2]^2$ and has been derived from the measured overall second-order decay of $i\text{-}C_3H_7O_2$ (k_0) by correcting for secondary removal of $i\text{-}C_3H_7O_2$.

(b) Molecular modulation study of the photolysis of 2,2'-azopropane in the presence of O_2 and N_2 at total pressures up to 710 Torr. $i\text{-}C_3H_7O_2$ radicals were monitored by absorption at 265 nm. The rate coefficient k has been calculated from the experimental value of $k_0 = (2.37 \pm 0.17) \times 10^{-12} \exp[-(2243 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1} and the branching ratio $k_2/k_1 = 1.39$ at 302 K determined in the subsequent study.[4]

(c) Flash photolysis of 2,2'-azopropane in the presence of O_2 and added N_2 at total pressures up to 720 Torr. $i\text{-}C_3H_7O_2$ radicals were monitored by absorption at 240 nm, for which $\sigma_0(240\text{ nm}) = 4.86 \times 10^{-18}$ cm^2 molecule^{-1}. The rate coefficient k has been calculated from the experimental value of $k_0 = (2.03 \pm 0.58) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K, on the basis of a proposed mechanism of 12 elementary reactions including secondary consumption of $i\text{-}C_3H_7O_2$ radicals.

(d) Pulsed radiolysis of H_2 at 1 atm in the presence of C_3H_6. $i\text{-}C_3H_7$ was generated from the reaction of H atoms with C_3H_6. The absorption spectrum of $i\text{-}C_3H_7O_2$ was observed on the addition of O_2 and the decay of $i\text{-}C_3H_7O_2$ monitored by UV absorption at 253 nm, and found to obey second-order kinetics. It is not clear if the reported value of the rate coefficient is k_0 or k.

(e) Steady-state photolysis of 2,2'-azopropane in the presence of O_2 and added N_2 at total pressures up to 500 Torr. Ratio of rate coefficients based on analyses of $(CH_3)_2CO$ and $(CH_3)_2CHOH$ by GC.

(f) Extension of the experiments by Kirsch *et al.*,[4] to obtain k_2/k_1 at 333 and 372 K. The Arrhenius equation calculated from these data and a value of k_2/k_1 at 302 K was reported by Kirsch *et al.*[4]

(g) See Comments on Preferred Values.

Preferred Values

$k = 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6 \times 10^{-12} \exp(-2200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the temperature range 300–400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0 \exp(-380/T)$ over the temperature range 300–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The recommended rate coefficient (k) at 298 K is the average of the rate coefficients from the data of Kirsch *et al.*[1,4] and Adachi and Basco,[2] which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk *et al.*,[3] for which experimental details are lacking.

The recommended temperature dependence of k is based on the results of Kirsch *et al.*,[1] which have been rounded-off and adjusted to the recommended value of k_{298}.

The branching ratio and its temperature dependence[4,5] appear to be reliable and have been adopted here, but require further confirmation.

The value of k_{298} is considerably lower than that for the analogous reaction of the n-$C_3H_7O_2$ radical, which is in keeping with the trend observed in studies of the interactions of alkylperoxy radicals in solution,[7] i.e.,

$$k(\text{primary } RO_2) > k(\text{secondary } RO_2) > k(\text{tertiary } RO_2).$$

References

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$CH_3COCH_2O_2 + CH_3COCH_2O_2 \rightarrow CH_3COCH_2OH + CH_3COCHO + O_2$ (1)

$\rightarrow 2CH_3COCH_2O + O_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 8.3 \times 10^{-12}$	298	Cox *et al.*, 1990[1]	(a,b)

Comments

(a) k is defined by $-d[CH_3COCH_2O_2]/dt = 2k[CH_3COCH_2O_2]^2$.

(b) Pulsed radiolysis experiments with CH_3COCH_3–O_2 mixtures in 1 atm SF_6. $CH_3COCH_2O_2$ radicals were monitored by absorption at 310 nm and the rate coefficient k was derived from the observed second-order decays at high O_2 concentrations. The derived value of $k_0 = (8.3 \pm 1.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit, owing to the possibility of secondary reactions producing an enhanced decay of $CH_3COCH_2O_2$ radicals.

Preferred Values

$k \leq 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient at 298 K, as determined by Cox *et al.*[1] The secondary chemistry in that system, along with the absorption cross-section of the $CH_3COCH_2O_2$ radical, require further studies before the rate coefficient can be established with greater certainty.

References

[1]R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, Chem. Phys. Lett. **173**, 206 (1990).

$$RCHOO + O_3 \rightarrow RCHO + 2O_2 \quad (1)$$
$$RCHOO + H_2O \rightarrow products \quad (2)$$
$$RCHOO + CO \rightarrow products \quad (3)$$
$$RCHOO + HCHO \rightarrow \overline{RCHOOCH_2O} \quad (4)$$
$$RCHOO + C_2H_4 \rightarrow products \quad (5)$$
$$RCHOO + NO \rightarrow RCHO + NO_2 \quad (6)$$
$$RCHOO + NO_2 \rightarrow RCHO + NO_3 \quad (7)$$
$$RCHOO + SO_2 \rightarrow products \quad (8)$$

(R=H or CH_3)

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Relative Rate Coefficients			
$k_2/k_8 = (6.1 \pm 0.3) \times 10^{-5}$	295	Calvert *et al.*, 1978[1]	(a)
$k_1:k_3:k_4:k_5:k_8 = 2.5 \times 10^{-3}:1.8 \times 10^{-3}:2.5 \times 10^{-1}:2.5 \times 10^{-3}:1.0$	296	Su, Calvert and Shaw, 1980[2]	(b)
$k_2/k_8 = (2.3 \pm 1) \times 10^{-4}$	298	Suto, Manzanares and Lee, 1984[3]	(c)
$k_7/k_8 = (1.4 \pm 0.4) \times 10^{-2}$	298	Manzanares, Suto and Lee, 1987[4]	(d)
Reviews and Evaluations			
$k_2 = 2 \times 10^{-19}$ to 1×10^{-15}	298	Herron, Martinez and Huie, 1982[5]	(e)
$k_4 = 2 \times 10^{-16}$ to 8×10^{-13}	298		(f)
$k_7 = 1 \times 10^{-17}$ to 7×10^{-14}	298		(g)
$k_8 = 3 \times 10^{-15}$ to 1.7×10^{-11}	298		(h)
$k_2:k_3:k_4:k_6:k_7:k_8 = 5 \times 10^{-5}:2 \times 10^{-3}:0.25:10^2:10:1$	298	Atkinson and Lloyd, 1984[6]	(i)
$k_2 \sim 4 \times 10^{-18}$	298		(j)
$k_4 \sim 2 \times 10^{-14}$	298		(j)
$k_6 = 7 \times 10^{-12}$	298		(k)
$k_7 \sim 7 \times 10^{-13}$	298		(j)
$k_8 \sim 7 \times 10^{-14}$	298		(j)
$k_2 = 4 \times 10^{-16}$	298	Kerr and Calvert, 1984[7]	(l)
$k_3 = 1.3 \times 10^{-14}$	298		(l)
$k_4 = 2 \times 10^{-12}$	298		(l)
$k_6 = 7 \times 10^{-12}$	298		(l)
$k_7 = 1.0 \times 10^{-13}$	298		(l)
$k_8 = 7 \times 10^{-12}$	298		(l)

Comments

(a) Derived from a reanalysis of the data of Cox and Penkett[8] from a study of the aerosol formation from SO_2 in the presence of O_3–O_2–*cis*-2-C_4H_8 mixtures at atmospheric pressure. In this system the biradical intermediate involved is believed to be $CH_3\dot{C}HO\dot{O}$.

(b) FTIR study of the C_2H_4–O_3 reaction in the presence of O_2–N_2 mixtures at a total pressure of 700 Torr and with added CO, HCHO, or SO_2. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.

(c) Flow system involving C_2H_4–O_3–SO_2–H_2O mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3, SO_2, and H_2O.

(d) Similar study to that of comment (c), with the inclusion of the effect of added NO_2 on the formation of the H_2SO_4 aerosol.

(e) Based on the ratio $k_2/k_8 \approx 6 \times 10^{-5}$, as derived by Calvert *et al.*[1] from the data of Cox and Penkett,[8] and taking $3 \times 10^{-15} < k_8 < 1.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [see comment (i)].

(f) Based on a study of the ozonide formation in the system O_3–O_2–*cis*-2-C_4H_8–HCHO by Niki *et al.*[9] and on thermochemical kinetic estimates of Nangia and Benson.[10] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(g) Derived from the ratio $k_4/k_7 \approx 14$, which has been estimated[5] from the data of Martinez *et al.*[11] from a study of the reduction in secondary ozonide formation from the O_3–O_2–*trans*-2-C_4H_8 reaction in the presence of NO_2. k_7 was calculated by taking $2 \times 10^{-16} < k_4 < 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [see comment (f)]. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(h) Based on the suppression of ozonide formation in the O_3–O_2–*cis*–2–C_4H_8–HCHO system by SO_2 observed by Niki *et al.*[9] and on thermochemical kinetic estimates of Nangia and Benson.[10] Details were not provided. It has been assumed that the reactivities of the $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ biradicals are identical.

(i) The relative rate coefficients are proposed on the basis that the data on $\dot{C}H_2O\dot{O}$ (Su *et al.*[2]) and on $CH_3\dot{C}HO\dot{O}$ (Cox and Penkett[8]) can be amalgamated, i.e., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ have the same reactivities. From the studies of Akimoto *et al.*[12,13] on the O_3–C_2H_4 and C_3H_6 system, it was estimated that k_6:k_7:k_8 = 10^2:10:1.

(j) Calculated from the above relative rate coefficients and assuming that $k_6 = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [see comment (k)].

(k) This rate coefficient was assumed to have a value similar to that for the reaction of alkylperoxy radicals with NO ($RO_2 + NO \rightarrow RO + NO_2$), and hence $k_6 = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(l) Calculated (i) on the assumption that $k_6 = k_8$ and taking the estimated value of $k_6 = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} of Atkinson and Lloyd[6] and (ii) from the relative rate data of Calvert *et al.*,[1] Su *et al.*[2] and of Suto *et al.*[3]

Preferred Values

No recommendation.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989.[14] Vibrationally excited Criegie intermediates or biradicals, $[R\dot{C}HO\dot{O}]^{\ddagger}$, are produced from the reactions of O_3 with alkenes.[15] These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated biradicals, $R\dot{C}HO\dot{O}$. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated biradicals.

Studies have been made of the reactions of $R\dot{C}HO\dot{O}$ with aldehydes,[2,9,16–19] SO_2[1,2,8,9,20] and H_2O,[1,8,12,21] but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert *et al.*,[1] Su *et al.*[2] and Suto *et al.*,[3] based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO_2 in systems involving $R\dot{C}HO\dot{O}$ biradicals. The only compound, other than SO_2, common to any of these studies is H_2O, for which the derived relative rate coefficients differ by a factor of ~4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the biradicals $CH_3\dot{C}HO\dot{O}$ with O_3, CO and alkenes are not important under atmospheric conditions. The reactions with H_2O, RCHO, NO_2, and SO_2 need to be considered, although for most tropospheric conditions the only effective reaction of the biradicals is likely to be that with H_2O forming acidic products.

Previous reviewers[6,7] have made the reasonable assumption that the reaction of $R\dot{C}HO\dot{O}$ with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2$. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd[6] have estimated the relative rate coefficients for $R\dot{C}HO\dot{O}$ reacting with NO and SO_3, corresponding to $k_6/k_7 = 10^2$, whereas Kerr and Calvert[7] propose $k_6/k_7 = 1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients of any of the $R\dot{C}HO\dot{O}$ bimolecular reactions, both Atkinson and Lloyd[6] and Kerr and Calvert[7] have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $RO_2 + NO \rightarrow RO + NO_2$, with $k_6 = 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made with $R\dot{C}HO\dot{O}$ systems involving O_3-alkene reactions owing to the complex chemistry involved. In this regard the recent studies of Hatakeyama *et al.*[21] involving the generation of $\dot{C}H_2O\dot{O}$ biradicals from the reaction of $CH_2(^3B_1)$ with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary to compare data obtained from different O_2-alkene systems and to assume that all the $R\dot{C}HO\dot{O}$ biradicals have equal reactivity, e.g., $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is very little direct experimental evidence on the products of any of the reactions (1) to (8). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

Recent studies of the reactions of O_3 with *trans*-2-butene,[22,23] isoprene[22,23] and monoterpenes[22,23] have reported varying amounts of H_2O_2 product. Since the yields of H_2O_2 were considerably enhanced by the presence of H_2O, it was proposed that H_2O_2 was formed in a direct reaction involving Criegie biradicals:

$$R_1R_2\dot{C}O\dot{O} + H_2O \rightarrow (R_1R_2COO \cdot H_2O)$$

$$(R_1R_2COO \cdot H_2O) \rightarrow R_1COR_2 + H_2O_2$$

In some of these experiments,[22] as in previous O_3-alkene studies,[24,25] hydroperoxides were also detected as products. The hydroperoxides were suggested to arise also from a direct Criegie biradical-H_2O interaction:

$$R_1R_2\dot{C}O\dot{O} + H_2O \rightarrow R_1R_2C(OH)OOH.$$

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$O_3 + C_2H_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.8 \pm 2.8) \times 10^{-20}$	303	Cadle and Schadt, 1953[1]	(a)
$5.3 \times 10^{-12} \exp[-(5435 \pm 201)/T]$	243–283	DeMore, 1969[2]	(b)
6.4×10^{-20}	298*		
$(3.0 \pm 0.5) \times 10^{-20}$	294	DeMore, 1971[3]	(c)
$(8.6 \pm 0.9) \times 10^{-20}$	298	Stedman and Niki, 1973[4]	(d)
$(3.8 \pm 0.6) \times 10^{-20}$	297	Pate, Atkinson and Pitts, 1976[5]	
$(7.8 \pm 1.2) \times 10^{-21}$	294	Atkinson and Aschmann, 1984[6]	(d)
Reviews and Evaluations			
1×10^{-20}	298	IUPAC, 1989[7]	(e)
$1.0 \times 10^{-14} \exp(-4100/T)$	~298	NASA, 1990[8]	(f)

Comments

(a) Static system with IR absorption detection of O_3 and C_2H_2. An approximate temperature dependence of 20 kJ·mol^{-1} was reported.
(b) Static system with UV absorption detection of O_3 at 253.7 nm.
(c) Static system with UV (253.7 nm) and/or IR (1053 cm^{-1}) absorption detection of O_3.
(d) Static system with chemiluminescence detection of O_3.
(e) See Comments on Preferred Values.
(f) The 298 K rate coefficient was based on the most recent (and lowest) measured rate coefficient of Atkinson and Aschmann,[6] and is identical to the previous[7] and present IUPAC recommendations. The temperature dependence was estimated.

Preferred Values

$k = 1 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The literature data show a large degree of scatter at room temperature. While the most recent and lowest rate coefficient of Atkinson and Aschmann[6] may be the most accurate (any impurities would lead to higher rate constants), the preferred value and its associated large uncertainty cover the available 298 K rate coefficients. No recommendation is made regarding the temperature dependence.

References

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[8]NASA Evaluation No. 9, 1990 (see references in Introduction).

$O_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.6 \pm 1.4) \times 10^{-18}$	303–323	Cadle and Schadt, 1952[1]	(a)
1.35×10^{-18}	~298	Hanst *et al.*, 1958[2]	(b)
$2.8 \times 10^{-15} \exp[-(2114 \pm 201)/T]$	303–373	Bufalini and Altshuller, 1965[3]	(c)
$(2.66 \pm 0.33) \times 10^{-18}$	303		
3.3×10^{-18}	298	Bufalini and Altshuller, 1965[3]	(d)
$3.3 \times 10^{-15} \exp[-(2365 \pm 101)/T]$	178–233	DeMore, 1969[4]	(e)
1.18×10^{-18}	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman, Wu and Niki, 1973[5]	(f)
$1.2 \times 10^{-14} \exp[-(2491 \pm 101)/T]$	~284–347	Becker, Schurath and Seitz, 1974[6]	(g)
2.8×10^{-18}	298		
$9.00 \times 10^{-15} \exp[-(2557 \pm 167)/T]$	235–362	Herron and Huie, 1974[7]	(h)
1.69×10^{-18}	298		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar, Wu and Niki, 1974[8]	(f)
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar, Wu and Niki, 1976[9]	(f)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby, Toby and O'Neal, 1976[10]	(e)
$(1.8 \pm 0.1) \times 10^{-18}$	298	Su, Calvert and Shaw, 1980[11]	(i)
$3.2 \times 10^{-14} \exp(-2920/T)$	260–294	Adeniji, Kerr and Williams, 1981[12]	(f)
1.6×10^{-18}	294		
1.8×10^{-18}	~298	Niki *et al.*, 1981[13]	(i)
$2.6 \times 10^{-14} \exp[-(2828 \pm 181)/T]$	283–304	Kan *et al.*, 1981[14]	(i,j)
1.97×10^{-18}	298		
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson *et al.*, 1982[15]	(f)
$7.72 \times 10^{-15} \exp[-(2557 \pm 30)/T]$	232–298	Bahta, Simonaitis and Heicklen, 1984[16]	(e)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
Reviews and Evaluations			
$1.20 \times 10^{-14} \exp(-2633/T)$	178–362	Atkinson and Carter, 1984[17]	(k)
$1.2 \times 10^{-14} \exp(-2630/T)$	180–360	IUPAC, 1989[18]	(l)
$1.2 \times 10^{-14} \exp(-2630/T)$	180–360	NASA, 1990[19]	(m)

Comments

(a) Static system, with IR absorption detection of C_2H_4 and O_3.

(b) Both static and stirred flow reaction systems were used, with IR absorption spectroscopic detection.

(c) Stirred flow reactor used with wet chemical analysis of O_3.

(d) Static system with wet chemical analysis of O_3.

(e) Static system, with UV absorption detection of O_3 at 253.7 nm.

(f) Static system, with chemiluminescence detection of O_3.

(g) Static system, with UV absorption detection of O_3 at 253.7 nm. Low total pressures used, and it was noted that insufficient O_2 was present to minimize the occurrence of secondary reactions. Hence these data are upper limits to the elementary rate coefficients.

(h) Stopped flow system, with MS detection of O_3. Carried out at total pressure of ~4 Torr, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3.

(i) Static system, with analysis of O_3 and C_2H_4 by FTIR absorption spectroscopy.

(j) Arrhenius expression derived from the data of Su *et al.*[11] and Kan *et al.*,[14] both of these studies being conducted by the same research group using the same experimental techniques.

(k) Derived from the rate coefficient data of DeMore,[4] Stedman *et al.*,[5] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Su *et al.*,[11] Adeniji *et al.*,[12] Kan *et al.*[14] and Atkinson *et al.*[15] The earlier data of Cadle and Schadt[1] and Bufalini and Altshuller[3] were not used because of questions regarding the validity of the experimental methods used, those of Hanst *et al.*[2] and Niki *et al.*[13] could not be used since the temperature was not specified, and the rate coefficients of Becker *et al.*[6] are recognized to be erroneously high due to the presence of insufficient O_2 to avoid or minimize secondary reactions removing O_3.

(l) See Comments on Preferred Values.

(m) Accepts the IUPAC, 1989, evaluation[18] based on the rate coefficient data of DeMore,[4] Stedman *et al.*,[5] Herron and Huie,[7] Japar *et al.*,[8,9] Toby *et al.*,[10] Su *et al.*,[11] Adeniji *et al.*,[12] Kan *et al.*,[14] Atkinson *et al.*[15] and Bahta *et al.*[16]

Preferred Values

$k = 1.7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-14} \exp(-2630/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 180–360 K.

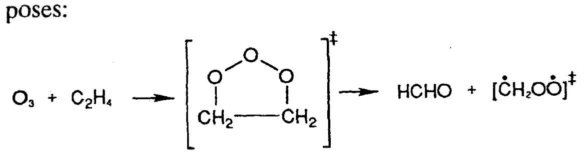
Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

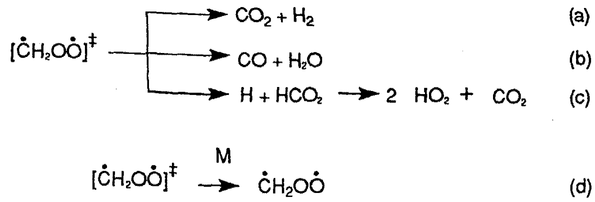
Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[18] The preferred rate coefficient is derived from the data set[4,5,7–12,14,15] utilized by Atkinson and Carter,[17] together with the more recent rate coefficients measured by Bahta *et al.*[16] (averaging the individual data given at each temperature studied to provide a single rate constant for each of the temperatures 232, 251, 272 and 298 K). As discussed by Atkinson and Lloyd[20] and Atkinson and Carter,[17] the initial reaction forms the energy-rich trioxane which rapidly decomposes:



to yield HCHO and the energy-rich biradical $[\dot{C}H_2O\dot{O}]^‡$

This energy-rich biradical can either decompose or be stabilized



At room temperature and atmospheric pressure, the fraction of stabilization is 0.37,[11,13,14,21] and the fractions of the overall reactions proceeding via pathways (a) through (c) are then approximately 0.13, 0.44, and 0.06, respectively.[17,20] The relative importance of these decomposition/stabilization reactions of the $[\dot{C}H_2O\dot{O}]^‡$ radical are, however, pressure dependent, with no quantitative data being available other than at ~1 bar of air.

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$O_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.2×10^{-18}	~298	Cadle and Schadt, 1952[1]	(a)
8.1×10^{-18}	~298	Hanst *et al.*, 1958[2]	(b)
1.26×10^{-17}	296	Cox and Penkett, 1972[3]	(c)
$(1.25 \pm 0.10) \times 10^{-17}$	299	Stedman, Wu and Niki, 1973[4]	(d)
$1.10 \times 10^{-14} \exp[-(1968 \pm 101)/T]$	286–358	Becker, Schurath, and Seitz, 1974[5]	(e)
1.45×10^{-17}	298		
$6.14 \times 10^{-15} \exp[-(1897 \pm 109)/T]$	235–362	Herron and Huie, 1974[6]	(f)
1.06×10^{-17}	298		
$(1.30 \pm 0.01) \times 10^{-17}$	299	Japar, Wu and Niki, 1974[7]	(d)
$(1.32 \pm 0.03) \times 10^{-17}$	299	Japar, Wu and Niki, 1976[8]	(d)
$1.3 \times 10^{-14} \exp(-2013/T)$	260–294	Adeniji, Kerr, and Williams, 1981[9]	(d)
1.26×10^{-17}	294		
$(1.04 \pm 0.14) \times 10^{-17}$	296	Atkinson *et al.*, 1982[10]	(d)
Reviews and Evaluations			
$1.32 \times 10^{-14} \exp(-2105/T)$	250–362	Atkinson and Carter, 1984[11]	(g)
$1.3 \times 10^{-14} \exp(-2105/T)$	250–360	IUPAC, 1989[12]	(h)
$6.5 \times 10^{-15} \exp(-1900/T)$	235–360	NASA, 1990[13]	(i)

Comments

(a) Static system, with wet chemical analysis for oxidant.

(b) Both static and stirred flow reaction systems were used, with IR absorption spectroscopic detection.

(c) Static system with detection of O_3 by both chemiluminescence and wet chemical analysis.

(d) Static system, with chemiluminescence detection of O_3.

(e) Static system, with UV absorption detection of O_3 at 253.7 nm. Low total pressures used, and it was observed that the presence of O_2 was necessary to minimize the occurrence of secondary reactions. It is possible that these data are still upper limits to the elementary rate coefficients.

(f) Stopped flow system, with MS detection of O_3. Carried out at total pressure of ~4 Torr, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3. [Due to a typographical error,[13] the lowest temperature studied was 235.0 K, and not 250.0 K as stated.[13]]

(g) Derived from the rate coefficients of Cox and Penkett,[3] Stedman *et al.*,[4] Herron and Huie,[6] Japar *et al.*,[7,8] Adeniji *et al.*,[9] and Atkinson *et al.*[10] The earlier data of Cadle and Schadt[1] were not used because of questions concerning the validity of the wet chemical analysis used, and in any case the temperature was not specified. This was also the case for the study of Hanst *et al.*[2] The data of Becker *et al.*[5] were not utilized in the evaluation since they were ~40% higher than the other data used,[3,4,6-10] possibly due to the presence of insufficient O_2 to avoid secondary reactions.

(h) See Comments on Preferred Values.

(i) Based mainly on the absolute rate coefficient data of Herron and Huie.[6]

Preferred Values

$k = 1.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5 \times 10^{-15} \exp(-1880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–370 K.

Reliability

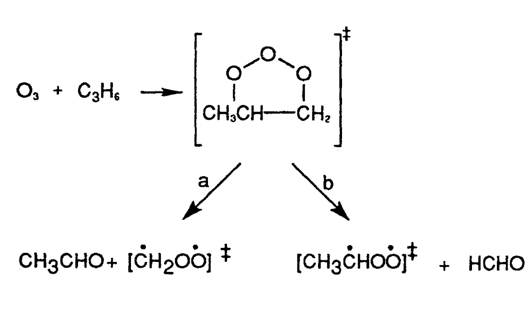
$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

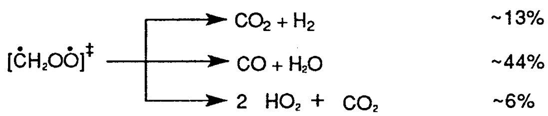
Comments on Preferred Values

Derived from a least-squares analysis of the absolute rate coefficient data of Cox and Penkett,[3] Stedman *et al.*,[4] Herron and Huie,[6] Japar *et al.*,[7,8] Adeniji *et al.*[9] and Atkinson *et al.*[10] While this data set was used by the earlier evaluations of Atkinson and Carter[11] and IUPAC, 1989,[12] the incorrect value of 250.0 K was previously used[11,12] for the lowest temperature studied by Herron and Huie[6] (rather than 235.0 K), due to a typographical error[13] in the publication of Herron and Huie.[6] The present evaluation uses the corrected data and is essentially identical to the recent NASA, 1990, evaluation.[13]

The reaction proceeds via the initial formation of a trioxane, which rapidly decomposes:

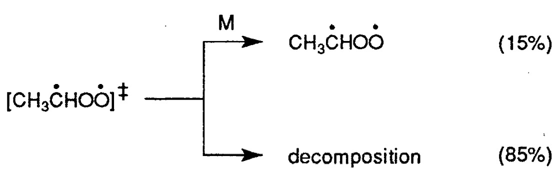


The rate coefficient ratio k_a/k_b has not been experimentally determined, and is assumed to be approximately unity. It is generally assumed[11,14] that the reactions of the energy-rich biradical $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from propene are similar to those for $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from ethene. Hence, as for the $O_3 + C_2H_4$ reaction, at room temperature and 1 bar of air[11,14,15]

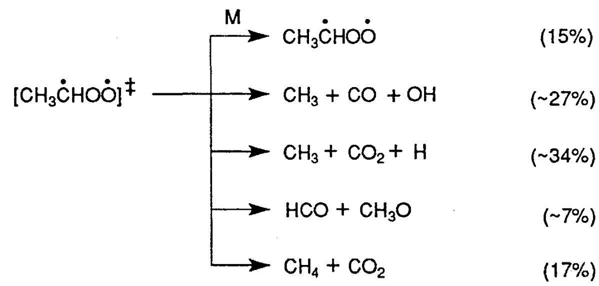


$$[\dot{C}H_2O\dot{O}]^{\ddagger} + M \longrightarrow \dot{C}H_2O\dot{O} + M \qquad 37\%$$

Less data are available concerning the stabilization and decomposition reactions of the $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ biradical. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama *et al.*[15] determined an overall stabilized biradical ($\dot{C}H_2O\dot{O}$ + $CH_3\dot{C}HO\dot{O}$) yield of 0.254 ± 0.023 at room temperature and atmospheric pressure. Assuming that $k_a = k_b$ and that the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ stabilization yield is 0.37, then the fraction of $[CH_3\dot{C}HO\dot{O}]^{+}$ biradicals which are stabilized at ~298 K and 1 bar of air is 0.14. While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[CH_3\dot{C}HO\dot{O}]$ biradicals which are stabilized at 298 K and 1 bar of air is similar to the measured yields of stabilized $CH_3\dot{C}HO\dot{O}$ from *trans*-2-butene (0.185[15]) and *cis*-2-butene (0.18[16]). A yield of stabilized $CH_3\dot{C}HO\dot{O}$ from $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ of 0.15 at 298 K and 1 bar of air is recommended, consistent with the product data of Hatakeyama *et al.*[15]:



The decomposition pathways are less well understood,[11,14] but are expected to involve formation of CH_3 + CO + OH, $CH_3 + CO_2$ + H, HCO + CH_3O, and $CH_4 + CO_2$, with approximate fractional overall yields as shown below (at ~1 bar of air).



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$HCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HCHO + h\nu \rightarrow H + HCO$	(1)	363.8	329
$\rightarrow H_2 + CO$	(2)	−1.9	–

Absorption cross-section data

Wavelength range/nm	Reference	Comments
300–360	Cantrell *et al.*, 1990[1]	(a)
235–365	Rogers, 1990[2]	(b)

Comments

(a) Cross-sections measured as a function of temperature (223–293 K) at different concentrations of HCHO and extrapolated to zero HCHO concentrations using high resolution FT spectroscopy.

(b) Cross-sections measured at 296 K over the pressure range 0.8–9 Torr by high resolution FT spectroscopy.

Preferred Values

Absorption cross-sections for HCHO photolysis over the wavelength region 240–360 nm, T = 285 K[a]

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
240	0.064	271	1.789
241	0.056	272	1.227
242	0.105	273	0.645
243	0.115	274	0.656
244	0.082	275	2.232
245	0.103	276	2.416
246	0.098	277	1.402
247	0.135	278	1.050
248	0.191	279	2.548
249	0.282	280	2.083
250	0.205	281	1.475
251	0.170	282	0.881
252	0.288	283	1.066
253	0.255	284	4.492
254	0.255	285	3.592
255	0.360	286	1.962
256	0.509	287	1.295
257	0.339	288	3.356
258	0.226	289	2.838
259	0.504	290	1.304
260	0.505	291	1.746
261	0.549	292	0.832
262	0.520	293	3.727
263	0.933	294	6.535
264	0.823	295	3.950
265	0.430	296	2.333
266	0.495	297	1.513
267	1.239	298	4.037
268	1.110	299	2.871
269	0.878	300	0.871
270	0.936	301	1.715

Absorption cross-sections for HCHO photolysis over the wavelength region 240–360 nm, T = 285 K[a] – Continued

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
302	1.064	333	0.215
303	3.201	334	0.171
304	6.902	335	0.143
305	4.914	336	0.194
306	4.632	337	0.417
307	2.100	338	2.360
308	1.494	339	4.712
309	3.407	340	2.481
310	1.950	341	0.759
311	0.521	342	0.681
312	1.120	343	1.953
313	1.116	344	1.137
314	4.747	345	0.323
315	5.247	346	0.113
316	2.899	347	0.066
317	5.373	348	0.122
318	2.975	349	0.032
319	0.918	350	0.038
320	1.262	351	0.104
321	1.529	352	0.713
322	0.669	353	2.212
323	0.345	354	1.536
324	0.816	355	0.676
325	1.850	356	0.135
326	5.950	357	0.036
327	3.485	358	0.0057
328	1.087	359	0.058
329	3.353	360	0.082
330	3.321		
331	1.073		
332	0.289		

[a]Averaged over 0.5 nm wavelength intervals centered at the cited wavelength [G. K. Moortgat and W. Schneider (unpublished data)].

Absorption cross-sections for HCHO photolysis over the wavelength region 301.25 – 356.25 nm[a] as a function of temperature (223–293 K)[b]

λ/nm	σ/cm² 223 K	σ/cm² 293 K	Intercept (273 K)	Temp. gradient
301.25	1.38E-20	1.36E-20	1.37E-20	−2.10E-24
303.75	4.67E-20	4.33E-20	4.43E-20	−4.73E-23
306.25	3.32E-20	3.25E-20	3.27E-20	−1.06E-23
308.75	2.27E-20	2.22E-20	2.24E-20	−7.24E-24
311.25	7.58E-21	9.31E-21	8.82E-21	2.48E-23
313.75	3.65E-20	3.40E-20	3.47E-20	−3.64E-23
316.25	4.05E-20	3.89E-20	3.94E-20	−2.30E-23
318.75	1.66E-20	1.70E-20	1.69E-20	6.59E-24
321.25	1.24E-20	1.13E-20	1.16E-20	−1.52E-23
323.75	4.65E-21	4.73E-21	4.71E-21	1.18E-24
326.25	5.06E-20	4.44E-20	4.61E-20	−8.86E-23
328.75	2.44E-20	2.29E-20	2.34E-20	−2.15E-23
331.25	1.39E-20	1.28E-20	1.31E-20	−1.53E-23
333.75	9.26E-22	1.23E-21	1.14E-21	4.32E-24
336.25	1.27E-21	1.13E-21	1.30E-21	5.03E-25
338.75	3.98E-20	3.36E-20	3.45E-20	−8.96E-23
341.25	8.05E-21	9.36E-21	8.98E-21	1.86E-23
343.75	1.44E-20	1.26E-20	1.31E-20	−2.64E-23
346.25	3.39E-23	7.10E-22	5.18E-22	9.57E-24
348.75	9.05E-23	3.97E-22	3.10E-22	4.38E-24
351.25	1.69E-21	2.35E-21	2.16E-21	9.48E-24
353.75	1.83E-20	1.55E-20	1.63E-20	−4.05E-23
356.25	3.54E-22	1.25E-21	9.19E-22	1.27E-23

[a]2.5 nm interval centered at given λ.
[b]At any temperature within the range 223–293 K, σ can be calculated from the listed temperature gradient (slope) and intercept fit parameters, with σ = (slope × T(°C) + intercept) [C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **94**, 3902 (1990)].

Quantum yields for HCHO photolysis

λ/nm	ϕ_1	ϕ_2
240	0.27	0.49
250	0.29	0.49
260	0.30	0.49
270	0.38	0.43
280	0.57	0.32
290	0.73	0.24
300	0.78	0.21
310	0.78	0.22
320	0.62	0.38
330	0.27	0.66
340	0.00	0.56
350	0.00	0.21
360	0.00	0.03

Comments on Preferred Values

The cross-sections reported by Cantrell *et al.*[1] are in good agreement with the recommended data in our previous evaluation,[3] which were taken from results of Moortgat and Schneider.[4] Here we have listed data from both studies and we recommend the use of the Moortgat and Schneider[4] data for λ ≤ 300 nm and the Cantrell *et al.*[1] data for λ = 301–356 nm, the latter providing a temperature dependence over the range 223–293 K.

The cross-sections measured by Rogers[2] do not agree as well with our previous recommendations.[3] This may be due to the failure in the study of Rogers[2] to observe non-linearity in the absorbance of HCHO as a function of HCHO concentration.

The recommended values of the quantum yields are unaltered from our previous evaluation,[3] which also contains plots of ϕ_1 and ϕ_2 as a function of wavelength.

The problem of understanding the measured quantum yields and branching ratios, $Y_2 = \phi_2/(\phi_1 + \phi_2)$, remains unresolved. If the photochemistry were governed by a sequence of light absorption into the first excited electronic state, internal conversion to the electronic ground state, and subsequent competition of the reactions HCHO* → H + HCO and HCHO* → H_2 + CO, then the measured values of Y_2 for λ ≤ 300 nm would be difficult to interpret. Simulations[5] of the rates of the competing processes of HCHO* and measurements of the product yields in molecular beams[7] would indicate that the radical channel (1), HCHO* → H + HCO dominates for λ ≤ 300 nm, with $Y_2 \ll 0.1$ at 284 nm.[6] An analysis of the details of the photophysical processes[7] has failed to resolve this discrepancy with the macroscopic photochemical observations. The branching ratios for ≤300 nm should therefore be treated with caution.

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$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CHO + h\nu \rightarrow CH_4 + CO$	(1)	−19.5	
$\rightarrow CH_3 + HCO$	(2)	349.0	343
$\rightarrow CH_3CO + H$	(3)	359.5	333

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement			Wavelengthλ/nm	Reference	Comments
$\phi_1 = 0.47$	$\phi_2 = 0.31$		260	Atkinson and Lloyd, 1984[1]	(a)
$\phi_1 = 0.33$	$\phi_2 = 0.38$		270		
$\phi_1 = 0.06$	$\phi_2 = 0.59$		280		
$\phi_1 = 0.01$	$\phi_2 = 0.55$	$\phi_3 = 0.026$	290		
$\phi_1 = 0.00$	$\phi_2 = 0.415$	$\phi_3 = 0.009$	300		
$\phi_1 = 0.00$	$\phi_2 = 0.235$		310		
		$\phi_3 = 0.002$	313		
$\phi_1 = 0.00$	$\phi_2 = 0.08$	$\phi_3 = 0.00$	320		
$\phi_1 = 0.00$	$\phi_2 = 0.00$		330		
		$\phi_3 = 0.00$	331–2		

Comments

(a) Evaluation of data of Horowitz and Calvert[2] and of Meyrahn *et al.*[3]

Preferred Values

Absorption cross-section and quantum yields for CH_3CHO photolysis (ϕ_1 and ϕ_2 for 1 atm air)

λ/nm	$10^{20}\ \sigma$/cm^2	ϕ_1	ϕ_2
200	0.77		
210	0.31		
220	≤0.1		
240	0.42		
250	1.0		
260	2.0	0.46	0.31
270	3.4	0.31	0.39
280	4.5	0.05	0.58
290	4.9	0.01	0.53
295	4.5	0.00	0.48
300	4.3		0.43
305	3.4		0.37
315	2.1		0.17
320	1.8		0.10
325	1.1		0.04
330	0.69		0.00
335	0.38		
340	0.15		
345	0.08		

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The evaluated data on ϕ_1 and ϕ_2 derived by Atkinson and Lloyd[1] from the experimental data of Horowitz and Calvert[2] and of Meyrahn *et al.*[3] are in essential agreement with our previous recommendations,[4] which remain unaltered.

References

[1]R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
[2]A. Horowitz and J. G. Calvert, J. Phys. Chem. **86**, 3105 (1982).
[3]H. Meyrahn, G. K. Moortgat, and P. Warneck, presented at the 15th Informal Conference on Photochemistry, Stanford, CA, July 1982.
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[5]IUPAC, Supplement III, 1989 (see references in Introduction).

$C_2H_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_2H_5CHO \rightarrow C_2H_5 + HCO$	(1)	343.1	349
$\rightarrow C_2H_6 + CO$	(2)	-7.1	
$\rightarrow C_2H_4 + HCHO$	(3)	131.0	913
$\rightarrow CH_3 + CH_2CHO$	(4)	336.4	356

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–300	Calvert and Pitts, 1966[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \approx 0.12$, $\phi_2 \approx 0.51$, $\phi_3 \approx 0.06$, $\phi_4 \approx 0.31$	187	Calvert and Pitts, 1966[1]	(b)
$\phi_4 \approx 0.08$	238		
$\phi_1 \geq 0.28$, $\phi_2 \geq 0.37$, $\phi_3 \approx 0.13$, $\phi_4 \approx 0.039$	253.7		
$\phi_1 \geq 0.28$, $\phi_2 \geq 0.34$, $\phi_3 \approx 0.13$, $\phi_4 \approx 0.012$	256.4		
$\phi_1 \geq 0.53$, $\phi_2 \geq 0.13$, $\phi_3 \approx 0.01$, $\phi_4 \approx 0.007$	280.4		
$\phi_1 \geq 0.48$, $\phi_2 \approx 0.022$, $\phi_3 \approx 0.03$, $\phi_4 \approx 0.00$	313		
$\phi_1 \approx 0.30 \pm 0.05$	313	Shepson and Heicklen, 1982[2]	(c)
$\phi_1 = 0.13$	254	Shepson and Heicklen, 1982[3]	(d)
$\phi_1 = 0.28$	280		
$\phi_1 = 0.22$	302		
$\phi_1 = 0.26$	313		
$\phi_1 = 0.067$	326		
$\phi_1 = 0.18$	334		
$\phi_1 = 0.89$	294	Heicklen *et al.*, 1986[4]	(e)
$\phi_1 = 0.85$	302		
$\phi_1 = 0.50$	313		
$\phi_1 = 0.26$	325		
$\phi_1 = 0.15$	334		

Comments

(a) Spectra were recorded in an 10 cm cell at 298 K and at several different pressures of C_2H_5CHO. The data were presented as a plot of ϵ/dm^3 mol^{-1} cm^{-1} versus wavelength.

(b) Summary of earlier data of Blacet and Pitts,[5] Blacet and Crane[6] and Borkowski and Ausloos.[7]

(c) Steady-state photolysis of C_2H_5CHO at 313 nm and 295 K in presence of O_2, O_2-He, O_2-N_2, O_2-NO and O_2-*cis*-2-C_4H_8 mixtures. Quantum yields for CO and other products measured as a function of the concentrations of O_2, C_2H_5CHO, etc. ϕ_{co} measurements indicated that $C_2H_5CHO^*$ from absorption was pressure quenched and the quoted value of ϕ_1 is for 1 atm of air.

(d) An extension of the experiments of Shepson and Heicklen[2] at a range of wavelengths and at 296 K. The quoted values of ϕ_1 are for 1 atm of air.

(e) Flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in presence of O_2 at 263 or 298 K. Quantum yields of CO and C_2H_6 were measured as a function of wavelength and of pressure of added O_2. From the proposed mechanism it was deduced that $\phi_1 = (\phi_{co} - \phi_{C_2H_6})$, and the values of ϕ quoted are for 1 atm of air.

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_1
230	0.00	
240	0.46	
250	1.1	
260	2.4	
270	4.1	
280	5.2	
290	5.7	
294		0.89
300	5.0	
302		0.85
310	3.7	
313		0.50
320	1.9	
325		0.26
330	0.80	
334		0.15
340	0.26	

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[8] The preferred values of the absorption cross-sections are taken from the plot of the extinction coefficient as a function of wavelength reported by Calvert and Pitts,[1] and are the actual values for the wavelengths indicated rather than averaged values.

The preferred values of the quantum yields for the photodissociation yielding C_2H_5 radicals are taken from the study of Heicklen *et al.*,[4] and refer to photolysis in air at a total pressure of 1 atm. No explanation has been put forward to account for the large differences in the reported values of ϕ_1 as a function of wavelength.[3,4]

References

[1]J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
[2]P. B. Shepson and J. Heicklen, J. Photochem. **18**, 169 (1982).
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[6]F. E. Blacet and A. C. Crane, J. Am. Chem. Soc. **76**, 5337 (1954).
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[8]IUPAC, Supplement III, 1989 (see references in Introduction).

$(CHO)_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$(CHO)_2 + h\nu \rightarrow H_2 + 2CO$	(1)	−9.1	
$\rightarrow 2HCO$	(2)	286.3	418
$\rightarrow CH_2O + CO$	(3)	−7.2	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
230–462	Plum *et al.*, 1983[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength/nm	Reference	Comments
$\phi_1/\phi_3 \approx 0.19$	253.7	Calvert and Pitts, 1966[2]	(b)
$\phi_1 \approx 0.15, \phi_2 \approx 0.0, \phi_3 \approx 0.85$	313		
$\phi_1/\phi_3 \approx 0.03, \phi_2 \approx 0.0$	366		
$\phi_1 \approx 0.01, \phi_3 \approx 0.6$	435.8		
$\phi = 0.29 \pm 0.018$	325–470	Plum *et al.*, 1983[1]	(c)
$\phi_2 = 0.4 \pm 0.2$	308	Langford and Moore, 1984[3]	(d)

Comments

(a) Measured with a Cary 17-D spectrophotometer at glyoxal pressures of ~3–13 Torr.

(b) Review of earlier data of Blacet and Moulton,[4] Calvert and Layne,[5] Herzberg and Ramsay[6] and Parmenter.[7]

(c) Study of the rate of photolysis of glyoxal in air mixtures at atmospheric pressure in an environmental chamber. The quantum yield for the photodissociation of glyoxal was obtained by dividing the observed ratio of the rate of photolysis of glyoxal to the rate of photolysis of NO_2 (measured under similar experimental conditions), by the same ratio calculated on the assumption that $\phi_\lambda = 1$ for glyoxal.

(d) Laser photolysis of 4.0 Torr glyoxal in 1000 Torr N_2 at 295 K. The HCO product was determined by time-resolved laser resonance absorption, and the quantum yield derived by comparing the HCO radical signals from HCHO and $(CHO)_2$ photolyses.

Preferred Values

Absorption cross-sections for glyoxal

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
230.5	0.30	390	3.14	427	10.76
235	0.30	391	3.45	428	16.65
240	0.42	392	3.25	429	4.06
245	0.57	393	2.23	430	5.07
250	0.84	394	2.64	431	4.87
255	1.15	395	3.04	432	4.06
260	1.45	396	2.64	433	3.65
265	1.88	397	2.44	434	4.06
270	2.30	398	3.25	435	5.07
275	2.60	399	3.04	436	8.12
280	2.87	400	2.84	437	5.28
285	3.33	401	3.25	438	10.15
290	3.18	402	4.46	439	7.71
295	3.33	403	5.28	440	24.76
300	3.60	404	4.26	441	8.12
305	2.76	405	3.05	442	6.09
310	2.76	406	3.05	443	7.51
312.5	2.88	407	2.84	444	9.34
315	2.30	408	2.44	445	11.37
320	1.46	409	2.84	446	5.28
325	1.15	410	6.09	447	2.44
327.5	1.46	411	5.27	448	2.84
330	1.15	412	4.87	449	3.86
335	0.30	413	8.32	450	6.09
340	0.00	414	7.51	451	10.96
345	0.00	415	8.12	452	12.18
350	0.00	416	4.26	453	23.95
355	0.00	417	4.87	454	17.05
360	0.23	418	5.89	455	40.60
365	0.30	419	6.70	456	10.14
370	0.80	420	3.86	457	1.63
375	1.03	421	5.68	458	1.22
380	1.72	422	5.28	459	0.41
382	1.57	423	10.55	460	0.41
384	1.49	424	6.09	461	0.20
386	1.49	425	7.31	462	0.00
388	2.87	426	11.77		

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[8] The preferred values listed above are taken from the results of Plum *et al.*[1] and are in good agreement with the earlier published data summarized by Calvert and Pitts.[2]

The selection of preferred quantum yields for the photolysis of glyoxal as a function of wavelength under atmospheric conditions must await further investigations. The "effective" quantum yield of $\phi = 0.029$ reported by Plum *et al.*[1] is strictly valid only for the particular spectral distributions used in their study. This value of ϕ may be used to calculate the rates of photolyses of glyoxal under tropospheric conditions within the spectral region 325–470 nm. For the lower wavelength band in the troposphere it is recommended that the value $\phi = 0.4$, reported by Langford and Moore[3] at 308 nm, be used in such calculations.

References

[1]C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).
[2]J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, (Wiley, New York, 1966).
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[6]G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. London Ser. A. **233**, 34 (1955).
[7]G. S. Parmenter, J. Chem. Phys. **41**, 658 (1964).
[8]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3COCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3COCHO + h\nu \rightarrow CH_4 + 2CO$	(1)	−24.7	
$\rightarrow CH_3CO + HCO$	(2)	284.0	421
$\rightarrow CH_3CHO + CO$	(3)	−5.2	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–480	Meller *et al.*, 1991[1]	(a)

Comments

(a) Measured over the range 220–480 nm by conventional UV spectroscopy with detection of light by a diode array camera, in a cell of path length 63 cm and with a spectral resolution of 0.07 nm. Also measured over the range 390–460 nm by *in situ* generation of methylglyoxal by the Cl atom-initiated modulated photooxidation of acetol.

Preferred Values

Absorption cross-sections for methylglyoxal between 225 and 410 nm, at 5 nm intervals

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

Preferred Values

Absorption cross-sections for methylglyoxal between 401 and 475 nm, at 1 nm intervals

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
401	5.90	434	10.54
402	6.07	435	10.81
403	6.35	436	11.13
404	6.54	437	9.99
405	6.91	438	10.59
406	7.20	439	11.01
407	7.58	440	9.94
408	7.94	441	10.39
409	8.12	442	10.20
410	8.52	443	10.17
411	8.63	444	11.17
412	9.07	445	9.61
413	9.37	446	8.90
414	9.62	447	9.84
415	9.68	448	9.18
416	9.71	449	10.13
417	10.04	450	8.67
418	10.07	451	6.34
419	10.12	452	6.33
420	10.21	453	6.08
421	10.34	454	4.46
422	10.51	455	3.69
423	10.45	456	3.08
424	10.15	457	2.46
425	10.34	458	1.81
426	10.24	459	1.28
427	9.84	460	0.914
428	10.01	461	0.795
429	9.94	462	0.642
430	10.41	463	0.479
431	10.53	464	0.332
432	9.79	465	0.268
433	10.64	466	0.227

Absorption cross-sections for methylglyoxal between 401 and 475 nm, at 1 nm intervals – Continued

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
467	0.187	472	0.089
468	0.160	473	0.077
469	0.133	474	0.067
470	0.108	475	0.062
471	0.099		

Comments on Preferred Values

The recent measurements of the cross-sections reported by Meller *et al.*[1] are approximately a factor of two higher than the previous measurements of Plum *et al.*[2] Here we have selected the former data[1] on the basis of the agreement between the cross-sections measured by Meller *et al.*[1] by conventional spectroscopy and from *in situ* generation of methylglyoxal. In addition, Meller *et al.*[1] found evidence of problems in the handling of methylglyoxal which were minimized by the *in situ* generation technique and which seem likely to have been present in the study of Plum *et al.*[2]

No further work has been reported on the quantum yields for the photolysis of methylglyoxal as a function of wavelength under atmospheric conditions. In our previous evaluation[3] we recommended under tropospheric conditions (within the spectral region 325–470 nm) the use of the "effective" quantum yield, $\phi = 0.107$, reported by Plum *et al.*[2] Since, however, Plum *et al.*[2] measured the rate of photolysis of methylglyoxal, and this is equal to $\int \sigma_\lambda \phi_\lambda J_\lambda d\lambda$, the previously recommended "effective" value of ϕ^3 must be reduced by a factor of ~2 to be consistent with the increased values of σ now being recommended.

References

[1]R. Meller, W. Raber, J. N. Crowley, M. E. Jenkin, and G. K. Moortgat, J. Photochem. Photobiol., A: Chemistry, **62**, 163 (1991).
[2]C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3COCH_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol⁻¹	$\lambda_{threshold}$/nm
$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$	(1)	338.9	353
$\rightarrow 2CH_3 + CO$	(2)	398.7	300

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–340	Calvert and Pitts, 1966[1]	(a)
250–350	Meyrahn *et al.*, 1986[2]	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength/nm	Reference	Comments
$\phi_2/\phi = 0.07$	313	Calvert and Pitts, 1966[1]	(c,e)
$\phi = 1.00$	313		(c,d)
$\phi_2/\phi = 0.22$	253.7		(c,e)
$\phi = 1.00$	253.7		(c,d)
$\phi = 0.074$	280	Gardner, Wijayaratne and Calvert, 1984[3]	(f)
$\phi = 0.080$	290		
$\phi = 0.076$	299		
$\phi = 0.074$	313		
$\phi_1 = 0.76$	250	Meyrahn *et al.*, 1986[2]	(g)
$\phi_1 = 0.80$	260		
$\phi_1 = 0.64$	270		
$\phi_1 = 0.55$	280		
$\phi_1 = 0.30$	290		
$\phi_1 = 0.15$	300		
$\phi_1 = 0.05$	310		
$\phi_1 = 0.028$	320		
$\phi_1 = 0.033$	330		

Comments

(a) Graphical presentation of $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$ (base 10) versus wavelength at 298 K. Spectrum determined in a 10 cm path length cell over a range of pressures of CH_3COCH_3 at an undefined spectral resolution.

(b) Absorption cross-sections measured from 250 to 360 nm in cells of 0.1 and 1 m pathlength, with a resolution of 0.04 nm at half-width. The tabulated cross-sections were derived by averaging the high-resolution data over 3 nm wavelength intervals.

(c) Review of earlier work on photolysis of acetone vapor alone by Noyes *et al.*,[4] Heicklen and Noyes,[5] Heicklen,[6] Ausloos and Murad[7] and Doepker and Mains.[8]

(d) Measured at 298 K.

(e) Measured above 373 K.

(f) Study of the quantum yields of acetone loss and formation of CO_2, CO, CH_3OH, and HCHO products in the photolysis of dilute mixtures of acetone (~0.36 Torr) in air (25–745 Torr) over the temperature range 271–301 K. Quantum yields for acetone loss and formation of CO_2 were equal, and the listed values of ϕ are averaged data for 298 K, which were taken as a measure of the extent of photodissociation of acetone.

(g) Study of the quantum yields of formation of CO_2 and CO in the photolysis of dilute mixtures of acetone (0.1–0.15 Torr) in air (753 Torr) at room temperature. In addition, the quantum yields of formation of peroxyacetyl nitrate (PAN) were measured when trace amounts of NO_2 (9.1×10^{-5} Torr) were added to the reactant mixtures. The listed values of ϕ_1 are the quantum yields of PAN, which were taken as a measure of the extent of primary process (1).

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	ϕ_1
250	2.37	0.76
260	3.66	0.80
270	4.63	0.64
280	5.05	0.55
290	4.21	0.30
300	2.78	0.15
310	1.44	0.05
320	0.48	0.028
330	0.08	0.033
340	0.01	
350	0.003	

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[9] The preferred absorption cross-sections, which are those measured by Meyrahn *et al.*,[2] are in substantial agreement with the absorption spectrum reported by Calvert and Pitts.[1]

The two recent studies[2,3] of the photodissociation of acetone in air are not in agreement regarding the quantum yield measurements. As pointed out by Meyrahn *et al.*,[2] further work on this system is needed to elucidate more quantitative details such as the collisional deactivation of photoexcited acetone. In the meantime, we have recommended the quantum yield data of Meyrahn *et al.*,[2] on the basis that the trend in ϕ_1 with wavelength observed by these authors appears to be reasonable.

References

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[9]IUPAC, Supplement III, 1989 (see references in Introduction).

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3OOH + h\nu \rightarrow CH_3O + HO$ (1)	188	637
$\rightarrow CH_3 + HO_2$ (2)	292	410
$\rightarrow CH_3O_2 + H$ (3)	359	333

[a]Calculated assuming $\Delta H^\circ_0 = \Delta H^\circ_{298}$, C_P data not available for CH_3OOH.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
210–350	Molina and Arguello, 1979[1]	(a)
210–280	Cox and Tyndall, 1979[2]	(b)
210–365	Vaghjiani and Ravishankara, 1989[3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 1.00 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[4]	(d)

(a) CH_3OOH prepared by standard method and the absorption measured in a long-path cell in 15 separate runs. Beers Law was obeyed. Similar spectrum was observed in aqueous solution, which agreed with earlier solution-phase work.

(b) Absorption of the product of the reaction of $CH_3O_2 + HO_2$ in the photolysis of Cl_2-CH_4-H_2-O_2 mixtures. The absorption was assumed to be due to CH_3OOH.

(c) CH_3OOH prepared by methylation of H_2O_2 and shown by ^1H NMR to be >97% pure [major impurity $(C_2H_5)_2O$]. CH_3OOH concentrations were determined by (i) trapping the vapor at 77 K and titrating with Fe^{2+} or I^-, or (ii) measurement of the absorbance due to CH_3OOH vapor by measuring its pressure in the absorption cell.

(d) Direct measurements of products; OH by LIF and $O(^3P)$ and H atoms by resonance fluorescence. Quantum yields for the formation of $O(^3P)$ and H atoms of $\phi_O < 0.007$ and $\phi_H = 0.038 \pm 0.007$ were also obtained.

Preferred Values

Absorption cross-sections

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Comments on Preferred Values

The preferred absorption cross-section data are those of Vaghjiani and Ravishankara,[3] which are approximately 25% lower than the previously recommended data of Molina and Arguello.[1] The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello[1] used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara[3] showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara,[4] who showed that $\phi_{OH} \sim 1.0$ at $\lambda = 248$ nm, we recommend that for atmospheric photolysis of CH_3OOH, ϕ_1 be taken to be unity for wavelengths >290 nm.

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$CH_3ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3ONO_2 + h\nu \rightarrow CH_3O + NO_2$	(1)	170.5	702
$\rightarrow HCHO + HONO$	(2)	−68.4	
$\rightarrow CH_3ONO + O$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–325	Calvert and Pitts, 1966[1]	(a)
235–303	Maria, McDonald, and McGlynn, 1973[2]	(b)
190–330	Taylor *et al.*, 1980[3]	(c)
270–330	Roberts and Fajer, 1989[4]	(d)

Comments

(a) Graphical presentation of ϵ/dm^3 mol^{-1} cm^{-1} (base 10) versus wavelength at 298 K. The spectrum was determined in a 10 cm pathlength cell, over a range of pressures of CH_3ONO_2 at an undefined spectral resolution.

(b) Graphical presentation of ϵ/dm^3 mol^{-1} cm^{-1} (base 10) versus wavelength. The experimental conditions were unspecified.

(c) Graphical presentation of absorption cross-section (cm^2) versus wavelength.

(d) Absorption cross-sections measured in a 10.2 cm path length cell, using a single-beam spectrometer with a photometric accuracy of $\pm 0.5\%$. Numerical data for cross-sections are available from Ref. 5.

Preferred Values

λ/nm	$10^{20}\ \sigma$/cm^2
270	2.4
275	2.0
280	1.6
285	1.2
290	0.83
295	0.56
300	0.35
305	0.21
310	0.12
315	0.067
320	0.035
325	0.017
330	0.008

Comments on Preferred Values

The preferred absorption cross-sections are those measured by Roberts and Fajer,[4] which are in reasonable agreement with the absorption spectrum reported by Calvert and Pitts[1] and with the cross-sections reported by Maria *et al.*[2] The results of Taylor *et al.*[3] are consistently higher than the values of the other three studies, by as much as a factor of 2 in the region 290–330 nm. There is no apparent explanation of this discrepancy.[5]

The sole evidence on the primary processes comes from the study of Gray and Style,[6] who concluded from the products of photolyses that reaction (1) occurred, but reported no quantum yield data. It has generally been assumed[5] that the lack of structure in the absorption spectra of $RONO_2$ molecules indicates that the quantum yield for dissociation is unity. In the case of ethyl and propyl nitrates this conclusion is supported by experimental data on the rates of photolysis of the nitrates in sunlight (see comments on photolyses of other alkyl nitrates).

References

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[4]J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).
[5]J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).
[6]J. A. Gray and D. W. G. Style, Trans. Faraday Soc. **49**, 52 (1953).

$C_2H_5ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_2H_5ONO_2 + h\nu \rightarrow C_2H_5O + NO_2$	(1)	170.0	704
$\rightarrow CH_3CHO + HONO$	(2)	−91.2	
$\rightarrow C_2H_5ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
175–225	Kaya, Kuwata and Nogakura, 1964[1]	(a)
245–303	Calvert and Pitts, 1966[2]	(b)
270–330	Roberts and Fajer, 1989[3]	(c)
185–330	Turberg *et al.*, 1990[4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \geq 0.24$	313	Rebbert, 1963[5]	(e)
$\phi_2 \leq 0.09$	313		
$\phi_3 \leq 0.14$	313		

Comments

(a) Graphical presentation of ϵ/dm^3 mol^{-1} cm^{-1} (base 10) versus wavelength. The spectrum was determined in 0.7 and 3 cm pathlength cells, at unspecified pressures of $C_2H_5ONO_2$ and at an undefined spectral resolution.

(b) Graphical presentation of ϵ/dm^3 mol^{-1} cm^{-1} (base 10) versus wavelength at 298 K. The spectrum was determined in a 10 cm pathlength cell, over a range of pressures of $C_2H_5ONO_2$ at an undefined spectral resolution.

(c) Absorption cross-sections were measured in a cell of 10.2 cm pathlength, using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Ref. 8.

(d) Absorption cross-sections were measured in cells of 2 and 10 cm pathlengths with a range of pressures of $C_2H_5ONO_2$ at an unspecified spectral resolution.

(e) Study of the products (C_2H_5ONO, CH_3CHO, NO_2, and O_2) of photolyses of $C_2H_5ONO_2$ alone and in the presence of NO at room temperature.

Preferred Values

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
185	1710	260	4.1
188	1760	265	3.7
190	1710	270	3.2
195	1490	275	2.8
200	1140	280	2.3
205	738	285	1.8
210	400	290	1.3
215	195	295	0.85
220	91	300	0.54
225	45	305	0.32
230	24	310	0.18
235	13	315	0.091
240	8.0	320	0.045
245	5.6	325	0.023
250	4.7	330	0.011
255	4.3		

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Turberg *et al.*[4] over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer[3] and of Turberg *et al.*[4] over the wavelength region 270–330 nm. These two studies[3,4] are in good agreement over the wavelength region 270–315 nm, but show variations in the cross-sections of up to a factor of two over the region 320–330 nm. The data of Calvert and Pitts[2] from 245 to 303 nm and of Kaya *et al.*[1] from 185 to 225 nm yield somewhat higher cross-sections than the preferred data.

There are insufficient definitive data to recommend values of the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation are unity. Evidence for this conclusion comes from direct measurements of the rates of formation of NO_2 from the photolyses of ethyl nitrate in sunlight.[6,7] These agreed well with the calculated rates of photolysis based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1 = 1$ throughout the region 290–340 nm.

References

[1]K. Kaya, K. Kuwata, and S. Nogakura, Bull. Chem. Soc. Jpn. **37**, 1055 (1964).
[2]J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
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[6]W. T. Luke and R. R. Dickerson, Geophys. Res. Lett. **15**, 1181 (1988).
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[8]J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

n-$C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol⁻¹	$\lambda_{threshold}$/nm
n-$C_3H_7ONO_2 + h\nu \rightarrow n$-$C_3H_7O + NO_2$	(1)	165.9	721
$\rightarrow C_2H_5CHO + HONO$	(2)	−92.8	
$\rightarrow C_3H_7ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989[1]	(a)
185–330	Turberg *et al.*, 1990[2]	(b)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm path length, using a single-beam spectrometer with a photometric accuracy of ±0.5%.
(b) Absorption cross-sections were measured in 2 and 10 cm path length cells with a range of pressures of n-$C_3H_7ONO_2$ at an unspecified spectral resolution.

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
185	1810	260	4.3
188	1830	265	4.0
190	1800	270	3.6
195	1600	275	3.0
200	1260	280	2.5
205	855	285	1.9
210	489	290	1.4
215	244	295	1.0
220	114	300	0.66
225	57	305	0.40
230	29	310	0.23
235	16	315	0.17
240	9.2	320	0.11
245	6.4	325	0.078
250	5.0	330	0.060
255	4.6		

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Turberg *et al.*[2] over the wavelength regions 185–265 nm and 315–330 nm, and are the average of the measurements of Roberts and Fajer[1] and of Turberg *et al.*[2] over the wavelength region 250–310 nm. These two studies[1,2] are in agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence for this conclusion comes from direct measurements of the rate of formation of NO_2 from the photolyses of n-$C_3H_7ONO_2$ in sunlight.[3] These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–340 nm.

References

[1]J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. 23, 945 (1989).
[2]M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. A51, 281 (1990).
[3]W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, J. Geophys. Res. 94, 14905 (1989).

i-$C_3H_7ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
i-$C_3H_7ONO_2 + h\nu \rightarrow C_3H_7O + NO_2$	(1)	171.7	697
$\rightarrow CH_3COCH_3 + HONO$	(2)	−105.9	
$\rightarrow i$-$C_3H_7ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989[1]	(a)
185–330	Turberg *et al.*, 1990[2]	(b)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm path length cell using a single-beam spectrometer with a photometric accuracy of ±0.5%. Numerical data for cross-sections are available from Ref. 4.

(b) Absorption cross-sections were measured in 2 and 10 cm path length cells with a range of pressures of *i*-$C_3H_7ONO_2$ at an unspecified spectral resolution.

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
185	1790	260	4.9
188	1810	265	4.6
190	1790	270	4.1
195	1610	275	3.6
200	1260	280	2.9
205	867	285	2.3
210	498	290	1.7
215	247	295	1.2
220	117	300	0.81
225	58	305	0.52
230	31	310	0.32
235	18	315	0.19
240	11	320	0.11
245	7.0	325	0.061
250	5.7	330	0.037
255	5.2		

Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Turberg *et al.*[2] over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer[1] and of Turberg *et al.*[2] over the wavelength region 270–330 nm. These two studies[1,2] are in good agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight supports this conclusion.[3] Thus the measured rates of formation of NO_2 matched well with calculated rates of photolyses of the $RONO_2$ based on measurements of the absorption cross-sections, solar irradiances and an assumed value of ϕ_1 = 1 throughout the wavelength region 290–330 nm.

References

[1]J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).

[2]M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, J. Photochem. Photobiol. **A51**, 281 (1990).

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[4]J. M. Roberts, Atmos. Environ. **24A**, 243 (1990).

$CH_3O_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2$	(1)	88	1359
$\rightarrow CH_3O + NO_3$	(2)	126	949

[a]Only approximate values of ΔH°_{298} values are given since the heat of formation of $CH_3O_2NO_2$ is not well known.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–310	Cox and Tyndall, 1979[1]	(a)
210–280	Morel, Simonaitis and Heicklen, 1980[2]	(b)
240–280	Sander and Watson, 1980[3]	(c)

Comments

(a) $CH_3O_2NO_2$ was prepared from the photolysis of Cl_2-CH_4-O_2-NO_2 mixtures at 275 K. Absorption cross-sections were based on the assumption that all CH_3O_2 radicals produced in the system reacted with NO_2. Correction for absorptions due to NO_2 and O_3 were also necessary.
(b) Similar to (a) using 366 nm photolysis and at 296 K.
(c) Derived from the residual absorption in the flash photolysis of Cl_2-CH_4 [or $(CH_3)_2N_2$] mixtures in the presence of O_2 and NO_2 at 298 K. σ was measured relative to the absorption cross-section for CH_3O_2 in the range 240–280 nm, assuming stoichiometric conversion of CH_3O_2 to $CH_3O_2NO_2$.

Preferred Values

Absorption cross-sections for $CH_3O_2NO_2$

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$, the measurement of the cross-sections for $CH_3O_2NO_2$ presents considerable experimental problems. Nevertheless the three studies yield values of σ in moderately good agreement at wavelengths <255 nm.[4] At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall,[1] which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter.[4] The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2 (this evaluation).

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the $-NO_2$ chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden n-π^* transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1 + \phi_2 = 1$.

References

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[2]O. Morel, R. Simonaitis, and J. Heicklen, Chem. Phys. Lett. **73**, 38, (1980).
[3]S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).
[4]CODATA, Supplement I, 1982 (see references in Introduction).

$CH_3CO_3NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol⁻¹	$\lambda_{threshold}$/nm
$CH_3CO_3NO_2 + h\nu \rightarrow CH_3CO_3 + NO_2$	(1)	119	1005
$\rightarrow CH_3CO_2 + NO_3$	(2)	115	1040

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–300	Senum, Lee and Gaffney, 1984[1]	(a)
210–250	Basco and Parmar, 1987[2]	(b)

Comments

(a) Measured at 298 K in a 10 cm cell with a spectral resolution of 2 nm, and over the pressure range 2.5 to 25 Torr of PAN. Cross-sections at $\lambda > 300$ nm were not recorded since the light absorption was negligible in this region under the experimental conditions.

(b) Derived from measurements following the flash photolysis of mixtures of Cl_2, CH_3CHO, O_2, N_2, and NO_2 at total pressures of 76–612 Torr. The absorption spectrum of PAN was obtained from the total residual absorption 10 s to 2 min after the photoflash using a xenon lamp as a monitoring source.

Preferred Values

Absorption cross-sections

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	317	255	7.9
205	237	260	5.7
210	165	265	4.04
215	115	270	2.79
220	77	275	1.82
225	55	280	1.14
230	39.9	285	0.716
235	29.0	290	0.414
240	20.9	295	0.221
245	15.9	300	0.105
250	10.9		

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred values of the absorption cross-sections are those reported by Senum, Lee and Gaffney,[1] which are in substantial agreement with the previously recommended provisional data,[4] and with the less direct measurements of Basco and Parmar.[2]

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes. In the meantime, by analogy with other organic nitrates it is again suggested that it be assumed that $(\phi_1 + \phi_2) = 1$ for absorption in the UV region. Channel (1) forming CH_3CO_3 and NO_2 would appear to be the more likely photochemical primary process.

References

[1]G. I. Senum, Y.-N. Lee, and J. S. Gaffney, J. Phys. Chem. **88**, 1269 (1984).
[2]N. Basco and S. S. Parmar, Int. J. Chem. Kinet. **19**, 115 (1987).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]CODATA, Supplement I, 1982 (see references in Introduction).

4.5. Sulfur Species

O + CS → CO + S

$\Delta H^\circ = -355$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.06 \pm 0.14) \times 10^{-11}$	305	Slagle *et al.*, 1975[1]	(a)
$(2.24 \pm 0.36) \times 10^{-11}$	300	Bida, Breckenridge and Kolln, 1976[2]	(b)
$2.6 \times 10^{-10} \exp[-(760 \pm 140)/T]$	156–215	Lilenfeld and Richardson, 1977[3]	(c)
2.0×10^{-11}	298*		
Relative Rate Coefficients			
2.2×10^{-11}	298	Hancock and Smith, 1971[4]	(d)
Reviews and Evaluations			
$2.7 \times 10^{-10} \exp(-760/T)$	150–300	CODATA, 1980[5]; IUPAC, 1989[6]	(e)

Comments

(a) Discharge flow system with detection of CS radicals by MS and $[O]/[CS]_0 \geq 20$. The rate coefficient was unaffected by a threefold variation of $[O]/[CS]_0$.

(b) Discharge flow system. CS radicals were monitored by absorbance at 257.6 nm and $O(^3P)$ by O + NO chemiluminescence reaction. $[CS]/[O] \geq 10$. $[O(^3P)]$ was maintained constant by the presence of O_2 which, through the reaction $S + O_2 \rightarrow SO + O$, regenerated $O(^3P)$ atoms consumed in the main reaction.

(c) Discharge flow system with EPR and MS detection. The rate coefficient was determined from CO formation in the presence of excess CS and CS disappearance in the presence of excess $O(^3P)$. At low temperature, the presence of O_2 produced an interfering chain reaction. To avoid this problem, at low temperature a discharge through NO rather than O_2 was used as a source of $O(^3P)$ atoms.

(d) Discharge flow system used. $O(^3P)$ was added to CS_2, and the infrared chemiluminescence from the O + CS reaction monitored. NO_2 was added to compete for O atoms. A rate coefficient ratio of $k/k(O + NO_2) = 2.3$ was obtained, and placed on an absolute basis by use of $k(O + NO_2) = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-10} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 150–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[5] Because of its significance in the CO chemical laser, this reaction has been the subject of a number of studies.[1–4] The rate coefficients k obtained at 298 K fall within a range of about 20%. The preferred value is the mean of these measurements, all of which seem reliable. To obtain the preferred temperature-dependent expression for k, the only available value of E/R is accepted[3] and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient.

References

[1] I. R. Slagle, R. E. Graham, J. R. Gilbert, and D. Gutman, Chem. Phys. Lett. **32**, 184 (1975).
[2] G. T. Bida, W. H. Breckenridge, and W. S. Kolln, J. Chem. Phys. **64**, 3296 (1976).
[3] H. V. Lilenfeld and R. J. Richardson, J. Chem. Phys. **67**, 3991 (1977).
[4] G. Hancock and I. W. M. Smith, Trans. Faraday Soc. **67**, 2586 (1971).
[5] CODATA, 1980 (see references in Introduction).
[6] IUPAC, Supplement III, 1989 (see references in Introduction).

$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$

$\Delta H^\circ = -132$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.11 \times 10^{-11} \exp[(460 \pm 41)/T]$	296–557	Nip, Singleton, and Cvetanovic, 1981[1]	(a)
5.11×10^{-11}	297		
Relative Rate Coefficients			
$(5.51 \pm 0.42) \times 10^{-11}$	298	Nip, Singleton, and Cvetanovic, 1981[1]	(b)
Reviews and Evaluations			
$1.3 \times 10^{-11} \exp(409/T)$	270–560	CODATA, 1984[2]; IUPAC, 1989[3]	(c)

Comments

(a) Modulated Hg photosensitization of N_2O used as the source of $O(^3P)$ atoms, which were detected by chemiluminescence from the $O(^3P)$ + NO reaction. First-order rate constants were measured in the presence of excess CH_3SCH_3 using a phase shift technique.

(b) Product analysis in the Hg photosensitization of N_2O-1-butene-CH_3SCH_3 mixtures. A rate coefficient ratio of $k/k(O(^3P) + \text{1-butene}) = 13.8 \pm 0.9$ was measured, and has been placed on an absolute basis by use of $k(O(^3P) + \text{1-butene}) = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 5.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-11} \exp(409/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–560 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The data of Nip *et al.*[1] are in excellent agreement, over the entire temperature range studied, with both of the studies of Lee *et al.*[5,6] The preferred 298 K rate coefficient and the temperature dependence are obtained from a least-squares fit of the data from these three studies.[1,5,6] Product studies[7] suggest that at high pressures (0.39–1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to $CH_3 + CH_3SO$.

References

[1] W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, J. Am. Chem. Soc. **103**, 3526 (1981).

[2] CODATA, Supplement II, 1984 (see references in Introduction).

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[4] D. L. Singleton and R. J. Cvetanovic, J. Am. Chem. Soc. **98**, 6812 (1976).

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$$O + CS_2 \rightarrow SO + CS \quad (1)$$
$$\rightarrow CO + S_2 \quad (2)$$
$$\rightarrow OCS + S \quad (3)$$

$\Delta H°(1) = -89$ kJ·mol^{-1}
$\Delta H°(2) = -348$ kJ·mol^{-1}
$\Delta H°(3) = -231$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.3) \times 10^{-12}$	298	Talrose *et al.*, 1978[1]	(a)
Branching Ratios			
$k_2/k = 0.006 \pm 0.002$	298	Talrose *et al.*, 1978[1]	(a)
$k_3/k = 0.006 \pm 0.002$	298		
Reviews and Evaluations			
$3.2 \times 10^{-11} \exp(-650/T)$	200–500	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$3.2 \times 10^{-11} \exp(-650/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) Diffusion cloud technique with MS detection of CS_2 in the presence of excess $O(^3P)$ atoms generated from discharge. Total pressure = 5–20 Torr.
(b) See Comments on Preferred Values.
(c) Based on the work of Westenberg and deHaas,[5] Callear and Hedges,[6] Slagle *et al.*,[7] Wei and Timmons,[8] Graham and Gutman,[9] Callear and Smith[10] and Homann *et al.*[11]

Preferred Values

$k = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-11} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.
$k_1/k \geq 0.90$ over the range 200–500 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] There are several determinations of k at 298 K using a variety of techniques, which are in good agreement. The preferred value is an average of the values of Westenberg and deHaas,[5] Callear and Hedges,[6] Slagle *et al.*,[7] Wei and Timmons,[8] Graham and Gutman,[9] Callear and Smith[10] and Homann *et al.*[11] The preferred temperature coefficient is that of Wei and Timmons.[8] The temperature dependence measured by Graham and Gutman[9] and Homann *et al.*[11] are in good agreement with the preferred value of E/R over the recommended temperature range.

There is little information on the branching ratios. The values of $k_3/k = 0.006$ and $k_2/k = 0.006$ obtained by Talrose *et al.*[1] at 298 K are lower than those found by Graham and Gutman[9] ($k_3/k = 0.096$) and Hsu *et al.*[12] ($k_2/k = 0.016$). At this stage our only recommendation for the branching ratios is that $k_1/k > 0.90$.

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O + $CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$

$\Delta H^\circ = -168$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.35 \times 10^{-11} \exp[(251 \pm 61)/T]$	298–571	Nip, Singleton, and Cvetanovic, 1981[1]	(a)
5.11×10^{-11}	298		
Relative Rate Coefficients			
$(9.82 \pm 0.61) \times 10^{-11}$	298	Nip, Singleton, and Cvetanovic, 1981[1]	(b)
Reviews and Evaluations			
$5.5 \times 10^{-11} \exp(250/T)$	290–570	CODATA, 1984[2]; IUPAC, 1989[3]	(c)

Comments

(a) Modulated Hg photosensitization of N_2O with $O(^3P)$ atoms being detected by chemiluminescence from the $O(^3P)$ + NO reaction. First-order rate constants were measured in the presence of excess CH_3SSCH_3 using a phase shift technique.

(b) Product analysis in Hg photosensitization of N_2O-1-butene-CH_3SSCH_3 mixtures. A rate coefficient ratio of $k/k(O(^3P) + \text{1-butene}) = 24.5 \pm 1.5$ was measured and placed on an absolute basis by use of $k(O(^3P) + \text{1-butene}) = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–570 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The data of Nip *et al.*[1] are about a factor of 2 lower than the earlier discharge flow-resonance fluorescence study of Lee *et al.*,[5] who reported no temperature dependence over the rather limited range 270–329 K. The cause of the discrepancy between the two measurements is not clear. The preferred value at 298 K is an average of the values from the two studies.[1,5] The temperature dependence is that from Nip *et al.*[1] with the A-factor adjusted to yield the preferred 298 K rate coefficient.

Product studies[6] suggest that at high pressures (0.39–1.58 bar) the reaction proceeds mainly by addition followed by rapid fragmentation to $CH_3S + CH_3SO$.

References

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$$O + OCS \rightarrow SO + CO \quad (1)$$
$$\rightarrow CO_2 + S \quad (2)$$

$\Delta H°(1) = -213$ kJ·mol^{-1}
$\Delta H°(2) = -224$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\sim 10^{-14}$	298	Rolfes, Reeves and Harteck, 1965[1]	(a)
$(9.0 \pm 1.3) \times 10^{-15}$	298	Sullivan and Warneck, 1965[2]	(b)
$2.0 \times 10^{-10} \exp(-2950/T)$	290–465	Hoyermann, Wagner and Wolfrum, 1967[3]	(c)
1.5×10^{-14}	300		
$1.08 \times 10^{-10} \exp(-2770/T)$	300–1150	Homann, Krome and Wagner, 1968[4]	(d)
9.8×10^{-15}	300*		
$3.2 \times 10^{-11} \exp(-2280/T)$	273–808	Westenberg and deHaas, 1969[5]	(e)
$(1.4 \pm 0.1) \times 10^{-14}$	297		
$(1.19 \pm 0.06) \times 10^{-14}$	297	Breckenridge and Miller, 1972[6]	(f)
$1.65 \times 10^{-11} \exp[-(2165 \pm 30)/T]$	263–502	Klemm and Stief, 1974[7]	(g)
$(1.2 \pm 0.1) \times 10^{-14}$	298		
$2.0 \times 10^{-11} \exp[-(2140 \pm 40)/T]$	239–404	Wei and Timmons, 1975[8]	(h)
$(1.35 \pm 0.13) \times 10^{-14}$	295		
$(1.39 \pm 0.14) \times 10^{-14}$	296	Manning, Braun and Kurylo, 1976[9]	(i)
$(1.17 \pm 0.12) \times 10^{-14}$	298	Yoshida and Saito, 1976[10]	(j)
Relative Rate Coefficients			
$1.51 \times 10^{-14} \exp(-1100/T)$	298–523	Krezenski, Simonaitis, and Heicklen, 1971[11]	(k)
Reviews and Evaluations			
$2.6 \times 10^{-11} \exp(-2250/T)$	220–600	CODATA, 1980[12]; IUPAC, 1989[13]	(l)
$2.1 \times 10^{-11} \exp(-2200/T)$	200–300	NASA, 1990[14]	(m)

Comments

(a) Discharge flow system with [O] > [OCS]. O(^{3}P) atoms were monitored by emission from the O(^{3}P) + SO reaction, and CO measured by MS. Authors quote unpublished result of Dondes and Safrany to the effect that $k_1/k_2 > 10^3$. CO_2 was not observed as a product of the reaction.

(b) Discharge flow system used, and CO and SO were monitored by MS.

(c) Discharge flow system with OCS in excess over O(^{3}P). O(^{3}P), SO and SO_2 monitored by EPR. Channel (2) was assumed to be unimportant.

(d) Discharge flow system with [O(^{3}P)] > [OCS]. OCS and SO were monitored by MS. The Arrhenius expression is based on the authors' results over the temperature range 764–1123 K together with the data of Ref. 3. Only small amounts of CO_2 were observed as products, and therefore channel (2) was considered unimportant.

(e) Discharge flow system with OCS in large excess. O(^{3}P) atoms and SO were monitored by EPR spectrometry, and CO by MS. No CO_2 was detected in the products.

(f) Method similar to that in reference 4 used. No details of measurement of k_1 were given since the main aim of the work was the investigation of the reaction of $O_2(^1\Delta_g)$ with SO($^3\Sigma^-$).

(g) Flash photolysis of OCS-O_2-Ar mixtures. O(^{3}P) atoms were monitored by resonance fluorescence. The measured rate coefficient was invariant over a wide range of reagent mixtures and total pressures (~40–200 Torr).

(h) Discharge flow system used, with O(^{3}P) atoms being monitored by EPR. The [OCS]/[O] ratio was varied over the range 20–150.

(i) Flash photolysis of OCS-O_2-Ar-CH_3F (or CH_2F_2) mixtures, with resonance fluorescence detection of O(^{3}P) atoms. The main purpose of the study was to investigate the effects of enhanced vibrational energy of OCS on the rate coefficient. Little effect was found.

(j) Discharge flow system used. SO radicals were measured by microwave spectroscopy under conditions such that [OCS] ≫ O(^{3}P).

(k) Mercury photosensitized photolysis of N_2O in the presence of OCS and 2-trifluoromethylpropene. CO, N_2 and the alkene products were determined by MS. The rate coefficient for reaction of O(^{3}P) atoms with 2-trifluoromethylpropene was taken from Ref. 15.

(l) See Comments on Preferred Values.

(m) Based on the work of Westenberg and deHaas,[5] Klemm and Stief,[7] Wei and Timmons,[8] Manning *et al.*[9] and Breckenridge and Miller.[6]

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11} \exp(-2150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–500 K.

Reliability
$\Delta\log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1980.[12] The rate coefficients obtained are in excellent agreement over a wide range of temperatures and pressures ($\leq$ 340 mbar). The available evidence suggests that at low temperatures the reaction proceeds by channel (1) and that channel (2) may only become significant at temperatures above 600 K.

Because of the possible enhancement of the rate by channel (2) at high temperatures, the recommended value of E/R is the mean of the values obtained by Wei and Timmons[8] and Klemm and Stief,[7] which were limited to temperatures below 502 K. The 298 K rate coefficient is the mean of the values in references 2–10, and the pre-exponential factor is adjusted to fit this value of k and the recommended value of E/R.

Approximate values of k_2/k_1 measured are: 10^{-3} at 298 K[16] and 10^{-2} at 500 K.[4]

References

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$O + SO_2 + M \rightarrow SO_3 + M$

$\Delta H^\circ = -348.1$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.1 \times 10^{-32} \exp(-1009/T)$ [Ar]	299–400	Atkinson and Pitts, 1978[1]	(a)
1.05×10^{-33} [Ar]	298		
1.37×10^{-33} [N_2]	298		
Reviews and Evaluations			
$1.1 \times 10^{-31}(T/1000)^{-4} \times \exp(-2646/T)$ [Ar]	250–2500	Troe, 1978[2]	(b)
$4.0 \times 10^{-32} \exp(-1000/T)$ [N_2]	200–400	CODATA, 1980[3]	(c)
$8.3 \times 10^{-31}(T/1000)^{-3.75} \times \exp(-2650/T)$ [Ar]	200–2500		

Comments

(a) Flash photolysis technique with detection of O(^{3}P) atoms by NO_2 chemiluminescence. Relative efficiencies of $k(M = N_2)$: $k(M = Ar)$: $k(M = SO_2)$ = 1.0:0.71:6.9 were determined.
(b) Theoretical analysis of dissociation and recombination data, fitting a barrier of 22 kJ·mol^{-1} for the spin-forbidden reaction $O(^3P) + SO_2(^1A_1) \rightarrow SO_3(^1A_1)$.
(c) Based on the data from reference 1, the high temperature dissociation results from Ref. 4, and the theoretical analysis from Ref. 2. Summary of earlier data also given.

Preferred Values

$k_0 = 4.0 \times 10^{-32} \exp(-1000/T)$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.
$k_0 = 1.4 \times 10^{-33}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta(E/R) = \pm 200$ K over the temperature range 200–400 K.

Comments on Preferred Values

See comment (c) for k_0. Because the reaction has an activation barrier, the Arrhenius form is chosen. The falloff transition to the high pressure range is expected at pressures not too far above 1 bar. However, as yet no experimental data are available in this pressure region.

References

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$S + O_2 \rightarrow SO + O$

$\Delta H^\circ = -22.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-12} \exp[(153 \pm 108)/T]$	296–393	Clyne and Whitefield, 1979[1]	(a)
$(2.6 \pm 0.3) \times 10^{-12}$	298		
Reviews and Evaluations			
2.1×10^{-12}	230–400	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
2.3×10^{-12}	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system used. S atoms were generated by a discharge in Ar-SO_2 mixtures and monitored by resonance fluorescence under conditions such that $[S] \ll [O_2]$.

(b) See Comments on Preferred Values.

(c) Based on the data of Clyne and Whitefield[1] and Refs. 5–9.

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 230–400 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[2] All of the measurements of the rate coefficients k are in good agreement. Clyne and Whitefield[1] observed a small decrease in k with increase in temperature, but until more definitive measurements of E/R are made a temperature independent rate coefficient is recommended with error limits encompassing the existing measured values. The preferred 298 K rate coefficient is the mean of those from Refs. 1 and 5–9.

References

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$S + O_3 \rightarrow SO + O_2$

$\Delta H^\circ = -415$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.3) \times 10^{-11}$	298	Clyne and Townsend, 1975[1]	(a)

Comments

(a) Discharge flow system, with S atoms produced by discharge in Ar-SO_2 mixture. The O_3-O_2 mixture was in large excess of S atoms. O_3 was monitored by absorption spectrophotometry and S atoms by resonance fluorescence.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available experimental determination[1] is accepted as the preferred value. The method was direct, and in the same study a number of other rate coefficients for S atom reactions were measured giving results in good agreement with other techniques.

References

[1]M. A. A. Clyne and L. W. Townsend, Int. J. Chem. Kinet., Symp. 1, 73 (1975).

$Cl + H_2S \rightarrow HCl + HS$

$\Delta H° = -50.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.3 \pm 0.9) \times 10^{-11}$	298	Nesbitt and Leone, 1980[1]	(a)
$(4.00 \pm 0.08) \times 10^{-11}$	296	Clyne and Ono, 1983[3]	(b)
$(5.1 \pm 0.7) \times 10^{-11}$	296	Clyne *et al.*, 1984[4]	(c)
$(6.29 \pm 0.46) \times 10^{-11}$	211–353	Nava, Brobst and Stief, 1985[5]	(d)
Relative Rate Coefficients			
$(1.05 \pm 0.04) \times 10^{-10}$	232–359	Lu, Iyer and Rowland, 1986[6]	(e)
Reviews and Evaluations			
5.7×10^{-11}	200–300	NASA, 1990[7]	(f)

Comments

(a) Pulsed laser photolysis of $S_2Cl_2 - H_2S$ mixtures at 300 nm in a flowing system. IR emission from $HCl(\nu=1)$ monitored, with negligible contribution from $HCl(\nu>1)$ states. These results supersede the earlier result [$k = (6.0 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}] obtained by Braithwaite and Leone[2] using the same technique.

(b) Discharge flow study. Cl atoms were generated by discharge in $Cl_2 - He$ mixtures and monitored by resonance fluorescence at 120.1 and 134.7 nm in the presence of excess H_2S.

(c) Discharge flow study. H_2S was monitored by MS in an excess of Cl atoms. Several products (SH, SCl and S_2) were also monitored.

(d) Flash photolysis of CCl_4-H_2S-Ar mixtures at 115 nm in flowing system. Cl atoms were monitored by resonance fluorescence. No effect of pressure was observed over the range 40–180 Torr.

(e) Hot atom technique. ^{38}Cl atoms were generated from neutron irradiation of $CClF_3$ (4000 Torr) and moderated to thermal energies. In the presence of H_2S, C_2H_6 and CH_2CHBr, the reactions $^{38}Cl + H_2S \rightarrow H^{38}Cl + HS$, $^{38}Cl + C_2H_6 \rightarrow H^{38}Cl + C_2H_5$, $^{38}Cl + CH_2CHBr \rightarrow CH_2CH^{38}Cl + Br$ are in competition. Measurement of the $CH_2CH^{38}Cl$ yield as a function of $[H_2S]$, $[C_2H_6]$, $[CH_2CHBr]$ yielded the rate coefficient ratios. The rate coefficient k was obtained using a value of $k(Cl + CH_2CHBr) = 7.7 \times 10^{-11} \exp(-90/T)$cm^3 molecule^{-1} s^{-1}, as quoted by Lu *et al.*[6]

(f) Based on the data of Nesbitt and Leone,[1] Clyne and Ono,[3] Clyne *et al.*[4] and Nava *et al.*[5]

Preferred Values

$k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

There is significant scatter in the measured rate coefficients which is difficult to attribute to any of the different techniques used. The preferred value at 298 K is a mean of the values of Nesbitt and Leone,[1] Clyne and Ono,[3] Clyne *et al.*[4] and Nava *et al.*[5] The result of Lu *et al.*[6] is not included because of the very different conditions used. Both studies in which the temperature was varied[5,6] showed no temperature dependence of the rate coefficient, which is accepted but with substantial error limits.

References

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$HO + H_2S \rightarrow H_2O + HS$

$\Delta H° = -117$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.6 \times 10^{-12} \exp(-57/T)$	245–450	Lin *et al.*, 1985[1]	(a)
$(4.4 \pm 0.7) \times 10^{-12}$	299		
$1.32 \times 10^{-11} \exp[-(394 \pm 190)/T]$	294–463	Lafage *et al.*, 1987[2]	(b)
$(3.3 \pm 0.5) \times 10^{-12}$	294		
Relative Rate Coefficients			
$(5.2 \pm 0.8) \times 10^{-12}$	300	Barnes *et al.*, 1986[3]	(c)
Reviews and Evaluations			
$6.3 \times 10^{-12} \exp(-80/T)$	200–300	IUPAC, 1989[4]	(d)
$6.0 \times 10^{-12} \exp(-75/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) Discharge-flow study with He as the carrier gas. HO produced by the $H + NO_2$ reaction. Passage of H_2-He mixture through a microwave discharge or over a heated filament used as source of H. HO radicals monitored by resonance fluorescence at 309 nm. Changes in pressure and use of N_2 or O_2 as carrier gases had no effect on the measured rate coefficient.
(b) Discharge flow study with He as the carrier gas. HO produced by the $H + NO_2$ reaction. Excess NO_2 scavenged any HS radicals produced. HO radicals were monitored by LIF resonance fluorescence. A minimum in the plot of k versus T observed, with the minimum rate coefficient being $k = (3.3 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 294 K.
(c) HO radicals produced by photolysis of CH_3ONO-O_2 mixtures in air at 1 atm pressure in a 38 liter reaction vessel. Removal of H_2S relative to reference hydrocarbon measured by GC. A rate coefficient ratio of k/k(HO + ethene) = 0.65 ± 0.10 was measured, and placed on an absolute basis by use of k(HO + ethene) = 8.0×10^{-12} cm^3 molecule^{-1} s^{-1}.
(d) See Comments on Preferred Values.
(e) Based on the results of Lin *et al.*,[1] Lafage *et al.*,[2] Barnes *et al.*,[3] Wine *et al.*,[6] Leu and Smith,[7] Michael *et al.*,[8] Lin,[9] Westenberg and deHaas,[10] Perry *et al.*[11] and Cox and Sheppard.[12]

Preferred Values

$k = 4.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.3 \times 10^{-12} \exp(-80/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 80$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The most recent studies[1-3] are in excellent agreement with previous work. Both Lin *et al.*[1] and Lafage *et al.*[2] confirm the finding of Leu *et al.*[7] that the rate coefficient exhibits non-Arrhenius behavior over the temperature range 245–450 K, with the Arrhenius plot appearing to have a shallow minimum at approximately 270–300 K. Also in agreement with Leu *et al.*,[7] Lin *et al.*[1] find that the value of k appears to be independent of pressure and the nature of the bath gas. These latter

cast some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstraction channels.

Despite the non-Arrhenius behavior of the rate coefficient k over an extended temperature range, the preferred expression is given in Arrhenius form, which is satisfactory for the limited temperature range covered by our recommendation.

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$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H° = -127$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.3) \times 10^{-32} \times \exp(640/T)$ [He]	280–413	Lee, Kao and Lee, 1990[1]	(a)
$(2.4 \pm 0.7) \times 10^{-31}$ [N_2]	298		
Reviews and Evaluations			
$5.0 \times 10^{-31}(T/300)^{-3.3}$ [N_2]	200–300	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
$3.0 \times 10^{-31}(T/300)^{-3.3}$ [air]	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with HO detection by resonance fluorescence. Rate coefficients for M = He, N_2 and SO_2 were measured in the pressure range 0.2–6 Torr.

(b) Based on the results of Wine *et al.*,[5] Martin *et al.*[6] and Barnes *et al.*,[7] evaluated with $F_c = 0.45$.

(c) Based on the value of Leu,[8] corrected for falloff using $F_c = 0.6$.

Preferred Values

$k_0 = 4.0 \times 10^{-31}(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The most recent measurements of Ref. 1 gave smaller rate coefficients than earlier studies. We included these values in the averaging of data which reduced the preferred values. The error limits include most of the earlier data. The difference in F_c values between Refs. 3 and 4, which leads to different k_0 and k_∞ values, should be noted.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2×10^{-12}	200–300	CODATA, 1980[2]; IUPAC, 1989[3]	(a)
1.5×10^{-12}	200–300	NASA, 1990[4]	(b)

Comments

(a) See comment (b) on k_0.
(b) Result from a fit of the data of Leu,[8] Paraskevopoulos *et al.*,[9] and Wine *et al.*[5]

Preferred Values

$k_\infty = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See comment on k_0. Falloff representation with F_c = 0.45 near 300 K.

References

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$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$\Delta H° = 4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 2) \times 10^{-13}$	250	Margitan, 1984[1]	(a)
$(4.0 \pm 2) \times 10^{-13}$	298		
$(3.5 \pm 1) \times 10^{-13}$	298	Martin, Jourdain and Le Bras, 1986[2]	(b)
$(4.37 \pm 0.66) \times 10^{-13}$	298	Gleason, Sinha, and Howard, 1987[3]	(c)
$1.34 \times 10^{-12} \exp(-330/T)$	297–423	Gleason and Howard, 1988[4]	(c)
$(4.37 \pm 0.66) \times 10^{-13}$	297		
Reviews and Evaluations			
4.0×10^{-13}	298	IUPAC, 1989[5]	(d)
$1.3 \times 10^{-12} \exp(-330/T)$	200–300	NASA, 1990[6]	(e)

Comments

(a) Pulsed laser photolysis of HNO_3-Ar-SO_2 mixtures at 226 nm. HO radicals monitored by resonance fluorescence. System was studied at 40 and 100 Torr Ar and at 250 and 298 K. HO radicals were removed by the $HO + SO_2 + M \rightarrow HOSO_2 + M$ reaction, but the addition of O_2 and NO regenerates HO by the reactions $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ and $HO_2 + NO \rightarrow HO + NO_2$. Effects of varying amounts of O_2 were studied. Same value of k found at 250 K and 298 K, but author suggested that this was due to lack of precision in the technique rather than indicating that k is temperature independent.
(b) Discharge flow study of the reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$. HO radicals were produced by the $H + NO_2$ reaction in He carrier gas and monitored by EPR, calibrated with NO. Effects of addition of NO and O_2 on HO radical decays were studied. System of 12 reactions used to model system to obtain the rate coefficient k.
(c) Discharge flow system used, with N_2 as the carrier gas. HO radicals were produced by the $H + NO_2$ reaction, and SO_2 and O_2 were added down-stream. $HOSO_2$ was monitored by sampling into a flowing afterglow containing Cl^- ions. SO_3^- ions, formed by the reaction $Cl^- + HOSO_2 \rightarrow SO_3^- + HCl$, were detected by quadrupole MS. SO_3 product of the reaction was also detected by $Cl^- + SO_3 + M \rightarrow (ClSO_3)^- + M$ with MS measurement of $(ClSO_3)^-$. The total pressure was varied over the range 2–8 Torr, and no change in k observed allowing a limit of 3.4×10^{-31} cm^6 molecule^{-2} s^{-1} (M = N_2) for the rate coefficient for the reaction $HOSO_2 + O_2 + M \rightarrow HOSO_2O_2 + M$ to be set.
(d) Accepted the data of Gleason *et al.*[3]
(e) Based on the work of Gleason *et al.*[3] and Gleason and Howard.[4]

Preferred Values

$k = 4.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–420 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1989,[5] with the addition of the work of Gleason and Howard.[4] In the earlier studies[1,2] HO radical decays due to the reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$ were monitored in the presence of NO and O_2. The reaction sequence $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ and $HO_2 + NO \rightarrow HO + NO_2$ then regenerates HO. Modeling of the NO decay leads to the rate coefficient k. This method of determining k is less direct than the more recent measurements of Gleason and Howard[4] and of Gleason *et al.*,[3] where $HOSO_2$ radicals were monitored by MS. We therefore accept the expression obtained by Gleason and Howard.[4] The other results, though less precise, are in good agreement with the preferred expression.

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HO + OCS → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.13 \times 10^{-13} \exp(-1200/T)$	255–483	Cheng and Lee, 1986[1]	(a)
$(2.0^{+0.4}_{-0.8}) \times 10^{-15}$	300		
$(1.92 \pm 0.25) \times 10^{-15}$	298	Wahner and Ravishankara, 1987[2]	(b)
Reviews and Evaluations			
$1.1 \times 10^{-13} \exp(-1200/T)$	250–500	IUPAC, 1989[3]	(c)
$1.1 \times 10^{-13} \exp(-1260/T)$	200–300	NASA, 1990[4]	(d)

Comments

(a) Discharge flow study with He as the carrier gas. HO generated by the $H + NO_2$ reaction and excess NO_2 used to ensure removal of H atoms that could lead to complicating side reactions. The purity of OCS was checked by FTIR spectroscopy, showing that H_2S was present at less than 0.005%. HO radicals were monitored by resonance fluorescence at 309 nm. The measured rate coefficient k was independent of pressure (0.9–5.9 Torr) and the addition of O_2 (up to 18%).

(b) Pulsed laser photolysis using a variety of HO sources (H_2O_2, HNO_3 and HONO). A Xe flash lamp was used in some experiments. HO radicals were monitored by LIF. The rate coefficient k was independent of pressure (90–300 Torr), the nature of buffer gas, and the addition of O_2 (up to 36 Torr).

(c) See Comments on Preferred Values.

(d) Based on the results of Cheng and Lee[1] and Wahner and Ravishankara.[2]

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-13} \exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC 1989.[3] The rate coefficients k measured by Cheng and Lee[1] and Wahner and Ravishankara[2] are approximately a factor of 3 lower at 298 K than the earlier value of Leu and Smith.[5] This may be due to the corrections applied by Leu and Smith[5] to allow for the presence of traces of H_2S in their system, since in the absence of such corrections there is reasonable agreement between the studies. Cheng and Lee[1] took care to keep the H_2S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara,[2] leads us to recommend their values. These recommendations are compatible with the earlier upper limit given by Atkinson *et al.*,[6] but not with the higher value obtained by Kurylo[7] which may have been due to interfering secondary chemistry and/or excited state reactions.

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$$HO + CS_2 + M \rightarrow HOCS_2 + M \quad (1)$$
$$HO + CS_2 \rightarrow HS + OCS \quad (2)$$

$\Delta H°(1) = -46$ kJ·mol^{-1}
$\Delta H°(2) = -155$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}[M]/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
10^{-12} at 70 Torr (N_2)	247–299	Hynes, Wine and Nicovich, 1988[1]	(a)
6×10^{-13} at 30 Torr (N_2)	259–318	Murrells, Lovejoy, and Ravishankara, 1990[2]	(b)
3.4×10^{-13} at 50 Torr (He)	299		
3.9×10^{-13} at 50 Torr (He)	274		
6.0×10^{-13} at 50 Torr (He)	249		
7.2×10^{-14} at 23 Torr (He)	298	Diau and Lee, 1991[3]	(c)
3.4×10^{-13} at 32 Torr (Ar)	246		

Comments

(a) Pulsed laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 with added He, N_2, air, and O_2. HO radicals monitored by LIF. Experiments conducted in the pressure range 65–690 Torr.
(b) Pulsed laser photolysis of H_2O_2 at 248 nm or 266 nm in mixtures of CS_2 in He–N_2 or He–SF_6 mixtures. HO radicals monitored by LIF. Pressure range was 9–60 Torr. The effect of O_2 (0.5–15 Torr) on the rate was studied.
(c) Pulsed laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 with added He or Ar. Pressure range 9–270 Torr of Ar or 9–270 Torr of He. Effect of CS_2 on rate studied.

Preferred Values

$k_{01} = 8 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 270–300 K.

Reliability
$\Delta \log k_{01} = \pm 0.5$.

Comments on Preferred Values
Because of the low thermal stability of $HOCS_2$, experimental studies have to account for the redissociation of the adduct. After clarification of the mechanism, rate coefficients can now be specified. Combining the data for M = N_2 from Refs. 1 and 2 in a falloff representation indicates that the low pressure limit is approached within 10% only at pressures below about 20 Torr. Because of the rather large scatter, the falloff data do not yet allow for the specification of a temperature dependence. The strong temperature dependence of k_{01} for M = He derived in Ref. 3 ($E/R = -1610$ K) is apparently not consistent with the results from Refs. 1 and 2. It appears that reaction (2) is slow, with a rate coefficient of

$$k_2 < 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}^2$$

High-pressure rate coefficient

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.8×10^{-12} at 680 Torr (N_2)	250–270	Hynes, Wine, and Nicovich, 1988[1]	(a)
3.1×10^{-12} at 660 Torr (N_2)	297		
1.9×10^{-12} at 760 Torr (Ar)	room temperature	Bulatov *et al.*, 1988[4]	(b)
1.3×10^{-12} at 760 Torr (air)	295	Becker *et al.*, 1985[5]	(c)
Relative Rate Coefficients			
2.0×10^{-12} at 760 Torr (air)	295	Becker *et al.*, 1988[5]	(d)
2.3×10^{-12} at 760 Torr (air)	295		(e)

Comments

(a) See comment (a) for k_{01}.

(b) Laser photolysis of O_3 in the presence of H_2O, CS_2 and Ar (presumably 1 bar) at room temperature (unspecified), with LIF detection of HO. The rates of $HOCS_2$ formation and decomposition were measured, with an equilibrium constant of $K_c = 2.6 \times 10^{-17}$ cm^3 molecule^{-1}. The rate of the reaction O_3 + $HOCS_2$ was also investigated, leading to $k(O_3 + HOCS_2) = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(c) Laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 and N_2–O_2 or Ar–O_2, with LIF detection of HO. The partial pressure of O_2 was in the range 0.24–760 Torr, at a total pressure of 760 Torr.

(d) 420 liter reaction vessel with White optics and FTIR detection used. HO radicals produced by photolysis of CH_3ONO (at wavelengths >300 nm) in the presence of NO–O_2 mixtures, photolysis of H_2O in O_2–N_2 mixtures at 254 nm, or the thermal decomposition of HO_2NO_2 in the presence of NO. The rate coefficient was based on the appearance rate of final products.

(e) Technique as in (d). The rate coefficient was based on the CS_2 removal rate.

Preferred Values

$k_{\infty 1} = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_{\infty 1} = \pm 0.5$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient $k_{1\infty}$ is based on a falloff representation of the data from Refs. 1 and 2, with high pressure data mostly from Ref. 1. The most weight is given to the measurements near 250 K, where the decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of $F_c = 0.8$ was employed for extrapolation. Experiments at 1 bar are apparently still far below the high pressure limit. An extensive discussion of the complicated mechanism is given in Refs. 6–8 as well as in Refs. 1, 2, and 9. Rate expressions combining adduct formation, dissociation and subsequent reactions with O_2 have been proposed which are not reproduced here. More experiments separating the individual steps are required.

References

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$HOCS_2 + M \rightarrow HO + CS_2 + M$

$\Delta H° = 46$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0[M]/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.3×10^4 at 75 Torr (N_2)	255	Hynes, Wine, and Nicovich, 1988[1]	(a)
2.6×10^4 at 81 Torr (N_2)	280		
4.3×10^3 at 15 Torr (N_2)	277	Murrells, Lovejoy, and Ravishankara, 1990[2]	(b)
3.0×10^4 at 24 Torr (N_2)	298		
2.0×10^4 at 50 Torr (He)	299		
5.2×10^3 at 50 Torr (He)	274		
1.2×10^3 at 50 Torr (He)	249		
7.8×10^3 at 23 Torr (He)	298	Diau and Lee, 1991[3]	(c)
1.3×10^3 at 32 Torr (Ar)	246		

Comments

(a) Pulsed laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 with added He, N_2, air and O_2. HO radicals were monitored by LIF. Experiments were conducted in the pressure range 65–690 Torr. A value of $K_c(297\ K) = 1.39 \times 10^{-17}$ cm^3 molecule^{-1} was obtained for the equilibrium $HO + CS_2 \rightleftharpoons HOCS_2$ as well as $K_c(247\ K) = 3.5 \times 10^{-16}$ cm^3 molecule^{-1}.

(b) Pulsed laser photolysis of H_2O_2 at 248 nm or 266 nm in He–N_2–CS_2 or He–SF_6–CS_2 mixtures, with HO being monitored by LIF. Pressure range = 9–60 Torr. The effect of O_2 (0.5–15 Torr) on the rate was studied. $K_c(299\ K) = 1.7 \times 10^{-17}$ cm^3 molecule^{-1}, $K_c(274\ K) = 7.5 \times 10^{-17}$ cm^3 molecule^{-1} and $K_c(249\ K) = 5.1 \times 10^{-16}$ cm^3 molecule^{-1} were obtained for the equilibrium $HO + CS_2 \rightleftharpoons HOCS_2$.

(c) Pulsed laser photolysis of H_2O_2 at 248 nm in mixtures of CS_2 with added He or Ar. Pressure range = 9–270 Torr of He. The effect of CS_2 on the rate was studied. $K_c(298\ K) = 0.87 \times 10^{-17}$ cm^3 molecule^{-1}, $K_c(273\ K) = 4.2 \times 10^{-17}$ cm^3 molecule^{-1} and $K_c(249\ K) = 2.6 \times 10^{-16}$ cm^3 molecule^{-1} were obtained for the equilibrium $HO + CS_2 \rightleftharpoons HOCS_2$.

Preferred Values

$k_0 = 4.8 \times 10^{-14}$ [N_2] s^{-1} at 298 K.
$k_0 = 1.6 \times 10^{-6} \exp(-5160/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_0 = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
The preferred values are based on a falloff representation from Refs. 1 and 2 of the data for the reverse process $HO + CS_2 + M \rightarrow HOCS_2 + M$ and the determination of the equilibrium constant from the same work. Most weight was given to the data from Ref. 2 which extends to lower pressures. The data from Refs. 3 are not consistent with this evaluation (with differences of a factor of ~2). $HOCS_2$ formation and dissociation are characterized by an equilibrium constant of

$$K_c = 5.16 \times 10^{-25} \exp(5160/T)\ \text{cm}^3\ \text{molecule}^{-1},$$

as derived from the data of Ref. 2.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.1×10^4 at 680 Torr (N_2)	252	Hynes, Wine, and Nicovich, 1988[1]	(a)
6.5×10^4 at 685 Torr (N_2)	270		
2.2×10^5 at 660 Torr (N_2)	297		
7.4×10^4	room temperature	Bulatov *et al.*, 1988[4]	(b)

Comments

(a) See comment (a) for k_0.

(b) Laser photolysis of O_3 in the presence of H_2O, CS_2 and Ar (presumably 1 bar) at room temperature. LIF detection of HO. Rates of $HOCS_2$ formation and decomposition measured, with an equilibrium constant of $K_c = 2.6 \times 10^{-17}$ cm^3 molecule^{-1}. The rate of the reaction $O_3 + HOCS_2$ was also investigated, leading to $k(O_3 + HOCS_2) = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_\infty = 4.8 \times 10^5$ s^{-1} at 298 K.

$k_\infty = 1.6 \times 10^{13} \exp(-5160/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant $K_c = 5.16 \times 10^{-25} \exp(5160/T)$ cm^3 molecule^{-1} from Ref. 2. Falloff curves are constructed with an estimated $F_c = 0.8$. The small preexponential factor of k_∞ can be explained theoretically as being due to the low bond energy of $HOCS_2$. For a discussion of the mechanism, see Refs. 1, 2 and 5–8.

References

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$HOCS_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-14} \exp[(217 \pm 301)/T]$	247–299	Hynes, Wine, and Nicovich, 1988[1]	(a)
$(3.26 \pm 0.70) \times 10^{-14}$	297		
$(2.6 \pm 1.0) \times 10^{-14}$	249–299	Murrells, Lovejoy, and Ravishankara, 1990[2]	(b)

Comments

(a) Pulsed laser photolysis of H_2O_2–CS_2 mixtures at 248 nm. HO radicals were monitored by LIF. The effects of He, N_2, air and O_2 were studied, and the total pressure was varied over the range 65–690 Torr. If the rate coefficient k is assumed to be temperature independent, the average of the measured values is $(2.9 \pm 1.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} over the range 247–299 K.

(b) Pulsed laser photolysis of H_2O_2–CS_2 mixtures at 248 or 266 nm. HO radicals monitored by LIF. The effects of N_2, He, SF_6, and O_2 were studied at total pressures over the range 9–60 Torr.

Preferred Values

$k = 2.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240–300 K.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 240–300 K.

Comments on Preferred Values

The reaction of $HOCS_2$ with O_2 is an intermediate step in the overall reaction of HO with CS_2 under atmospheric conditions. The $HOCS_2$ is formed by the addition of HO to CS_2; once formed it may undergo dissociation back to HO and CS_2 or react with O_2. In previous evaluations, the $HOCS_2 + O_2$ reaction has been considered on the data sheet for HO + CS_2 because only in recent studies has the mechanism of the HO + CS_2 reaction been clarified and the individual reactions involved studied separately.

The two studies[1,2] of the kinetics of this reaction are in good agreement. Basically the same technique was used in both and a similar temperature range was covered. Similar results were obtained over a range of bath gas pressures.

The results of Hynes *et al.*[1] could equally well be represented by an Arrhenius expression with a small negative temperature coefficient for k or by a temperature-independent rate coefficient k. The results of Murrell *et al.*[2] favor the latter. For the preferred values we assume the rate coefficient k to be temperature independent over the temperature range studied and take a mean of the values of Hynes *et al.*[1] and Murrells *et al.*[2]

Lovejoy *et al.*[3] have studied product formation from the $HOCS_2 + O_2$ reaction using a flow tube with product detection by LMR and chemionization MS. They concluded that the overall stoichiometry of the reaction is

$$HOCS_2 + 2O_2 \rightarrow HO_2 + SO_2 + OCS$$

This reaction cannot occur in a single step to yield these products, and Lovejoy *et al.*[3] conclude that there are unidentified intermediate stages in the reaction. The same conclusion was reached by Becker *et al.*[4] Further work to establish the detailed mechanism is desirable.

The main steps in the atmospheric oxidation of CS_2 initiated by HO are

$$HO + CS_2 \rightleftharpoons HOCS_2$$

$$HOCS_2 + 2O_2 \rightarrow HO_2 + SO_2 + OCS$$

Because of the nature and number of the steps involved, the overall rate of reaction of HO with CS_2 in the presence of O_2 is a complex function of both the total pressure and the pressure of O_2. Studies over a range of pressures and gas composition have established k_{eff}, the rate coefficient for HO removal in air. Hynes *et al.*[1] have obtained the following expression for k_{eff} in air at 298 K:

$$k_{eff} = \frac{1.25 \times 10^{-16} \exp(4550/T)}{T + 1.81 \times 10^{-3} \exp(3400/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Studies by Murrells *et al.*[2] and by Becker *et al.*[4] are in good agreement with this expression.

Despite the concordancy of measurements of k_{eff}, significant differences are found between values for k_{eff} based on measurements of HO removal and those based on relative rate studies of product formation. Becker *et al.*[4] have used both types of technique in the same laboratory, employing a number of variations of the relative rate method, but the results have only confirmed the difference. The studies based on product formation give values of k_{eff} up to 50% higher than the real-time studies based on HO removal. These differences point to the need for further studies of the chemistry of the later stages of the reaction involving O_2.

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$HO + CH_3SH \rightarrow$ products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.89 \times 10^{-12} \exp[(398 \pm 151)/T]$	300–423	Atkinson, Perry, and Pitts, 1977[1]	(a)
$(3.39 \pm 0.34) \times 10^{-11}$	300		
$1.15 \times 10^{-11} \exp[(338 \pm 100)/T]$	244–366	Wine *et al.*, 1981[2]	(a)
$(3.37 \pm 0.41) \times 10^{-11}$	298		
$(2.1 \pm 0.2) \times 10^{-11}$	293	Mac Leod, Poulet, and Le Bras, 1983[3]; Mac Leod *et al.*, 1984[4]	(b)
$(2.56 \pm 0.44) \times 10^{-11}$	296	Lee and Tang, 1983[5]	(c)
$1.01 \times 10^{-11} \exp[(347 \pm 59)/T]$	254–430	Wine, Thompson, and Semmes, 1984[6]	(a)
3.24×10^{-11}	298		
3.69×10^{-11}	270	Hynes and Wine, 1987[7]	(d)
3.17×10^{-11}	300		
Relative Rate Coefficients			
$(9.68 \pm 0.97) \times 10^{-11}$	297	Cox and Sheppard, 1980[8]	(e)
$(3.72 \pm 0.37) \times 10^{-11}$	300	Barnes *et al.*, 1986[9]	(f)
$(3.50 \pm 0.49) \times 10^{-11}$	313		
Reviews and Evaluations			
$9.9 \times 10^{-12} \exp(356/T)$	240–430	IUPAC, 1989[10]	(g)
$9.97 \times 10^{-12} \exp(356/T)$	244–430	Atkinson, 1989[11]	(h)
$9.9 \times 10^{-12} \exp(360/T)$	244–430	NASA, 1990[12]	(i)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.

(b) Discharge flow system with electron paramagnetic resonance detection of HO.

(c) Discharge flow system with resonance fluorescence detection of HO.

(d) Laser photolysis system with LIF detection of HO. The rate coefficients were observed to be independent of total pressure and of the presence or absence of O_2, up to 147 Torr O_2 (270 K) or 700 Torr O_2 (300 K).

(e) Relative rate method. HO radicals generated by photolysis of HONO–NO–air mixtures at atmospheric pressure. Decay rate of CH_3SH measured relative to that of C_2H_4, and the relative rate coefficient placed on an absolute basis by use of $k(HO + C_2H_4) = 8.57 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.[11]

(f) Relative rate method. HO radicals generated by photolysis of H_2O_2 in N_2 at atmospheric pressure. Decay rate of CH_3SH measured relative to that for propene, and the relative rate coefficient placed on an absolute basis by use of $k(HO + \text{propene}) = 4.85 \times 10^{-12} \exp(504/T)$ cm³ molecule⁻¹ s⁻¹.[11]

(g) See Comments on Preferred Values.

(h) Derived from a least-squares analysis of the absolute rate coefficient data of Atkinson *et al.*,[1] Wine *et al.*,[2,6] and Hynes and Wine[7] and the relative rate coefficients of Barnes *et al.*[9]

(i) Derived from the absolute rate coefficient data of Atkinson *et al.*,[1] Wine *et al.*[2,6] and Hynes and Wine.[7]

Preferred Values

$k = 3.3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 9.9 \times 10^{-12} \exp(356/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 240–430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[10] The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson *et al.*,[1] Wine *et al.*,[2,6] and Hynes and Wine,[7] which are in excellent agreement. The recent relative rate study of Barnes *et al.*[9] shows that erroneous rate coefficient data are obtained in the presence of O_2 and NO, thus accounting for the much higher value of Cox and Sheppard.[8]

The study of Hynes and Wine[7] shows that there is no observable effect of O_2 on the measured rate coefficient and the rate coefficients at 298 K for the reactions of the HO radical with CD_3SH[7] and CH_3SD[6] are within 15% of that for $HO + CH_3SH$. These data indicate[6,7,11] that the reaction proceeds via initial addition of HO to form the adduct $CH_3S(OH)H$[6].

Tyndall and Ravishankara[13] have determined, by monitoring the CH_3S radical by LIF, a CH_3S radical yield from the reaction of the HO radical with CH_3SH of 1.1 ± 0.2. The reaction then proceeds by $HO + CH_3SH \rightarrow [CH_3S(OH)H] \rightarrow H_2O + CH_3S$.

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$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$ (1)
$\rightarrow CH_3S(OH)CH_3$ (2)

$\Delta H°(1) = -107.9$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (3.5 \pm 0.2) \times 10^{-12}$	295 ± 2	Nielsen *et al.*, 1989[1]	(a)
Relative Rate Coefficients			
$k_1 = (4.69 \pm 0.43) \times 10^{-12}$	298 ± 3	Barnes, Bastian, and Becker, 1988[2]	(b)
$k = (8.52 \pm 0.52) \times 10^{-12}$ (760 Torr air)	298 ± 3	Barnes, Bastian, and Becker, 1988[2]	(b)
Reviews and Evaluations			
$k_1 = 9.6 \times 10^{-12} \exp(-234/T)$	250–400	IUPAC, 1989[3]	(c)
$k_2 = \left[\frac{1.7 \times 10^{-42} [O_2] \exp(7810/T)}{1 + 5.5 \times 10^{-31} [O_2] \exp(7460/T)]}\right]$	260–360		
$k_1 = 1.03 \times 10^{-11} \exp(-243/T)$	248–397	Atkinson, 1989[4]	(d)
$k_2 = \left[\frac{1.68 \times 10^{-42} [O_2] \exp(7812/T)}{[1 + 5.53 \times 10^{-31} [O_2] \exp(7460/T)]}\right]$	~260–400		
$k_1 = 1.1 \times 10^{-11} \exp(-240/T)$	248–397	NASA, 1990[5]	(e)

Comments

(a) HO radicals generated by the pulsed radiolysis of $Ar-H_2O$ mixtures at 1 atm total pressure, and detected by UV absorption at 309 nm.

(b) Relative rate study. HO radicals generated by the photolysis of H_2O_2 at 254 nm in N_2-O_2 mixtures at 760 Torr total pressure. Decay rates of dimethyl sulfide and ethene monitored by GC and the measured rate coefficient ratio was placed on an absolute basis by use of $k(HO + \text{ethene}) = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4] The pressure of O_2 was varied from zero to 760 Torr. The cited value for k is at 760 Torr total pressure of air.

(c) See Comments on Preferred Values.

(d) The rate coefficient for the abstraction process [channel (1)] was derived from the data of Wine *et al.*,[6] Hynes *et al.*[7] and Barnes *et al.*[2] The rate coefficient for the addition process [channel (2)] is that of Hynes *et al.*[7]

(e) The rate coefficient for the abstraction process [channel (1)] was derived from the absolute rate coefficient data of Wine *et al.*,[6] Hynes *et al.*[7] and Hsu *et al.*[8]

Preferred Values

$k = 4.4 \times 10^{-12} + \{(4.1 \times 10^{-31} [O_2])/(1 + 4.1 \times 10^{-20} [O_2])\}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 4.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 9.6 \times 10^{-12} \exp(-234/T)$ over the temperature range 250–400 K.

$k_2 = 4.1 \times 10^{-31}\ [O_2]/(1 + 4.1 \times 10^{-20}\ [O_2])$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_2 = 1.7 \times 10^{-42} \exp(7810/T)\ [O_2]/(1 + 5.5 \times 10^{-31} \exp(7460/T)\ [O_2])$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–360 K.

Reliability

$\Delta\log k_1 = \pm 0.10$ at 298 K.

$\Delta(E_1/R) = \pm 300$ K.

$\Delta\log k_2 = \pm 0.3$ at 298 K and 1 bar of air.

Comments on Preferred Values

It is now recognized[2–4,7] that this reaction proceeds via the two reaction steps (1) and (2). The $CH_3S(OH)CH_3$ adduct radical decomposes sufficiently rapidly that in the absence of O_2 only the rate coefficient k_1 is measured. In the presence of O_2, the $CH_3S(OH)CH_3$ radical reacts by

$$CH_3S(OH)CH_3 + O_2 \rightarrow \text{products}$$

Hence only in the presence of O_2 is the addition channel (2) observed, with the observed rate constant being dependent on the O_2 concentration (but, to at least a first approximation, not on the concentration of other third bodies such as N_2, Ar or SF_6).[7]

The relative rate study of Wallington *et al.*[9] shows that previous relative rate studies were complicated by secondary reactions, and that all relative rate coefficient studies carried out in the presence of NO are of dubious quality. The most recent absolute rate coefficients measured in the absence of O_2[1,6–10] agree that the earliest absolute rate coefficients of Atkinson *et al.*[11] and Kurylo[12] are erroneously high, and those of Mac Leod *et al.*[13] were in error owing to heterogeneous wall reactions.[10] The preferred rate coefficient k_1 for the H-atom abstraction channel is based upon the two studies of Wine and coworkers,[6,7] and the rate coefficient for the HO radical addition channel (step 2) utilizes the data of Hynes *et al.*[6] While the expression for k_2 is strictly valid only for 0.93 bar of air[6] (in that the rate coefficients for HO addition to CH_3SCH_3 and the reverse dissociation step may be in the fall-off regime), this equation fits the room temperature data obtained at pressures of air from 0.07 to 0.93 bar well.

References

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$HO + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.9 \times 10^{-11} \exp[(380 \pm 160)/T]$	249–367	Wine *et al.*, 1981[1]	(a)
$(1.98 \pm 0.18) \times 10^{-10}$	298		
Reviews and Evaluations			
$6.0 \times 10^{-11} \exp(380/T)$	250–370	CODATA, 1984[2]; IUPAC,1989[3]	(b)
$5.83 \times 10^{-11} \exp(383/T)$	249–367	Atkinson, 1989[4]	(c)
$5.7 \times 10^{-11} \exp(380/T)$	249–367	NASA, 1990[5]	(c)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO, carried out over the total pressure range 50–200 Torr of Ar.

(b) See Comments on Preferred Values.

(c) Based on the absolute rate coefficient study of Wine *et al.*[1]

Preferred Values

$k = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.0 \times 10^{-11} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The direct determinations of the rate coefficient by Wine *et al.*[1] are in excellent agreement with the previous room temperature relative rate coefficient of Cox and Sheppard.[6] The preferred 298 K rate coefficient is the mean of all of the individual determinations of the rate coefficient at 298 K (four from Wine *et al.*[1] and one from Cox and Sheppard[6]). The temperature dependence is that of Wine *et al.*,[1] with the *A* factor being adjusted to yield the preferred 298 K rate coefficient. The magnitude of the rate coefficient and the negative temperature dependence indicates that the reaction proceeds by initial HO radical addition to the S atoms:

$$HO + CH_3SSCH_3 \rightarrow CH_3SS(OH)CH_3$$

References

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$HO_2 + SO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 4.3 \times 10^{-17}$	~298	Burrows *et al.*, 1979[1]	(a)
Reviews and Evaluations			
$\leq 1 \times 10^{-18}$	298	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
$\leq 1 \times 10^{-18}$	298	NASA, 1990[4]	(c)

Comments

(a) Fast-flow discharge study. HO_2 radicals were generated by a discharge in H_2O_2 and by reaction of F atoms with H_2O_2. HO_2 and HO radicals were monitored by LMR to yield the rate coefficient ratio $k/k(HO + H_2O_2)$. A value of $k/k(HO + H_2O_2)$ was not quoted, but from the cited value of $k \leq 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} and the rate coefficient $k(HO + H_2O_2) = 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} used,[1] we obtain $k/k(HO + H_2O_2) \leq 2.5 \times 10^{-3}$. Using $k(HO + H_2O_2) = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained. The quoted value of k was assigned to the reaction $HO_2 + SO_2 \rightarrow HO + SO_3$, but results suggest other channels are also slow.

(b) See Comments on Preferred Values.

(c) Accepts the upper limit to the rate coefficient of Graham *et al.*[6]

Preferred Values

$k \leq 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA 1982.[2] The most recent determination[1] confirms that the reaction is slower than some earlier results[5] had suggested and supports the even lower limit set by Graham *et al.*,[6] which we take as the preferred value.

References

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$NO_3 + H_2S \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3 \times 10^{-14}$	298	Wallington *et al.*, 1986[1]	(a)
$<8 \times 10^{-16}$	298	Dlugokencky and Howard, 1988[2]	(b)
Relative Rate Coefficients			
$<3 \times 10^{-14}$	298	Cantrell *et al.*, 1987[3]	(c)
Reviews and Evaluations			
$<1 \times 10^{-15}$	298	IUPAC, 1989[4]	(d)
$<8 \times 10^{-16}$	298	NASA, 1990[5]	(e)

Comments

(a) Flash photolysis system with optical absorption detection of NO_3.
(b) Flow system with LIF detection of NO_3.
(c) Relative rate method. NO_3 generated by the thermal decomposition of N_2O_5, and the rate coefficient placed on an absolute basis by use of an equilibrium constant for the $NO_3 + NO_2 \rightleftharpoons N_2O_5$ reactions of 3.41×10^{-11} cm^3 molecule^{-1}.[6]
(d) See Comments on Preferred Values.
(e) Based upon the upper limit to the rate coefficient determined by Dlugokencky and Howard.[2]

Preferred Values

$k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred upper limit to the rate coefficient is based upon the study of Dlugokencky and Howard.[2]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[2] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[3] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).
[6] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CS_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	298	Burrows, Tyndall and Moortgat, 1985[1]	(a)
Relative Rate Coefficients			
$<1.1 \times 10^{-15}$	297	Mac Leod *et al.*, 1986[2]	(b)
Reviews and Evaluations			
$<1 \times 10^{-15}$	298	IUPAC, 1989[3]	(c)
$<4.0 \times 10^{-16}$	298	NASA, 1990[4]	(d)

Comments

(a) Molecular modulation system with optical absorption detection of NO_3.
(b) Relative rate method. NO_3 generated by thermal decomposition of N_2O_5 at atmospheric pressure of air. Decay rates of CS_2 and propene monitored by FTIR absorption spectroscopy. Upper limit to the rate coefficient obtained by use of $k(NO_3 + \text{propene}) = 9.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(c) See Comments on Preferred Values.
(d) Based on the upper limit to the rate coefficient determined by Burrows *et al.*[1]

Preferred Values

$k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred value is based upon the absolute study of Burrows *et al*.,[1] which is consistent with the slightly higher upper limit derived by Mac Leod *et al*.[2]

References

[1]J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[2]H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$NO_3 + OCS \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<4.6 \times 10^{-17}$	297	Mac Leod *et al*., 1986[1]	(a)
Reviews and Evaluations			
$<3 \times 10^{-15}$	298	IUPAC, 1989[2]	(b)
$<3.0 \times 10^{-15}$	298	NASA, 1990[3]	(c)

Comments

(a) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 at atmospheric pressure of air. Decay rates of COS and propene monitored by FTIR absorption spectroscopy. Upper limit to the rate coefficient obtained by use of $k(NO_3 +$ propene$) = 9.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based upon the upper limit to the rate coefficient determined by Mac Leod *et al*.[1] Due to a typographical error, the incorrect reference reaction and rate coefficient were used.

(c) Based upon the upper limit to the rate coefficient determined by Mac Leod *et al*.[1]

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the sole study of Mac Leod *et al*.,[1] with a somewhat higher upper limit than reported.

References

[1]H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$NO_3 + SO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1 \times 10^{-17}$	295 ± 2	Canosa-Mas *et al*., 1988[1]	(a)
$<1.2 \times 10^{-17}$	473	Canosa-Mas *et al*., 1988[2]	(a)
Reviews and Evaluations			
$<1 \times 10^{-19}$	298	IUPAC, 1989[3]	(b)
$<7.0 \times 10^{-21}$	298	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with optical absorption detection of NO_3.
(b) See Comments on Preferred Values.
(c) Based upon the study of Daubendiek and Calvert.[5]

Preferred Values

$k < 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the relative rate study of Daubendiek and Calvert,[5] with a much higher upper limit. This preferred upper limit to the 298 K rate coefficient is consistent with the upper limits determined in the absolute rate coefficient studies of Burrows *et al.*,[6] Wallington *et al.*,[7] Dlugokencky and Howard[8] and Canosa-Mas *et al.*[1,2]

References

[1]C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 247 (1988).
[2]C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 263 (1988).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]R. L. Daubendiek and J. G. Calvert, Environ. Lett. **8**, 103 (1975).
[6]J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[7]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[8]E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

$NO_3 + CH_3SH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.0 \times 10^{-13} \exp[(600 \pm 400)/T]$	280–350	Wallington *et al.*, 1986[1]	(a)
$(8.1 \pm 0.6) \times 10^{-13}$	298		
$(7.7 \pm 0.5) \times 10^{-13}$	298	Rahman *et al.*, 1988[2]	(b)
$1.09 \times 10^{-12} \exp[(0 \pm 50)/T]$	254–367	Dlugokencky and Howard, 1988[3]	(c)
$(1.09 \pm 0.13) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.00 \pm 0.22) \times 10^{-12}$	297	Mac Leod *et al.*, 1986[4]	(d)
Reviews and Evaluations			
9.2×10^{-13}	250–370	IUPAC, 1989[5]	(e)
$4.4 \times 10^{-13} \exp(210/T)$	250–370	NASA, 1990[6]	(f)
9.3×10^{-13}	254–367	Atkinson, 1991[7]	(g)

Comments

(a) Flash photolysis system with optical absorption of NO_3. Carried out at total pressures of 50–100 Torr of N_2.
(b) Discharge flow system with MS detection of CH_3SH in the presence of excess concentrations of NO_3 radicals. Carried out at total pressures of ~1 Torr. Corrections were made for the reaction of CH_3SH with F_2 used as the precursor to generate NO_3 radicals.
(c) Flow system with LIF detection of NO_3. Carried out at a total pressure of ~1 Torr.
(d) Relative rate method. NO_3 radicals generated by the thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. Decay rates of CH_3SH and *trans*-2-butene monitored, and the rate coefficient placed on an absolute basis by use of $k(NO_3 + trans\text{-2-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[7]
(e) See Comments on Preferred Values.
(f) Derived from the absolute rate coefficient data of Wallington *et al.*,[1] Rahman *et al.*[2] and Dlugokencky and Howard.[3]
(g) The 298 K rate coefficient was the average of the absolute rate coefficient studies of Wallington *et al.*,[1] Rahman *et al.*[2] and Dlugokencky and Howard[3] and the relative rate coefficient of Mac Leod *et al.*[4] The temperature dependence was that of Dlugokencky and Howard.[3]

Preferred Values

$k = 9.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–370 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The preferred value at 298 K is the mean of the four studies carried out to date,[1-4] which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington *et al*.,[1] this is due to the rate coefficient measured at 350 K, since the rate coefficients at 280 and 298 K are identical.[1] The temperature independence determined by Dlugokencky and Howard[3] is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~0.0013–1 bar.

The magnitude of the rate coefficient and the lack of temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield CH_3S radicals (see also the data sheet on the $NO_3 + CH_3SCH_3$ reaction)

$$NO_3 + CH_3SH \rightleftarrows [CH_3S(ONO_2)H]^{\ddagger} \rightarrow CH_3S + HNO_3$$

References

[1]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[2]M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges Phys. Chem. **92**, 91 (1988).
[3]E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[4]H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9 (see references in Introduction).
[7]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.3) \times 10^{-12}$	298 ± 1	Daykin and Wine, 1990[1]	(a)
Reviews and Evaluations			
1.9×10^{-13} exp(500/T)	250–380	IUPAC, 1989[2]	(b)
1.9×10^{-13} exp(500/T)	256–376	NASA, 1990[3]	(c)
1.87×10^{-13} exp(519/T)	256–376	Atkinson, 1991[4]	(d)

Comments

(a) NO_3 radicals generated by pulsed laser photolysis of HNO_3, and detected by optical absorption.

(b) The 298 K rate coefficient was derived from the absolute rate coefficients of Tyndall *et al*.[5] and Dlugokencky and Howard[6] and the relative rate coefficient of Atkinson *et al*.[7] The temperature dependence was that of Dlugokencky and Howard.[6]

(c) Derived from the absolute rate coefficients of Wallington *et al*.,[8] Tyndall *et al*.[5] and Dlugokencky and Howard.[6]

(d) Derived from a least-squares analysis of the absolute rate coefficients of Tyndall *et al*.,[5] Dlugokencky and Howard[6] and Daykin and Wine[1] and the relative rate coefficient of Atkinson *et al*.[7]

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-13}$ exp(520/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute[1,5,6,8,9] and relative[7] rate coefficient studies are in reasonable agreement, although the data of Wallington *et al*.[8,9] are ~20% lower than the other data. The absolute rate coefficients measured by Tyndall *et al*.,[5] Dlugokencky and Howard[6] and Daykin and Wine[1] and the relative rate coefficient of Atkinson *et al*.[7] have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013–1 bar.

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO_3 radical to the S atom. The kinetic data of Daykin and Wine[1] for CH_3SCH_3 and CD_3SCD_3 show that the rate determining step involves H−(or D−) atom abstraction, indicating that the reaction is $NO_3 + CH_3SCH_3 \rightleftarrows [CH_3S(ONO_2)CH_3]^{\ddagger} \rightarrow CH_3SCH_2 + HNO_3$.

References

[1]E. P. Daykin and P. H. Wine, Int. J. Chem. Kinet. **22**, 1083 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[5]G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, Chem. Phys. Lett. **130**, 463 (1986).
[6]E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[7]R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, J. Phys. Chem. **88**, 1584 (1984).
[8]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[9]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **40**, 4640 (1986).

$NO_3 + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.9 \times 10^{-13} \exp[(290 \pm 50)/T]$	280–350	Wallington *et al.*, 1986[1]	(a)
$(4.9 \pm 0.8) \times 10^{-13}$	298		
$7.4 \times 10^{-13} \exp[(0 \pm 200)/T]$	334–382	Dlugokencky and Howard, 1988[2]	(b)
$(7.4 \pm 1.5) \times 10^{-13}$	298*		
Relative Rate Coefficients			
(See comment)	297	Mac Leod *et al.*, 1986[3]	(c)
Reviews and Evaluations			
7×10^{-13}	300–380	IUPAC, 1989[4]	(d)
$1.3 \times 10^{-12} \exp(-270/T)$	280–380	NASA, 1990[5]	(e)
7×10^{-13}	300–380	Atkinson, 1991[6]	(f)

Comments

(a) Flash photolysis system with optical absorption detection of NO_3. Carried out at total pressures of 50–100 Torr of N_2.
(b) Flow system with LIF detection of NO_3. Carried out at total pressures of ~1 Torr.
(c) Relative rate method. NO_3 radicals generated by thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. Relative decay rates of CH_3SSCH_3 and *trans*-2-butene monitored. The more recent study of Atkinson *et al.*[7] has shown that reliable rate coefficient data cannot be obtained from the chemical system used.
(d) See Comments on Preferred Values.
(e) Derived from the absolute rate coefficients of Wallington *et al.*[1] and Dlugokencky and Howard.[2]
(f) Derived mainly from the absolute rate coefficient study of Dlugokencky and Howard,[2] taking into account the data of Wallington *et al.*[1]

Preferred Values

$k = 7 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, independent of temperature over the range ~300–380 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The two absolute studies[1,2] are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study[3] is an order of magnitude lower than the absolute data, the recent study of Atkinson *et al.*[7] shows that this is due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and then mainly on the most recent data of Dlugokencky and Howard,[2] with the error limits being sufficient to encompass the data of Wallington *et al.*[1]

As for the NO_3 radical reactions with CH_3SH and CH_3SCH_3, the NO_3 radical reaction with CH_3SSCH_3 is expected to proceed by initial addition, followed by decomposition of the addition adduct, possibly to yield CH_3S radicals[3]

$$NO_3 + CH_3SSCH_3 \rightleftarrows [CH_3SS(ONO_2)CH_3]^{\ddagger} \rightarrow CH_3S + CH_3SONO_2$$

References

[1]T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).
[2]E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[3]H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9 (see references in Introduction).
[6]R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).
[7]R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Geophys. Res. **93**, 7125 (1988).

$HS + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4 \times 10^{-17}$	298	Black, 1984[1]	(a)
$\leq 1 \times 10^{-17}$	298	Friedl, Brune and Anderson, 1985[2]	(b)
$<1 \times 10^{-14}$	298	Schoenle, Rahman and Schindler, 1987[3]	(c)
$<4 \times 10^{-19}$	298	Stachnik and Molina, 1987[4]	(d)
$<1.5 \times 10^{-17}$	295	Wang, Lovejoy and Howard, 1987[5]	(e)
Reviews and Evaluations			
$<4 \times 10^{-19}$	298	IUPAC, 1989[6]	(f)
$<4 \times 10^{-19}$	298	NASA, 1990[7]	(g)

Comments

(a) Pulsed laser photolysis of H_2S at 193 nm. HS radicals were monitored by LIF. There was no observable decay of HS in the presence of 500 Torr of O_2.
(b) Discharge flow study, with He as the carrier gas. HS radicals were generated by the $H + H_2S$ reaction and monitored by LIF.
(c) Discharge flow study, with He as the carrier gas. HS radicals were generated by the $F + H_2S$ reaction and monitored by MS.
(d) Pulsed laser photolysis of H_2S at 193 nm. HS radicals were monitored by UV absorption at 324 nm using a multipass cell. Sufficient CO was added to scavenge HO radicals by the $CO + HO \rightarrow CO_2 + H$ reaction.
(e) Discharge flow study, with He as the carrier gas. HS radicals were generated by $F + H_2S$ or $H + C_2H_4S$ and monitored by LMR.
(f) See Comments on Preferred Values.
(g) Accepted the upper limit determined by Stachnik and Molina.[4]

Preferred Values

$k \leq 4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits that fall in the range 4×10^{-19} to 4×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K. The preferred value is from the study of Stachnik and Molina,[4] which gives the lowest value of the upper limit to the rate coefficient, and which seems reliable.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1987).
[3] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).
[4] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
[5] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[6] IUPAC, Supplement III, 1989 (see references in Introduction).
[7] NASA Evaluation No. 9, 1990 (see references in Introduction).

$HS + O_3 \rightarrow HSO + O_2$

$\Delta H^\circ = -290\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.2 \pm 1.0) \times 10^{-12}$	298	Friedl, Brune and Anderson, 1985[1]	(a)
$(2.9 \pm 0.6) \times 10^{-12}$	298	Schoenle, Rahman and Schindler, 1987[2]; Schindler and Benter, 1988[3]	(b)
$1.1 \times 10^{-11} \exp[(-280 \pm 50)/T]$	296–431	Wang and Howard, 1990[4]	(c)
$(4.39 \pm 0.88) \times 10^{-12}$	298		
Reviews and Evaluations			
3.6×10^{-12}	298	IUPAC, 1989[5]	(d)
$9.0 \times 10^{-12} \exp(-280/T)$	200–300	NASA, 1990[6]	(e)

Comments

(a) Discharge flow study, with He as the carrier gas. HS radicals were generated by the $H + H_2S$ reaction and monitored by LIF.

(b) Discharge flow study, with He as the carrier gas. HS radicals were produced by the $F + H_2S$ reaction. HS and HSO radicals were monitored by MS. An error in the sensor calibration was noted in a later publication,[3] and the corrected rate coefficient is given in the table.

(c) Discharge flow study, with He as the carrier gas. HS radicals were produced by the $H + C_2H_4S \rightarrow HS + C_2H_4$ reaction. HS, HSO, and HO radicals were monitored by LMR.

(d) Mean of the uncorrected value of Schoenle *et al.*[2] and that of Friedl *et al.*[1]

(e) The temperature coefficient was taken from Wang and Howard.[4] The pre-exponential factor was based on the studies of Wang and Howard,[4] Schoenle *et al.*[2] and Friedl *et al.*[1]

Preferred Values

$k = 3.7 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 9.5 \times 10^{-12} \exp(-280/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is reproduced largely from our previous evaluation, IUPAC, 1989,[5] with the addition of the recent data of Wang and Howard.[4] The measured rate coefficients k at 298 K agree reasonably well. A mean of the rate coefficients from the three studies[1,3,4] is taken as the preferred value. There is only one measurement of the temperature coefficient, which is the basis of the recommended expression, with the pre-exponential factor chosen to fit the recommended value of k at 298 K.

Since there is only one determination of the temperature dependence of k, and in view of the complexity of the secondary chemistry in these systems, substantial error limits are assigned.

References

[1] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[2] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges Phys. Chem. **91**, 66 (1987).

[3] R. N. Schindler and Th. Benter, Ber. Bunsenges Phys. Chem. **92**, 558 (1988).

[4] N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).

[5] IUPAC, Supplement III, 1989 (see references in Introduction).

[6] NASA Evaluation No. 9, 1990 (see references in Introduction).

HS + NO + M → HSNO + M

$\Delta H^\circ = -139$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.7 \times 10^{-31}(T/300)^{-2.48}$ [N$_2$]	250–445	Black *et al.*, 1984[1]	(a)
1.4×10^{-30} [N$_2$]	298	Bulatov, Kozliner and Sarkisov, 1985[2]	(b)
Reviews and Evaluations			
$2.4 \times 10^{-31}(T/300)^{-2.5}$ [N$_2$]	200–300	IUPAC, 1989[3]	(c)
$2.4 \times 10^{-31}(T/300)^{-3}$ [air]	200–300	NASA, 1990[4]	(c)

Comments

(a) Laser flash photolysis of H_2S at 193 nm with HS detection by LIF at 354.5 nm. The pressure dependence was studied over the range 30–760 Torr. The relative rate coefficients obtained were k_0(M = He) : k_0(Ar) : k_0(N$_2$) = 0.88 : 0.92 : 1. Falloff curves were represented with $F_c = 0.6$ and $k_\infty = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Theoretical modeling with the given value of ΔH° was carried out.

(b) Flash photolysis with intracavity laser spectroscopy of HSO. Measurements were conducted at 13 Torr total pressure.

(c) Based on Ref. 1.

Preferred Values

$k_0 = 2.4 \times 10^{-31}(T/300)^{-2.5}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The pressure- and temperature-dependent measurements from Ref. 1 give a consistent picture for the association reaction and are preferred.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.5) \times 10^{-11}$	250–300	Black *et al.*, 1984[1]	(a)
Reviews and Evaluations			
2.7×10^{-11}	200–300	IUPAC, 1989[3]	(b)
2.7×10^{-11}	200–300	NASA, 1989[4]	(b)

Comments

(a) See comment (a) for k_0.

(b) Based on Ref. 1.

Preferred Values

$k_\infty = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

The falloff extrapolation with $F_c = 0.6$ of Ref. 1 toward k_∞ appears less certain than that to k_0.

Intermediate Falloff Range

The given k_0 and k_∞ values from Ref. 1 were based on an assumed F_c value of 0.6.

References

[1]G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).
[2]V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **4**, 1353 (1985).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HS + NO_2 \rightarrow HSO + NO$

$\Delta H° = -90$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.4) \times 10^{-11}$	298	Black, 1984[1]	(a)
$(2.4 \pm 0.2) \times 10^{-11}$	298	Bulatov, Kozliner, and Sarkisov, 1984[2]	(b)
$(3.0 \pm 0.8) \times 10^{-11}$	298	Friedl, Brune, and Anderson, 1985[3]	(c)
$(8.6 \pm 0.9) \times 10^{-11}$	298	Schoenle, Rahman, and Schindler, 1987[4]	(d)
$(4.8 \pm 1.0) \times 10^{-11}$	298	Stachnik and Molina, 1987[5]	(e)
$2.9 \times 10^{-11} \exp(237/T)$	221–415	Wang, Lovejoy, and Howard, 1987[6]	(f)
$(6.7 \pm 1.0) \times 10^{-11}$	298		
Reviews and Evaluations			
$2.6 \times 10^{-11} \exp(240/T)$	220–450	IUPAC, 1989[7]	(g)
$2.9 \times 10^{-11} \exp(240/T)$	200–300	NASA, 1990[8]	(h)

Comments

(a) Pulsed laser dissociation of H_2S at 193 nm. Decays of HS radicals were monitored by LIF. He, Ar and N_2 were used as buffer gases. The rate coefficient was determined to be independent of He pressure over the range 28.5–300 Torr. A rate coefficient of

$$k(HS + NO_2 + He) \leq 7 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

was also obtained.

(b) Pulsed laser photolysis of H_2S–NO_2 mixtures. HSO radicals were monitored by intracavity laser absorption.

(c) Discharge flow study, with He as the carrier gas. HS radicals were generated by the reaction of H + H_2S with H_2S in excess, and monitored by LIF.

(d) Discharge flow study, with He as the carrier gas. HS radicals were generated by the F + H_2S reaction and monitored by MS. HSO radicals were also monitored in some experiments.

(e) Pulsed laser photolysis of H_2S at 193 nm. HS radicals were monitored by absorption at 324 nm using a multipass cell. O_2 was added to suppress secondary chemistry arising from the presence of H atoms. N_2 was used as the buffer gas, and the total pressure varied over the range 30–730 Torr.

(f) Discharge flow study with He as the carrier gas. HS radicals were generated by the reactions F + H_2S and H + C_2H_4S, and monitored by LMR.

(g) See Comments on Preferred Values.

(h) Accepted the value of Wang *et al.*[6]

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6 \times 10^{-11} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–450 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[7] There is considerable scatter in the measured rate coefficients, with no obvious correlation with the conditions or techniques used. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H_2S. In more recent studies,[5,6] care has been taken to eliminate or model such effects, but significant differences persist. The preferred value at 298 K is the mean of the results of Stachnik and Molina[5] and Wang *et al.*[6] The temperature coefficient is that of Wang *et al.*[6] and the pre-exponential factor has been adjusted to fit the recommended value of k at 298 K.

The absence of any pressure effect on the rate constant at pressures up to 0.96 bar[1,5] indicates that any addition channel is unimportant up to these pressures.

References

[1]G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2]V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. 3, 1300 (1984).
[3]R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[4]G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges Phys. Chem. **91**, 66 (1987), revised by R. N. Schindler and Th. Benter, Ber. Bunsenges Phys. Chem. **92**, 558 (1988).
[5]R. A. Stachnik and M. J. Molina **91**, 4603 (1987).
[6]N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[7]IUPAC, Supplement III, 1989 (see references in Introduction).
[8]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HSO + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-17}$	296	Lovejoy, Wang, and Howard, 1987[1]	(a)
Reviews and Evaluations			
$\leq 2.0 \times 10^{-17}$	298	IUPAC, 1989[2]	(b)
$<2.0 \times 10^{-17}$	298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow study with He as the carrier gas. HSO radicals were generated by the O + CH_3SH reaction and monitored by LMR. HO_2 or OH, which are possible reaction products, were not observed.
(b) See Comments on Preferred Values.
(c) Based on the rate coefficient of Lovejoy *et al.*[1]

Preferred Values

$k \leq 2.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The reaction is slow and only an upper limit to the rate coefficient is available.[1]

References

[1]E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HSO + O_3 \rightarrow HS + 2O_2$ (1)
$\rightarrow HO + SO + O_2$ (2)
$\rightarrow HSO_2 + O_2$ (3)

$\Delta H°(1) = 4$ kJ·mol^{-1}
$\Delta H°(2) = -94$ kJ·mol^{-1}
$\Delta H°(3) = -360$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.1×10^{-13}	297	Wang and Howard, 1990[1]	(a)
$k_1 = 7 \times 10^{-14}$	297		
Relative Rate Coefficients			
1.1×10^{-13}	298	Friedl, Brune, and Anderson, 1985[2]	(b)
Reviews and Evaluations			
1.1×10^{-13}	298	IUPAC, 1989[3]	(c)
1.0×10^{-13}	298	NASA, 1990[4]	(c)

Comments

(a) Discharge flow study with He as the carrier gas. The $HS + O_3 \rightarrow HSO + O_3$ reaction was studied, with the HSO radical subsequently reacting with O_3. HS, HSO and HO radicals were monitored by LMR. The rate coefficients k and k_1 were obtained from modeling the variation of the HS and HSO concentrations with time.
(b) Discharge flow system with He as the carrier gas. The $HS + O_3$ reaction was studied, with HS being generated by the $H + H_2S$ reaction. HS radicals were monitored by LIF. Addition of O_3 gave an initial decrease in the HS concentration, which finally attained a steady state indicating regeneration of HS, postulated to be by the $HSO + O_3$ reaction. A rate coefficient ratio of $k/k(HS + O_3) = 0.031 \pm 0.005$ was obtained and has been placed on an absolute basis by use of $k(HS + O_3) = 3.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation). A rate coefficient k was also obtained by modeling the HS profiles, giving $k = (1.1 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the best fit. When SD was used, no isotope effect on k was observed. The authors suggest that reaction leads to $HS + 2O_2$.
(c) Based on the study of Friedl *et al.*[2]

Preferred Values

$k = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta \log k_1 = \pm 0.4$ at 298 K.

Comments on Preferred Values
There are now two identical values of k at 298 K obtained by different techniques,[1,2] which are accepted as our preferred value. The one measured value of k_1 is also accepted, but with fairly large error limits.

The isotopic studies[2] favor the occurrence of channel (1) rather than (2), but the evidence is indirect and requires confirmation by product studies.

References

[1]N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).
[2]R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

HSO + NO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.6×10^{-14}	296	Bulatov, Kozliner and Sarkisov, 1985[1]	(a)
$\leq 1.0 \times 10^{-15}$	298	Lovejoy, Wang and Howard, 1987[2]	(b)
Reviews and Evaluations			
$<1.0 \times 10^{-15}$	298	IUPAC, 1989[3]	(c)
$<1.0 \times 10^{-15}$	298	NASA, 1990[4]	(d)

Comments

(a) Pulsed laser photolysis of H_2S-NO_2-NO mixtures. HSO radicals were monitored by intracavity laser absorption. The total pressure was varied from 10–100 Torr.
(b) Discharge flow study with He as the carrier gas. HSO radicals were generated by the $O(^3P) + CH_3SH$ and $HS + NO_2$ reactions and monitored by LMR.
(c) See Comments on Preferred Values.
(d) Accepted the results of Lovejoy *et al.*[2]

Preferred Values

$k \leq 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The only two available measurements of the rate coefficient k differ by at least a factor of 26. This is unlikely to be due to the higher pressures used in the Bulatov *et al.*[1] study, but may arise from secondary chemistry in their HSO source, which employed relatively large H_2S concentrations. Provisionally, the upper limit to the rate coefficient reported by Lovejoy *et al.*[2] is preferred.

References

[1]V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. 4, 1353 (1985).
[2]E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. 91, 5749 (1987).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HSO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
4.1×10^{-12}	298	Bulatov, Kozliner and Sarkisov, 1984[1]	(a)
$(9.6 \pm 2.4) \times 10^{-12}$	298	Lovejoy, Wang and Howard, 1987[2]	(b)
Reviews and Evaluations			
9.6×10^{-12}	298	IUPAC, 1989[3]	(c)
9.6×10^{-12}	298	NASA, 1990[4]	(d)

Comments

(a) Pulsed laser photolysis of H_2S–NO_2 mixtures. HSO radicals were monitored by intracavity laser absorption.
(b) Discharge flow study with He as the carrier gas. HSO radicals were generated by the $O(^3P) + CH_3SH$ or $HS + NO_2$ reactions. HSO, HS, HO and HO_2 radicals were monitored by LMR.
(c) See Comments on Preferred Values.
(d) Accepts the rate coefficient of Lovejoy *et al.*[2]

Preferred Values

$k = 9.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The only two measurements of k differ by at least a factor of 2. Lovejoy *et al.*[2] have suggested that the relatively high H_2S concentrations used by Bulatov *et al.*[1] may have led to side reactions regenerating HSO. The value of Lovejoy *et al.*[2] is preferred, but wide error limits are assigned awaiting confirmatory studies.

HO_2 was observed as a product of the reaction by Lovejoy *et al.*,[2] which they suggest arises from the reaction sequence

$$HSO + NO_2 \rightarrow HSO_2 + NO$$

$$HSO_2 + O_2 \rightarrow HO_2 + SO_2.$$

References

[1]V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. 3, 988 (1984).
[2]E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. 91, 5749 (1987).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HSO_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.0×10^{-13}	296	Lovejoy, Wang and Howard, 1987[1]	(a)
Reviews and Evaluations			
3.0×10^{-13}	298	IUPAC, 1989[2]	(b)
3.0×10^{-13}	298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow study with He as the carrier gas. HSO radicals were generated by the $O(^3P)$ + CH_3SH and HS + NO_2 reactions. The HSO + NO_2 reaction was studied, with HSO, HO_2 and HO radicals being monitored by LMR. O_2 addition to the system led to an increase in the HO_2 concentration, assumed to be due to the reactions HSO + NO_2 → HSO_2 + NO and HSO_2 + O_2 → HO_2 + SO_2. The rate coefficient k was deduced from the HO_2 radical time-concentration profile.
(b) See Comments on Preferred Values.
(c) Based on the rate coefficient of Lovejoy *et al.*[1]

Preferred Values

$k = 3.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta\log k = \pm 0.8$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The indirect nature of the sole measurement of the rate coefficient k leads us to suggest substantial error limits, despite the high quality of the experimental work.

References

[1]E. R. Lovejoy, W. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$SO + O_2 \rightarrow SO_2 + O$

$\Delta H^\circ = -52.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16) \times 10^{-16}$	298	Black, Sharpless and Slanger, 1982[1]	(a)
$2.4 \times 10^{-13} \exp[-(2370^{+200}_{-250})/T]$	230–420	Black, Sharpless and Slanger, 1982[2]	(a)
8.4×10^{-17}	298		
$1.00 \times 10^{-13} \exp[-(2180 \pm 117)/T]$	262–363	Goede and Schurath, 1983[3]	(b)
4.9×10^{-17}	298		
Reviews and Evaluations			
$1.4 \times 10^{-13} \exp(-2275/T)$	230–420	CODATA, 1984[4]; IUPAC, 1989[5]	(c)
$2.6 \times 10^{-13} \exp(-2400/T)$	200–300	NASA, 1990[6]	(d)

Comments

(a) Laser photolysis of SO_2 at 193 nm, with SO radicals being detected by chemiluminescence from the SO + O_3 reaction. Pseudo-first-order decay of SO monitored in the presence of excess O_2. Total pressure = 100–500 Torr of O_2 + He.
(b) SO produced from the O + OCS reaction in a flow system. Controlled admission of SO radicals to a static volume where the pseudo-first-order decay of SO in excess O_2 was followed by SO + O_3 chemiluminescence. Total pressure = 1–200 mTorr O_2.
(c) See Comments on Preferred Values.
(d) Based on the work of Black *et al.*[1,2]

Preferred Values

$k = 6.7 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-13} \exp(-2280/T)$ over the temperature range 230–420 K.

Reliability
$\Delta\log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] This reaction is very slow and measurement of the rate coefficient k is subject to error due to impurities. For this reason, Black *et al.*[1,2] favor their lower value of k at 298 K obtained in the temperature dependence study.[2] The Goede and Schurath[3] values are systematically about 35% lower than those from Ref. 2, but appear to have less experimental uncertainty at temperatures <300 K. The preferred value for the rate coefficient k at 298 K and for the temperature dependence are the mean values from Ref. 2 and 3. The A-factor has been adjusted to give the preferred 298 K rate coefficient.

References

[1]G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[2]G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).
[3]H.-J. Goede and U. Schurath, Bull. Soc. Chim. Belg. **92**, 661 (1983).
[4]CODATA, Supplement II, 1984 (see references in Introduction).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).

$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H^\circ = -445$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.06 \pm 0.16) \times 10^{-13}$	298	Black, Sharpless and Slanger, 1982[1]	(a)
$4.8 \times 10^{-12} \exp[-(1170^{+80}_{-120})/T]$	230–420	Black, Sharpless, and Slanger, 1982[2]	(a)
9.46×10^{-14}	298		
Reviews and Evaluations			
$4.5 \times 10^{-12} \exp(-1170/T)$	230–420	CODATA, 1984[3]; IUPAC, 1989[4]	(b)
$3.6 \times 10^{-12} \exp(-1100/T)$	200–300	NASA, 1990[5]	(c)

Comments

(a) Laser flash photolysis of SO_2–O_3 mixtures at 193 nm with SO_2 being monitored by chemiluminescence from the $SO + O_3$ reaction. Excess O_3 was determined by UV absorption. The total pressure = 200 Torr of He.

(b) See Comments on Preferred Values.

(c) Based on the studies of Black *et al.*,[1,2] Halstead and Thrush[6] and Robertshaw and Smith.[7]

Preferred Values

$k = 8.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.5 \times 10^{-12} \exp(-1170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The data of Black *et al.*[1,2] are in good agreement with earlier work.[6,7] The preferred 298 K rate coefficient is the mean of the measurements from Refs. 1, 2, 6 and 7. The temperature dependence of Black *et al.*[2] is accepted since this study covered a much larger temperature range than the earlier work,[6] which nevertheless gave a value of E/R within the experimental error of the later study.[2]

References

[1]G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[2]G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).
[3]CODATA, Supplement II, 1984 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]C. J. Halstead and B. A. Thrush, Proc. R. Soc. London Ser. A, **295**, 380 (1966).
[7]J. S. Robertshaw and I. W. M. Smith, Int. J. Chem. Kinet. **12**, 729 (1980).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H^\circ = -245$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.37 \pm 0.07) \times 10^{-11}$	210–363	Brunning and Stief, 1986[1]	(a)
$(1.37 \pm 0.07) \times 10^{-11}$	298		
Reviews and Evaluations			
1.4×10^{-11}	210–360	IUPAC, 1989[2]	(b)
1.4×10^{-11}	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow study with He as the carrier gas. SO radicals were generated by discharge in a He–SO_2 mixture and quantified by titration with NO_2. SO concentrations were monitored by quadrapole MS under pseudo-first-order conditions.
(b) See Comments on Preferred Values.
(c) Based on the studies of Black *et al.*,[4] Clyne and co-workers[5,6] and Brunning and Stief.[1]

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The measurements of Brunning and Stief[1] are the only available temperature dependence study of the rate coefficient, and indicate no measurable change in the rate coefficient k over the temperature range 210–363 K. This finding is the basis for our present recommendation for the temperature coefficient. All of the studies[1,4–6] are in good agreement with respect to the 298 K rate coefficient.

References

[1]J. Brunning and L. J. Stief, J. Chem. Phys. **84**, 4371 (1986).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[5]M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. Roy. Soc. London, Ser. A **295**, 355 (1966).
[6]M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).

$SO_3 + H_2O \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
9×10^{-13}	300	Castleman *et al.*, 1974[1]	(a)
$\leq (5.7 \pm 0.9) \times 10^{-15}$	298	Wang *et al.*, 1989[2]	(b)
Reviews and Evaluations			
No recommendation		CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$<6.0 \times 10^{-15}$	298	NASA, 1990[5]	(d)

Comments

(a) Fast flow system. The reactant concentrations were monitored by MS in the presence of an excess concentration of H_2O.
(b) Flow system with He and N_2 as carrier gases and H_2O in large excess over SO_3. SO_3 was monitored by the photo-dissociation of SO_3 at 147 nm and detection of SO_2 fluorescence at 300–390 nm. A halocarbon wall coating of the flow tube was used.
(c) The data of Castleman *et al.*[1] were considered suspect due to the possibility of wall reactions.
(d) Accepted the upper limit of Wang *et al.*[2]

Preferred Values

$k < 6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This reaction was first considered in our previous evaluation, CODATA, 1980.[3] No recommendation was made as the only available data at that time, those of Castleman *et al.*,[1] were suspect due to the likely interference of wall reactions in their work. The recent study of Wang *et al.*[2] has now confirmed that suspicion. Wang *et al.*[2] obtained an upper limit to the rate coefficient which is more than two orders of magnitude lower than the value of Castleman *et al.*,[1] by treatment of the flow tube walls to reduce wall effects. The upper limit to the rate coefficient of Wang *et al.*[2] is accepted as our preferred value.

References

[1]A. W. Castleman, Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and W. P. Wood, Int. J. Chem. Kinet. **Symp. 1**, 629 (1975).
[2]X. Wang, Y. G. Yin, M. Suto, and L. C. Lee, J. Chem. Phys. **89**, 4853 (1989).
[3]CODATA, 1980 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$$CS + O_2 \rightarrow CO + SO \quad (1)$$
$$\rightarrow OCS + O \quad (2)$$

$\Delta H°(1) = -378$ kJ·mol^{-1}
$\Delta H°(1) = -165$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 3 \times 10^{-18}$	298	Callear and Dickson, 1971[1]	(a)
$< 8 \times 10^{-18}$	300–670	Breckenridge, Kolln, and Moore, 1975[2]	(b)
$k_2 = (4.5 \pm 1.7) \times 10^{-19}$	293	Richardson, 1975[3]	(c)
$k_2 = (5.9 \pm 1.3) \times 10^{-18}$	495		
$(2.9 \pm 0.4) \times 10^{-19}$	298	Black, Jusinski, and Slanger, 1983[4]	(d)
Branching Ratios			
$k_2/k_1 = 1.2$	298	Wood and Heicklen, 1971[5], 1973/74[6]	(e)
$k_2/k_1 = 1.2$	341–415	Wood and Heicklen, 1971[7]	(f)
Reviews and Evaluations			
No recommendation		CODATA, 1980[8]; IUPAC, 1989[9]	
2.9×10^{-19}	298	NASA, 1990[10]	(g)

Comments

(a) Flash photolysis of CS_2–O_2 mixtures, with CS radicals being monitored by light absorption.

(b) Discharge flow system used. CS radicals were produced by discharge through a Ar–CS_2 mixture and monitored by light absorption.

(c) Discharge flow system used. CS radicals were produced by a discharge through CS_2. CS, SO_2, CO and OCS were measured by MS. A very slow linear flow rate (≈ 100 cm s^{-1}) was necessary to observe reaction. SO_2, a product formed via channel (1), was at least one order of magnitude lower in concentration than CO and OCS.

(d) CS radicals were produced by pulsed laser photolysis of CS_2 in He bath gas (24 Torr), and were monitored by LIF at 257.7 nm.

(e) Photolysis of CS_2–O_2 mixtures, with analysis of CO, OCS, SO_2 and S_2O products by GC. Light of wavelength 313 nm was used in Ref. 5, which has insufficient energy to dissociate the CS_2, but CS was postulated to have been formed by reaction of electronically excited CS_2 with O_2. In the later study,[6] $\lambda = 213.9$ nm was used which can photodissociate CS_2.

(f) Explosion limits of CS_2–O_2 mixtures were determined by GC. The [CO]/[OCS] ratio was relatively unaffected by pressure and temperature changes, and the value of 0.84 found for this ratio is the same as that observed in photochemical studies.[4,5] The explosion limits were modeled on the basis of an assumed mechanism of eight reactions, and a computer fit to the data yielded the value for k_2/k_1.

(g) Accepted the rate coefficient of Black *et al.*[4]

Preferred Values

$k = 2.9 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.6$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced largely from our previous evaluation, CODATA, 1980,[8] with the addition of the more recent work of Black *et al.*[4] The reaction of CS with O_2 is slow at 298 K and difficult to study. The technique used by Black *et al.*[4] seems the most suitable for avoiding the difficulties associated with the slowness of the reaction, and their rate coefficient at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies[5–7] indicate a comparable importance of channels (1) and (2) but in the more direct flow system study[3] k_1 was found to be at least an order of magnitude less than k_2. However, the value of k_2 obtained in the fast flow study[3] appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of k at higher temperatures,[3] when combined with the 298 K values, leads to an Arrhenius expression with an extremely low pre-exponential factor. No recommendation is hence made for the temperature dependence.

References

[1] Reported in G. Hancock and I. W. M. Smith, Trans. Faraday Soc. **67**, 2586 (1971).

[2] W. H. Breckenridge, W. S. Kolln, and D. S. Moore, Chem. Phys. Lett. **32**, 290 (1975).

[3] R. J. Richardson, J. Phys. Chem. **79**, 1153 (1975).

[4]G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[5]W. P. Wood, and J. Heicklen, J. Phys. Chem. **75**, 854 (1971).
[6]W. P. Wood, and J. Heicklen, J. Photochem. **2**, 173 (1973/74).
[7]W. P. Wood, and J. Heicklen, J. Phys. Chem. **75**, 861 (1971).
[8]CODATA, 1980 (see references in Introduction).
[9]IUPAC, Supplement III, 1989 (see references in Introduction).
[10]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CS + O_3 \rightarrow OCS + O_2$

$\Delta H^\circ = -556.7\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.4) \times 10^{-16}$	298	Black, Jusinski, and Slanger, 1983[2]	(a)
Reviews and Evaluations			
3.0×10^{-16}	298	NASA, 1990[2]	(b)

Comments

(a) CS radicals were produced by pulsed laser photolysis of CS_2 at 193 nm, with He as the buffer gas at a total pressure of 50–300 Torr. CS radicals were monitored by LIF at 257.7 nm.
(b) Accepted the rate coefficient of Black *et al.*[1]

Preferred Values

$k = 3.0 \times 10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values
The only available measurement of the rate coefficient k is that of Black *et al.*[1] Their value is accepted with substantial error limits.

References

[1]G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CS + NO_2 \rightarrow OCS + NO$

$\Delta H^\circ = -357\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.6 \pm 1.1) \times 10^{-17}$	298	Black, Jusinski, and Slanger, 1983[1]	(a)
Reviews and Evaluations			
7.6×10^{-17}	298	NASA, 1990[2]	(b)

Comments

(a) CS radicals were produced by pulsed laser photolysis of CS_2 at 193 nm and monitored by LIF at 257.7 nm. He (24 Torr total pressure) was used as the buffer gas.
(b) Accepted the rate coefficient of Black *et al.*[1]

Preferred Values

$k = 7.6 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of k is that of Black *et al.*[1] Their value is accepted, but with substantial error limits.

References

[1]G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CH_3S + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2 \times 10^{-17}$	298	Balla, Nelson, and McDonald, 1986[1]	(a)
$<1 \times 10^{-16}$	298	Black and Jusinski, 1986[2]	(b)
$<2.5 \times 10^{-18}$	298	Tyndall and Ravishankara, 1989[3]	(c)
Relative Rate Coefficients			
2×10^{-14}	298	Hatakeyama and Akimoto, 1983[4]	(d)
2.8×10^{-17}	298	Grosjean, 1984[5]	(e)
$>2.3 \times 10^{-16}$	296	Balla and Heicklen, 1985[6]	(f)
Reviews and Evaluations			
$<3.0 \times 10^{-18}$	298	NASA, 1990[7]	(g)

Comments

(a) CH_3S radicals were produced by pulsed laser photolysis of $(CH_3S)_2$ at 266 nm in a flowing system, and monitored by LIF at 371.7 nm.

(b) CH_3S radicals were generated by pulsed laser photolysis of $(CH_3S)_2$ at 248 nm and CH_3SH at 193 nm in a flowing system. CH_3S radicals were monitored by LIF at 371.3 nm and 377.0 nm.

(c) CH_3S radicals were generated by pulsed laser photolysis of $(CH_3S)_2$ at 248 nm in a flowing system, and monitored at 371.4 and 377.0 nm. The decay of CH_3S in N_2 was compared with the decay in O_2 in back-to-back experiments over the pressure range 38–300 Torr to obtain the cited upper limit to the rate coefficient k.

(d) Photolysis of $(CH_3S)_2$–RONO–NO–air mixtures. The products were analyzed by FTIR and GC–MS and the yields of SO_2 and CH_3SNO measured. From an assumed mechanism, the rate coefficient ratio $k(CH_3S + NO)/k = 2 \times 10^3$ was derived. A rate coefficient of $k(CH_3S + NO) = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation) was used to obtain the rate coefficient given in the table.

(e) Environmental chamber study using the oxidation of organo-sulphur compounds in air by natural sunlight. Major products were SO_2, CH_3SO_3H and HCHO. Production of SO_2 and sulphur were related to an unidentified compound (assumed to be CH_3SNO_2) formed from $CH_3S + NO_2$. A rate coefficient ratio of $k(CH_3S + NO_2)/k = 2 \times 10^6$ was derived, and placed on an absolute basis by use of $k(CH_3S + NO_2) = 5.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(f) From the photolysis of $(CH_3S)_2$–O_2–N_2 mixtures at 253.7 nm, with product analysis by GC and MS. The SO_2 yield was measured as a function of $[(CH_3S)_2]$, $[O_2]$ and light intensity. From an assumed mechanism, a value of $k^2/2k(CH_3S + CH_3S) > 6 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1} was derived. A rate coefficient of $k(CH_3S + CH_3S) = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (from Graham *et al.*[8]) was used to obtain the rate coefficient given in the table.

(g) Based on the data of Tyndall and Ravishankara.[3]

Preferred Values

$k < 2.5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

All of the direct studies lead to an upper limit to the rate coefficient which indicates that the reaction between CH_3S and O_2 is extremely slow. The lowest value, due to Tyndall and Ravishankara,[3] was obtained using carefully controlled conditions and is taken as the preferred value. The relative rate coefficient values were based on assumed mechanisms in complex reaction systems and cannot be considered reliable.

References

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, J. Chem. Phys. **109**, 101 (1986).
[2]G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, **86**, 2143 (1986).
[3]G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).
[4]S. Hatakeyama and H. Akimoto, J. Phys. Chem. **87**, 2387 (1983).
[5]D. Grosjean, Environ. Sci. Technol. **18**, 460 (1984).
[6]R. J. Balla and J. Heicklen, J. Photochem. **29**, 297 (1985).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).
[8]D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, Can. J. Chem. **42**, 2250 (1964).

$CH_3S + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<8 \times 10^{-14}$	298	Black and Jusinski, 1986[1]	(a)
$(4.1 \pm 2.0) \times 10^{-12}$	298	Tyndall and Ravishankara, 1989[2]	(b)
Reviews and Evaluations			
4.1×10^{-12}	298	NASA, 1990[3]	(c)

Comments

(a) CH_3S radicals were generated by pulsed laser photolysis of CH_3SH at 193 nm and monitored by LIF at 371.3 nm and 377.0 nm in a flowing system.

(b) Pulsed laser photolysis of CH_3SH–H_2O–O_3 mixtures at 248 nm. The photodissociation of O_3 produced $O(^1D)$ which generated CH_3S by the reaction sequence $O(^1D) + H_2O \rightarrow 2\ OH$ and $OH + CH_3SH \rightarrow CH_3S + H_2O$. CH_3S radicals were monitored by LIF at 371.4 nm. Non-exponential decays of CH_3S were found to be due to CH_3S regeneration, postulated to be from the reactions $CH_3S + O_3 \rightarrow CH_3SO + O_2$ and $CH_3SO + O_3 \rightarrow CH_3S + 2O_2$ (with the detailed mechanism of the last of these reactions being uncertain.)

(c) Accepted the rate coefficient of Tyndall and Ravishankara.[2]

Preferred Values

$k = 4.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

There are two measurements of the rate coefficient k using basically the same technique, but yielding very different values for k. Tyndall and Ravishankara[2] have shown that complications can arise in the rate coefficient measurements due to the regeneration of CH_3S from the reaction of O_3 with one of the products of the initial step ($CH_3S + O_3$) in the reaction. They postulate[2] that CH_3SO is the product which is able to react in this way with O_3, but it is unlikely that this reaction occurs in a single step to give CH_3S since $CH_3SO + O_3 \rightarrow CH_3S + 2O_2$ is thought to be substantially endothermic. This aspect of the reaction requires further study.

Under the conditions used by Black and Jusinski,[1] the initial, and rapid, reaction of O_3 with CH_3S would be masked by the regeneration of CH_3S hence leading to an erroneously low value for the rate coefficient of CH_3S removal. Tyndall and Ravishankara[2] used a different CH_3S source from Black and Jusinski[1] and as a result were able to work under conditions in which the initial decay of CH_3S radicals could be observed. Their rate coefficient value[1] is accepted as our preferred value, but with substantial error limits.

References

[1]G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, **82**, 2143 (1986).
[2]G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CH_3S + NO + M \rightarrow CH_3SNO + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.24 \pm 0.36) \times 10^{-29}$ [N_2]	295	Balla, Nelson, and McDonald, 1986[1]	(a)
$(1.43 \pm 0.36) \times 10^{-29}$ [N_2]	351		
$(1.13 \pm 0.20) \times 10^{-29}$ [N_2]	397		
$(5.84 \pm 0.66) \times 10^{-30}$ [N_2]	453		

Comments

(a) Pulsed laser photolysis of $(CH_3S)_2$–NO–N_2 (or SF_6) mixtures at 266 nm, with CH_3S being monitored by LIF. Lower part of the falloff curves were measured over the pressure range 1.5–300 Torr of N_2. Falloff extrapolations were carried out with fitted values of F_c of 0.6, 0.86, 0.77, and 0.94 at 295, 351, 397, and 453 K, respectively.

Preferred Values

$k_0 = 3.2 \times 10^{-29}(T/298)^{-4}$ [N_2] cm³ molecule⁻¹ s⁻¹ over the temperature range 250–450 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

Although the falloff extrapolations were made with a theoretically improbable temperature coefficient of F_c, the low-pressure rate coefficients are much less influenced by this extrapolation than are the high-pressure rate coefficients.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.81 \times 10^{-12} \exp(900/T)$	295–453	Balla, Nelson, and McDonald, 1986[1]	(a)

Comments

(a) See comment (a) for k_0. High-pressure limit was obtained from measurements at 200 and 300 Torr of SF_6.

Preferred Values

$k_\infty = 4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ over the temperature range 250–450 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 250–450 K.

Comments on Preferred Values

The negative temperature coefficient of k_∞ reported in Ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We recommend the use of the extrapolated k_∞ value at 298 K over large temperature ranges together with $F_c = \exp(-T/580)$.

Reference

[1]R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986).

$CH_3S + NO_2 \rightarrow CH_3SO + NO$

$\Delta H^\circ = -134$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.3 \times 10^{-11} \exp[(80 \pm 60)/T]$	295–511	Balla, Nelson, and McDonald, 1986[1]	(a)
9.8×10^{-11}	295		
$(6.10 \pm 0.90) \times 10^{-11}$	298	Tyndall and Ravishankara, 1989[2]	(b)
5.1×10^{-11}	298	Domine, Murrells, and Howard, 1990[3]	(c)
Reviews and Evaluations			
5.6×10^{-11}	298	NASA, 1990[4]	(d)

Comments

(a) CH_3S radicals were produced by pulsed laser photolysis of $(CH_3S)_2$ at 266 nm and monitored by LIF at 371.3 nm in a flowing system. The total pressure (buffer gas N_2 or SF_6) was varied from 1 Torr to 200 Torr.

(b) CH_3S radicals were generated by pulsed laser photolysis of $(CH_3S)_2$ at 248 nm and monitored at 371.4 nm and 377.0 nm in a flowing system. The total pressure (He, N_2 bath gases) was varied over the range 34–140 Torr. The presence of O_2 was found to decrease the apparent rate coefficient. The yield of NO from reaction was measured to be 0.8 ± 0.2.

(c) Discharge flow system with He as the carrier gas. Various sources of CH_3S were used [$O(^3P) + (CH_3S)_2$, $(CH_3S)_2 + h\nu$, and $Cl + CH_3SH$]. Lyman-α photoionization MS detection of CH_3S and CH_3SO was employed.

(d) Based on the results of Tyndall and Ravishankara[2] and Domine *et al.*[3]

Preferred Values

$k = 5.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The two most recent measurements[2,3] of the rate coefficient at 298 K using different techniques are in good agreement. The earlier measurements by Balla *et al.*[1] gives a value approximately a factor of two higher. It has been suggested[2] that this could be due to secondary chemistry arising from the higher radical concentrations used by Balla *et al.*[1] The preferred value at 298 K is therefore taken as the mean of the results of Domine *et al.*[3] and Tyndall and Ravishankara.[2] No recommendation is made for the temperature dependence at this stage; further studies are required.

An alternative addition channel to give CH_3SNO_2 is possible, but there is no evidence for its occurrence up to a total pressure of 260 mbar. Both of the studies[1,2] in which the pressure was varied have reported no appreciable effect of pressure on the measured rate coefficient, and product studies[2,5] are consistent with the reaction occurring predominantly by formation of NO and CH_3SO. Other reaction channels are likely to be very minor.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986).

[2] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).

[3] F. Domine, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).

[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

[5] I. Barnes, V. Bastian, K. H. Becker, and H. Niki, Chem. Phys. Lett. **140**, 451 (1987).

$CH_3SO + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1×10^{-12}	298	Tyndall and Ravishankara, 1989[1]	(a)
Reviews and Evaluations			
1×10^{-12}	298	NASA, 1990[2]	(b)

Comments

(a) Study of the $CH_3S + O_3$ reaction by pulsed laser photolysis of $CH_3SH–H_2O–O_3$ mixtures. CH_3S radicals were monitored by LIF at 371.4 nm. CH_3SO radicals were produced by $CH_3S + O_3 \rightarrow CH_3SO + O_2$, and the reaction of CH_3SO with O_3 yielded CH_3S radicals through an uncertain mechanism. Modeling of the CH_3S time-concentration profile gave the rate coefficient k.

(b) Accepted the rate coefficient of Tyndall and Ravishankara.[1]

Preferred Values

$k = 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

Comments on Preferred Values

The only available value for this rate coefficient was obtained from the analysis of secondary reactions in a complex system.[1] This value[1] is accepted, but because of the indirect nature of the measurement very substantial error limits are recommended.

References

[1]G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CH_3SO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3 \pm 2) \times 10^{-11}$	298	Mellouki, Jourdain, and Le Bras, 1988[1]	(a)
$(8 \pm 5) \times 10^{-12}$	298	Tyndall and Ravishankara, 1989[2]	(b)
$(1.2 \pm 0.25) \times 10^{-11}$	298	Domine, Murrells and Howard, 1990[3]	(c)
Reviews and Evaluations			
1.2×10^{-11}	298	NASA, 1990[4]	(d)

Comments

(a) Discharge flow study of the $Cl + CH_3SH$ reaction in the presence of NO_2. Cl atoms were generated by a discharge in Cl_2–He mixtures. Cl atoms were monitored by EPR, other species (CH_3SH, NO, SO_2, CH_3SO) by MS. The NO, CH_3SH and NO time-concentration profiles were modeled using an assumed reaction mechanism, and the rate coefficient k derived from a best fit.

(b) A study of $CH_3S + NO_2$ reaction by pulsed laser photolysis of $(CH_3S)_2–NO_2–He–N_2$ mixtures at 248 nm. CH_3S, OH and NO were monitored by LIF. NO was produced from the reaction of NO_2 with CH_3SO. The NO time-concentration was modeled to give the rate coefficient k. Yield of NO from reaction = 0.8 ± 0.2.

(c) Discharge flow study with He as the carrier gas. CH_3SO radicals were produced by the reaction $O(^3P) + (CH_3S)_2 \rightarrow CH_3S + CH_3SO$. CH_3S and CH_3SO radicals were monitored by Lyman-α photoionization MS. Some work was carried out using the $O(^3P) + CH_3SSC_2H_5$ reaction as a source of CH_3SO radicals.

(d) Accepted the rate coefficient of Domine *et al.*[3]

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The measured rate coefficients[1-3] at 298 K agree within their error limits (some of which are substantial). The preferred value is that of Domine *et al.*,[3] which lies between the other two values,[1,2] both of which have much larger error limits. This rate coefficient is difficult to measure because of the lack of a clean primary source of CH_3SO radicals and the complexity of the secondary chemistry; substantial error limits are suggested.

References

[1]A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett. **148**, 231 (1988).
[2]G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).
[3]F. Domine, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$O_3 + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<8.3 \times 10^{-19}$	296	Martinez and Herron, 1978[1]	(a)
Reviews and Evaluations			
$<1 \times 10^{-18}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Static system with MS detection of O_3.
(b) See Comments on Preferred Values.

Preferred Values

$k < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989[2]. The preferred value is based upon the sole study of Martinez and Herron.[1]

References

[1]R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet. **10**, 433 (1978).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

OCS + $h\nu \rightarrow$ products

Primary photochemical processes

Reactions	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
OCS + $h\nu \rightarrow$ CO + S(^{3}P) (1)	308	388
$\rightarrow$ CO + S(^{1}D) (2)	419	286

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–270	Rudolf and Inn, 1981[1]	(a)
185–300	Molina, Lamb, and Molina, 1981[2]	(b)
196–257	Locker *et al.*, 1983[3]	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.72 \pm 0.08$	214–253.7	Rudolf and Inn, 1981[1]	(d)

Comments

(a) At a spectral resolution of 0.01 nm at temperatures of 297 K and 195 K. A value of $\sigma_{max} = 3.13 \times 10^{-19}$ cm^2 was determined at 223.5 nm and 297 K. With a decrease in temperature from 297 to 195 K, σ increased by ~5% at $\lambda < 226$ nm but at $\lambda > 226$ nm σ decreased with a decrease of temperature. The 297 K data were tabulated. A residual absorption at $\lambda < 280$ nm with $\sigma \approx 2 \times 10^{-22}$ cm^2 was also reported, extending to at least 300 nm. These results were first reported in Turco *et al.*[4]

(b) At a spectral resolution of 0.2 nm, at temperatures of 295 and 225 K. Data were given in figures and tables showing values averaged over 1 nm and averaged over wavelength intervals generally used in stratospheric photodissociation calculations. A value of $\sigma_{max} = 3.27 \times 10^{-19}$ cm^2 was determined at 223 nm. The observed temperature effects were similar to those reported in Ref. 1 and earlier work. The cross-sections at $\lambda < 280$ nm are significantly lower than those proposed by Rudolf and Inn.[1]

(c) σ measured at six temperatures (195, 273.2, 308.8, 335.2, 365.2, and 403.6 K). The COS was carefully purified, and sample pressures 2–100 Torr were employed, with a 50 cm path length with data points being obtained at 0.5 nm intervals. The results were presented in graphical form.

(d) Quantum yields for CO formation were determined using resonance fluorescence detection of CO in the fourth positive system of CO centered at 172.9 nm. Light sources were a deuterium lamp (220, 225.8, and 230 nm), Zn lamp (214 nm) and Hg lamp (253.7 nm) with appropriate filter systems. Temperature = 297 K. ϕ was independent of λ over this range. The quantum yield value was based on the assumption that all of the S atoms produced (^{3}P and ^{1}D) reacted with OCS to produce CO, for which earlier work[5,6] provided support.

Preferred Values

λ/nm	$10^{21}\ \sigma$/cm^2 295 K	225 K	ϕ	ϕ_2
300	0.0009			
295	0.0023	0.0013		
290	0.0077	0.0035		
285	0.0218	0.0084		
280	0.0543	0.0206		
275	0.1504	0.0607		
270	0.376	0.156		
265	0.960	0.423		
260	2.52	1.16	0.8	0.6
255	6.64	3.46	0.8	0.6
250	16.5	9.79	0.8	0.6
245	38.2	25.1	0.8	0.6
240	81.3	59.3	0.8	0.6
235	153.6	123.7	0.8	0.6
230	243.8	211.8	0.8	0.6
225	310.4	283.0	0.8	0.6
220	304.8	287.5	0.8	0.6
215	241.6	236.2	0.8	0.6
210	150.8	151.6		
205	82.0	82.5		
200	39.3	39.3		
195	20.2	18.9		
190	39.7	26.8		
185	190.3	135.7		

Comments on Preferred Values

There is good agreement among all of the recent cross-section studies for $\lambda < 280$ nm. At $\lambda > 280$ nm the data of Molina *et al.*[2] appear to be the most accurate. The higher values in Ref. 1 may be due to the presence of CS_2 or other unidentified trace contaminants or alternatively dimerization of OCS in the pressurized cell employed. The preferred values are 5 nm averages based on the data of Molina *et al.*[2] The results of Locker *et al.*,[3] presented in graphical form, agree with these values.

The preferred overall quantum yield of 0.80 is an average of the results of Rudolf and Inn[1] and the earlier work of Sidhu *et al.*,[5] which gave slightly higher values ($\phi_1 + \phi_2 = 0.9$), with $\phi_2/\phi \geq 0.72$. Breckenridge and Taube[6] obtained $\phi_2/\phi = 0.74 \pm 0.04$ and their results suggest strongly that S(^{3}P) production accounts for the balance. They did not, however, determine absolute values for the quantum yields. There is currently no evidence for fluorescence from OCS. This is difficult to reconcile with a photodissociation yield significantly less than unity.

References

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[6]W. H. Breckenridge and H. Taube, J. Chem. Phys. **53**, 1750 (1970).

$CS_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H^\circ_{298}/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CS_2 + h\nu \rightarrow CS_2^*$	(1)		>277
$\rightarrow CS + S(^3P)$	(2)	432	277
$\rightarrow CS + S(^1D)$	(3)	543	220

Absorption cross-section data

Wavelength range/nm	Reference	Comments
280–360	Wine, Chameides and Ravishankara, 1981[1]	(a)
318–330	Wu and Judge, 1981[2]	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi_{OCS} = 0.012$	281–350	Jones, Cox, and Penkett, 1983[3]	(c)

Comments

(a) At a spectral resolution of 0.4 nm. A value of $\sigma_{max} \approx 1 \times 10^{-19}$ cm^2 was determined at 320 nm. Temperature variation over range $250 < T < 325$ K produced little change in the averaged σ values. 298 K values were shown in graphical form.
(b) At a spectral resolution of 0.06 nm. A value of $\sigma_{max} = 1.1 \times 10^{-19}$ cm^2 was determined at 321.5 nm. Temperature = 294 K. A synchrotron continuum source was used, and the spectrum shown in graphical form.
(c) Quantum yield for OCS formation in overall photooxidation of CS_2 over wavelength region indicated. From steady-state photolysis of low partial pressures of CS_2 in air at 1 atm, $CS_2^* + O_2$ was suggested as the source of OCS.

Preferred Values

λ/nm	10^{21} σ/cm^2	λ/nm	10^{21} σ/cm^2
295	9.6	335	5.3
305	46	345	2.6
315	72	355	0.5
325	48		

Quantum Yield

$\phi_{OCS} = 0.012$ for 290–360 nm region in 1 bar air.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[4] The most recent studies confirm the structured nature of the absorption in the near UV band (290–350 nm). Since there is insufficient energy to dissociate CS_2 at $\lambda < 281$ nm, the photochemical reaction yielding OCS and SO_2 products, reported by Jones *et al.*[3] and in earlier work,[5,6] must arise from reactions involving excited CS_2 molecules. The quantum yield reported by

Jones *et al.*[3] is in good agreement with that estimated for CS_2 photolysis in air at 1 atm by Wine *et al.*[1] from the earlier data of Wood and Heicklen[5] (i.e., ϕ_{OCS} = 0.01–0.015). The preferred value is based on the data of Ref. 3 but might best be considered an upper limit since the observed slow oxidation of CS_2 could have been due, at least in part, to other mechanisms.

References

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$CH_3SSCH_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H^\circ_{298}/kJ \cdot mol^{-1}$	$\lambda_{threshold}$/nm
$CH_3SSCH_3 \rightarrow CH_3SS + CH_3$	(1)	238	502
$\rightarrow 2CH_3S$	(2)	273	438

Absorption cross-section data

Wavelength range/nm	Reference	Comments
201–360	Hearn, Turcu, and Joens, 1990[1]	(a)

Quantum yield data

No data available.

Comments

(a) Cary 2300 double beam UV spectrophotometer used with a resolution of 0.10 nm. Photolysis of $(CH_3)_2S_2$–N_2 mixtures at a constant pressure of 100 Torr. Temperature = 300 ± 2 K.

Preferred Values

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

Comments on Preferred Values

The preferred cross-section values are those of Hearn *et al.*,[1] which agree well with the earlier values of McMillan[2] and with the single value at 228.0 nm (σ = 116 × 10^{-20} cm^2) quoted by Wine *et al.*[3] While the spectrum of Sheraton and Murray[4] agrees qualitatively with the other studies, the reported absorption coefficients are significantly lower.

The thermochemistry suggests that formation of CH_3S is the sole dissociation process at wavelengths of importance to atmospheric photochemistry. Balla and Heiklen[5] reported a quantum yield for CH_3S formation of 2.04 ± 0.06 for light absorption in the range 280–300 nm, but as yet there are no definitive measurements of the quantum yields.

References

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$CH_3SNO + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3SNO \rightarrow CH_3S + NO$	(1)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190–430	Niki *et al.*, 1983[1]	(a)

Quantum yield data

No data available.

Comments

(a) Cary 14 double beam spectrophotometer used; the spectral resolution was not reported. Measurements of σ were made over the range 190–600 nm, but only the results in the range 190–430 nm were given in graphical form. Values of σ = 2.4 × 10^{-20} and 5.8 × 10^{-20} cm^2 were quoted for 510 and 545 nm, respectively. Values given in the table were taken from graph. Temperature = 298 K.

Preferred Values

λ/nm	10^{19} σ/cm^2	λ/nm	10^{19} σ/cm^2
190	5	310	14.9
195	104	320	18.5
200 (max)	162	330	21.3
205	91	335 (max)	21.6
210 (min)	81	340	21.5
215	98	350	19.6
218 (max)	104		
220	96	360	16.5
225	73	370	12.7
230	40	380	9.6
240	16	390	6.7
250	3.5	400	4.5
260	1.7	410	2.9
264 (min)	1.5	420	2.0
270	1.8	430	1.3
280	2.7		
290	5.2	510	0.24
300	9.3	545	0.58

Comments on Preferred Values

The spectrum of CH_3SNO consists of a weak transition in the 500–600 nm region showing some vibrational fine structure and stronger continuous bands at shorter wavelengths.[2] The CH_3S–NO dissociation energy has been estimated[3] to be ~ 110 kJ·mol^{-1}, but because more reliable data are not available we do not give wavelength limits for this dissociation channel.

The only available cross-section data in the gas phase appear to be those of Niki *et al.*,[1] who have published their results mainly in the form of graphs covering the range 190–430 nm. Their published spectrum shows no fine structure but appears to consist of overlapping continua with three maxima at approximately 200, 218 and 335 nm. The preferred values of σ in the range 190–430 nm are taken from the graphs of Niki *et al.*[1] and cannot be considered to be very precise. The two values at 510 and 545 nm are numerical values quoted in the same study.[1]

There have been no quantum yield measurements. By analogy with CH_3ONO photolysis, the primary products are expected to be CH_3S and NO. This is supported by the work of McCoustra and Pfab[2] who studied the photodissociation of CH_3SNO in a molecular beam and the study of Niki *et al.*[1] who found CH_3SSCH_3 and NO to be the only major products from CH_3SNO photolysis at 300–400 nm.

References

[1]H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **87**, 7 (1983).

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4.6 Fluorine Species

$O + FO \rightarrow O_2 + F$

$\Delta H° = -279$ kJ·mol^{-1}

Rate coefficient data: no available experimental data

Preferred Values

$k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[1] There are no experimental data. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of ClO and BrO. The temperature dependence of the rate constant is expected to be small, as for the analogous ClO reaction.

References

[1]CODATA, 1980 (see references in Introduction).

$O + FO_2 \rightarrow O_2 + FO$

$\Delta H° = -166$ kJ·mol^{-1}

Rate coefficient data: no available experimental data

Preferred Values

$k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[1] There are no experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency and is not expected to exhibit a strong temperature dependence.

Reference

[1]CODATA, 1980 (see references in Introduction).

$O(^1D) + HF \rightarrow HO + F$ (1)
$\rightarrow O(^3P) + HF$ (2)

$\Delta H°(1) = -47$ kJ·mol^{-1}
$\Delta H°(2) = -190$ kJ·mol^{-1}

Rate coefficient data: no available experimental data.

Preferred Values

$k = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[1] k is assumed to be comparable to most other $O(^1D)$ rate constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence.

Reference

[1]CODATA, 1980 (see references in Introduction).

$$O(^1D) + COF_2 \rightarrow CO_2 + F_2 \quad (1)$$
$$\rightarrow O(^3P) + COF_2 \quad (2)$$

$\Delta H°(1) = -197$ kJ·mol^{-1}
$\Delta H°(2) = -190$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.6 \pm 0.4) \times 10^{-10}$	298	Fletcher and Husain, 1978[1]	(a)
$(7.4 \pm 1.2) \times 10^{-11}$	298	Wine and Ravishankara, 1983[2]	(b)
Relative Rate Coefficients			
4.8×10^{-11}	298	Jayanty, Simonaitis, and Heicklen, 1976[3]	(c)
$k_1 = 3.4 \times 10^{-11}$	298	Atkinson *et al.*, 1976[4]	(d)
Branching Ratios			
$k_2/k = 0.71 \pm 0.07$	298	Wine and Ravishankara, 1983[2]	(b)
Reviews and Evaluations			
$k_1 = 2.2 \times 10^{-11}$	298	CODATA, 1984[5]; IUPAC, 1989[6]	(e)
$k_2 = 5.2 \times 10^{-11}$	298		
7.4×10^{-11}	298	NASA, 1990[7]	(f)

Comments

(a) Flow system. $[O(^1D)]$ monitored by time-resolved resonance absorption at 115 nm. Data analysis used modified Beer-Lambert law.

(b) Pulsed laser photolysis of O_3 at 248 nm. $[O(^3P)]$ monitored by time-resolved resonance fluorescence. Relative importance of deactivation determined by comparison of $[O(^3P)]$ with N_2 as dominant quencher to that with COF_2 as predominant quencher.

(c) Photolysis of O_3–N_2O–COF_2 mixtures at 254 nm. Rate of formation of N_2 measured. Value of k derived from measured ratio, $k/k[O(^1D) + N_2O] = 0.41$ and $k[O(^1D) + N_2O] = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Evidence presented for some chemical reaction.

(d) Photolysis of NO_2 at 229 nm. $[COF_2]$ and $[N_2O]$ monitored by infrared absorption spectroscopy. Value of k_1 derived from measured ratio, $k_1/k[O(^1D) + N_2O] = 0.29 \pm 0.04$ and $k[O(^1D) + N_2O] = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) See Comments on Preferred Values.

(f) Based on results of Wine and Ravishankara.[2]

Preferred Values

$k_1 = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1 = \Delta\log k_2 = \pm 0.2$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[5] The preferred values for k_1 and k_2 are based on the results reported in the study of Wine and Ravishankara,[1] which is much more direct than the other studies. Both the overall rate and the branching ratio reported in this study are accepted. The technique of Fletcher and Husain[1] has given problems in the past for well-studied similar reactions, and the value reported appears unacceptably high.

References

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[6] IUPAC, Supplement III, 1989 (see references in Introduction).
[7] NASA Evaluation No. 9, 1990 (see references in Introduction).

O(^{1}D) + HFCs → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×10^{-10} CH_3F	298	Force and Wiesenfeld, 1981[1]	(a)
8.4×10^{-12} CHF_3	298		
9.8×10^{-11} CHF_3	298	Fletcher and Husain, 1976[2]	(b)
Relative Rate Coefficients			
4.8×10^{-11} CH_2F_2	298	Green and Wayne, 1976[3]	(c)
6×10^{-11} CH_3CF_3	298		
4.8×10^{-11} CHF_2CF_3	298		
Reviews and Evaluations			
1.4×10^{-10} CH_3F	200–300	NASA, 1990[4]	(d)
9×10^{-11} CH_2F_2	200–300		
8.4×10^{-12} CHF_3	200–300		
1×10^{-10} CH_3CHF_2	200–300		
1×10^{-10} CH_3CF_3	200 300		
1×10^{-10} CH_2FCF_3	200–300		
5×10^{-11} CHF_2CF_3	200–300		

Comments

(a) Laser flash photolysis of O_3 at 248 nm. Time-resolved production of O(^{3}P) was monitored by resonance absorption at 130 nm.

(b) Flash photolysis of O_3. O(^{1}D) was monitored by time-resolved resonance absorption at 115 nm. The data analysis used modified Beer-Lambert law.

(c) O(^{1}D) produced by photolysis of NO_2 at 229 nm. Monitored Δ[HFC]/Δ[N_2O] by IR absorption spectrometry. Relative rate coefficients k/k(O(^{1}D) + N_2O) placed on an absolute basis by use of k(O(^{1}D) + N_2O) from this evaluation. The cited rate coefficients refer to chemical reaction only and do not include physical quenching.

(d) CH_3F and CHF_3: based on results of Force and Wiesenfeld.[1] CH_2F_2, CH_3CF_3, and CHF_2CF_3: based on results of Green and Wayne.[3] CH_3CHF_2 and CH_2FCF_3: estimated by analogy.

Preferred Values

CH_3F $k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2F_2 $k = 9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CHF_3 $k = 8.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CHF_2 $k = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_3CF_3 $k = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CH_2FCF_3 $k = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
CHF_2CF_3 $k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

Δlog k = ±0.5 at 298 K for CH_3F, CH_2F_2, CHF_3, CH_3CF_3, and CHF_2CF_3.

Δlog k = ±0.7 at 298 K for CH_3CHF_2 and CH_2FCF_3.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of O(^{1}D) atoms and include both physical quenching and chemical reaction. Because these rate coefficients have such high values (nearly collisional) at 298 K, they can be assumed to be temperature-independent. Specific comments are as follows:

CH_3F Based on the results of Force and Wiesenfeld[1] who also reported 25% physical quenching.

CH_2F_2 Based on the results of the relative rate study of Green and Wayne[3] with an estimated 50% physical quenching.

CHF_3 Based on the results of Force and Wiesenfeld,[1] who also reported 77% physical quenching.

CH_3CHF_2 Estimated by analogy with CH_3CF_3 and CH_3F.

CH_3CF_3 Based on the results of Green and Wayne.[3]

CH_2FCF_3 Estimated by analogy with CH_2F_2.

CHF_2CF_3 Based on the results of Green and Wayne.[3]

References

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[2]I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[3]R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1976).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$F + H_2 \rightarrow HF + H$

$\Delta H^\circ = -135$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.2×10^{-10} exp[$-(470 \pm 30)/T$]	221–376	Stevens, Brune and Anderson, 1989[1]	(a)
Reviews and Evaluations			
1.9×10^{-10} exp($-570/T$)	190–770	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
1.4×10^{-10} exp($-500/T$)	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system. F atoms reacted with D_2 to produce D atoms. D atom decay monitored by resonance fluorescence.

(b) Based on the temperature-dependent studies of Heidner *et al.*,[5] Wurzberg and Houston,[6] Igoshin *et al.*,[7] and the room temperature studies of Zhitneva and Pshezhetskii,[8] Dodonov *et al.*[9] and Clyne *et al.*[10]

(c) Based on the results cited in (b) and those of Clyne and Hodgson[11] and Stevens *et al.*[1]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-10}$ exp($-500/T$) cm^3 molecule^{-1} s^{-1} over the range 200–375 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The value of k at 298 K seems to be well established with the results reported by Zhitneva and Pshezhetskii,[8] Heidner *et al.*,[5] Wurzberg and Houston,[6] Dodonov *et al.*,[9] Clyne *et al.*,[10] Igoshin *et al.*,[7] Clyne and Hodgson[11] and Stevens *et al.*[1] being in good agreement; the preferred value at 298 K is the mean of these values. Reported values of E/R range from 433–595 K (Refs. 1 and 5–7). The preferred value of E/R is derived from a least-squares fit to the data in these studies, and the A-factor was chosen to fit the recommended room temperature value.

References

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$F + H_2O \rightarrow HF + HO$

$\Delta H^\circ = -72$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.1) \times 10^{-11}$	298	Frost *et al.*, 1986[1]	(a)
$1.6 \times 10^{-11} \exp[-(28 \pm 42)/T]$	240–373	Stevens, Brune and Anderson, 1989[2]	(b)
Reviews and Evaluations			
$4.2 \times 10^{-11} \exp(-400/T)$	240–370	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
1.4×10^{-11}	240–370	NASA, 1990[5]	(d)

Comments

(a) Laser flash photolysis at 308 nm; HF chemiluminescence monitored.
(b) Discharge flow system. F atoms reacted with D_2 to yield D atoms. D atom decay monitored by resonance fluorescence.
(c) Based on results of Walther and Wagner.[6]
(d) Based on results of Stevens *et al.*[2]

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 240–370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommended temperature-independent value is based on the results reported by Stevens *et al.*[2] This value is in good agreement with the room temperature results of Frost *et al.*[1] and Walther and Wagner.[6] The latter authors in a limited temperature study reported an E/R value of 400 K. Although these data have not been used in derivation of the preferred value, with the exception of the one low temperature data point they are within the stated uncertainty limit.

References

[1] R. J. Frost, D. S. Green, M. K. Osborn, and I. W. M. Smith, Int. J. Chem. Kinet. **18**, 885 (1986).
[2] P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).
[3] CODATA, Supplement II, 1984 (see references in Introduction).
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$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H° = -53$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3 \pm 0.4) \times 10^{-33}(T/300)^{-1}$ [Ar]	295–359	Pagsberg *et al.*, 1987[1]	(a)
$(2.8 \pm 0.2) \times 10^{-33}$ [He]	298	Lyman and Holland, 1988[2]	(b)
$(3.1 \pm 0.2) \times 10^{-33}$ [Ar]	298		
Reviews and Evaluations			
$4.3 \times 10^{-33}(T/300)^{-1.4}$ [N_2]	200–300	IUPAC, 1989[3]	(c)
$4.4 \times 10^{-33}(T/300)^{-1.2}$ [air]	200–300	NASA, 1990[4]	(d)

Comments

(a) Pulsed radiolysis of $Ar–F_2–O_2$ mixtures, with UV absorption detection of FO_2 radicals at 220 nm. The rate coefficient and the equilibrium constant were determined by varying the O_2 concentration. A value of $\Delta H° = -52.8$ kJ·mol^{-1} was derived.

(b) Laser photolysis of F_2 at 248 nm in the presence of O_2 and bath gases. The reaction mechanism with six reactions was followed via the analysis of transient absorption signals at 215 nm. The forward and backward rate coefficients of the reactions $F + O_2 + M \rightarrow FO_2 + M$ and $F + FO_2 + M \rightarrow F_2O_2 + M$ were determined. A value of $\Delta H° = -(56.4 \pm 1.7)$ kJ·mol^{-1} was derived.

(c) Based on the data of reference 1. It was assumed that $k_0(Ar):k_0(N_2) = 1$. The calculated temperature coefficient[5] is in accord with the experimental observation from Ref. 1.

(d) Based on data from reference 1 and on earlier measurements.[6-11] The value of k_0(Ar) from reference 2 is slightly smaller than previous measurements.

Preferred Values

$k_0 = 3.7 \times 10^{-33}(T/300)^{-1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred rate coefficient is an average of the two most recent determinations[1,2] for M = Ar. We assume k_0 to be similar for M = Ar and N_2.

References

[1] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).

[2] J. L. Lyman and R. Holland, J. Phys. Chem. **92**, 7232 (1988).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

[5] R. Patrick and D. M. Golden, Int. J. Chem. Kinet. **15**, 1189 (1983).

[6] V. S. Arutyunov, K. S. Popov, and A. M. Chaikin, Kinetika i Kataliz. **17**, 286 (1976).

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[8] N. F. Shamonina and A. G. Kotov, Kinetika i Kataliz **20**, 233 (1979).

[9] I. W. M. Smith and D. J. Wrigley, Chem. Phys. Lett. **70**, 481 (1980).

[10] I. W. M. Smith and D. J. Wrigley, Chem. Phys. **63**, 321 (1981).

[11] H. L. Chen, D. W. Trainor, R. E. Center, and W. I. Fyfe, J. Chem. Phys. **66**, 5513 (1977).

$FO_2 + M \rightarrow F + O_2 + M$

$\Delta H° = 53$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.8×10^{-17} [Ar]	295	Pagsberg *et al.*, 1987[1]	(a)
3.1×10^{-17} [Ar]	312.5		
2.8×10^{-16} [Ar]	359		
$(2.5 \pm 1.0) \times 10^{-18}$ [He]	298	Lyman and Holland, 1988[2]	(b)
Reviews and Evaluations			
2.2×10^{-17} [N_2]	298	IUPAC, 1989[3]	(c)

Comments

(a) Pulsed radiolysis of Ar–F_2–O_2 mixtures with UV absorption detection of FO_2 radicals at 220 nm. The rate of approach to equilibrium was monitored and the equilibrium constant measured. A value of $\Delta H° = 52.8$ kJ·mol^{-1} was derived by a third-law analysis.
(b) Laser photolysis of F_2 at 248 nm in the presence of O_2 and bath gases. Transient absorption at 215 nm was monitored and approach of equilibrium was analyzed. A value of $\Delta H° = 56.4$ kJ·mol^{-1} was derived.
(c) Based on Ref. 1.

Preferred Values

No recommendation.

Comments on Preferred Values

Although the data in Refs. 1 and 2 on the formation of FO_2 in the reverse reaction $F + O_2 + M \rightarrow FO_2 + M$ agree, the derived equilibrium constants and the corresponding values of k_0 differ by more than a factor of 5. Since the origin of this discrepancy is not understood, we cannot make a recommendation.

References

[1] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).
[2] J. L. Lyman and R. Holland, J. Phys. Chem. **92**, 7232 (1988).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).

$F + O_3 \rightarrow FO + O_2$

$\Delta H° = -113$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.8×10^{-11} exp[$-(226 \pm 200)/T$]	253–365	Wagner, Zetzsch, and Warnatz, 1972[1]	(a)
1.3×10^{-11}	298		
Reviews and Evaluations			
2.8×10^{-11} exp($-230/T$)	250–365	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
2.8×10^{-11} exp($-230/T$)	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with MS detection of O_3.
(b) See Comments on Preferred Values.
(c) Based on data of Wagner *et al.*[1]

Preferred Values

$k = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-11}$ exp($-230/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 250–365 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[2] This is the only experimental study of this reaction. The value appears to be quite reasonable by analogy with the reactivity of atomic chlorine with ozone.

References

[1]H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).
[2]CODATA, 1980 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$F + HONO_2 \rightarrow HF + NO_3$

$\Delta H° = -153$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.5) \times 10^{-11}$	298	Mellouki, Le Bras and Poulet, 1987[1]	(a)
$(2.1 \pm 1) \times 10^{-11}$	298	Rahman *et al.*, 1988[2]	(b)
$6.0 \times 10^{-12} \exp[(400 \pm 120)/T]$	260–320	Wine, Wells and Nicovich, 1988[3]	(c)
$(2.3 \pm 0.1) \times 10^{-11}$	298		
Reviews and Evaluations			
$6.0 \times 10^{-12} \exp(400/T)$	200–300	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with EPR detection of F.
(b) Discharge flow system with MS detection of HF, NO_3 and HNO_3.
(c) Pulsed laser photolysis at 351 nm with long-path laser absorption of NO_3 at 662 nm. At higher temperatures (335–373 K), the rate coefficient was found to be independent of temperature with a value of $(2.0 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
(d) Based on results of the temperature-dependent study of Wine *et al.*[3] and the room temperature results of Mellouki *et al.*[1] and Rahman *et al.*[2]

Preferred Values

$k = 2.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.0 \times 10^{-12} \exp(400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–320 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommendation is based on results of the temperature-dependent study of Wine *et al.*[3] and the room temperature results of Mellouki *et al.*[1] and Rahman *et al.*[2] The values at room temperature are in good agreement. The study of Wine *et al.*[3] was over the temperature range 260–373 K; below 320 K the authors fitted their data with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

References

[1]A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **91**, 5760 (1987).
[2]M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).
[3]P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. **92**, 2223 (1988).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$F + CH_4 \rightarrow HF + CH_3$

$\Delta H° = -132$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.72 \pm 0.30) \times 10^{-11}$	298	Fasano and Nogar, 1982[1]	(a)
Reviews and Evaluations			
$3.0 \times 10^{-10} \exp(-400/T)$	250–450	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$3.0 \times 10^{-10} \exp(-400/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) Infrared multiphoton dissociation of SF_6 in mixture of CH_4, D_2, and Ar. First-order decay of [F] monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gave values for k and for k ($F + D_2 \rightarrow DF + D$).
(b) See Comments on Preferred Values.
(c) Based on absolute values of Wagner *et al.*,[5] Clyne *et al.*[6] and Kompa and Wanner,[7] and on relative results of Foon and Reid[8] and Pollock and Jones.[9]

Preferred Values

$k = 8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.0 \times 10^{-10} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The preferred value is based on the room-temperature results of Clyne *et al.*,[6] Kompa and Wanner,[7] Pollock and Jones[9] and Fasano and Nogar,[1] the 298–450 K results of Wagner *et al.*,[5] and the 253–348 K results of Foon and Reid.[8]

References

[1]D. M. Fasano and N. S. Nogar, Chem. Phys. Lett. **92**, 411 (1982).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]H. Gg. Wagner, J. Warnatz, and C. Zetzsch, An. Assoc. Ouim. Argentina **59**, 169 (1971).
[6]M. A. A. Clyne, D. J. McKenney, and R. F. Walker, Can. J. Chem. **51**, 3596 (1973).
[7]K. L. Kompa and J. Wanner, Chem. Phys. Lett. **12**, 560 (1972).
[8]R. Foon and G. P. Reid, Trans. Faraday Soc. **67**, 3513 (1971).
[9]T. L. Pollock and W. E. Jones, Can. J. Chem. **51**, 2041 (1973).

$HO + CH_3F$ (HFC-41) $\rightarrow H_2O + CH_2F$

$\Delta H° = -80.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.35) \times 10^{-14}$	296 ± 2	Howard and Evenson, 1976[1]	(a)
$(2.17 \pm 0.18) \times 10^{-14}$	297 ± 2	Nip *et al.*, 1979[2]	(b)
$7.96 \times 10^{-25} T^{4.32} \exp[-(277 \pm 730)/T]$	292–480	Jeong and Kaufman, 1982[3,4]	(c)
$(1.40 \pm 0.09) \times 10^{-14}$	292		
$(1.71 \pm 0.24) \times 10^{-14}$	308	Bera and Hanrahan, 1988[5]	(d)
Reviews and Evaluations			
$5.51 \times 10^{-18} T^2 \exp(-1005/T)$	292–480	Atkinson, 1989[6]	(e)
$5.4 \times 10^{-12} \exp(-1700/T)$	292–400	NASA, 1990[7]	(f)

Comments

(a) Discharge flow system with LMR detection of HO.
(b) Flash photolysis system with UV absorption detection of HO.
(c) Discharge flow system with resonance fluorescence detection of HO.
(d) Pulsed radiolysis generation of HO radicals with detection by UV absorption.
(e) Derived from the absolute rate coefficient data of Howard and Evenson,[1] Nip *et al.*[2] and Jeong and Kaufman.[3,4]
(f) The 298 K rate coefficient was derived from the absolute rate coefficients of Howard and Evenson,[1] Nip *et al.*[2] and Jeong and Kaufman.[3,4] The temperature dependence was derived from the data of Jeong and Kaufman[3,4] below 400 K.

Preferred Values

$k = 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-12} \exp(-1600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range ~270–340 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson,[1] Nip *et al.*,[2] Jeong and Kaufman[3,4] and Bera and Hanrahan[5] are in reasonably good agreement at around room temperature. Since secondary reactions of HO radicals with CH_2F radicals and other radical species were expected to have occurred in the study of Bera and Hanrahan,[5] the rate coefficient of Bera and Hanrahan[5] was not used in the evaluation. The absolute rate coefficients of Howard and Evenson,[1] Nip *et al.*[2] and Jeong and Kaufman[3,4] were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 5.51 \times 10^{-18} T^2 \exp(-1005/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 292–480 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. Note that no experimental rate coefficient data are available below 292 K.

References

[1]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2]W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[3]K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
[4]K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[5]R. K. Bera and R. J. Hanrahan, Radiat. Phys. Chem. **32**, 579 (1988).
[6]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

$\Delta H^\circ = -67.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.8 \pm 1.2) \times 10^{-15}$	296 ± 2	Howard and Evenson, 1976[1]	(a)
$7.4 \times 10^{-12} \exp[-(2100 \pm 200)/T]$	293–429	Clyne and Holt, 1979[2]	(b)
$(5.8 \pm 0.3) \times 10^{-15}$	293		
$(1.17 \pm 0.14) \times 10^{-14}$	297 ± 2	Nip *et al.*, 1979[3]	(c)
$2.52 \times 10^{-21} T^{3.09} \exp[-(679 \pm 458)/T]$	250–492	Jeong and Kaufman, 1982[4,5]	(b)
$(1.12 \pm 0.075) \times 10^{-14}$	298		
$(8.8 \pm 1.4) \times 10^{-15}$	308	Bera and Hanrahan, 1988[6]	(d)
$1.57 \times 10^{-12} \exp[-(1470 \pm 100)/T]$	222–381	Talukdar *et al.*, 1991[7]	(e)
$(1.13 \pm 0.10) \times 10^{-14}$	298		
Reviews and Evaluations			
$5.06 \times 10^{-18} T^2 \exp(-1107/T)$	250–492	Atkinson, 1989[8]	(f)
$2.5 \times 10^{-12} \exp(-1650/T)$	250–400	NASA, 1990[9]	(g)

Comments

(a) Discharge flow system with LMR detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) Flash photolysis system with UV absorption detection of HO.
(d) HO radicals generated by pulsed radiolysis and detected by UV absorption.
(e) Flash photolysis system with LIF detection of HO.
(f) Derived from the absolute rate coefficient data of Howard and Evenson,[1] Nip *et al.*[3] and Jeong and Kaufman.[4]
(g) The 298 K rate coefficient was obtained from the rate coefficients of Howard and Evenson,[1] Nip *et al.*[3] and Jeong and Kaufman.[4] The temperature dependence was derived from the rate coefficient data of Jeong and Kaufman[4] below 400 K, with the A-factor being adjusted to fit the 298 K rate coefficient.

Preferred Values

$k = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-12} \exp(-1545/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta\log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The room temperature rate coefficients of Nip *et al.*,[3] Jeong and Kaufman[4] and Talukdar *et al.*[7] are in good agreement, but are ~30% higher than those of Howard and Evenson,[1] Clyne and Holt[2] and Bera and Hanrahan.[6] The data of Clyne and Holt[2] are not considered reliable,[8,9] and that of Bera and Hanrahan[6] may have been subject to secondary reactions. The rate coefficients measured by Jeong and Kaufman[4] (250–492 K) and Talukdar *et al.*[7] (222–381 K) are in good agreement over the temperature range where they overlap. The rate coefficient data of Howard and Evenson,[1] Nip *et al.*,[3] Jeong and Kaufman[4] and Talukdar *et al.*,[7] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.84 \times 10^{-18} T^2 \exp(-1016/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 222–492 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

[1]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[3]W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[4]K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
[5]K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[6]R. K. Bera and R. J. Hanrahan, Radiat. Phys. Chem. **32**, 579 (1988).
[7]R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).
[8]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[9]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CHF_3$ (HFC–23) $\rightarrow H_2O + CF_3$

$\Delta H° = -50.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2^{+2}_{-1.5}) \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976[1]	(a)
$(5.5\text{–}9.3) \times 10^{-13}$	1255–1445	Ernst, Wagner and Zellner,1978[2]	(b)
$(1.3 \pm 0.4) \times 10^{-15}$	296	Clyne and Holt, 1979[3]	(c)
$(1.4 \pm 0.6) \times 10^{-15}$	430		
$(3.5 \pm 1.7) \times 10^{-16}$	297 ± 2	Nip *et al.*, 1979[4]	(d)
$2.98 \times 10^{-12} \exp[-(2909 \pm 156)/T]$	387–480	Jeong and Kaufman, 1982[5,6]	(c)
1.7×10^{-16}	298*		
Reviews and Evaluations			
$1.49 \times 10^{-18} T^2 \exp(-1887/T)$	387–1445	Atkinson, 1989[7]	(e)
$1.5 \times 10^{-12} \exp(-2650/T)$	296–410	NASA, 1990[8]	(f)

Comments

(a) Discharge flow system with LMR detection of HO.
(b) Flash photolysis study (gas mixture heated by shock wave) with UV absorption detection of HO. Reference should be consulted for rate coefficients at the various temperatures studied.
(c) Discharge flow system with resonance fluorescence detection of HO.
(d) Flash photolysis system with UV absorption detection of HO.
(e) Derived from the absolute rate coefficient data of Ernst *et al.*[2] and Jeong and Kaufman,[5,6] using the three parameter equation $k = CT^2 \exp(-D/T)$.
(f) Derived from the 296 K rate coefficient of Howard and Evenson[1] and the 387 and 410 K rate coefficients of Jeong and Kaufman.[5,6]

Preferred Values

$k = 2.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.0 \times 10^{-12} \exp(-2490/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range ~270–340 K.

Reliability
$\Delta\log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The rate coefficients measured at ~298 K by Howard and Evenson,[1] Nip *et al.*[4] and Clyne and Holt[3] are highly uncertain, due to the low rate coefficient (note the reported invariance of the rate coefficient over the range 296–430 K from the study of Clyne and Holt[3]). The absolute rate coefficients of Ernst *et al.*[2] and Jeong and Kaufman[5,6] have been fitted to the three parameter equation, $k = CT^2 \exp(-D/T)$, resulting in $k = 1.49 \times 10^{-18} T^2 \exp(-1887/T)$ cm^3 molecule^{-1} s^{-1} over the range 387–1445 K. At 298 K, this equation yields $k = 2.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, in agreement within the error limits with the room temperature rate coefficients of Howard and Evenson[1] and Nip *et al.*[4] The preferred Arrhenius expression, $k = A \exp(-B/T)$, was obtained from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$, and is centered at 300 K.

References

[1]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2]J. Ernst, H. Gg. Wagner, and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 409 (1978).
[3]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[4]W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[5]K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
[6]K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[7]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).
[8]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_3CH_2F$ (HFC–161) $\rightarrow H_2O + CH_3CHF$ (1)
$\rightarrow H_2O + CH_2CH_2F$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.32 \pm 0.37) \times 10^{-13}$	297 ± 2	Nip *et al.*, 1979[1]	(a)
Branching Ratios			
$k_1/k = 0.85 \pm 0.03$	297	Singleton, Paraskevopoulos and Irwin, 1980[2]	(b)
Reviews and Evaluations			
$1.3 \times 10^{-11} \exp(-1200/T)$	~298	NASA, 1990[3]	(c)

Comments

(a) Flash photolysis system with UV absorption detection of HO.
(b) Product study carried out using GC.
(c) The 298 K rate coefficient was based on the rate coefficient of Nip *et al.*,[1] and the temperature dependence was estimated.

Preferred Values

$k = 2.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.85$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta k_1/k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The 298 K rate coefficient and branching ratio are taken from the studies of Nip *et al.*[1] and Singleton *et al.*[2]

References

[1]W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[2]D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Phys. Chem. **84**, 2339 (1980).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_3CHF_2$ (HFC–152a) $\rightarrow H_2O + CH_2CHF_2$ (1)
$\rightarrow H_2O + CH_3CF_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$9.6 \times 10^{-13} \exp[-(940 \pm 130)/T]$	270–400	Liu, Huie and Kurylo, 1990[1]	(a)
$(4.22 \pm 0.45) \times 10^{-14}$	298		
$1.42 \times 10^{-12} \exp[-(1050 \pm 250)/T]$	220–423	Brown *et al.*, 1990[2]	(b)
$(5.6 \pm 2.3) \times 10^{-14}$	303		
$1 \times 10^{-12} \exp[-(980 \pm 50)/T]$	212–349	Gierczak *et al.*, 1991[3]	(c)
$(3.76 \pm 0.60) \times 10^{-14}$	298		
Reviews and Evaluations			
3.4×10^{-14}	298	IUPAC, 1989[4]	(d)
3.4×10^{-14}	295	Atkinson, 1989[5]	(d)
$1.5 \times 10^{-12} \exp(-1100/T)$	212–400	NASA, 1990[6]	(e)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) Laser photolysis system with LIF detection of HO and a discharge flow system with LMR detection of HO used.
(d) Mean of the room temperature rate coefficients of Howard and Evenson,[7] Handwerk and Zellner[8] and Nip *et al.*[9] The data of Clyne and Holt[10] were not used in the evaluation.
(e) The rate expression was derived from the rate coefficient data of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*[1] and the, as then unpublished, data of Gierczak *et al.*[3]

Preferred Values

$k = 3.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.0 \times 10^{-12} \exp(-990/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The absolute rate coefficient data of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*,[1] Brown *et al.*[2] and Gierczak *et al.*[3] are in reasonably good agreement at room temperature, and the temperature dependent studies of Liu *et al.*,[1] Brown *et al.*[2] and Gierczak *et al.*[3] also agree well. As in previous evaluations[4–6] the data of Clyne and Holt[10] are omitted; they are significantly higher than the other literature data[1–3,7–9] over the entire temperature range studied by Clyne and Holt.[10] The absolute rate coefficients measured by Brown *et al.*[2] are subject to large uncertainties, as evidenced by the high standard deviations cited at several temperatures, especially at 220 K and 303 K. Because of this and the observations that in general the rate coefficients of Brown *et al.*[2] are significantly higher than those of other recent studies (see the data sheets for other OH + HCFC and HFC reactions in this evaluation), these data of Brown *et al.*[2] were not used in the evaluation of the rate coefficient for this reaction.

The absolute rate coefficient data of Howard and Evenson,[7] Handwerk and Zellner,[8] Nip *et al.*,[9] Liu *et al.*[1] and Gierczak *et al.*[3] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in

$$k = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 212–423 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

[1]R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).
[2]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).
[3]T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
[7]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).
[8]V. Handwerk and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 1161 (1978).
[9]W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. **83**, 2440 (1979).
[10]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

$HO + CH_3CF_3$ (HFC–143a) → $H_2O + CH_2CF_3$

$\Delta H° = -49.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.9 \times 10^{-11} \exp[-(3200 \pm 500)/T]$	293–425	Clyne and Holt, 1979[1]	(a)
$<1 \times 10^{-15}$	293		
$(1.71 \pm 0.44) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983[2]	(b)
$2.12 \times 10^{-12} \exp[-(2200 \pm 200)/T]$	261–374	Talukdar *et al.*, 1991[3]	(c)
$(1.35 \pm 0.25) \times 10^{-15}$	298		
Reviews and Evaluations			
$6.0 \times 10^{-13} \exp(-1750/T)$	~298	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) Flash photolysis system with UV absorption detection of HO.
(c) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.
(d) The 298 K rate coefficient was that of Martin and Paraskevopoulos.[2] The temperature dependence was estimated.

Preferred Values

$k = 1.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.05 \times 10^{-12} \exp(-1990/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature rate coefficients of Martin and Paraskevopoulos[2] and Talukdar *et al.*[3] are in reasonable agreement. The rate coefficients of Clyne and Holt[1] are not used in the evaluation since their rate coefficients at 333 K and 378 K are significantly higher than those of Talukdar *et al.*[3] and have large associated cited uncertainties. The rate coefficients of Martin and Paraskevopoulos[2] and Talukdar *et al.*[3] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 2.02 \times 10^{-18}\, T^2 \exp(-1459/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–374 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\, e^2\, T^2$ and $B = D + 2T$.

References

[1]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[2]J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
[3]R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_2FCHF_2$ (HFC–143) → $H_2O + CH_2FCF_2$ (1)
→ $H_2O + CHFCHF_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.5 \times 10^{-12} \exp[-(1000 \pm 100)/T]$	293–441	Clyne and Holt, 1979[1]	(a)
$(4.68 \pm 0.40) \times 10^{-14}$	294		
$(1.83 \pm 0.18) \times 10^{-14}$	298	Martin and Paraskevopoulos, 1983[2]	(b)
Reviews and Evaluations			
$2.8 \times 10^{-12} \exp(-1500/T)$	~298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) Flash photolysis system with UV absorption detection of HO.
(c) 298 K rate coefficient based on the rate coefficient of Martin and Paraskevopoulos.[2] The temperature dependence was estimated.

Preferred Values

$k = 1.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is that determined by Martin and Paraskevopoulos.[2] The data of Clyne and Holt[1] were not used in the evaluation.

References

[1]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[2]J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_2FCF_3$ (HFC–134a) → $H_2O + CHFCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.7 \times 10^{-12} \exp[-(1990 \pm 280)/T]$	270–440	Liu, Huie and Kurylo, 1990[1]	(a)
$(5.18 \pm 0.7) \times 10^{-15}$	298		
$5.8 \times 10^{-13} \exp[-(1350 \pm 100)/T]$	231–423	Brown *et al.*, 1990[2]	(b)
$(6.9 \pm 1.5) \times 10^{-15}$	301		
$5.7 \times 10^{-13} \exp[-(1430 \pm 60)/T]$	223–324	Gierczak *et al.*, 1991[3]	(c)
$(4.34 \pm 0.35) \times 10^{-15}$	298		
Review and Evaluations			
$6.6 \times 10^{-13} \exp(-1300/T)$	249–473	IUPAC, 1989[4]	(d)
$1.27 \times 10^{-18} T^2 \exp(-769/T)$	249–473	Atkinson, 1989[5]	(d)
$1.7 \times 10^{-12} \exp(-1750/T)$	223–440	NASA, 1990[6]	(e)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.
(d) Obtained from a least-squares analysis of the absolute rate coefficients of Martin and Paraskevopoulos[7] and Jeong *et al.*[8] The data of Clyne and Holt[1] were not utilized in the evaluation because of discrepancies with other data for the haloalkanes.[4,5]
(e) Derived from the rate coefficient data of Martin and Paraskevopoulos,[7] Liu *et al.*[1] and Gierczak *et al.*[3]

Preferred Values

$k = 4.9 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 8.4 \times 10^{-13} \exp(-1535/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The measured rate coefficients,[1-3,7-9] both at room temperature and as a function of temperature, do not agree well. In particular, the rate coefficients of Jeong *et al.*[8] are significantly higher than those of Martin and Paraskevopoulos,[7] Liu *et al.*[1] and Gierczak *et al.*,[3] probably because of the presence of reactive impurities in the CH_2FCF_3 sample used. To a lesser extent, the rate coefficients of Brown *et al.*[2] are also consistently higher than those of Martin and Paraskevopoulos,[7] Liu *et al.*[1] and Gierczak *et al.*,[3] especially at the lower temperatures studied, again indicating the presence of reactive impurities.

The rate coefficients of Martin and Paraskevopoulos,[7] Liu *et al.*[1] and Gierczak *et al.*[3] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.61 \times 10^{-18} T^2 \exp(-1005/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 223–450 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C\, e^2\, T^2$ and $B = D + 2T$.

References

[1]R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).
[2]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).
[3]T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
[7]J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
[8]K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).
[9]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

$HO + CHF_2CHF_2$ (HFC–134) $\rightarrow H_2O + CF_2CHF_2$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-12} \exp[-(1800 \pm 400)/T]$	294–434	Clyne and Holt, 1979[1]	(a)
$(5.3 \pm 1.5) \times 10^{-15}$	294		
Reviews and Evaluations			
$8.7 \times 10^{-13} \exp(-1500/T)$	~298	NASA, 1990[2]	(b)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) The 298 K rate coefficient was derived from the rate coefficient of Clyne and Holt.[1] The temperature dependence was estimated.

Preferred Values

$k = 5.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the 294 K rate coefficient of Clyne and Holt,[1] extrapolated to 298 K. Since the temperature dependencies measured by Clyne and Holt[1] for other halocarbons are generally in disagreement with other literature studies,[2,3] no temperature dependence is recommended.

References

[1]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).
[3]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

HO + CHF_2CF_3 (HFC–125) → H_2O + CF_2CF_3

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-13} \exp[-(1100 \pm 100)/T]$	294–441	Clyne and Holt, 1979[1]	(a)
$(4.9 \pm 1.4) \times 10^{-15}$	294		
$(2.49 \pm 0.28) \times 10^{-15}$	298	Martin and Paraskevopoulos, 1983[2]	(b)
$2.8 \times 10^{-13} \exp[-(1350 \pm 100)/T]$	226–423	Brown *et al.*, 1990[3]	(c)
$(2.9 \pm 1.0) \times 10^{-15}$	303		
$5.41 \times 10^{-13} \exp[-(1700 \pm 100)/T]$	220–364	Talukdar *et al.*, 1991[4]	(d)
$(1.90 \pm 0.27) \times 10^{-15}$	298		
Reviews and Evaluations			
$8.9 \times 10^{-13} \exp(-1750/T)$	~298	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.

(b) Flash photolysis system with UV absorption detection of HO.

(c) Discharge flow system with resonance fluorescence detection of HO.

(d) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.

(e) The 298 K rate coefficient was based on the rate coefficient measured by Martin and Paraskevopoulos.[2] The temperature dependence was estimated.

Preferred Values

$k = 1.9 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 4.9 \times 10^{-13} \exp(-1655/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

At room temperature, the measured rate coefficients cover a range of a factor of ~3, with the rate coefficient of Talukdar *et al.*[4] being the lowest. Combined with the temperature dependence observed by Talukdar *et al.*[4] being the highest, this suggests the presence of reactive impurities in the CHF_2CF_3 samples used in the studies of Clyne and Holt[1] and Brown *et al.*[3] Accordingly, the preferred rate coefficient is derived from the data of Martin and Paraskevopoulos[2] and Talukdar *et al.*[4]

These rate coefficient data[2,4] were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 9.46 \times 10^{-19} T^2 \exp(-1126/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 220–364 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

[1]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

[2]J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

[3]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

[4]R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).

[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CF_3CHO \rightarrow H_2O + CF_3CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.11 \pm 0.54) \times 10^{-12}$	299 ± 3	Dóbé, Khachatryan and Bérces, 1989[1]	(a)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the absolute rate coefficient study of Dóbé *et al.*[1]

References

[1]S. Dóbé L. A. Khachatryan, and T. Bérces, Ber. Bunsenges Phys. Chem. 93, 847 (1989).

$FO + O_3 \rightarrow F + 2O_2$ (1)
$\rightarrow FO_2 + O_2$ (2)

$\Delta H^\circ(1) = -172$ kJ·mol^{-1}
$\Delta H^\circ(2) = -226$ kJ·mol^{-1}

Rate coefficient data: no direct experimental data available

Comments

The $FO + O_3$ reaction has two possible pathways which are exothermic, resulting in the production of $F + 2O_2$ or $FO_2 + O_2$. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have provided some relevant kinetic information. Starrico *et al.*[1] measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2F + O_2$ (the latter reaction has been studied twice (by Wagner *et al.*[2] and Clyne and Watson,[3]) but although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity it has not been accurately determined). Consequently it is impossible to ascertain from the experimental results of Starrico *et al.*[1] whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner *et al.*[2] utilized a low pressure discharge flow – mass spectrometric system to study the $F + O_3$ and $FO + FO$ reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of $k(FO + FO)$ of 3×10^{-11} cm^3 molecule^{-1} s^{-1} is about a factor of 4 greater than that reported by Clyne and Watson,[3] which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or that the $FO + O_3$ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the $FO + O_3$ reaction rate constant from existing experimental data. It is worth noting that the analogous $ClO + O_3$ reactions are reported[4] to be extremely slow ($< 10^{-18}$ cm^3 molecule^{-1} s^{-1}), and upper limits of 8×10^{-14} cm^3 molecule^{-1} s^{-1} [5] and 5×10^{-15} cm^3 molecule^{-1} s^{-1} [6] have been reported for $k(BrO + O_3)$.

Preferred Values

None.

References

[1]E. H. Starrico, S. E. Sicre, and H. J. Schumacher, Z. Physik Chem. N.F. **31**, 385 (1962).
[2]H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).
[3]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 1109 (1974).
[4]W. B. DeMore, C. L. Lin, and S. Jaffe, results presented at ACS meeting Philadelphia, 1975, and 12th Informal Conference on Photochemistry, Washington, D.C. (1976).
[5]M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2214 (1970).
[6]S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).

$FO + NO \rightarrow F + NO_2$

$\Delta H° = -86$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Ray and Watson, 1981[1]	(a)
Reviews and Evaluations			
2.6×10^{-11}	298	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
2.6×10^{-11}	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with MS detection of FO.
(b) See Comments on Preferred Values.
(c) Based on data of Ray and Watson.[1]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[2] The preferred value is based on results reported by Ray and Watson.[1] The temperature dependence of the rate coefficient is expected to be small for such a radical-radical reaction. The temperature dependences for the analogous ClO and BrO reactions are small and negative.

References

[1]G. W. Ray and R. T. Watson, J. Phys Chem. **85**, 2955 (1981).
[2]CODATA, Supplement I, 1982 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$$FO + FO \rightarrow 2F + O_2 \quad (1)$$
$$\rightarrow FO_2 + F \quad (2)$$
$$\rightarrow F_2 + O_2 \quad (3)$$

$\Delta H°(1) = -59$ kJ·mol^{-1}
$\Delta H°(2) = -112$ kJ·mol^{-1}
$\Delta H°(3) = -218$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5 \pm 2.8) \times 10^{-12}$	298	Clyne and Watson, 1974[1]	(a)
Relative Rate Coefficients			
3.3×10^{-11}	298	Wagner *et al.*, 1972[2]	(b)
Reviews and Evaluations			
1.5×10^{-11}	298	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
1.5×10^{-11}	298	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with MS detection of FO and NO_2 (unreacted FO was converted to NO_2 by reaction with NO).
(b) Discharge flow system with MS detection of F, FO, F_2, and O_3. From the time behavior of these species a value for k was derived together with information concerning the relative importance of the three channels. The value of k derived is sensitive to the value of $k(F + O_3)$ and the assumed mechanism.
(c) See Comments on Preferred Values.
(d) Based on data of Clyne and Watson[1] and Wagner *et al.*[2]

Preferred Values

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1980.[3] The value of k reported by Clyne and Watson[1] was obtained in a more direct manner than that of Wagner *et al.*,[2] and as such is less susceptible to error due to complicating secondary reactions. The value recommended in this evaluation is a weighted average of the results from the two studies. From the data of Wagner *et al.*[2] it can be seen that the dominant channel is that producing $2F + O_2$. However, their data base is not adequate to conclude that this is the only process.

References

[1]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 1109 (1974).
[2]H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).
[3]CODATA, 1980 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$COF_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$COF_2 + h\nu \rightarrow COF + F$	(1)	543	220
$\rightarrow CO + 2F$	(2)	683	175
$\rightarrow CF_2 + O(^3P)$	(3)	690	173

Preferred Values

Absorption cross-sections for COF_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186.0	5.5	205.1	0.69
187.8	4.8	207.3	0.50
189.6	4.2	209.4	0.34
191.4	3.7	211.6	0.23
193.2	3.1	213.9	0.15
195.1	2.6	216.2	0.10
197.0	2.1	218.6	0.06
199.0	1.6	221.0	0.04
201.0	1.3	223.5	0.03
203.0	0.95		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Molina and Molina.[1] The spectrum shows considerable structure, and the values listed are averages over 500 cm^{-1} intervals. The quantum yield for photodissociation at 206 nm was reported in the same study to be approximately 0.25. In view of the preliminary nature of these data, no quantum yield recommendation is given.

References

[1]L. T. Molina and M. J. Molina, presented at the 182nd American Chemical Society National Meeting, New York, August 1982.

$HCOF + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HCOF + h\nu \rightarrow HF + CO$	(1)	5.4	22,000
$\rightarrow F + HCO$	(2)	507	236
$\rightarrow H + FCO$	(3)	436	274

Absorption cross-section data

Wavelength range/nm	Reference	Comments
195–270	Giddings and Innes, 1961[1]	(a)

Quantum yield data

There are no reported quantum yield data. Klimeck and Berry[2] have observed infra-red laser emission from HF* following flash photolysis of HCOF (λ > 165 nm). The results indicate the occurrence of both reactions (1) and/or (2).

Comments

(a) The absorption spectra of HCOF and DCOF were studied using conventional methods. Low resolution spectrophotometric measurements were made as well as high resolution plate photometry. The spectrum of HCOF shows a characteristic vibrational progression of many sharp bands, with an origin of structured absorption at 268 nm and a maximum of intensity near 210 nm, where a value of 50 l mol^{-1} cm^{-1} was reported for the molar extinction coefficient ($\sigma = 1.9 \times 10^{-19}$ cm^2 molecule^{-1}). The spectra were illustrated in figures and the positions of the bands were listed. There was no effect of temperature on the bands on cooling to 196 K.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
220	22.3	250	2.74	275	0.38
225	18.1	255	1.77	280	0.26
230	14.0	260	1.17	285	0.16
235	9.96	265	0.80	290	0.10
240	6.92	270	0.55	295	0.06
245	4.29				

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data for the absolute absorption coefficients reported by Giddings and Innes[1] and on a digital spectrum of HCOF recorded at a resolution of 1 nm by a diode array spectroscopic analysis of the products of the photooxidation of CF_3CFH_2.[3] The listed values are averaged over 5 nm intervals.

References

[1] L. K. Giddings and K. K. Innes, J. Molecular Spectr. **6**, 528 (1961).
[2] E. Klimeck and M. J. Berry, Chem. Phys. Lett. **20**, 141 (1973).
[3] G. D. Hayman (private communication to IUPAC subcommittee, 1991).

$CF_3COF + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH/kJ·mol⁻¹	$\lambda_{threshold}$/nm
$CF_3COF + h\nu \rightarrow CF_3 + COF$	(1)	146	819
$\rightarrow CF_3CO + F$	(2)		
$\rightarrow CF_4 + CO$	(3)	−255	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–340	Rattigan, Jones and Cox, 1991[1]	(a)

Quantum yield data

There are no reported data for ϕ_1 or ϕ_2.

Comments

(a) Absolute absorption cross-sections measured using a dual beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of CF_3COF shows a single band with a maximum at 215 nm ($\sigma = 1.36 \times 10^{-19}$ cm² molecule⁻¹) extending out to 315 nm where there is a significant temperature dependence. Values of σ given at 5 nm intervals at 298 K and 240 K, as well as temperature coefficients in the long wavelength tail at >270 nm.

Preferred Values

Absorption cross-sections at 293 K and 238 K

λ/nm	10^{20} σ/cm^2		λ/nm	10^{20} σ/cm^2	
	293 K	238 K		293 K	238 K
200	9.35	9.46	255	0.552	0.491
205	11.5	11.6	260	0.216	0.179
210	13.1	13.1	265	0.0703	0.0465
215	13.6	13.7	270	0.0262	0.0099
220	12.9	13.1	275	0.0098	0.0031
225	11.1	11.4	280	0.0031	0.0010
230	8.78	9.11	285	0.0016	0.0004
235	6.30	6.55	290	0.0008	0.0
240	4.07	4.18	295	0.0003	0.0
245	2.35	2.30	300	0.0	0.0
250	1.22	1.16			

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan *et al.*,[1] which also provide the temperature dependence.

Reference

[1]O. Rattigan, R. L. Jones, and R. A. Cox, J. Photochem., submitted for publication.

4.7 Chlorine Species

O + HOCl → HO + ClO

$\Delta H^\circ = -30$ kJ·mol^{-1}

Comments

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[1] There are still no experimental data on this reaction. In this evaluation we prefer to make no recommendation, rather than the estimated preferred value of $1 \times 10^{-11} \exp(-2200/T)$ cm^3 molecule^{-1}s^{-1} given in our earlier evaluation.[2]

References

[1]IUPAC, Supplement III, 1989 (see references in Introduction).
[2]CODATA, 1980 (see references in Introduction).

O + ClO → Cl + O_2

$\Delta H^\circ = -230$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-11}$	252–347	Schwab *et al.*, 1984[1]	(a)
$1.55 \times 10^{-11} \exp[(263 \pm 60)/T]$	231–367	Nicovich, Wine and Ravishankara, 1988[2]	(b)
$(3.8 \pm 0.6) \times 10^{-11}$	298		
Relative Rate Coefficients			
$(3.5 \pm 0.6) \times 10^{-11}$	298	Ongstad and Birks, 1984[3]	(c)
$2.61 \times 10^{-11} \exp[(97 \pm 64)/T]$	220–387	Ongstad and Birks, 1986[4]	(c)
Reviews and Evaluations			
3.8×10^{-11}	200–300	IUPAC, 1989[5]	(d)
$3.0 \times 10^{-11} \exp(70/T)$	200–300	NASA, 1990[6]	(e)

Comments

(a) Discharge flow system with LMR detection of ClO radicals and resonance fluorescence detection of O(^{3}P) and Cl atoms. Pseudo-first order decay of O(^{3}P) atoms in the presence of excess ClO and decay of ClO in the presence of excess O(^{3}P) gave good agreement for the rate coefficient k. No discernible temperature dependence over the range studied. Pressure range 0.8 – 2.0 Torr.

(b) Dual laser flash photolysis system with resonance fluorescence detection in slow flow reactor. ClO produced by reaction of excess Cl, produced by 351 nm excimer laser photolysis of Cl_2, with known amount of O_3. O(^{3}P) produced by 266 nm laser photolysis of ClO after appropriate delay time. O(^{3}P) monitored by time-resolved resonance fluorescence. The measured O(^{3}P) atom decay rate was corrected for losses due to reaction with Cl_2 and other routes. Pressure range 15 – 500 Torr, M = N_2. No pressure effect on k.

(c) Discharge flow system with detection of O(^{3}P) by NO + O + M chemiluminescence in presence of excess ClO. [ClO] determined indirectly by in-situ conversion to NO_2 by addition of NO and k measured relative to $k(O + NO_2 \rightarrow NO + O_2) = 6.58 \times 10^{-12} \exp[(142 \pm 23)/T]$ cm^3 molecule^{-1} s^{-1}, determined in the same system concurrently. Pressure = 2.3 Torr. No effect of O_2 at 230 K.

(d) See Comments on Preferred Values.

(e) Based on a least-squares fit to the data from Leu,[7] Margitan,[8] Schwab *et al.*,[1] Ongstad and Birks,[3,4] Zahniser and Kaufman[11] and Nicovich *et al.*[2]

Preferred Values

$k = 3.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The most recent studies all give values of $k_{298\ K}$ about 30% lower than the earlier work of Bemand *et al.*[9] and Clyne and Nip.[10] The two most recent studies[2,4] give a negative temperature dependence, in contrast to the earlier work which showed zero or positive temperature coefficients. The preferred value is independent of temperature and is obtained by averaging the 298 K values from Schwab *et al.*,[1] Nicovich *et al.*,[2] Ongstad and Birk[3,4] Leu,[7] Margitan[8] and Zahniser and Kaufman.[11] The uncertainty on E/R allows for a temperature dependence consistent with all studies. Leu and Yung[12] have recently shown that the yields of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ in the reaction are $<2.5 \times 10^{-2}$ and $(4.4 \pm 1.1) \times 10^{-4}$, respectively.

References

[1] J. J. Schwab, D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Geophys. Res. **89**, 9581 (1984).
[2] J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. **89**, 5670 (1988).
[3] A. P. Ongstad and J. W. Birks, J. Chem. Phys. **81**, 3922 (1988).
[4] A. P. Ongstad and J. W. Birks, J. Chem. Phys. **85**, 3359 (1986).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] NASA Evaluation No. 9, 1990 (see references in Introduction).
[7] M. T. Leu, J. Phys. Chem. **88**, 1394 (1984).
[8] J. J. Margitan, J. Phys. Chem. **88**, 3638 (1984).
[9] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).
[10] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 1, **72**, 221 (1976).
[11] M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).
[12] M. T. Leu and Y. Yung, Geophys. Res. Lett. **14**, 949 (1987).

$O + OClO \rightarrow O_2 + ClO$

$\Delta H° = -248\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5 \pm 2) \times 10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	(a)
$(1.6 \pm 0.4) \times 10^{-13}$	298	Colussi, 1990[2]	(b)
See Comment	248–312	Colussi, Sander, and Friedl, 1992[3]	(c)
$2.5 \times 10^{-12} \exp(-950/T)$	243–400	Gleason, Nesbitt, and Stief, 1991[4]	(d)
$(1.05 \pm 0.21) \times 10^{-13}$	298		
Reviews and Evaluations			
5×10^{-13}	298	IUPAC, 1989[5]	(e)
$2.8 \times 10^{-11} \exp(-1200/T)$	200–300	NASA, 1990[6]	(f)

Comments

(a) Discharge flow system. Two independent methods used: $O(^3P)$ decay in excess OClO determined by resonance fluorescence, and OClO decay in excess $O(^3P)$ determined by MS. There was only fair agreement between the two methods.

(b) Laser flash photolysis of OClO at 308 nm, with the $O(^3P)$ decay being determined by resonance fluorescence. The results were extrapolated to zero laser flash intensity. Measurements were over the pressure range 10–780 Torr Ar. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. The value reported was not directly measured but was derived from fitting a falloff curve to the experimental data over the entire pressure range.

(c) Laser flash photolysis of OClO at 308 nm, with the $O(^3P)$ decay being determined by resonance fluorescence. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. A negative temperature dependence was observed, with the reported values of k increasing from $1.5 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 312 K to $4.0 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 248 K. These values were not directly measured but were derived quantities which are consistent with falloff curves fitted to the experimental data over the pressure range 20–600 Torr Ar.

(d) Discharge flow system with resonance fluorescence detection of $O(^3P)$. Pressure = 1 Torr. Measurements were made over the temperature range 200–400 K. The data for the temperature range 243–400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.

(e) Based on the results of Bemand *et al.*[1]

(f) Estimated Arrhenius parameters based on the 298 K results of Bemand *et al.*[1]

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.5 \times 10^{-12} \exp(-950/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability
$\Delta\log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values
The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason *et al.*[4] Over the temperature range of the recommendation (240–300 K), the data were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence. The extrapolated 298 K rate coefficient of Colussi[2] supports this value. It appears that the experiments of Bemand *et al.*[1] were complicated by secondary chemistry. The experiments of Colussi[1] and Colussi *et al.*[2] over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on O + OClO + M).

References

[1]P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).
[2]A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).
[3]A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).
[4]J. F. Gleason, F. L. Nesbitt, and L. J. Stief, presented at the Spring Meeting of the American Geophysical Union, Baltimore, MD, May 1991.

$O + OClO + M \rightarrow ClO_3 + M$

$\Delta H^\circ = -117.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-31}$ [Ar]	298	Colussi, 1990[1]	(a)
$1.8 \times 10^{-31}(T/298)^{-1}$ [Ar]	248–312	Colussi, Sander and Friedl, 1992[2]	(b)

Comments

(a) Laser flash photolysis study of OClO at pressures of Ar between 8 and 760 Torr. The oxygen atoms produced were monitored by resonance fluorescence. The recombination reaction is coupled with the bimolecular channel $O + OClO \rightarrow O_2 + ClO$ for which a rate constant of $(1.6 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} value was determined. The second order rate coefficients were fitted by falloff curves using $F_c = 0.6$. A bond energy of $E_o = 112.4$ kJ·mol^{-1} was derived from unimolecular rate theory. The above ΔH° value was derived from the reported value of $\Delta H_f^\circ(ClO_3) = 232.6$ kJ·mol^{-1}.

(b) See comment (a). Extension of measurements of Ref. 1; pressure range 20–600 Torr of Ar. Discussion of the mechanism $O + OClO \rightarrow ClO_3^*$, $ClO_3^* \rightarrow O + OClO$, $ClO_3^* + M \rightarrow ClO_3 + M$, $ClO_3^* \rightarrow ClO + O_2$, $O + OClO \rightarrow ClO + O_2$ was given. Fitted values of F_c were 0.5 at 249 K, 0.48 at 273 K, and 0.45 at 312 K.

Preferred Values

$k_0 = 1.8 \times 10^{-31}(T/298)^{-1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta\log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values
This is the first determination of rate data for this reaction. The preferred values correspond to falloff curves with $F_c = 0.48$ at 298 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.8) \times 10^{-11}$	298	Colussi, 1990[1]	(a)
$3.1 \times 10^{-11}(T/298)^1$	248–312	Colussi, Sander and Friedl, 1992[2]	(b)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 3.1 \times 10^{-11}(T/298)^1$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values
See comment on k_0.

References

[1]A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).
[2]A. J. Colussi, S. P. Sander, and R. R. Friedl **96**, 4442 (1992).

$O + Cl_2O \rightarrow ClO + ClO$

$\Delta H° = -127$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.7 \times 10^{-11} \exp[-(560 \pm 80)/T]$	236–295	Miziolek and Molina, 1978[1]	(a)
$(4.1 \pm 0.5) \times 10^{-12}$	295		
$3.3 \times 10^{-11} \exp[-(700 \pm 150)/T]$	237–297	Wecker, Johanssen and Schindler, 1982[2]	(b)
$(3.1 \pm 0.5) \times 10^{-12}$	297		
Reviews and Evaluations			
$2.9 \times 10^{-11} \exp(-630/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system. The pseudo-first-order decay of [O] in excess [Cl_2O] detected by NO_2 chemiluminescence.
(b) Discharge flow system. The pseudo-first-order decay of [O] in excess [Cl_2O] detected by EPR.
(c) Based on results of Miziolek and Molina[1] and of Wecker *et al.*[2]

Preferred Values

$k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-11} \exp(-630/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 235–300 K.

Reliability
$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The preferred value averages the results of Miziolek and Molina[1] with the approximately 30% lower values of Wecker *et al.*[2] The earlier, higher results of Basco and Dogra[4] and of Freeman and Phillips[5] have not been included in derivation of the preferred value due to data analysis difficulties in both studies.

References

[1]A. W. Miziolek and M. J. Molina, J. Phys. Chem. **82**, 1769 (1978).
[2]D. Wecker, R. Johanssen, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **86**, 532 (1982).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]N. Basco and S. K. Dogra, Proc. Roy. Soc. London A, **323**, 29 (1971).
[5]G. G. Freeman and L. F. Phillips, J. Phys. Chem. **72**, 3025 (1968).

$$O + ClONO_2 \rightarrow ClO + NO_3 \quad (1)$$
$$\rightarrow OClO + NO_2 \quad (2)$$
$$\rightarrow O_2 + ClONO \quad (3)$$

$\Delta H°(1) = -106$ kJ·mol^{-1}
$\Delta H°(2) = -138$ kJ·mol^{-1}
$\Delta H°(3) = -216$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.2) \times 10^{-13}$	245	Ravishankara *et al.*, 1977[1]	(a)
$3.4 \times 10^{-12} \exp[-(840 \pm 60)/T]$	213–295	Molina, Spencer, and Molina, 1977[2]	(b)
$(2.0 \pm 0.4) \times 10^{-13}$	295		
$1.9 \times 10^{-12} \exp[-692 \pm 167)/T]$	225–273	Kurylo, 1977[3]	(c)
1.8×10^{-13}	298*		
$(2.3 \pm 0.6) \times 10^{-13}$	298	Adler-Golden and Wiesenfeld, 1981[4]	(d)
Reviews and Evaluations			
$3.0 \times 10^{-12} \exp(-808/T)$	213–295	CODATA, 1980[5]; IUPAC, 1989[6]	(e)
$2.9 \times 10^{-12} \exp(-800/T)$	200–300	NASA, 1990[7]	(f)

Comments

(a) Static flash photolysis system with resonance fluorescence detection of O(^{3}P).
(b) Discharge flow system with chemiluminescence detection of O(^{3}P).
(c) Flash photolysis system with resonance fluorescence detection of O(^{3}P).
(d) Flash photolysis system with absorption spectroscopy detection of O(^{3}P).
(e) See Comments on Preferred Values.
(f) Based on data of Molina *et al.*,[2] Kurylo[3] and Adler-Golden and Wiesenfeld.[4]

Preferred Values

$k = 2.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.0 \times 10^{-12} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213–295 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our prevous evaluation, CODATA, 1980.[5] The results reported by Molina *et al.*,[2] Kurylo[3] and Adler-Golden and Wiesenfeld[4] are in good agreement and have been used to derive the preferred Arrhenius expression. The value reported by Ravishankara *et al.*[1] is a factor of two greater, and this may possibly be attributed to secondary kinetic complications, the presence of NO_2 as a reactive impurity, or the formation of reactive photolytic products. None of the studies reported identification of the reaction products.

References

[1]A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. **4**, 7 (1977).
[2]L. T. Molina, J. E. Spencer, and M. J. Molina, Chem. Phys. Lett. **45**, 158 (1977).
[3]M. J. Kurylo, Chem. Phys. Lett. **45**, 158 (1977).
[4]S. M. Adler-Golden and J. R. Wiesenfeld, Chem. Phys. Lett. **82**, 281 (1981).
[5]CODATA, 1980 (see references in Introduction).
[6]IUPAC, Supplement III, 1989 (see references in Introduction).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).

$O(^1D)$ + HCFCs → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.4×10^{-10} CHF_2Cl	298	Fletcher and Husain, 1976[1]	(a)
4.8×10^{-10} $CHFCl_2$	298		
9.5×10^{-11} CHF_2Cl	173–343	Davidson *et al.*, 1978[2]	(b)
1.9×10^{-10} $CHFCl_2$	173–343		
Relative Rate Coefficients			
1.0×10^{-10} CHF_2Cl	298	Green and Wayne, 1976[3]	(c)
1.4×10^{-10} CH_3CF_2Cl	298		
1.5×10^{-10} CH_2ClCF_3	298		
1.6×10^{-10} CH_2ClCF_2Cl	298		
2.2×10^{-10} $CHCl_2CF_3$	298		
1.9×10^{-10} CHF_2Cl	298	Atkinson *et al.*, 1976[4]	(c)
Reviews and Evaluations			
9.5×10^{-11} CHF_2Cl	200–300	NASA, 1990[5]	(d)
1.9×10^{-10} $CHFCl_2$	200–300		
1.4×10^{-10} CH_3CF_2Cl	200–300		
1.5×10^{-10} CH_3CFCl_2	200–300		
1.5×10^{-10} CH_2ClCF_3	200–300		
1.6×10^{-10} CH_2ClCF_2Cl	200–300		
1.0×10^{-10} $CHFClCF_3$	200–300		
2.2×10^{-10} $CHCl_2CF_3$	200–300		

Comments

(a) $O(^1D)$ atoms generated by flash photolysis of O_3 and monitored by time-resolved resonance absorption at 115 nm. Data analysis used the modified Beer-Lambert law.

(b) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(c) $O(^1D)$ produced by photolysis of NO_2 at 229 nm. Monitored $\Delta[HFC]/\Delta[N_2O]$ by IR absorption spectrometry. The measured rate coefficient ratios $k/k(O(^1D) + N_2O)$ have been placed on an absolute basis by use of $k(O(^1D) + N_2O)$ from this evaluation. The cited rate coefficients refer to chemical reaction only, and do not include physical quenching.

(d) CHF_2Cl and $CHFCl_2$: based on results of Davidson *et al.*[2] CH_3CF_2Cl, CH_2ClCF_3, CH_2ClCF_2Cl, and $CHCl_2CF_3$: based on results of Green and Wayne.[3] CH_3CFCl_2 and $CHFClCF_3$: estimated by analogy.

Preferred Values

CHF_2Cl $k = 9.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 175–340 K.

$CHFCl_2$ $k = 1.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the temperature range 175–340 K.

CH_3CF_2Cl $k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

CH_3CFCl_2 $k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

CH_2ClCF_3 $k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

CH_2ClCF_2Cl $k = 1.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$CHFClCF_3$ $k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$CHCl_2CF_3$ $k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ for CHF_2Cl and $CHFCl_2$ over the temperature range 175–340 K.

$\Delta \log k = \pm 0.3$ at 298 K for CH_3CF_2Cl, CH_2ClCF_3, CH_2ClCF_2Cl, and $CHCl_2CF_3$.

$\Delta \log k = \pm 0.5$ at 298 K for CH_3CFCl_2 and $CHFClCF_3$.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of $O(^1D)$ and include both physical quenching and chemical reaction. The rate coefficients for CHF_2Cl and $CHFCl_2$ have been determined to be temperature-independent over the range 175–340 K. Rate coefficients for the other HCFCs are also assumed to be temperature-independent by analogy with these two compounds and because they have such high values at 298 K. Specific comments are as follows:

CHF_2Cl Based on the results of Davidson *et al.*[2] The results of the relative rate study by Green and Wayne,[3] which refer to chemical reaction only, are in good agreement whereas those of a similar relative study by Atkinson *et al.*[4] are a factor of two higher. Addison *et al.*[6] reported that reaction leads to the formation of ClO (55 ± 10%) and to the elimination of HCl (40%). The latter process is accompanied by formation of CF_2 and $O(^3P)$. The OH yield is 5%.

$CHFCl_2$	Based on the results of Davidson *et al.*[2]
CH_3CF_2Cl	Based on the results of Green and Wayne.[3]
CH_3CFCl_2	Estimated by analogy with CH_3CF_2Cl.
CH_2ClCF_3	Based on the results of Green and Wayne.[3]
CH_2ClCF_2Cl	Based on the results of Green and Wayne.[3]
$CHFClCF_3$	Estimated by analogy with similar compounds.
$CHCl_2CF_3$	Based on the results of Green and Wayne.[3]

References

[1] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[2] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[3] R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1976).
[4] R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).
[6] M. C. Addison, R. J. Donovan, and J. Garraway, J. Chem. Soc. Faraday Discussions **67**, 286 (1979).

$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl$ (1)

$\rightarrow O(^3P) + CF_2Cl_2$ (2)

$\rightarrow COF_2 + Cl_2$ (3)

$\rightarrow COFCl + FCl$ (4)

$\Delta H°(1) = -113$ kJ·mol^{-1}
$\Delta H°(2) = -190$ kJ·mol^{-1}
$\Delta H°(3) = -580$ kJ·mol^{-1}
$\Delta H°(4) = -423$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.2) \times 10^{-10}$	298	Force and Wiesenfeld, 1981[1]	(a)
Branching Ratios			
$k_1/k > 0.47$	298	Gillespie, Garraway, and Donovan, 1977[2]	(b)
$k_1/k = 0.55 \pm 0.15$	298	Donovan, 1980[3]	(c)
$k_2/k = 0.20 \pm 0.10$	298		
$k_2/k = 0.14 \pm 0.07$	295	Force and Wiesenfeld, 1981[1]	(a,d)
Reviews and Evaluations			
1.4×10^{-10}	298	CODATA, 1982[4]; IUPAC, 1989[5]	(e)
1.4×10^{-10}	298	NASA, 1990[6]	(f)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time resolved production of $O(^3P)$ was monitored by resonance absorption at 130 nm.
(b) Flash photolysis with plate photometric detection (ultraviolet absorption) of ClO and O_3.
(c) Flash photolysis. Plate photometric detection of ClO and resonance absorption detection of $O(^3P)$ at 130 nm. Channels (1) and (2) were shown to be the dominant, but not necessarily exclusive, pathways.
(d) The rate constant for the quenching channel, k_2, was determined to be $(2 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
(e) See Comments on Preferred Values.
(f) Based on the results of Davidson *et al.*[7] and Force and Wiesenfeld.[1]

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.15$ at 298 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values
This data sheet is largely reproduced from our previous evaluation, CODATA, 1982.[4] The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[7] which are in excellent agreement. The weight of evidence from many $O(^1D)$ rate studies suggests that the results of Fletcher and Husain[8] contain a systematic error. The results from the relative rate coefficient studies[9-11] were not considered in this evaluation. However,

combining the values of $k/k(O^1D + N_2O)$ reported in references[9] and [11] with the IUPAC preferred value for $k(O^1D + N_2O)$ yields values of k in good agreement with the preferred value. Both Donovan[3] and Force and Wiesenfeld[1] report that the quenching channel (2) is a significant removal pathway for $O(^1D)$. Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k.

References

[1] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2] H. M. Gillespie, J. Garraway, and R. J. Donovan, J. Photochem. **7**, 29 (1977).
[3] R. J. Donovan, private communication (1980).
[4] CODATA, Supplement I, 1982 (see references in Introduction).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] NASA Evaluation No. 9, 1990 (see references in Introduction).
[7] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[8] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[9] R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).
[10] R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).
[11] R. G. Green and R. P. Wayne, J. Photochem. **6**, 371 (1977).

$$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2 \quad (1)$$
$$\rightarrow O(^3P) + CFCl_3 \quad (2)$$
$$\rightarrow COFCl + Cl_2 \quad (3)$$
$$\rightarrow COCl_2 + FCl \quad (4)$$

$\Delta H^\circ(1) = -141$ kJ·mol^{-1}
$\Delta H^\circ(2) = -190$ kJ·mol^{-1}
$\Delta H^\circ(3) = -581$ kJ·mol^{-1}
$\Delta H^\circ(4) = -425$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.2) \times 10^{-10}$	295	Force and Wiesenfeld, 1981[1]	(a)
Branching Ratios			
$k_1/k > 0.39$	298	Gillespie, Garraway, and Donovan, 1977[2]	(b)
$k_1/k = 0.6 \pm 0.15$	298	Donovan, 1980[3]	(c)
$k_2/k = 0.25 \pm 0.10$	298		
$k_2/k = 0.13 \pm 0.04$	295	Force and Wiesenfeld, 1981[1]	(a,d)
Reviews and Evaluations			
2.3×10^{-10}	298	CODATA, 1982[4]; IUPAC, 1989[5]	(e)
2.3×10^{-10}	298	NASA, 1990[6]	(f)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time resolved production of $O(^3P)$ was monitored by resonance absorption at 130 nm.
(b) Flash photolysis with plate photometric detection (ultraviolet absorption) of ClO and O_3.
(c) Flash photolysis. Plate photometric detection of ClO and resonance absorption detection of $O(^3P)$ at 130 nm. Channels (1) and (2) were shown to be the dominant, but not necessarily exclusive, pathways.
(d) The quenching rate constant, k_2, was determined to be $(3 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
(e) See Comments on Preferred Values.
(f) Based on the results of Davidson *et al.*[7] and Force and Wiesenfeld.[1]

Preferred Values

$k = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.16$ at 298 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, CODATA, 1982.[4] The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[7] which are in excellent agreement. The weight of evidence from many $O(^1D)$ rate studies suggests that the results of Fletcher and Husain[8] contain a systematic error.

The results from the relative rate coefficient studies[9,10] were not considered in this evaluation. However, combining the values of $k/k(O^1D + N_2O)$ reported in references 9 and 10 with the IUPAC preferred value for $k(O(^1D) + N_2O)$ yields rate coefficients in good agreement with the preferred value. Both Donovan[3] and Force and Wiesenfeld[1] report that the quenching channel (2) is a significant removal pathway for $O(^1D)$. Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k.

References

[1] A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2] H. M. Gillespie, J. Garraway, and R. J. Donovan, J. Photochem. **7**, 29 (1977).
[3] R. J. Donovan, private communication (1980).
[4] CODATA, Supplement I, 1982 (see references in Introduction).
[5] IUPAC, Supplement III, 1989 (see references in Introduction).
[6] NASA Evaluation No. 9, 1990 (see references in Introduction).
[7] J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[8] I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[9] R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).
[10] R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).

$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ (1)

$\rightarrow O(^3P) + CCl_4$ (2)

$\rightarrow COCl_2 + Cl_2$ (3)

$\Delta H°(1) = -170$ kJ·mol^{-1}
$\Delta H°(2) = -190$ kJ·mol^{-1}
$\Delta H°(3) = -563$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.3) \times 10^{-10}$	295	Force and Wiesenfeld, 1981[1]	(a)
Branching Ratios			
$k_2/k = 0.14 \pm 0.06$	295	Force and Wiesenfeld, 1981[1]	(b)
Reviews and Evaluations			
3.3×10^{-10}	298	CODATA, 1982[2]; IUPAC, 1989[3]	(c)
3.3×10^{-10}	298	NASA, 1990[4]	(d)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time production of $O(^3P)$ was monitored by resonance absorption at 130 nm.
(b) The quenching rate constant, k_2, was determined to be $(4.9 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
(c) See Comments on Preferred Values.
(d) Based on the results of Davidson *et al.*[5] and Force and Wiesenfeld.[1]

Preferred Values

$k = 3.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.14$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, CODATA, 1982.[2] The preferred values are based on the results of Force and Wiesenfeld[1] and Davidson *et al.*,[5] which are in excellent agreement. The weight of evidence from many $O(^1D)$ rate studies suggests that the data of Fletcher and Husain[6] contain a systematic error. The results from the relative rate coefficient study[7] was not considered in this evaluation. Combining the value of $k/k(O^1D + N_2O)$ reported in reference[7] with the IUPAC preferred value of $k(O^1D + N_2O)$ yields a value

~25% lower than the preferred value. The observation of a quenching channel in this reaction is consistent with the results from the $O(^1D)$ atom reactions with CF_2Cl_2 and $CFCl_3$. Consequently, preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k.

References

[1]A. P. Force and J. R. Wiesenfeld, J. Phys. Chem. **85**, 782 (1981).
[2]CODATA, 1980 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, J. Chem. Phys. **69**, 4277 (1978).
[6]I. S. Fletcher and D. Husain, J. Phys. Chem. **80**, 1837 (1976).
[7]R. K. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **4**, 381 (1975).

$O(^1D) + COFCl \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.4) \times 10^{-10}$	298	Fletcher and Husain, 1978[1]	(a)
Relative Rate Coefficients			
1.1×10^{-10}	298	Jayanty, Simonaitis, and Heicklen, 1976[2]	(b)
3.2×10^{-10}	298	Atkinson *et al.*, 1975[3]	(c)
Reviews and Evaluations			
1.9×10^{-10}	298	NASA, 1990[4]	(d)

Comments

(a) Flow system used, with $O(^1D)$ atoms being monitored by time-resolved resonance absorption at 115 nm. The data analysis used modified Beer-Lambert law.

(b) Photolysis of O_3–N_2O–COFCl mixtures at 254 nm. Rate of formation of N_2 measured. Value of k derived from measured rate coefficient ratio, $k/k(O(^1D) + N_2O) = 0.96$, and $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Photolysis of NO_2 at 229 nm. COFCl and N_2O monitored by infrared absorption spectroscopy. Value of k derived from measured rate coefficient ratio, $k_1/k(O(^1D) + N_2O) = 2.8 \pm 0.4$, and $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Note that this is based on measurement of the rate of loss of COFCl and so does not include simple physical deactivation.

(d) Based on results of Fletcher and Husain,[1] multiplied by a scaling factor of 0.5.

Preferred Values

$k = 1.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$.

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain[1] by use of a scaling factor of 0.5. The weight of evidence from many $O(^1D)$ rate studies suggests that $O(^1D)$ rates reported by Husain and co-workers[1] contain a systematic error, and that these results can be made consistent with other $O(^1D)$ recommended values in this evaluation by use of this scaling factor.

References

[1]I. S. Fletcher and D. Husain, J. Photochem. **8**, 355 (1978).
[2]R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **5**, 217 (1976).
[3]R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, J. Geophys. Res. **81**, 5765 (1976).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$O(^1D) + COCl_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.1 \pm 0.9) \times 10^{-10}$	298	Fletcher and Husain, 1978[1]	(a)
Relative Rate Coefficients			
1.8×10^{-10}	298	Jayanty, Simonaitis, and Heicklen, 1976[2]	(b)
Reviews and Evaluations			
3.6×10^{-10}	298	NASA, 1990[3]	(c)

Comments

(a) Flow system. $O(^1D)$ atoms monitored by time-resolved resonance absorption at 115 nm. The data analysis used a modified Beer-Lambert law.

(b) Photolysis of O_3–N_2O–$COCl_2$ mixtures at 254 nm. The rate of formation of N_2 was measured. The value of k was derived from the measured rate coefficient ratio, $k/k(O(^1D) + N_2O) = 1.57$ and $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (this evaluation). The authors interpreted the high yields of CO as evidence that the reaction channel to produce ClO + ClCO is important.

(c) Based on the results of Fletcher and Husain[1] multiplied by a scaling factor of 0.5.

Preferred Values

$k = 3.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$.

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain[1] by use of the scaling factor of 0.5. The weight of evidence from many $O(^1D)$ atom rate studies suggests that $O(^1D)$ rates reported by Husain and coworkers[1] contain a systematic error, and that these results can be made consistent with other $O(^1D)$ recommended values in this evaluation by use of this scaling factor. Note that Jayanty *et al.*[2] present evidence, based on high yields of CO, that the reaction channel to produce ClO + ClCO is very important.

References

[1]I. S. Fletcher and D. Husain, J. Photochem. **8**, 355 (1978).
[2]R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **5**, 217 (1976).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Cl + H_2 \rightarrow HCl + H$

$\Delta H° = 4.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.6 \times 10^{-11} \exp[-(2310/T)]$	200–500	Miller and Gordon, 1981[1]	(a)
$(1.5 \pm 0.2) \times 10^{-14}$	298		
$6.0 \times 10^{-11} \exp[-(2470 \pm 100)/T)]$	297–425	Kita and Stedman, 1982[2]	(b)
$(1.46 \pm 0.22) \times 10^{-14}$	297		
Reviews and Evaluations			
$3.7 \times 10^{-11} \exp(-2300/T)$	200–300	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$3.7 \times 10^{-11} \exp(-2300/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Flash photolysis-resonance fluorescence technique. Also measured rate coefficients for reverse reaction by same technique and found the rate coefficient ratio to agree with equilibrium constant data.
(b) Discharge flow-resonance fluorescence technique. Also measured rate coefficient for reverse reaction by same technique and found the rate coefficient ratio to agree with equilibrium constant data.
(c) See Comments on Preferred Values.
(d) Based on data below 300 K reported by Watson *et al.*,[6] Lee *et al.*,[7] Miller and Gordon[1] and Kita and Stedman.[2]

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-11} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The preferred value is derived from a least-squares fit to data below 300 K reported by Watson *et al.*,[6] Lee *et al.*,[7] Miller and Gordon[1] and Kita and Stedman.[2] The results of these studies are in excellent agreement below 300 K; at higher temperatures the data are in poorer agreement. After extrapolation, the results of Watson *et al.*,[6] Miller and Gordon[1] and Kita and Stedman[2] agree with the results of Benson *et al.*[8] and Steiner and Rideal.[9] Note that the two newest studies[1,2] have measured both the forward and reverse rates and have shown that the rate coefficient ratio agrees with equilibrium constant data.

References

[1]L. C. Miller and R. I. Gordon, J. Chem. Phys. **75**, 5305 (1991).
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$Cl + HO_2 \rightarrow HCl + O_2$ (1)
$\rightarrow ClO + HO$ (2)

$\Delta H°(1) = -228$ kJ·mol^{-1}
$\Delta H°(2) = 5.4$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.23 \pm 0.07) \times 10^{-11}$	250–414	Lee and Howard, 1982[1]	(a)
$k_1 = (4.4 \pm 1.5) \times 10^{-11}$	308	Cattell and Cox, 1986[2]	(b)
$k_2 = (9.4 \pm 1.2) \times 10^{-12}$			
Branching Ratios			
$k_2/k = 1.09 \exp(-478/T)$	250–414	Lee and Howard, 1982[1]	(a)
Reviews and Evaluations			
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	NASA, 1990[5]	(d)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		

Comments

(a) Discharge flow system with LMR detection of HO_2, HO, and ClO. On the basis of the temperature independent overall rate coefficient and the temperature dependent branching ratio, the authors derived the rate coefficient expressions $k_1 = 1.8 \times 10^{-11} \exp[(170 \pm 80)/T]$ cm^3 molecule^{-1} s^{-1} and $k_2 = 4.1 \times 10^{-11} \exp[-(450 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1}.

(b) Molecular modulation technique over the pressure range 50–760 Torr.

(c) See Comments on Preferred Values.

(d) Based on direct study of Lee and Howard,[1] supported by room temperature results of Cattell and Cox.[2]

Preferred Values

$k_1 = 3.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2 = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.8 \times 10^{-11} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–420 K.

$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–420 K.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 298 K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is largely reproduced from our earlier evaluation, CODATA, 1984[3] and incorporates the Comment in IUPAC, 1989.[4] The preferred values for k_1 and k_2 are based on results of the direct study by Lee and Howard.[1] These expressions were derived by the authors from data on the overall rate coefficient and the branching ratio. The total rate coefficient is temperature independent over the range 250–420 K with a value of 4.2×10^{-11} cm^3 molecule^{-1} s^{-1}. The room temperature results of Cattell and Cox[2] are in good agreement with this recommendation. Based on the combined results of these two studies, neither channel shows any pressure dependence between 1 mbar and 1 bar showing that stabilization of the HOOCl* intermediate does not occur and that the two bimolecular channels make up the entire reaction pathway. Results of earlier indirect studies[6-9] were not used.

The value of k_2 combined with the rate coefficient $k(ClO + HO \rightarrow Cl + HO_2)$ [this evaluation] leads to a heat of formation of HO_2 at 298 K of 13.8 kJ·mol^{-1}, in reasonably good agreement with the value of $\Delta H_f(HO_2)$ = 10.5 kJ·mol^{-1} of Howard.[10]

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$Cl + H_2O_2 \rightarrow HCl + HO_2$

$\Delta H° = -63$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.2×10^{-13}	298	Watson *et al.*, 1976[1]	(a)
6.2×10^{-13}	295	Leu and DeMore, 1976[2]	(b)
$1.24 \times 10^{-12} \exp[-(384 \pm 168)/T]$	265–400	Michael *et al.*, 1977[3]	(c)
$(3.6 \pm 0.5) \times 10^{-13}$	299		
$(4.0 \pm 0.4) \times 10^{-13}$	298	Poulet *et al.*, 1978[4]	(b)
$1.05 \times 10^{-11} \exp[-(982 \pm 102)/T]$	298–424	Keyser, 1980[5]	(d)
$(4.1 \pm 0.2) \times 10^{-13}$	298		
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(-980/T)$	265–424	CODATA, 1980[6]; IUPAC, 1989[7]	(e)
$1.1 \times 10^{-11} \exp(-980/T)$	200–300	NASA, 1990[8]	(f)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl.
(b) Discharge flow system with MS detection of H_2O_2.
(c) Flash photolysis system in a flowing reactor cell with resonance fluorescence detection of Cl.
(d) Discharge flow system with resonance fluorescence detection of Cl. A fast flow sampling procedure limited H_2O_2 decomposition to less than 5%.
(e) See Comments on Preferred Values.
(f) Based on results of Keyser.[5]

Preferred Values

$k = 4.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-11} \exp(-980/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 265–424 K.

Reliability
$\Delta\log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
This data sheet is largely reproduced from our previous evaluation, CODATA, 1980.[6] The room temperature rate coefficients reported in references 1–5 range from (3.6–6.2) $\times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The studies of Michael *et al.*,[3] Poulet *et al.*[4] and Keyser[5] are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser.[5] The data of Michael *et al.*[3] below 300 K are in good agreement; however, the A-factor reported is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 above 300 K. More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson[9] using mass spectrometry confirmed that this reaction proceeds only by the H-atom abstraction mechanism.

References

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$Cl + O_2 + M \rightarrow ClOO + M$

$\Delta H^\circ = -23.8$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.9 \pm 2.9) \times 10^{-33}$ [O_2]	186.5	Nicovich *et al.*, 1991[1]	(a)
$1.6 \times 10^{-33}(T/300)^{-2.9}$ [O_2]	160–260	Baer *et al.*, 1991[2]	(b)
6.4×10^{-33} [O_2]	186.5		
$1.4 \times 10^{-33}(T/300)^{-3.9}$ [N_2]	160–260		
Reviews and Evaluations			
1.7×10^{-33} [N_2]	298	IUPAC, 1989[3]	(c)
$2.7 \times 10^{-33}(T/300)^{-1.5}$ [air]	200–300	NASA, 1990[4]	(d)

Comments

(a) Laser flash photolysis of Cl_2–O_2 mixtures at 181–200 K and O_2 pressures of 15–40 Torr. Resonance fluorescence detection of Cl($^2P_{3/2}$). An equilibrium constant for the reaction of K_p = 18.9 atm^{-1} was determined at 185.4 K.
(b) Laser flash photolysis of Cl_2–O_2–M mixtures with M = He, Ar, O_2 and N_2, with ClOO detection through UV absorption at 248 nm. Redetermination of the ClOO absorption cross section gave σ(248 nm) = 3.4×10^{-17} cm^2 molecule^{-1}. Measurements over the temperature range 160–260 K and pressure range 1–1000 bar were in agreement with Ref. 5. Negligible deviations from third-order behavior were observed at pressures below 10 bar. At higher pressures, an anomalous transition to a high pressure plateau was observed. This and the anomalously strong temperature dependence suggest a radical-complex mechanism. An equilibrium constant of $K_p = 5.3 \times 10^{-6} \exp(23.4$ kJ·mol$^{-1}/RT)$ bar^{-1} was determined over the range 180–300 K.
(c) Based on the limited data from Ref. 6.
(d) Based on preliminary data from Ref. 1 and a temperature dependence calculated[7] for an assumed energy-transfer mechanism of the reaction.

Preferred Values

$k_0 = 1.4 \times 10^{-33}(T/300)^{-3.9}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 160–300 K.

$k_0 = 1.6 \times 10^{-33}(T/300)^{-2.9}$ $[O_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 160–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 200 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The two recent determinations are in good agreement and are also consistent with the older data of Ref. 6, if one takes into account the strong temperature dependence of k_0. The most extensive measurements of Ref. 2 are the basis for the preferred value. No falloff expressions are reported here, because deviations from third-order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism operating in this case. $\Delta H°$ is obtained from the analysis of Ref. 2.

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$ClOO + M \rightarrow Cl + O_2 + M$

$\Delta H° = 23.8$ $kJ \cdot mol^{-1}$

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.9×10^{-14} $[O_2]$	185.4	Nicovich *et al.*, 1991[1]	(a)
2.8×10^{-10} $\exp(-1820/T)$ $[N_2]$	160–260	Baer *et al.*, 1991[2]	(a)
6.2×10^{-13} $[N_2]$	298*		
6.3×10^{-10} $\exp(-2030/T)$ $[O_2]$	160–260		
1.1×10^{-14} $[O_2]$	185.4		
Reviews and Evaluations			
1.5×10^{-8} $\exp(-3285/T)$ $[N_2]$	200–300	IUPAC, 1989[3]	(b)
2.4×10^{-13} $[N_2]$	298		
1.1×10^{-12} [air]	298	NASA, 1990[4]	(c)

Comments

(a) From measurements of the reverse reaction and the equilibrium constant.

(b) Based on the data of Refs. 5 and 6.

(c) Based on the data of Ref. 1 and calculations of the equilibrium constant, using $\Delta H_f°(ClOO) = 97.5$ $kJ \cdot mol^{-1}$ as in this evaluation. Estimated temperature dependence for the reverse reaction assuming an energy transfer mechanism.

Preferred Values

$k_0 = 6.2 \times 10^{-13}$ $[N_2]$ s^{-1} at 298 K.

$k_0 = 2.8 \times 10^{-10} \exp(-1820/T)$ $[N_2]$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the most extensive data of Ref. 2. No falloff effects are observed at pressures below 1 bar. The reaction probably does not proceed via an energy transfer mechanism (see comments on the reverse reaction $Cl + O_2 + M \rightarrow ClOO + M$).

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$Cl + O_3 \rightarrow ClO + O_2$

$\Delta H^\circ = -162\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.49 \times 10^{-11} \exp[-(233 \pm 46)/T]$	269–385	Nicovich, Kreutter, and Wine, 1990[1]	(a)
$1.19 \times 10^{-11} \exp[-(33 \pm 37)/T]$	189–269		
1.14×10^{-13}	298		
Relative Rate Coefficients			
9.7×10^{-12}	197	DeMore, 1991[2]	(b)
1.1×10^{-11}	217		
Reviews and Evaluations			
$2.7 \times 10^{-11} \exp(-257/T)$	205–298	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$2.9 \times 10^{-11} \exp(-260/T)$	205–300	NASA, 1990[5]	(c)

Comments

(a) Laser flash photolysis system with resonance fluorescence detection of Cl atoms. Cl atoms produced by 355 nm photolysis of Cl_2.

(b) Competitive chlorination of O_3–CH_4 mixtures. Cl atoms were produced by the 320–400 nm photolysis of Cl_2. The rate coefficient ratios $k/k(Cl + CH_4)$ placed on an absolute basis by use of $k(Cl + CH_4) = 9.6 \times 10^{-12} \exp(-1350/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(c) Based on the data of Watson *et al.*,[6] Zahniser *et al.*,[7] Kurylo and Braun[8] and Clyne and Nip.[9]

Preferred Values

$k = 1.2 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 2.9 \times 10^{-11} \exp(-260/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 205–298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a fit to the data within the temperature range 205–298 K reported from the studies of Watson *et al.*,[6] Zahniser *et al.*,[7] Kurylo and Braun[8] and Clyne and Nip.[9] In this temperature range the rate constants at any particular temperature agree to within 30–40%. Results of the recent study by Nicovich *et al.*[1] show non-Arrhenius behavior over the temperature range 189–385 K. The new results are in very good agreement with the present recommendation above about ~250 K; at lower temperatures they are higher than the recommendation although still within its stated uncertainty down to about 220 K.

Vanderzanden and Birks[10] have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1–0.5%) of $O_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore[11] in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu[12] were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the $Cl + O_3$ system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2}, respectively. They suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder *et al.*[13] in a study of infrared line intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the $Cl + O_3$ reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals. These authors point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[ClO] : [O_3]_0$ when using the $Cl + O_3$ reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

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$Cl + HONO_2 \rightarrow HCl + NO_3$

$\Delta H^\circ = -14$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5.0 \times 10^{-16}$	298	Zagogianni, Mellouki and Poulet, 1987[1]	(a)
$<2.0 \times 10^{-16}$	298–400	Wine, Wells and Nicovich, 1988[2]	(b)
Reviews and Evaluations			
$<2.0 \times 10^{-16}$	298	IUPAC, 1989[3]	(c)
$<2.0 \times 10^{-16}$	298	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system with EPR detection of Cl in excess HNO_3. The same upper limit to the rate coefficient was found for the reaction of ClO with HNO_3.

(b) Laser photolysis of Cl_2-HNO_3 mixtures at 351 nm. Reaction was followed by observation of NO_3 formation using long-path laser absorption spectroscopy, and also by monitoring Cl atom decay by resonance fluorescence. No evidence was found for any reaction between Cl and HNO_3.

(c) See Comments on Preferred Values.

(d) Based on results of Wine *et al.*[2]

Preferred Values

$k < 2.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred upper limit to the rate coefficient is based on the work of Wine *et al.*[2] The new data[1,2] show that the measurements of Kurylo *et al.*,[5] upon which previous recommended upper limits were based, were well above the true value for the rate coefficient of this reaction.

References

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$Cl + NO_3 \rightarrow ClO + NO_2$

$\Delta H^\circ = -50$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Mellouki, Le Bras and Poulet, 1987[1]	(a)
Relative Rate Coefficients			
$(7.6 \pm 1.1) \times 10^{-11}$	296	Cox *et al.*, 1984[2]	(b)
$(2.7 \pm 1.0) \times 10^{-11}$	298	Burrows, Tyndall and Moortgat, 1985[3]	(c)
$(5.5 \pm 2.0) \times 10^{-11}$	278–338	Cox *et al.*, 1987[4]	(d)
Reviews and Evaluations			
2.6×10^{-11}	200–300	IUPAC, 1989[5]	(e)
2.6×10^{-11}	200–300	NASA, 1990[6]	(f)

Comments

(a) Discharge flow system with EPR detection of Cl and NO, the latter being used to titrate NO_3 radicals. Pseudo-first order decay of Cl monitored in the presence of excess NO_3. Pressure was 0.8 Torr.
(b) Time-dependent measurements of NO_3 absorption at 662 nm in the photolysis of Cl_2–$ClONO_2$–N_2 mixtures. First-order loss of NO_3 assumed to be due to reaction with Cl and rate coefficient k determined from steady state [Cl] computed from model chemistry. Rate coefficient measured relative to k(Cl + $ClONO_2$) = 1.18×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (this evaluation) using $\sigma_{NO_3} = 1.7 \times 10^{-17}$ cm^2 $molecule^{-1}$ at 662 nm. Pressure = 1 atm.
(c) Steady-state NO_3 radical concentrations measured by absorption in steady-state photolysis of Cl_2–$ClONO_2$–N_2 mixtures. Rate coefficient measured relative to k(Cl + $ClONO_2$) = 1.18×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (this evaluation). Used $\sigma_{NO_3} = 1.85 \times 10^{-17}$ cm^2 $molecule^{-1}$ at 662 nm.
(d) Steady-state NO_3 radical concentrations measured in modulated photolysis of Cl_2–$ClONO_2$–N_2 mixtures. Rate coefficient measured relative to k(Cl + $ClONO_2$) = 1.18×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (this evaluation). Used $\sigma_{NO_3} = 1.7 \times 10^{-17}$ cm^2 $molecule^{-1}$ at 662 nm. Pressure = 1 atm.
(e) See Comments on Preferred Values.
(f) Based on results of Mellouki *et al.*[1]

Preferred Values

$k = 2.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 400$ K

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5] The agreement between the earlier relative rate measurements is not good and probably arises from complications in the chemistry of the systems used. The preferred value is based on the recent direct measurement from Mellouki *et al.*[1]

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Cl + OClO → ClO + ClO

$\Delta H° = -18$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.0 \times 10^{-12}$	300	Clyne and Coxon, 1968[1]	(a)
$(8.5 \pm 1.2) \times 10^{-12}$	300	Basco and Dogra, 1971[2]	(b)
$5.9 \times 10^{-11} \exp[(0 \pm 120)/T]$	298–588	Bemand, Clyne and Watson, 1973[3]	(c)
$(5.9 \pm 0.9) \times 10^{-11}$	298		
$(6.1 \pm 0.9) \times 10^{-11}$	298		
$3.1 \times 10^{-11} \exp(160/T)$	229–428	Toohey, 1988[4]	(d)
5.45×10^{-11}	298		
Relative Rate Coefficients			
$3.7 \times 10^{-10} \exp[-(3020 \pm 101)/T]$	355–365	Gritsan, Panfilov and Sukhanov, 1975[5]	(e)
Reviews and Evaluations			
$3.4 \times 10^{-11} \exp(160/T)$	298–430	IUPAC, 1989[6]	(f)
$3.4 \times 10^{-11} \exp(160/T)$	200–300	NASA, 1990[7]	(g)

Comments

(a) Discharge flow system with UV absorption of OClO and ClO product. Lower limit to the rate coefficient only determined.
(b) Flash photolysis of OClO with UV absorption detection of OClO and ClO.
(c) Discharge flow system with resonance fluorescence detection of Cl decay in excess OClO and MS determination of OClO decay in excess Cl. The first 298 K value is the average obtained from the two techniques; temperature independence determined from Cl atom decay data at 300, 431 and 588 K. The second 298 K value was obtained from OClO decay in the presence of excess NO and Cl, in the unscavenged NO + OClO reaction at large extents of reaction.
(d) Discharge flow system with resonance fluorescence detection of Cl.
(e) Thermal decomposition of OClO. Complex system.
(f) See Comments on Preferred Values.
(g) Based on data of Toohey[4] and Bemand *et al.*[3]

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.4 \times 10^{-11} \exp(160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–450 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The new data of Toohey[4] agree well with the previous work of Bemand *et al.*[3] at 298 K, but show a small negative temperature dependence over a similar range to that over which Bemand *et al.*[3] saw little change in k. The preferred value is the average of the 298 K values from these two studies and the temperature dependence of Toohey is accepted but with error limits covering the possibility that k is independent of temperature. Earlier work in Ref. 2 and 5 is rejected following the recommendation of Bemand *et al.*[3]

References

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[7]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Cl + Cl_2O \rightarrow Cl_2 + ClO$

$\Delta H° = -101$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.33 \pm 0.54) \times 10^{-11}$	298	Ray, Keyser and Watson, 1980[1]	(a)
$(1.03 \pm 0.08) \times 10^{-10}$	298	Ray, Keyser and Watson, 1980[1]	(b)
Relative Rate Coefficients			
$(1.1 \pm 0.35) \times 10^{-10}$	298	Burrows and Cox, 1981[2]	(c)
Reviews and Evaluations			
9.8×10^{-11}	200–300	NASA, 1990[3]	(d)

Comments

(a) Discharge flow system with MS monitoring of the pseudo-first-order decay of [Cl_2O] in excess [Cl], at a pressure of 2 Torr He.
(b) Discharge flow system with resonance fluorescence detection of pseudo-first-order decay of [Cl] in excess [Cl_2O], at a pressure of 2 Torr He.
(c) Modulated photolysis of mixtures of Cl_2, Cl_2O, H_2, O_2, and N_2, at 1 atmosphere pressure. Value of k derived from $k/k(Cl + H_2) = 6900$ and $k(Cl + H_2) = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(d) Based on results of Ray *et al.*[1]

Preferred Values

$k = 9.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred value is the mean of the values obtained by Ray *et al.*[1] using two completely independent techniques. This value has been confirmed by the relative rate study of Burrows and Cox.[2] The much lower value reported earlier by Basco and Dogra[4] has been rejected. The Arrhenius parameters have not been determined experimentally; however, the high value of k determined at 298 K precludes a substantial positive activation energy. The agreement between the low-pressure studies and the high-pressure study implies that there is no apparent pressure dependence over the pressure range 1 mbar – 1 bar.

References

[1]G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
[2]J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1, **77**, 2465 (1981).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]N. Basco and S. K. Dogra, Proc. Roy. Soc. London, Series A, **323**, 401 (1971).

$Cl + Cl_2O_2 \rightarrow Cl_2 + ClOO$

$\Delta H° = -154$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.4) \times 10^{-10}$	298	Friedl, 1991[1]	(a)
Relative Rate Coefficients			
1.0×10^{-10}	233	Cox and Hayman, 1988[2]	(b)
Reviews and Evaluations			
1.0×10^{-10}	298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow – mass spectrometric study.
(b) Static photolysis of $Cl_2/Cl_2O/N_2$ mixtures at 350 nm. Time-dependence of $[Cl_2O_2]$ and $[Cl_2O]$ monitored by photodiode array UV spectroscopy. Value of k determined relative to $k(Cl + Cl_2O)$.
(c) Based on results of the absolute rate study of Friedl[1] and the relative rate study of Cox and Hayman.[2]

Preferred Values

$k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred value is based on results of the discharge flow – mass spectrometric study of Friedl[1] and the relative rate study of Cox and Hayman.[2] The Arrhenius parameters have not been determined experimentally; however, the agreement of the room temperature value and that at 233 K along with the high value of k precludes a significant temperature dependence.

References

[1]R. R. Friedl, manuscript in preparation (1991).
[2]R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$

$\Delta H° = -80$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.3 \times 10^{-12} \exp(150/T)$	219–298	Margitan, 1983[1]	(a)
$(1.04 \pm 0.04) \times 10^{-11}$	298		
$7.3 \times 10^{-12} \exp(165/T)$	220–296	Kurylo, Knable and Murphy, 1983[2]	(b)
$(1.20 \pm 0.24) \times 10^{-11}$	296		
Reviews and Evaluations			
$6.8 \times 10^{-12} \exp(160/T)$	219–298	CODATA, 1984[3]; IUPAC, 1989[4]	(c)
$6.8 \times 10^{-12} \exp(160/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Flash photolysis of Cl_2 at 355 nm. First-order decay of [Cl] monitored by resonance fluorescence. $O(^3P)$-atom abstraction channel to give $ClO + ClONO$ shown to be unimportant based on results of experiments with added NO, in which Cl was not regenerated by the fast reaction $ClO + NO \rightarrow Cl + NO_2$.

(b) Flash photolysis of CCl_4 or $COCl_2$. First-order decay of [Cl] monitored by resonance fluorescence. Results supersede earlier results[6] from same laboratory.

(c) See Comments on Preferred Values.

(d) Based on results of Margitan[1] and Kurylo *et al.*[2]

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.8 \times 10^{-12} \exp(160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 219–298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[3] The preferred value averages the results of Margitan[1] and Kurylo *et al.*,[2] which are in good agreement. These results show that the rate coefficient for this reaction is two orders of magnitude greater than was indicated by the only earlier published study.[6] In that study it now seems likely that the reaction actually being observed was the slower reaction $O(^3P) + ClONO_2$. Margitan[1] has shown that the reaction proceeds by Cl atom abstraction rather than by O-atom abstraction.

References

[1] J. J. Margitan, J. Phys. Chem. **87**, 674 (1983).
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[3] CODATA, Supplement II, 1984 (see references in Introduction).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).
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$Cl + CH_4 \rightarrow HCl + CH_3$

$\Delta H^\circ = 7.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.93 \pm 0.13) \times 10^{-14}$	298	Dobis and Benson, 1987[1]	(a)
$(9.17 \pm 0.75) \times 10^{-14}$	294 ± 1	Sawerysyn *et al.*, 1987[2]	(b)
Reviews and Evaluations			
$9.6 \times 10^{-12} \exp(-1350/T)$	200–300	CODATA, 1982[3]; IUPAC, 1989[4]	(c)
$1.1 \times 10^{-11} \exp(-1400/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Very low pressure reactor system with MS detection of reactants and products.
(b) Discharge flow system with MS detection.
(c) See Comments on Preferred Values.
(d) The 298 K rate coefficient was the average of the absolute rate coefficients reported by Watson *et al.*,[6] Manning and Kurylo,[7] Whytock *et al.*,[8] Michael and Lee,[9] Lin *et al.*,[10] Zahniser *et al.*,[11] Keyser[12] and Ravishankara and Wine[13] and the relative rate coefficients of Pritchard *et al.*,[14,15] Knox,[16] Knox and Nelson[17] and Lin *et al.*[10] The preferred Arrhenius expression was derived to best fit all of the reliable experimental data between 200 and 300 K.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred value at 298 K is obtained by taking the mean from the most reliable absolute (Watson *et al.*,[6] Manning and Kurylo,[7] Whytock *et al.*,[8] Michael and Lee,[9] Lin *et al.*,[10] Zahniser *et al.*,[11] Keyser,[12] and Ravishankara and Wine[13]) and the most reliable relative (Prichard *et al.*,[14,15] Knox,[16] Knox and Nelson[17] and Lin *et al.*[10]) rate coefficient studies. The recent room temperature absolute rate coefficients of Dobis and Benson[1] and Sawerysyn *et al.*[2] are in good agreement with this preferred value.

The preferred Arrhenius expression is derived to best fit all the reliable experimental data between 200 and 300 K. Data obtained above 300 K are not considered due to the non-linear Arrhenius behavior observed in the absolute rate coefficient studies.[8,10,12,13] The average values of k at 230 K are: 3.19×10^{-14} cm^3 molecule^{-1} s^{-1} (flash photolysis);[6,8,9,13] 2.67×10^{-14} cm^3 molecule^{-1} s^{-1} (discharge flow);[11,12] and 2.27×10^{-14} cm^3 molecule^{-1} s^{-1} (competitive chlorination).[10,14–17] These differences increase at lower temperatures. Ravishankara and Wine[13] have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures ($T < 240$ K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine[13] is proven, it is assumed that the discharge flow and competitive chlorination results are reliable. The Arrhenius expression is derived to yield the preferred values of k at 298 K (1.04×10^{-13} cm^3 molecule^{-1} s^{-1}) and at 230 K (2.71×10^{-14} cm^3 molecule^{-1} s^{-1}—this is a simple mean of the three average values obtained from each of the three techniques). The preferred expression of $9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} essentially yields rate coefficients similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used, then an alternate expression of $6.4 \times 10^{-12} \exp(-1220/T)$ cm^3 molecule^{-1} s^{-1} is obtained (k at 298 K = 1.07×10^{-13} cm^3 molecule^{-1} s^{-1} and k at 230 K = 3.19×10^{-14} cm^3 molecule^{-1}s^{-1}). It should be noted that the rate coefficient ratios $k(Cl + O_3)/k(Cl + CH_4)$ determined by DeMore[18] at 197 K and 217 K are in reasonable agreement with the present evaluations for these reactions (see the data sheet on the $Cl + O_3$ reaction).

References

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$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$

Low-pressure rate coefficient

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.15 \pm 0.30) \times 10^{-21}\ T^{-3.5}$ [Ar]	210–361	Brunning and Stief, 1985[1]	(a)
6.9×10^{-30} [Ar]	298		
Relative Rate Coefficients			
$(5.2 \pm 0.7) \times 10^{-30}$ [air]	295	Wallington *et al.*, 1990[2]	(b)
Reviews and Evaluations			
$8.0 \times 10^{-30}(T/300)^{-3.5}$ [air]	200–300	NASA, 1990[3]	(c)

Comments

(a) Cl atoms formed by flash photolysis of CCl_4 at 165 nm and detected by resonance fluorescence. The concentration of the bath gas Ar was varied in the range $(2.7–120) \times 10^{17}$ molecule cm^{-3}. Some experiments with M = N_2 were also conducted. Falloff exrapolations were made using $F_c = 0.6$.

(b) Relative rate measurements. Cl atoms generated by photolysis of Cl_2 in the presence of C_2H_2 and C_2H_6 (or C_2H_5Cl). Decay of C_2H_2, C_2H_6 (or C_2H_5Cl) followed by FTIR spectroscopy. Relative rate coefficients have been placed on an absolute basis using $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Measurements were conducted over the pressure range 10–5800 Torr. Falloff extrapolations were made with $F_c = 0.6$.

(c) Based mainly on the data at pressures below 1 atm of Refs. 1 and 2. The temperature dependence was from Brunning and Stief.[1]

Preferred Values

$k_0 = 6 \times 10^{-30}(T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

References 1 and 2 provide the largest data base for extrapolation to the low pressure limit. Falloff curves were constructed with $F_c = 0.6$. The preferred values are averages of k_0 from Refs. 1 and 2, assuming equal rates for M = Ar and N_2. The temperature dependence is from Ref. 1. The low-pressure data for M = He at 295 K from Ref. 4 [$k_0 = (2 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 0.5–2 Torr] appear consistent with the data from Refs. 1 and 2.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.52 \pm 0.15) \times 10^{-4}\, T^{-2.63}$	210–361	Brunning and Stief, 1985[1]	(a)
4.7×10^{-11}	298		
Relative Rate Coefficients			
$(2.3 \pm 0.7) \times 10^{-10}$	295	Wallington *et al.*, 1990[2]	(b)
Reviews and Evaluations			
$1.0 \times 10^{-10}(T/300)^{-2.6}$	200–300	NASA, 1990[3]	(c)

Comments

(a)– (c) See comments (a)– (c) for k_0.

Preferred Values

$k_\infty = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Only the study of reference 2, on which the preferred values are based, extends over a sufficiently large pressure range to allow for an extrapolation to k_∞. It should be noted that the falloff curve of reference 1 only covers the low pressure part and is too uncertain in its extrapolation to k_∞. A series of earlier measurements[4–7] were made near 1 atm and room temperature. Under these conditions, the reaction is close to the center of the falloff curve. The results of these measurements are in close agreement [$\Delta \log k(1\text{ atm}) = 0.2$] with the falloff curve of reference 2 (see Intermediate Falloff Range).

Intermediate Falloff Range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
5.6×10^{-11}	550	$CClF_3$	295	Lee and Rowland, 1977[5]	(a)
1.26×10^{-10}	4200	$CClF_3$	295		
7.2×10^{-11}	735	air	296 ± 2	Atkinson and Aschmann, 1985[6]	(b)
7.1×10^{-11}	740	air	295 ± 2	Wallington, Skewes and Siegl, 1988[7]	(b)
9.5×10^{-11}	740	air	295	Wallington *et al.*, 1990[2]	(c)

Comments

(a) Measurements with neutron irradiation and GC relative to the reaction Cl + HI (evaluated with k(Cl + HI) = 1.26×10^{-10} cm^3 molecule^{-1} s^{-1}, see discussion in reference 2).
(b) Measurements with steady-state photolysis using GC, relative to the reaction Cl + n-butane (evaluated with k(Cl + n-butane) = 2.25×10^{-10} cm^3 molecule^{-1} s^{-1}, see discussion in reference 2).
(c) See comment (b) for k_0.

References

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$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$

$\Delta H^\circ = -92.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.6^{+1}_{-0.3}) \times 10^{-29}$ [air]	295	Wallington *et al.*, 1990[1]	(a)

Comments

(a) Measurements of k performed by a relative rate technique. Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_4 and C_2H_6 (or C_2H_5Cl). Decay of C_2H_4, C_2H_6 (or C_2H_5Cl) monitored by FTIR spectroscopy. Using a value of 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} for the rate coefficient for the $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$ reaction, the relative data were placed on an absolute basis. The reaction was studied over the pressure range 10–3000 Torr and the measured rate coefficients fitted with $F_c = 0.6$.

Preferred Values

$k_0 = 1.6 \times 10^{-29}(T/298)^{-3.5}$[air] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Reference 1 is the only measurement in the falloff range which allows for extrapolation to k_0. The preferred values are based on reference 1 and an estimated temperature dependence such as observed for $Cl + C_2H_2 + M \rightarrow ClC_2H_2 + M$ (see this evaluation).

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(3.05^{+2}_{-0.4}) \times 10^{-10}$	295	Wallington *et al.*, 1990[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The falloff extrapolation of the data from reference 1 with $F_c = 0.6$ is consistent with results in the intermediate falloff range.

Intermediate Falloff Range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
9.3×10^{-11}	640	$CClF_3$	295	Lee and Rowland, 1977[2]	(a)
1.27×10^{-10}	1060	$CClF_3$	295		
1.70×10^{-10}	4100	$CClF_3$	295		
1.66×10^{-10}	4000	$CClF_3$	298	Iyer, Rogers and Rowland, 1983[3]	(b)
1.21×10^{-10}	735	air	296 ± 2	Atkinson and Aschmann, 1985[4]	(c)
9.8×10^{-11}	735	air	298 ± 2	Atkinson and Aschmann, 1987[5]	(d)
1.21×10^{-10}	740	air	295 ± 2	Wallington, Skewes and Siegl, 1988[6]	(c)

Comments

(a) Measurements with neutron irradiation and GC relative to the reaction Cl + HI (evaluated with k(Cl + HI) = 1.26×10^{-10} cm^3 molecule^{-1} s^{-1}, see discussion in reference 2).

(b) Measurements with neutron irradiation and GC relative to the reaction Cl + C_2H_6 (evaluated with k(Cl + C_2H_6) = 5.7×10^{-11} cm^3 molecule^{-1} s^{-1}, see discussion in reference 1).

(c) Measurements with steady-state photolysis gas chromatography relative to Cl + n-butane (evaluated with k(Cl + n-butane) = 2.25×10^{-10} cm^3 molecule^{-1} s^{-1}, see discussion in reference 1).

(d) As comment (c) but relative to Cl + C_2H_6 with k(Cl + C_2H_6) = 5.7×10^{-11} cm^3 molecule^{-1} s^{-1}.

References

[1]T. J. Wallington, J. M. Andino, S. M. Lovkovic, E. W. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).

[2]F. S. C. Lee and F. S. Rowland, J. Phys. Chem. **81**, 1235 (1977).

[3]S. R. Iyer, P. J. Rogers, and F. S. Rowland, J. Phys. Chem. **87**, 3799 (1983).

[4]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[5]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **19**, 1097 (1987).

[6]T. J. Wallington, L. M. Skewes, W. O. Siegl, J. Photochem. Photobiol. **A45**, 167 (1988).

$Cl + C_2H_6 \rightarrow HCl + C_2H_5$

$\Delta H° = -11.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.95 \pm 0.28) \times 10^{-11}$	298	Ray, Keyser and Watson, 1980[1]	(a)
$9.01 \times 10^{-11} \exp[-(133 \pm 15)/T]$	220–604	Lewis *et al.*, 1980[2]	(b)
$(5.48 \pm 0.30) \times 10^{-11}$	298		
$(6.10 \pm 0.11) \times 10^{-11}$	298	Dobis and Benson, 1990[3]	(c)
Reviews and Evaluations			
$7.7 \times 10^{-11} \exp(-90/T)$	220–350	CODATA, 1980;[4] IUPAC, 1989[5]	(d)
$7.7 \times 10^{-11} \exp(-90/T)$	220–350	NASA, 1990[6]	(e)

Comments

(a) Discharge flow system with MS detection of ethane.
(b) Discharge flow system with resonance fluorescence detection of Cl.
(c) Very low pressure reactor study. Cl atoms generated by microwave discharge of Cl_2–He mixtures, with MS analysis of reactants and products.
(d) Derived from the absolute rate coefficient data of Manning and Kurylo[7] and Lewis *et al.*[2]
(e) The 298 K rate coefficient was the mean of the absolute rate coefficients of Davis *et al.*,[8] Manning and Kurylo,[7] Ray *et al.*[1] and Lewis *et al.*,[2] with the temperature dependence being that which best fit the data of Manning and Kurylo[7] and Lewis *et al.*[2]

Preferred Values

$k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.2 \times 10^{-11} \exp(-100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–600 K.

Reliability
$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature rate coefficients of Davis *et al.*[8] (reduced by 10% as discussed previously[4]), Manning and Kurylo,[7] Ray *et al.*,[1] Lewis *et al.*[2] and Dobis and Benson,[3] all of which are in excellent agreement. The temperature dependence is the average of those from the two temperature-dependent studies of Manning and Kurylo[7] and Lewis *et al.*[2]

References

[1]G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
[2]R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[3]O. Dobis and S. W. Benson, J. Am. Chem. Soc. **112**, 1023 (1990).
[4]CODATA, 1980 (see references in Introduction).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
[7]R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).
[8]D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).

$Cl + C_3H_8 \rightarrow HCl + n\text{-}C_3H_7$ (1)
$\rightarrow HCl + i\text{-}C_3H_7$ (2)

$\Delta H°(1) = -8.4$ kJ·mol^{-1}
$\Delta H°(2) = -20.1$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.22 \pm 0.10) \times 10^{-10}$	295 ± 2	Wallington *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$1.3 \times 10^{-10} \exp(40/T)$	220–600	IUPAC, 1989[2]	(b)
$1.4 \times 10^{-10} \exp(40/T)$	220–607	NASA, 1990[3]	(c)

Comments

(a) Relative rate method. Cl atoms generated by photolysis of Cl_2 in one atmosphere of air. Relative disappearance rates of the organics studied were measured, leading to $k(Cl + C_3H_8)/k(Cl + n\text{-}C_4H_{10}) = 0.711 \pm 0.019$ and $k(Cl + C_2H_6)/k(Cl + n\text{-}C_4H_{10}) = 0.344 \pm 0.026$ at 295 ± 2 K. This results in $k(Cl + C_3H_8)/k(Cl + C_2H_6) = 2.07 \pm 0.17$. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).
(b) Based on the absolute rate coefficient data of Lewis *et al.*,[4] which are in generally good agreement with the relative rate coefficient measurements of Pritchard *et al.*,[5] Knox and Nelson[6] and Atkinson and Aschmann.[7]
(c) Based on the absolute rate coefficient data of Lewis *et al.*,[4] which are consistent with the relative rate coefficients of Pritchard *et al.*,[5] Knox and Nelson,[6] Atkinson and Aschmann[7] and Wallington *et al.*[1]

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2 \times 10^{-10} \exp(40/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–600 K.

Reliability
$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the absolute rate coefficient of Lewis *et al.*[4] and the relative rate measurements of Pritchard *et al.*,[5] Knox and Nelson,[6] Atkinson and Aschmann[7] and Wallington *et al.*,[1] all of which are in reasonable agreement. The temperature dependence is that determined by Lewis *et al.*[4]

References

[1]T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
[5]H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).
[6]J. H. Knox and R. L. Nelson, Trans Faraday Soc. **55**, 937 (1959).
[7]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$Cl + HCHO \rightarrow HCl + HCO$

$\Delta H^\circ = -67.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(6.84 \pm 0.71) \times 10^{-11}$	298	Poulet, Laverdet, and Le Bras, 1981[1]	(a)
Reviews and Evaluations			
$8.2 \times 10^{-11} \exp(-34/T)$	200–500	CODATA, 1984;[2] IUPAC, 1989[3]	(b)
$8.1 \times 10^{-11} \exp(-30/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with MS detection of reactants. Value of k derived from the measured ratio of $k(Cl + HCHO)/k(Cl + C_2H_6) = 1.16$ and $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) See Comments on Preferred Values.

(c) The 298 K rate coefficient was obtained from the absolute rate coefficients of Michael *et al.*,[5] Anderson and Kurylo[6] and Fasano and Nogar[7] and the relative rate coefficients of Niki *et al.*[8] and Poulet *et al.*[1] The temperature dependence was derived from a least-squares analysis of the absolute rate coefficient data of Michael *et al.*[5] and Anderson and Kurylo.[6] The A-factor was adjusted to fit the 298 K rate coefficient.

Preferred Values

$k = 7.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.2 \times 10^{-11} \exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The preferred temperature dependence is based on a least-squares fit to the 200–500 K data of Michael *et al.*[5] and the 223–323 K data of Anderson and Kurylo.[6] The preferred 298 K rate coefficient is based on these absolute studies and the room-temperature data of Niki *et al.*,[8] Fasano and Nogar[7] and Poulet *et al.*,[1] all of which are in good agreement.

References

[1]G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 1147 (1979).
[6]P. C. Anderson and M. J. Kurylo, J. Phys. Chem. **83**, 2053 (1979).
[7]D. M. Fasano and N. S. Nogar, Int. J. Chem. Kinet. **13**, 325 (1981).
[8]H. Niki, P. D. Maker, L. P. Breitenbach, and C. M. Savage, Chem. Phys. Lett. **57**, 596 (1978).

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad (1)$$
$$\rightarrow HCl + CH_2CHO \quad (2)$$

$\Delta H°(1) = -72.1$ kJ·mol^{-1}
$\Delta H°(2) = -44.8$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.6 \pm 1.4) \times 10^{-11}$	210–343	Payne *et al.*, 1990[1]	(a)
Relative Rate Coefficients			
$(8.15 \pm 0.82) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1988[2]	(b)
$(6.14 \pm 0.54) \times 10^{-11}$	298	Bartels, Hoyermann and Lange, 1989[3]	(c)
Branching Ratio			
$k_2/k < 0.07$	298	Bartels, Hoyermann and Lange, 1989[3]	(c)
Reviews and Evaluations			
7.6×10^{-11}	298	IUPAC, 1989[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl atoms.

(b) Relative rate method. Cl atoms generated in Cl_2–N_2–CH_3CHO–C_2H_6 mixtures from the photolysis of Cl_2 and the relative decay rates of CH_3CHO and C_2H_6 measured. The measured rate coefficient ratio was placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Discharge flow system with MS detection of CH_3CHO and of the C_2H_6 reference compound. Relative decay rates of CH_3CHO and C_2H_6 monitored, and the measured rate coefficient ratio placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation). Branching ratio derived from the products observed by MS.

(d) Based on the relative rate coefficient study of Niki *et al.*[5]

Preferred Values

$k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–340 K.

$k_2/k < 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Payne *et al.*[1] and the relative rate coefficients of Niki *et al.*,[5] Wallington *et al.*[2] and Bartels *et al.*[3] The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne *et al.*[1] The branching ratio is derived from the data of Niki *et al.*[5] and Bartels *et al.*[3]

References

[1]W. A. Payne, D. F. Nava, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. **94**, 7190 (1990).
[2]T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
[3]M. Bartels, K. Hoyermann, and U. Lange, Ber Bunsenges Phys. Chem. **93**, 423 (1989).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem. **89**, 588 (1985).

Cl + C_2H_5CHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.17 \pm 0.10) \times 10^{-10}$	295 ± 2	Wallington *et al.*, 1988[1]	(a)

Comments

(a) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2–air mixtures, and the decay rates of C_2H_5CHO and C_2H_6 monitored by GC. The measured rate coefficient ratio was placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Wallington *et al.*,[1] with expanded uncertainty limits.

Reference

[1]T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

Cl + CH_3COCH_3 → HCl + CH_3COCH_2

$\Delta H° = -20.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)

Comments

(a) Relative rate study. Cl atoms were generated by the photolysis of Cl_2–air (or N_2)–CH_3COCH_3–C_2H_5Cl mixtures. From the relative decays of CH_3COCH_3 and C_2H_5Cl, a rate coefficient ratio of $k(Cl + CH_3COCH_3)/k(Cl + C_2H_5Cl) = 0.295 \pm 0.015$ was obtained. Combined with a measurement of $k(Cl + C_2H_5Cl)/k(Cl + C_2H_6) = 0.201 \pm 0.027$[1] and $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the value cited in the table is obtained.

Preferred Values

$k = 3.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington *et al.*,[1] with expanded uncertainties.

Reference

[1]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$Cl + CH_3OH \rightarrow HCl + CH_2OH$

$\Delta H° = -37.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.33 \pm 0.70) \times 10^{-11}$	200–500	Michael *et al.*, 1979[1]	(a)
Relative Rate Coefficients			
$(4.73 \pm 0.42) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1988[2]	(b)
$(4.79 \pm 0.36) \times 10^{-11}$	298 ± 2	Nelson *et al.*, 1990[3]	(c)
Reviews and Evaluations			
5.7×10^{-11}	200–500	NASA, 1990[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl.

(b) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2–CH_3OH–C_2H_6–air (or N_2) mixtures at 740 Torr total pressure. Concentrations of CH_3OH and C_2H_6 monitored by GC and a rate coefficient ratio $k(Cl + CH_3OH)/k(Cl + C_2H_6) = 0.802 \pm 0.071$ determined. Rate coefficient ratio placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate study. Cl atoms generated from the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)–CH_3OH–cyclohexane mixtures at atmospheric pressure. Concentrations of CH_3OH and cyclohexane were measured by GC, and the rate coefficient ratio was placed on an absolute basis by use of k(Cl + cyclohexane) $= 3.11 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[5]

(d) Based on the rate coefficient data of Michael *et al.*[1] over the temperature range 200–500 K and the 298 K rate coefficient of Payne *et al.*[6] for the reaction $Cl + CH_3OD \rightarrow HCl + CH_2OD$.

Preferred Values

$k = 5.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–500 K.

Reliability

$\Delta \log k = 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The 298 K preferred value is the average of the rate coefficients of Michael *et al.*,[1] Wallington *et al.*[2] and Nelson *et al.*[3] and is in excellent agreement with the absolute rate coefficient of $(5.1 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K determined by Payne *et al.*[6] for the reaction $Cl + CH_3OD \rightarrow HCl + CH_2OD$. The zero temperature dependence is taken from the work of Michael *et al.*[1]

References

[1] J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 3652 (1979).

[2] T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[3] L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[4] NASA Evaluation No. 9, 1990 (see reference in Introduction).

[5] R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

[6] W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

$Cl + C_2H_5OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(8.75 \pm 0.95) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1988[1]	(a)
$(1.01 \pm 0.06) \times 10^{-10}$	298 ± 2	Nelson *et al.*, 1990[2]	(b)

Comments

(a) Relative rate study. Cl atoms generated by photolysis of Cl_2 in Cl_2–C_2H_5OH–C_2H_6–air (or N_2) mixtures at 740 Torr total pressure. C_2H_5OH and C_2H_6 monitored by GC and a rate coefficient ratio $k(Cl + C_2H_5OH)/k(Cl + C_2H_6) = 1.483 \pm 0.160$ determined. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate study. Cl atoms generated by photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)–ethanol–cyclohexane mixtures at atmospheric pressure. Concentrations of ethanol and cyclohexane measured by GC, and the rate constant ratio placed on an absolute basis by use of k(Cl + cyclohexane) $= 3.11 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[3]

Preferred Values

$k = 9.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Wallington *et al.*[1] and Nelson *et al.*,[2] which are in good agreement.

References

[1]T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[2]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[3]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$Cl + n\text{-}C_3H_7OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.49 \pm 0.12) \times 10^{-10}$	295 ± 2	Wallington *et al.*, 1988[1]	(a)
$(1.49 \pm 0.07) \times 10^{-10}$	298 ± 2	Nelson *et al.*, 1990[2]	(b)

Comments

(a) Relative rate study. Cl atoms generated by photolysis of Cl_2 in Cl_2–n-C_3H_7OH–C_2H_6–air (or N_2) mixtures at 740 Torr total pressure. n-C_3H_7OH and C_2H_6 monitored by GC and a rate coefficient ratio $k(Cl + n\text{-}C_3H_7OH)/k(Cl + C_2H_6) = 2.518 \pm 0.202$ determined. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Relative rate study. Cl atoms generated by the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–N_2 (or O_2)–n-propanol–cyclohexane mixtures at atmospheric pressure. Decay rates of n-propanol and cyclohexane measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(Cl + cyclohexane) $= 3.11 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[3]

Preferred Values

$k = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the data of Wallington *et al.*[1] and Nelson *et al.*,[2] which are in excellent agreement.

References

[1]T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).

[2]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).

[3]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$Cl + i\text{-}C_3H_7OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(8.40 \pm 0.35) \times 10^{-11}$	298 ± 2	Nelson *et al.*, 1990[1]	(a)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)–isopropyl alcohol–cyclohexane–O_2 (or N_2) mixtures at atmospheric pressure. Decay rates of isopropyl alcohol and cyclohexane measured, and rate coefficient ratio placed on an absolute basis by use of $k(Cl + \text{cyclohexane}) = 3.11 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[2]

Preferred Values

$k = 8.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
Based on the sole study of Nelson *et al.*[1]

References

[1]L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
[2]R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).

$Cl + CH_3OOH \rightarrow HCl + CH_3O_2$ (1)
$\rightarrow HCl + CH_2OOH$ (2)

$\Delta H°(1) = -72$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.9 \pm 0.3) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)

Comments

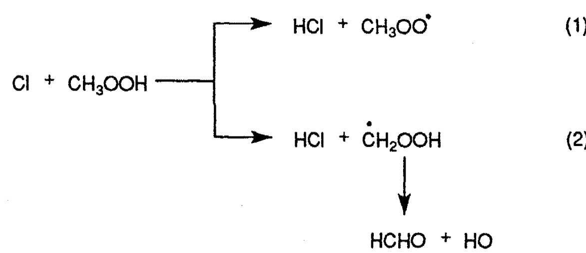
(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–N_2–CH_3OOH–C_2H_6 mixtures at 700 Torr total pressure, and CH_3OOH and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. Relative rate coefficient ratio placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values
The sole study carried out to date is that of Wallington *et al.*[1] The reaction may occur by the two pathways



and the formation of HO may have led to secondary reactions involving HO radicals. Since the room temperature rate coefficient for the Cl atom reaction with H_2O_2 (this evaluation) is two orders of magnitude lower than that for $Cl + CH_3OOH$, it is expected that channel (2) will dominate. Wallington *et al.*[1] concluded that secondary reactions involving HO radicals did not contribute $\geq 15\%$ to the observed CH_3OOH consumption. The cited uncertainty limits on the preferred values reflect this possibility of HO radical involvement in the Wallington *et al.*[1] study.

Reference

[1]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$$Cl + HCOOH \rightarrow HCl + HCO_2 \quad (1)$$
$$\rightarrow HCl + COOH \quad (2)$$

$\Delta H°(2) = -58$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.08 \pm 0.12) \times 10^{-13}$	295 ± 2	Wallington *et al.*, 1990[1]	(a,b)
$(1.83 \pm 0.10) \times 10^{-13}$	295 ± 2	Wallington *et al.*, 1990[1]	(a,c)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–air–HCOOH–CH_3Cl (or CH_4) mixtures at 700 Torr total pressure. HCOOH and CH_3Cl (or CH_4) monitored by FTIR absorption spectroscopy during the experiments.

(b) Relative to $k(Cl + CH_3Cl)$. Placed on an absolute basis by use of $k(Cl + CH_3Cl) = 4.75 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative to $k(Cl + CH_4)$. Placed on an absolute basis by use of $k(Cl + CH_4) = 9.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 2.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the rate coefficients obtained by Wallington *et al.*[1] relative to $k(Cl + CH_3Cl)$ and $k(Cl + CH_4)$, which are in good agreement. The relative importance of reaction channels (1) and (2) is not presently known.

Reference

[1]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$$Cl + CH_3COOH \rightarrow HCl + CH_2COOH \quad (1)$$
$$\rightarrow HCl + CH_3COO \quad (2)$$

$\Delta H°(2) = 10.9$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.8 \pm 0.4) \times 10^{-14}$	298 ± 1	Koch and Moortgat, 1990[1]	(a)

Comments

(a) Cl atoms generated by the photolysis of Cl_2 in Cl_2–CH_3COOH–CH_4–N_2 mixtures at 760 Torr total pressure. The concentrations of CH_3COOH and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio of $k(Cl + CH_3COOH)/k(Cl + CH_4) = 0.28 \pm 0.04$ was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation). An analogous experiment using CD_3COOH yielded a rate coefficient of $k(Cl + CD_3COOH) = (7.5 \pm 0.2) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, indicating that the majority of the reaction proceeds by reaction channel (1).

Preferred Values

$k = 2.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Koch and Moortgat.[1] The measured rate coefficient ratio of k(Cl + CH_3COOH)/k(Cl + CD_3COOH) = 3.7 at 298 ± 1 K[1] indicates that channel (1) dominates at 298 K.

Reference

[1]S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).

Cl + CH_3ONO_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.42 \pm 0.02) \times 10^{-13}$	298 ± 2	Nielsen *et al.*, 1991[1]	(a)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–CH_3ONO_2–C_2H_6–N_2 mixtures at atmospheric pressure. Concentrations of methyl nitrate and ethane measured by GC and the rate coefficient ratio placed on an absolute basis by use of k(Cl + C_2H_6) = 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 2.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Nielsen *et al.*[1] The reaction probably occurs via H-atom abstraction from the $-CH_3$ group.[1]

Reference

[1]O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1991).

Cl + $C_2H_5ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.5 \pm 0.8) \times 10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)
$(3.95 \pm 0.15) \times 10^{-12}$	298 ± 2	Nielsen *et al.*, 1991[2]	(b)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–ethyl nitrate–C_2H_5Cl–air mixtures at atmospheric pressure. Ethyl nitrate and C_2H_5Cl were measured by GC, and a rate coefficient ratio of k(Cl + ethyl nitrate)/k(Cl + C_2H_5Cl) = 0.46 ± 0.03 determined. Combined with k(Cl + C_2H_5Cl)/k(Cl + C_2H_6) = 0.201 ± 0.027[3] and k(Cl + C_2H_6) = 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

(b) Relative rate method. Cl atoms generated by the photolysis of Cl_2–ethyl nitrate–C_2H_6–N_2 mixtures at atmospheric pressure. Concentrations of ethyl nitrate and ethane measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(Cl + C_2H_6) = 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 4.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*[2] The reaction probably proceeds by H atom abstraction from the C–H bonds.[2]

References

[1]T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2]O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem Phys. Lett., **178**, 163 (1991).
[3]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos Chem. **10**, 301 (1990).

$Cl + n\text{-}C_3H_7ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(3.17 \pm 0.47) \times 10^{-11}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)
$(2.28 \pm 0.14) \times 10^{-11}$	298 ± 2	Nielsen *et al.*, 1990[2]	(b)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–n-propyl nitrate–C_2H_5Cl–air mixtures at atmospheric pressure. n-Propyl nitrate and C_2H_5Cl concentrations were measured by GC and a rate coefficient ratio of $k(Cl + n\text{-propyl nitrate})/k(Cl + C_2H_5Cl) = 2.67 \pm 0.16$ determined. Combined with $k(Cl + C_2H_5Cl)/k(Cl + C_2H_6) = 0.201 \pm 0.027$[3] and $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

(b) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–n-propyl nitrate–C_2H_6–N_2 mixtures at atmospheric pressure. Concentrations of n-propyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*[1] and Nielsen *et al.*[2] The reaction probably proceeds by H-atom abstraction from the C–H bonds.[2]

References

[1]T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2]O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, Chem. Phys. Lett. **178**, 163 (1990).
[3]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

Cl + i-$C_3H_7ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.8 \pm 1.1) \times 10^{-12}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)

Comments

(a) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2-isopropyl nitrate–C_2H_5Cl–air mixtures at atmospheric pressure. Concentrations of isopropyl nitrate and C_2H_5Cl measured by GC, and a rate coefficient ratio of k(Cl + isopropyl nitrate)/k(Cl + C_2H_5Cl) = 0.49 ± 0.06 determined. Combined with k(Cl + C_2H_5Cl)/k(Cl + C_2H_6) = 0.201 ± 0.027[2] and k(Cl + C_2H_6) = 5.9×10^{-11} cm^3 molecule^{-1} s^{-1} (this evaluation), the rate coefficient cited in the table is obtained.

Preferred Values

$k = 5.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington *et al.*[1]

References

[1]T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl and S. M. Japar, Int. J. Chem. Kinet. **22**, 665 (1990).
[2]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

Cl + $CH_3CO_3NO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 1.7) \times 10^{-13}$	298	Tsalkani *et al.*, 1988[1]	(a)
Relative Rate Coefficients			
$<7 \times 10^{-15}$	295 ± 2	Wallington *et al.*, 1990[2]	(b)

Comments

(a) Discharge flow system with EPR detection of Cl atoms.
(b) Relative rate method. Cl atoms generated by the photolysis of Cl_2 in Cl_2–air–$CH_3C(O)OONO_2$–CH_4 mixtures at 700 Torr total pressure, with the $CH_3C(O)OONO_2$ and CH_4 concentrations being monitored by FTIR absorption spectroscopy. Upper limit to relative rate coefficient ratio placed on an absolute basis by use of k(Cl + CH_4) = 9.9×10^{-14} cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k < 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington *et al.*,[2] in which no reaction of $CH_3C(O)OONO_2$ was observed in the presence of Cl atoms. In both studies,[1,2] the major impurity in the $CH_3C(O)OONO_2$ samples would be the C_{12}[1] or C_{13}[2] alkane solvent. While this is of no consequence in the relative rate study of Wallington *et al.*,[2] the presence of ~0.1% tridecane in the $CH_3C(O)OONO_2$ sample used by Tsalkani *et al.*[1] could account for the Cl reaction rate observed; their $CH_3C(O)OONO_2$ sample was >99% pure from IR measurements. The upper limit cited here is a factor of ~3 higher than measured by Wallington *et al.*[2] to allow for higher uncertainties.

References

[1]N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, J. Atmos. Chem. **7**, 409 (1988).
[2]T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

$Cl + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984[1]	(a)
$3.46 \times 10^{-11} \exp[-(2785 \pm 115)/T]$	478–723	Poulet *et al.*, 1984[2]	(b)
$(8.89 \pm 1.24) \times 10^{-15}$	295		
Relative Rate Coefficients			
$8 \times 10^{-11} \exp(-3000/T)$	370–413	Olbregts, Brasseur and Arijs, 1984[3]	(c)
Reviews and Evaluations			
$\leq 2.0 \times 10^{-15}$	298	IUPAC, 1989[4]	(d)
$< 2.0 \times 10^{-15}$	298	NASA, 1990[5]	(e)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl.

(b) Discharge flow system with MS detection of Cl. Data were obtained over the range 295–723 K, and a curved Arrhenius plot was observed.

(c) Relative rate method. Relative formation rates of products monitored in a competitive chlorination system between CH_3CN and $CHCl_3$. Placed on an absolute basis by use of $k(Cl + CHCl_3) = 1.15 \times 10^{-11} \exp(-1686/T)$ cm^3 molecule^{-1} s^{-1}.

(d) See Comments on Preferred Values.

(e) Based upon the upper limit to the rate coefficient measured by Kurylo and Knable.[1]

Preferred Values

$k \leq 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred 298 K rate coefficient is based on the upper limit to the rate coefficient determined by Kurylo and Knable.[1] The low temperature ($\leq$ 410 K) rate coefficient data of Poulet *et al.*[2] could have been influenced by a heterogeneous reaction. The rate coefficients of Olbregts *et al.*[3] at 370 and 413 K are in good agreement with the higher temperature data of Poulet *et al.*[2]

References

[1]M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).
[2]G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).
[3]J. Olbregts, G. Brasseur and E. Arijs, J. Photochem. **24**, 315 (1984).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Cl + HCOCl \rightarrow HCl + ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
8.8×10^{-13}	305	Sanhueza and Heicklen, 1975[1]	(a)
$(7.8 \pm 1.0) \times 10^{-13}$	298 ± 2	Niki *et al.*, 1980[2]	(b)
$1.2 \times 10^{-11} \exp(-815/T)$	266–321	Libuda *et al.*, 1990[3]	(c)
7.8×10^{-13}	298		

Comments

(a) Relative rate study. Rate coefficient ratios of $k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.85 \pm 0.43$ and $k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2) = 1.66 \pm 0.15$ (the errors are two standard deviations) derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidations of CH_2Cl_2 and CH_3Cl. Placed on an absolute basis by use of $k(Cl + CH_3Cl) = 5.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(Cl + CH_2Cl_2) = 4.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation). The rate coefficient cited in the table is the average of the two values obtained.

(b) Relative rate study. Rate coefficient ratio of $k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.6 \pm 0.2$ determined using FTIR absorption spectroscopy in irradiated Cl_2–CH_3Cl–O_2–N_2 mixtures at 700 Torr total pressure. Rate coefficient ratio placed on an absolute basis by use of $k(Cl + CH_3Cl) = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2–HC(O)Cl–CH_4–N_2 mixtures at 750 Torr total pressure. The concentrations of HC(O)Cl) and CH_4 were measured by FTIR absorption spectroscopy (HC(O)Cl) and/or gas chromatography (CH_4). Rate coefficient ratios were determined over the temperature range 265.8–321.3 K, and placed on an absolute basis by use of $k(Cl + CH_4) = 9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-11} \exp(-815/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 265–325 K.

Reliability

$\Delta \log k = 0.15$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

At 298 K, the rate coefficients of Niki *et al.*[2] and Libuda *et al.*[3] are in excellent agreement and are in reasonably good agreement with the 305 K rate coefficient data of Sanhueza and Heicklen.[1] The preferred 298 K rate coefficient is that of Niki *et al.*[2] and Libuda *et al.*,[3] and the temperature dependence is that derived from the study of Libuda *et al.*[3]

References

[1] E. Sanhueza and J. Heicklen, J. Phys. Chem. **79**, 7 (1975).

[2] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 915 (1980).

[3] H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. **94**, 5860 (1990).

$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$

$\Delta H^\circ = -9.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(4.8 \pm 0.4) \times 10^{-13}$	295 ± 2	Wallington *et al.*, 1990[1]	(a)
Reviews and Evaluations			
$3.4 \times 10^{-11} \exp(-1260/T)$	233–350	CODATA, 1980;[2] IUPAC, 1989[3]	(b)
$3.3 \times 10^{-11} \exp(-1250/T)$	200–300	NASA, 1990[4]	(c)

Comments

(a) Relative rate coefficient study. Cl atoms generated from the photolysis of Cl_2 in Cl_2–CH_3Cl–CH_4–air mixtures at 700 Torr total pressure. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl + CH_4) = 4.79 \pm 0.39$ determined. Placed on an absolute basis by use of $k(Cl + CH_4) = 9.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) The 298 K rate coefficient was based on the room temperature absolute rate coefficients of Clyne and Walker,[5] Manning and Kurylo[6] and Watson *et al.* (unpublished data). The temperature dependence was derived from those of Manning and Kurylo[6] and Watson *et al.* (unpublished data).

(c) Based on the absolute rate coefficient data of Manning and Kurylo.[6]

Preferred Values

$k = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.3 \times 10^{-11} \exp(-1250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–322 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

At 298 K, the absolute rate coefficients of Clyne and Walker[5] and Manning and Kurylo[6] and the relative rate coefficient of Wallington *et al.*[1] are in good agreement. However, the temperature dependencies measured by Clyne and Walker[5] and Manning and Kurylo[6] do not agree. The preferred 298 K rate coefficient is the average of those of Manning and Kurylo[6] and Wallington *et al.*,[1] and the temperature dependence is that of Manning and Kurylo.[6] The preferred Arrhenius expression is identical to the NASA recommendation.[4]

References

[1] T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).

[2] CODATA, 1980 (see references in Introduction).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

[5] M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Faraday Trans. 1, **69**, 1547 (1973).

[6] R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).

$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$

$\Delta H^\circ = -19.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 0.5) \times 10^{-13}$	298	Davis, Braun and Bass, 1970[1]	(a)
$8.4 \times 10^{-11} \exp[-(1448 \pm 60)/T]$	298–621	Clyne and Walker, 1973[2]	(b)
$(7.52 \pm 1.0) \times 10^{-13}$	298		
Relative Rate Coefficients			
$9.6 \times 10^{-12} \exp(-910/T)$	273–563	Knox, 1962[3]	(c)
4.5×10^{-13}	298		
$(3.74 \pm 0.40) \times 10^{-13}$	298 ± 2	Niki *et al.*, 1980[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of Cl atoms. The reported rate coefficient has been decreased by 10%, as discussed previously.[5]

(b) Discharge flow system with MS detection of CH_2Cl_2 in the presence of excess Cl atom concentrations.

(c) Relative rate method. Cl atoms generated by photolysis of Cl_2 in Cl_2–CH_2Cl_2–CH_4 mixtures. Organic reactants and products were monitored by GC, and the rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_4) = 1.0 \exp[(440 \pm 20)/T]$ placed on an absolute basis by use of $k(Cl + CH_4) = 9.6 \times 10^{-12} \exp(-1350/T)$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2–CH_2Cl_2–CH_3Cl–air mixtures at 700 Torr total pressure. Concentrations of CH_3Cl and CH_2Cl_2 were monitored by FTIR absorption spectroscopy, and a rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_3Cl) = 0.76 \pm 0.09$ determined. This rate coefficient ratio has been placed on an absolute basis by use of $k(Cl + CH_3Cl) = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 4.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.7 \times 10^{-12} \exp(-910/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–330 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The reported rate coefficient data exhibit appreciable scatter in both the room temperature rate coefficients as well as in the temperature dependencies. At room temperature, the rate coefficients derived from the relative rate studies of Knox[3] and Niki *et al.*[4] are in reasonable agreement, and suggest a self-consistent data set for the rate coefficients of the Cl atom reactions with CH_4, CH_3Cl and CH_2Cl_2. Accordingly, the preferred 298 K rate coefficient is the average of those of Knox[3] and Niki *et al.*,[4] with the temperature dependence being that derived from the data of Knox.[3] Analogous to the Cl + CH_4 reaction, the room temperature rate coefficients of Davis *et al.*[1] and Clyne and Walker[2] and the temperature dependence of Clyne and Walker[2] are higher than the preferred values.

References

[1]D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).
[2]M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Faraday Trans. 1, **69**, 1547 (1973).
[3]J. H. Knox, Trans. Faraday Soc. **58**, 275 (1962).
[4]H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **12**, 1001 (1980).
[5]CODATA, 1980 (see references in Introduction).

$Cl + CHCl_3 \rightarrow HCl + CCl_3$

$\Delta H^\circ = -39.2\ kJ{\cdot}mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.45 \times 10^{-11} \exp[-(1379 \pm 44)/T]$	297–652	Clyne and Walker, 1973[1]	(a)
$(1.47 \pm 0.35) \times 10^{-13}$	297		
Relative Rate Coefficients			
$2.7 \times 10^{-12} \exp(-1090/T)$	286–593	Knox, 1962[2]	(b,c)
7.0×10^{-14}	298		
$8.6 \times 10^{-12} \exp(-1385/T)$	240–593	Knox, 1962[2]	(b,d)
8.2×10^{-14}	298		

Comments

(a) Discharge flow system with MS detection of $CHCl_3$ in the presence of excess Cl atom concentrations.

(b) Relative rate study. Cl atoms generated by photolysis of Cl_2 in Cl_2–$CHCl_3$–CH_4 or Cl_2–$CHCl_3$–CH_3Cl mixtures. Organic reactants and products monitored by GC.

(c) Rate coefficient ratio of $k(Cl + CHCl_3)/k(Cl + CH_4) = 0.286 \exp(259/T)$ obtained, and placed on an absolute basis by use of $k(Cl + CH_4) = 9.6 \times 10^{-12} \exp(-1350/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

(d) Rate coefficient ratio of $k(Cl + CHCl_3)/k(Cl + CH_3Cl) = 0.26 \exp(-133/T)$ obtained, and placed on an absolute basis by use of $k(Cl + CH_3Cl) = 3.3 \times 10^{-11} \exp(-1250/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (this evaluation).

Preferred Values

$k = 7.6 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 4.9 \times 10^{-12} \exp(-1240/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the temperature range 240–330 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are based on the relative rate studies of Knox,[2] with the uncertainty limits being sufficient to encompass the data of Clyne and Walker.[1]

References

[1]M. A. A. Clyne and R. F. Walker, J. Chem. Soc., Faraday Trans. 1, **69**, 1547 (1973).

[2]J. H. Knox, Trans. Faraday Soc. **58**, 275 (1962).

$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2.40 \times 10^{-14}$	259	Wine, Semmes, and Ravishankara, 1982[1]	(a)
$<3.68 \times 10^{-14}$	298		
$<7.74 \times 10^{-14}$	356		
Reviews and Evaluations			
$<4 \times 10^{-14}$	298	CODATA, 1984;[2] IUPAC, 1989[3]	(b)
$<4.0 \times 10^{-14}$	298	NASA, 1990[3]	(c)

Comments

(a) Pulsed laser photolysis of Cl_2 with resonance fluorescence detection of Cl. Experiments were also performed at 403 K, at which temperature nonexponential decays of Cl atoms were observed. The authors concluded that the presence of a reactive impurity accounted for a significant fraction of the observed Cl atom decay, and therefore reported only upper limits for k.

(b) See Comments on Preferred Values.

(c) Based on results of Wine *et al.*[1]

Preferred Values

$k < 4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA 1984.[2] The preferred value is based on the only reported study[1] of this reaction. The observed decay rate included a significant contribution from a reactive impurity and therefore only an upper limit for the rate coefficient could be derived. This reaction is too slow to be of importance in atmospheric chemistry.

References

[1]P. H. Wine, D. H. Semmes, and A. R. Ravishankara, Chem. Phys. Lett. **90**, 128 (1982).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + HCl \rightarrow H_2O + Cl$

$\Delta H° = -67.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.8 \pm 0.25) \times 10^{-13}$	298	Cannon *et al.*, 1984[1]	(a)
$2.94 \times 10^{-12} \exp[-(446 \pm 32)/T]$	300–700	Husain, Plane and Xiang, 1984[2]	(b)
$(6.7 \pm 0.46) \times 10^{-13}$	298		
$4.6 \times 10^{-12} \exp[-(500 \pm 60)/T]$	240–295	Molina, Molina and Smith, 1984[3]	(c)
$(8.5 \pm 0.4) \times 10^{-13}$	298		
$2.1 \times 10^{-12} \exp[-(285 \pm 40)/T]$	258–334	Keyser, 1984[4]	(d)
$(7.9 \pm 0.4) \times 10^{-13}$	298		
$2.4 \times 10^{-12} \exp[-(327 \pm 28)/T]$	240–363	Ravishankara *et al.*, 1985[5]	(e)
$(8.01 \pm 0.44) \times 10^{-13}$	298		
Reviews and Evaluations			
$2.4 \times 10^{-12} \exp(-330/T)$	200–300	IUPAC, 1989[6]	(f)
$2.6 \times 10^{-12} \exp(-350/T)$	200–300	NASA, 1990[7]	(g)

Comments

(a) Flash photolysis system with LIF detection of HO.
(b) Flash photolysis of H_2O with the HO radical decay being monitored by time-resolved resonance fluorescence.
(c) Flash photolysis system with HO decay monitored by both resonance fluorescence and resonance absorption (298 K only) techniques.
(d) Discharge flow system with resonance fluorescence detection using high pressure flow system.
(e) Flash photolysis of H_2O or laser photolysis (266 nm) of O_3/H_2O or H_2O_2 to produce HO. Time resolved resonance fluorescence detection. Data obtained over temperature range 240–1055 K best represented by the three parameter expression $k = 4.5 \times 10^{-17}$ $T^{1.65}$ $\exp(112/T)$ cm^3 $molecule^{-1}$ s^{-1}.
(f) See Comments on Preferred Values.
(g) Based on data of Molina *et al.*,[3] Keyser[4] and Ravishankara *et al.*,[5] which gave higher room temperature values than earlier data.

Preferred Values

$k = 8.1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 2.4 \times 10^{-12} \exp(-330/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The most recent studies of Molina *et al.*,[3] Keyser[4] and Ravishankara *et al.*,[5] which paid careful attention to the [HCl] present in the experiments all show room temperature values higher by about 20-25% than the other studies.[8-13] Ravishankara *et al.* showed that HCl losses can be a problem, leading to low *k* values, and this is a plausible cause of these discrepancies. The higher value, $k(298) = 8.1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (average of the three studies) is the most reliable value. The preferred temperature dependent expression for the range 200–300 K is obtained by weighted linear least squares fit to the data from these three studies.[3-5] Ravishankara *et al.*[5] reported the three parameter expression $k = 4.5 \times 10^{-17}$ $T^{1.65}$ $\exp(112/T)$ cm^3 $molecule^{-1}$ s^{-1} for the temperature range 240–1055 K, which gives a good description of the non-Arrhenius behavior.

References

[1]B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).
[2]D. Husain, J. M. C. Plane, and C. C. Xiang, J. Chem. Soc. Faraday 2, **80**, 713 (1984).
[3]M. J. Molina, L. T. Molina, and C. A. Smith, Int. J. Chem. Kinet. **16**, 1151 (1984).
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[5]A. R. Ravishankara, P. H. Wine, J. R. Wells, and R. L. Thompson, Int. J. Chem. Kinet. **17**, 1281 (1985).
[6]IUPAC, Supplement III, 1989 (see references in Introduction).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).
[8]G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).
[9]M. S. Zahniser, F. Kaufman, and J. G. Anderson, Chem. Phys. Lett. **27**, 507 (1974).
[10]I. W. M. Smith and R. Zellner, J. Chem. Soc. Faraday 2, **70**, 1045 (1974).
[11]A. R. Ravishankara, G. Smith, R. T. Watson, and D. D. Davis, J. Phys. Chem. **81**, 2220 (1977).
[12]W. Hack, G. Mex, and H.-Gg. Wagner, Ber. Bunsenges Phys. Chem. **81**, 677 (1977).
[13]D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday 2, **77**, 1949 (1981).

$HO + HOCl \rightarrow ClO + H_2O$

$\Delta H^\circ = -101$ $kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7 - 9.5) \times 10^{-13}$	298	Ennis and Birks, 1988[1]	(a)
Reviews and Evaluations			
$3.0 \times 10^{-12} \exp(-500/T)$	200–300	IUPAC, 1989[2]	(b)
$3.0 \times 10^{-12} \exp(-500/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with MS detection of HOCl and LIF detection of HO decay in excess HOCl. Corrections made for reaction of HO with Cl_2 (k = 5.5×10^{-14} cm^3 molecule^{-1} s^{-1} [4]) and with Cl_2O (k = 9.4×10^{-12} cm^3 molecule^{-1} s^{-1} measured in the same study) and also secondary reactions which could complicate the kinetics.
(b) See Comments on Preferred Values.
(c) Based on data from reference 1 and assuming the A factor is the same as that for the HO + H_2O_2 reaction.

Preferred Values

$k = 5.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.0 \times 10^{-12} \exp(-500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The only reported experimental value[1] has a large uncertainty. Following the NASA evaluation[3], the preferred value is based on the mid-range value of 5×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K from the study of Ennis and Birks[1] and an A factor of 3.0×10^{-12} cm^3 molecule^{-1} s^{-1}, i.e., equal to that for the HO + H_2O_2 reaction.

References

[1]C. A. Ennis and J. W. Birks, J. Phys. Chem. **92**, 1119 (1988).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]M. T. Leu and C. L. Lin, Geophys. Res. Lett. **6**, 425 (1979).

$HO + ClO \rightarrow HO_2 + Cl$ (1)
$\rightarrow HCl + O_2$ (2)

$\Delta H°(1) = -5$ kJ·mol^{-1}
$\Delta H°(2) = -234$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.0 \times 10^{-12} \exp[(235 \pm 46)/T]$	219–373	Hills and Howard, 1984[1]	(a)
$(1.75 \pm 0.31) \times 10^{-11}$	298		
$(1.19 \pm 0.09) \times 10^{-11}$	243–298	Burrows, Wallington and Wayne, 1984[2]	(b)
$(1.94 \pm 0.38) \times 10^{-11}$	298	Poulet, Laverdet and Le Bras, 1986[3]	(c)
Relative Rate Coefficients			
$k_1/k = 0.86 \pm 0.14$	298	Hills and Howard, 1984[1]	(a)
$k_1/k = 0.85 \pm 0.07$	243–298	Burrows, Wallington and Wayne, 1984[2]	(b)
$k_1/k = 0.98 \pm 0.12$	298	Poulet, Laverdet and Le Bras, 1986[3]	(c)
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(120/T)$	200–373	IUPAC, 1989[4]	(d)
$1.1 \times 10^{-11} \exp(120/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system with LMR detection of HO, ClO and HO_2. Pseudo-first order with [ClO] >> [HO]. Branching ratio determined from HO_2 production after correction for secondary chemistry arising from Cl + HO_2 reaction.
(b) Discharge flow system with resonance fluorescence detection of HO, and indirectly for ClO and HO_2 after conversion to Cl and HO by titration with NO. Corrected HO_2 yield used to determine branching ratio.
(c) Discharge flow system with LIF detection of HO in presence of excess ClO. Molecular beam MS detection of Cl, ClO, HCl, NO_2, OClO, etc. Rate coefficient k determined by two direct methods and one relative rate method in which k(HO + OClO) = 6.9×10^{-12} cm^3 molecule^{-1} s^{-1} [5] was used as a reference reaction. Branching ratio determined from yield of HCl, after correction for HCl production from Cl + HO_2 reaction.
(d) See Comments on Preferred Values.
(e) Based on data of Hills and Howard,[1] Burrows *et al.*[2] and Poulet *et al.*[3] Earlier data[6,7] not used because [ClO] was not measured directly.

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-11} \exp(120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–373 K.
$k_1/k = 0.98$ at 298 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.
$\Delta(k_1/k) = ^{+0.02}_{-0.13}$ at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred rate coefficient k is based on the three recent studies[1-3] in which [ClO] was measured directly. The uncertainty reflects the differences in the 298 K values and the reported temperature coefficients. The measurement of the branching ratio for HCl formation based on measurement of the HCl stable product[3] is more accurate since this is clearly the minor channel. However the uncertainties do not allow the occurrence of this HCl channel to be eliminated completely.

References

[1]A. J. Hills and C. J. Howard, J. Chem. Phys. **81**, 4458 (1984).
[2]J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday 2, **80**, 957 (1984).
[3]G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **90**, 159 (1986).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **78**, 1140 (1983).
[7]M. T. Leu and C. L. Lin, Geophys. Res. Lett. **6**, 425 (1979).

$HO + OClO \rightarrow HOCl + O_2$ (1)
$\rightarrow HO_2 + ClO$ (2)

$\Delta H°(1) = -218$ kJ·mol^{-1}
$\Delta H°(2) = -24$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.50 \times 10^{-13} \exp[(804 \pm 114)/T]$	293–473	Poulet, Zagogianni and Le Bras, 1986[1]	(a)
$(6.86 \pm 0.44) \times 10^{-12}$	298		
Reviews and Evaluations			
$4.5 \times 10^{-13} \exp(800/T)$	290–480	IUPAC, 1989[2]	(b)
$4.5 \times 10^{-13} \exp(800/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with EPR and LIF detection of pseudo-first order decay of HO in excess OClO. HOCl product detected by modulated molecular beam mass spectrometry, calibrated using the HO + Cl_2 reaction as a source of HOCl. A relative rate coefficient of $k_1/k > 0.80$ was obtained, and the results suggest that reaction (1) is the exclusive channel. Pressure = 0.5 − 1.4 Torr.
(b) See Comments on Preferred Values.
(c) Based on the single study of Poulet *et al.*[1]

Preferred Values

$k_1 = 7.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 4.5 \times 10^{-13} \exp(800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–480 K.
$k_2 = 0$.

Reliability
$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred values are based on the single experimental study of Poulet *et al.*[1] Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range.

References

[1]G. Poulet, H. Zagogianni, and G. Le Bras, Int. J. Chem. Kinet. **18**, 847 (1986).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + ClNO_2 \rightarrow HOCl + NO_2$

$\Delta H^\circ = -97$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.7) \times 10^{-14}$	298	Ganske *et al.*, 1991[1]	(a)

Comments

(a) Fast flow discharge system used. Pseudo-first-order decays of HO in the presence of excess $ClNO_2$ monitored by resonance fluorescence. The value reported is based on the results with halocarbon wax and phosphoric acid coated tubes; the results with a boric acid coated tube were significantly higher. Mass spectrometry showed HOCl to be the major product, and no $HONO_2$ or Cl_2 were detected.

Preferred Values

$k = 3.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on results of Ganske *et al.*[1] from the only reported study of this rate coefficient. Mass spectrometric studies showed HOCl to be the major product, with no evidence for production of $HONO_2$ or Cl_2, thereby showing that the only reaction pathway is that yielding HOCl + NO_2.

Reference

[1] J. A. Ganske, M. J. Ezell, H. N. Berko, and B. J. Finlayson-Pitts, Chem. Phys. Lett. **179**, 204 (1991).

$HO + ClONO_2 \rightarrow HOCl + NO_3$ (1)

$\rightarrow HO_2 + ClONO$ (2)

$\rightarrow HONO_2 + ClO$ (3)

$\Delta H^\circ(1) = -76$ kJ·mol^{-1}
$\Delta H^\circ(2) = 8$ kJ·mol^{-1}
$\Delta H^\circ(2) = -95$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.4) \times 10^{-13}$	245	Ravishankara *et al.*, 1977[1]	(a)
$1.19 \times 10^{-12} \exp(-333/T)$	246–387	Zahniser *et al.*, 1977[2]	(b)
$(3.93 \pm 0.11) \times 10^{-13}$	295		
Reviews and Evaluations			
$1.2 \times 10^{-12} \exp(-330/T)$	246–387	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$1.2 \times 10^{-12} \exp(-330/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Static system using a flash photolysis system with resonance fluorescence detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) See Comments on Preferred Values.
(d) Based on data of Zahniser *et al.*[2]

Preferred Values

$k = 3.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 246–387 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1980.[3] The results of the only two reported studies are in good agreement at 245 K (within 25%) considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser *et al.*[2] Neither study reported any data on the reaction products.

References

[1]A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. 4, 7 (1977).
[2]M. S. Zahniser, J. S. Chang, and F. Kaufman, J. Chem. Phys. 67, 997 (1977).
[3]CODATA, 1980 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$

$\Delta H° = -77.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.21 \times 10^{-21} T^{3.08} \exp[-(232 \pm 423)/T]$	247–483	Jeong and Kaufman, 1982[1,2]	(a)
$(3.95 \pm 0.26) \times 10^{-14}$	293		
$8.38 \times 10^{-18} T^{1.38} \exp[-(1202 \pm 72)/T]$	295–800	Taylor *et al.*, 1989[3]	(b)
$(4.9 \pm 0.6) \times 10^{-14}$	295		
$(5.3 \pm 0.8) \times 10^{-14}$	298	Brown, Canosa-Mas and Wayne, 1990[4]	(a)
Reviews and Evaluations			
$1.9 \times 10^{-12} \exp(-1120/T)$	247–350	CODATA, 1982[5]; IUPAC, 1989[6]	(c)
$3.50 \times 10^{-18} T^2 \exp(-585/T)$	247–483	Atkinson, 1989[7]	(d)
$2.1 \times 10^{-12} \exp(-1150/T)$	247–400	NASA, 1990[8]	(e)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) Laser photolysis system with LIF detection of HO.
(c) Derived from the rate coefficient data of Howard and Evenson,[9] Perry *et al.*,[10] Davis *et al.*,[11] Paraskevopoulos *et al.*[12] and Jeong and Kaufman.[1] The preferred Arrhenius expression was obtained from the data obtained at ≤ 350 K.
(d) Derived from the absolute rate coefficient data of Howard and Evenson,[9] Perry *et al.*,[10] Davis *et al.*,[11] Paraskevopoulos *et al.*[12] and Jeong and Kaufman,[1] using the three parameter equation $k = CT^2 \exp(-D/T)$. The data of Taylor *et al.*,[3] which are in good agreement with this recommended rate coefficient expression at temperatures ≤ 378 K (but are significantly higher over the range 428–800 K), were not used in the evaluation.
(e) Derived from the rate coefficient data of Howard and Evenson,[9] Perry *et al.*,[10] Davis *et al.*,[11] Paraskevopoulos *et al.*[12] and Jeong and Kaufman,[1] using only the rate coefficients obtained at temperatures < 400 K.

Preferred Values

$k = 4.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8 \times 10^{-12} \exp(-1115/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature and below, the absolute rate coefficients of Howard and Evenson,[9] Perry *et al.*,[10] Davis *et al.*,[11] Paraskevopoulos *et al.*,[12] Jeong and Kaufman[1] and Taylor *et al.*[3] are in good agreement. However, the rate coefficients determined by Taylor *et al.*[3] at temperatures of ~428–485 K are significantly higher than those of Perry *et al.*[10] and Jeong and Kaufman,[1] and use of the rate data of Taylor *et al.*[3] leads to a rate expression which predicts rate coefficients at ~250 K which are ~30% lower than those reported by Davis *et al.*[11] and Jeong and Kaufman.[1] The room temperature rate coefficient of Brown *et al.*[4] is ~20–25% higher than other data,[1,9–12] and is not used in the evaluation. The rate coefficients of Howard and Evenson,[9] Perry *et al.*,[10] Davis *et al.*[11] Paraskevopoulos *et al.*[12] and Jeong and Kaufman[1] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.50 \times 10^{-18}\ T^2 \exp(-585/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 247–483 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$.

The preferred rate coefficient expression is very similar to our previous evaluation, CODATA, 1982,[5] and uses the same rate coefficient data set.

References

[1] K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
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$HO + CH_2FCl$ (HCFC–31) → $H_2O + CHFCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.6) \times 10^{-14}$	296	Howard and Evenson, 1976[1]	(a)
$(2.84 \pm 0.3) \times 10^{-12} \exp[-(1259 \pm 50)/T]$	245–375	Watson *et al.*, 1977[2]	(b)
$(4.21 \pm 0.41) \times 10^{-14}$	298		
$(3.1 \pm 0.9) \times 10^{-12} \exp[-(1320 \pm 100)/T]$	273–373	Handwerk and Zellner, 1978[3]	(c)
$(3.5 \pm 0.7) \times 10^{-14}$	293		
$(4.45 \pm 0.66) \times 10^{-14}$	297	Paraskevopoulos, Singleton and Irwin, 1981[4]	(c)
$1.57 \times 10^{-19}\ T^{2.41} \exp[-(307 \pm 382)/T]$	250–486	Jeong and Kaufman, 1982[5,6]	(d)
$(4.94 \pm 0.30) \times 10^{-14}$	295		
Reviews and Evaluations			
$2.6 \times 10^{-12} \exp(-1210/T)$	245–350	CODATA, 1982[7]; IUPAC, 1989[8]	(e)
$3.77 \times 10^{-18}\ T^2 \exp(-604/T)$	245–486	Atkinson, 1989[9]	(f)
$3.0 \times 10^{-12} \exp(-1250/T)$	245–400	NASA, 1990[10]	(g)

Comments

(a) Discharge flow system with LMR detection of HO.

(b) Flash photolysis system with resonance fluorescence detection of HO.

(c) Flash photolysis system with UV absorption detection of HO.

(d) Discharge flow system with resonance fluorescence detection of HO.

(e) Derived from the absolute rate coefficients of Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] Paraskevopoulos *et al.*[4] and Jeong and Kaufman,[5] using only the rate coefficients obtained at temperatures ≤350 K.

(f) Derived from the absolute rate coefficients of Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] Paraskevopoulos *et al.*[4] and Jeong and Kaufman,[5] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(g) Derived from the absolute rate coefficients of Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] Paraskevopoulos *et al.*[4] and Jeong and Kaufman,[5] using only the rate coefficients obtained at temperatures <400 K.

Preferred Values

$k = 4.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-12} \exp(-1135/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The rate coefficients measured by Howard and Evenson,[1] Watson *et al.*,[2] Handwerk and Zellner,[3] Paraskevopoulos *et al.*[4] and Jeong and Kaufman[5] are in reasonably good agreement at ≳290 K, although there is a significant discrepancy between the rate coefficients of Watson *et al.*[2] and Jeong and Kaufman[5] at ~250 K. The data from all five studies[1-5] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.77 \times 10^{-18} T^2 \exp(-604/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–486 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

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[10]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CHF_2Cl$ (HCFC-22) → $H_2O + CF_2Cl$

$\Delta H° = -66.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.58 \pm 0.58) \times 10^{-15}$	297	Paraskevopoulos, Singleton and Irwin, 1981[1]	(a)
$5.03 \times 10^{-28} T^{5.11} \exp[(252 \pm 780)/T]$	293–482	Jeong and Kaufman, 1982[2,3]	(b)
$(4.83 \pm 0.32) \times 10^{-15}$	293		
Reviews and Evaluations			
$1.1 \times 10^{-12} \exp(-1620/T)$	250–360	CODATA, 1982[4]; IUPAC, 1989[5]	(c)
$1.51 \times 10^{-18} T^2 \exp(-1000/T)$	250–482	Atkinson, 1989[6]	(d)
$1.2 \times 10^{-12} \exp(-1650/T)$	250–400	NASA, 1990[7]	(e)

Comments

(a) Flash photolysis system with UV absorption detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) Derived from the absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*[1] and Jeong and Kaufman,[2] using only the rate coefficients obtained at temperatures ≤ 360 K.
(d) Derived from the absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevoupolos *et al.*[1] and Jeong and Kaufman,[2] using the three parameter equation $k = CT^2 \exp(-D/T)$.
(e) Derived from the rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*[1] and Jeong and Kaufman,[2] using only the rate coefficients obtained at temperatures < 400 K.

Preferred Values

$k = 4.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.8 \times 10^{-13} \exp(-1530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson *et al.*,[8] Howard and Evenson,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Handwerk and Zellner,[12] Paraskevopoulos *et al.*[1] and Jeong and Kaufman[2] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.51 \times 10^{-18} T^2 \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–482 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. This preferred Arrhenius expression yields rate coefficients at 298 K and 250 K which are within 5% of the IUPAC, 1989[5] and NASA, 1990[7] evaluations.

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$HO + CHFCl_2$ (HCFC–21) $\rightarrow H_2O + CFCl_2$

$\Delta H^\circ = -85.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.39 \pm 0.86) \times 10^{-14}$	297	Paraskevopoulos, Singleton, and Irwin, 1981[1]	(a)
$1.97 \times 10^{-18} T^{1.94} \exp[-(382 \pm 413)/T]$	250–483	Jeong and Kaufman, 1982[2,3]	(b)
$(3.37 \pm 0.22) \times 10^{-14}$	295		
Reviews and Evaluations			
$1.1 \times 10^{-12} \exp(-1070/T)$	240–350	CODATA, 1982[4]; IUPAC, 1989[5]	(c)
$1.70 \times 10^{-18} T^2 \exp(-479/T)$	241–483	Atkinson, 1989[6]	(d)
$1.2 \times 10^{-12} \exp(-1100/T)$	241–400	NASA, 1990[7]	(e)

Comments

(a) Flash photolysis system with UV absorption detection of HO.
(b) Discharge flow system with resonance fluorescence detection of HO.
(c) Derived from the absolute rate coefficients of Howard and Evenson,[8] Perry *et al.*,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Paraskevopoulos *et al.*[1] and Jeong and Kaufman,[2] using only the rate coefficients obtained at temperatures ≤ 350 K.
(d) Derived from the absolute rate coefficients of Howard and Evenson,[8] Perry *et al.*,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Paraskevopoulos *et al.*[1] and Jeong and Kaufman,[2] using the three parameter equation $k = CT^2 \exp(-D/T)$.
(e) Derived from the absolute rate coefficients of Howard and Evenson,[8] Perry *et al.*,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Paraskevopoulos *et al.*[1] and Jeong and Kaufman,[2] using only rate coefficients obtained at temperatures <400 K.

Preferred Values

$k = 3.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.8 \times 10^{-13} \exp(-1010/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson,[8] Perry *et al.*,[9] Watson *et al.*,[10] Chang and Kaufman,[11] Paraskevopoulos *et al.*[1] and Jeong and Kaufman[2] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.70 \times 10^{-18} T^2 \exp(-479/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 241–483 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The preferred Arrhenius expression yields rate coefficients at 298 K and 250 K which are within 5% of those calculated from the IUPAC, 1989[5] and NASA, 1990[7] evaluations.

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$HO + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

$\Delta H° = -87.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.52 \times 10^{-16} T^{1.58} \exp[-(622 \pm 60)/T]$	298–775	Taylor *et al.*, 1989[1]	(a)
$(1.76 \pm 0.20) \times 10^{-13}$	298		
Reviews and Evaluations			
$4.4 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1989[2]	(b)
$8.54 \times 10^{-18} T^2 \exp(-500/T)$	245–455	Atkinson, 1989[3]	(c)
$5.8 \times 10^{-12} \exp(-1100/T)$	245–400	NASA, 1990[4]	(d)

Comments

(a) Laser photolysis system with LIF detection of HO.
(b) See Comments on Preferred Values.
(c) Derived from the absolute rate coefficient data of Howard and Evenson,[5] Perry *et al.*,[6] Davis *et al*[7] and Jeong and Kaufman,[8] using the three parameter equation $k = CT^2 \exp(-D/T)$.
(d) Derived from the absolute rate coefficient data of Howard and Evenson,[5] Perry *et al.*,[6] Davis *et al.*,[7] and Jeong and Kaufman,[8] using only the rate coefficients obtained at temperatures <400 K.

Preferred Values

$k = 1.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.4 \times 10^{-12} \exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred values are derived from the absolute rate coefficients of Howard and Evenson,[5] Perry *et al.*,[6] Davis *et al.*[7] and Jeong and Kaufman.[8] These data have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 8.54 \times 10^{-18} T^2 \exp(-500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–455 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The absolute rate coefficients of Taylor *et al.*,[1] especially those obtained at temperatures ≥ 350 K, are in excellent agreement with the preferred three parameter equation.

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$HO + CHCl_3 \rightarrow H_2O + CCl_3$

$\Delta H^\circ = -106.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.92 \times 10^{-20}\, T^{2.78} \exp[-(95 \pm 60)/T]$	295–775	Taylor *et al.*, 1989[1]	(a)
1.06×10^{-13}	295		
Reviews and Evaluations			
$3.3 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1989[2]	(b)
$6.30 \times 10^{-18}\, T^2 \exp(-504/T)$	245–487	Atkinson, 1989[3]	(c)
$4.3 \times 10^{-12} \exp(-1100/T)$	245–400	NASA, 1990[4]	(d)

Comments

(a) Laser photolysis system with LIF detection of HO.
(b) See Comments on Preferred Values.
(c) Derived using the absolute rate coefficient data of Howard and Evenson,[5] Davis *et al.*[6] and Jeong and Kaufman,[7] using the three parameter equation $k = CT^2 \exp(-D/T)$.
(d) Derived from the absolute rate coefficients of Howard and Evenson,[5] Davis *et al.*[6] and Jeong and Kaufman,[7] using only rate coefficients obtained at temperatures <400 K.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.3 \times 10^{-12} \exp(-1030/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson,[5] Davis *et al.*[6] and Jeong and Kaufman,[7] which are in excellent agreement, have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 6.30 \times 10^{-18}\, T^2 \exp(-504/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 245–487 K. The rate coefficients of Taylor *et al.*[1] are in excellent agreement with this three parameter expression. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

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HO + $CFCl_3$ (CFC-11) → HOCl + $CFCl_2$

$\Delta H° = 78.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	297–424	Atkinson, Hansen and Pitts, 1975[1]	(a)
$<5 \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976[2]	(b)
$<5 \times 10^{-16}$	480	Chang and Kaufman, 1977[3]	(c)
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979[4]	(d)
Relative Rate Coefficients			
$<4 \times 10^{-17}$	298	Cox *et al.*, 1976[5]	(e)
Reviews and Evaluations			
$<1.0 \times 10^{-12} \exp(-3650/T)$	250–480	IUPAC, 1989[6]	(f)
$<5.0 \times 10^{-18}$	298		
$<1 \times 10^{-17}$	298	Atkinson, 1989[7]	(g)
$<1.0 \times 10^{-12} \exp(-3700/T)$	<480	NASA, 1990[8]	(g)
$<5.0 \times 10^{-18}$	298		

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.

(b) Discharge flow system with LMR detection of HO.

(c) Discharge flow system with resonance fluorescence detection of HO. The upper limit rate coefficient obtained at 480 K was combined with an estimated Arrhenius preexponential factor of 10^{-12} cm^3 molecule^{-1} s^{-1} to derive an estimated Arrhenius activation energy of ≥ 29 kJ·mol^{-1}.

(d) Discharge flow system with resonance fluorescence detection of HO.

(e) Relative rate study. HO radicals generated by photolysis of HONO-air mixtures at one atmosphere total pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added $CFCl_3$ and $k(HO + CH_4) = 7.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the upper limit given in the table is obtained.

(f) See Comments on Preferred Values.

(g) Derived by assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and using the upper limit to the rate coefficient measured by Chang and Kaufman at 480 K.[3]

Preferred Values

$k < 5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 1 \times 10^{-12} \exp(-3650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–480 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The preferred values are based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 480 K in the absolute rate study of Chang and Kaufman.[3] This yields $k < 1 \times 10^{-12} \exp(-3650/T)$ cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[5] in their relative rate study.

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[8]NASA Evaluation No. 9, 1990 (see references in Introduction).

HO + CF_2Cl_2 (CFC-12) → HOCl + CF_2Cl

ΔH° = 107 kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	297–424	Atkinson, Hansen and Pitts, 1975[1]	(a)
$<4 \times 10^{-16}$	296 ± 2	Howard and Evenson, 1976[2]	(b)
$<6 \times 10^{-16}$	478	Chang and Kaufman, 1977[3]	(c)
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979[4]	(d)
Relative Rate Coefficients			
$<1.0 \times 10^{-16}$	298	Cox *et al.*, 1976[5]	(e)
Reviews and Evaluations			
$<1 \times 10^{-12} \exp(-3540/T)$	250–478	IUPAC, 1989[6]	(f)
$<7 \times 10^{-18}$	298		
$<1 \times 10^{-17}$	298	Atkinson, 1989[7]	(g)
$<1 \times 10^{-12} \exp(-3600)/T)$	<478	NASA, 1990[8]	(g)
$<6.0 \times 10^{-18}$	298		

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.

(b) Discharge flow system with LMR detection of HO.

(c) Discharge flow system with resonance fluorescence detection of HO. The upper limit rate coefficient obtained at 478 K was combined with an estimated Arrhenius preexponential factor of 10^{-12} cm^3 molecule^{-1} s^{-1} to derive an estimated Arrhenius activation energy of ≥29 kJ·mol^{-1}.

(d) Discharge flow system with resonance fluorescence detection of HO.

(e) Relative rate study. HO radicals generated by photolysis of HONO–air mixtures at one atmosphere total pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added CF_2Cl_2 and a rate coefficient of $k(HO + CH_4) = 7.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation), the upper limit given in the table is obtained.

(f) See Comments on Preferred Values.

(g) Derived by assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and using the upper limit to the rate coefficient measured by Chang and Kaufman at 478 K.[3]

Preferred Values

$k < 7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 1 \times 10^{-12} \exp(-3540/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–478 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[6] The preferred values are based upon an estimated Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} and the upper limit to the rate coefficient determined at 478 K in the absolute rate study of Chang and Kaufman.[3] This yields $k < 1 \times 10^{-12} \exp(-3540/T)$ cm^3 molecule^{-1} s^{-1}, and is consistent with the lack of reaction observed by Cox *et al.*[5] in their relative rate study.

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$HO + CCl_4 \rightarrow HOCl + CCl_3$

$\Delta H° = 49.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4 \times 10^{-15}$	296 ± 2	Howard and Evenson, 1976[1]	(a)
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979[2]	(b)
Relative Rate Coefficients			
$<1.0 \times 10^{-16}$	298	Cox *et al.*, 1976[3]	(c)
Reviews and Evaluations			
$<1 \times 10^{-12} \exp(-2320/T)$	~250–300	IUPAC, 1989[4]	(d)
$<4 \times 10^{-16}$	298		
$<5 \times 10^{-16}$	298	Atkinson, 1989[5]	(e)
$<1 \times 10^{-12} \exp(-2300/T)$	~250–300	NASA, 1990[6]	(f)
$<5.0 \times 10^{-16}$	298		

Comments

(a) Discharge flow system with LMR detection of HO.

(b) Discharge flow system with resonance fluorescence detection of HO.

(c) Relative rate study. HO radicals generated by photolysis of HONO–air mixtures at one atmosphere total pressure. Relative rate coefficients were obtained from measurement of the rates of NO formation as a function of the HONO and organic concentrations. Based upon the lack of NO formation as a function of added CCl_4 and a rate coefficient of $k(HO + CH_4) = 7.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (this study), the upper limit given in the table is obtained.

(d) Based upon the rate coefficient data of Howard and Evenson[1] (due to a typographical error, this was incorrectly cited), Clyne and Holt[2] and Cox *et al.*[3] An Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1} was assumed to derive the temperature dependent expression.

(e) Based on the relative rate study of Cox *et al.*[3]

(f) Based on the relative rate study of Cox *et al.*,[3] with an assumed Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k < 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k < 1 \times 10^{-12} \exp(-2260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range ~250–300 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the relative rate study of Cox *et al.*,[5] with their upper limit to the rate coefficient being increased by a factor of 5. Assuming an Arrhenius preexponential factor of 1×10^{-12} cm^3 molecule^{-1} s^{-1}, this leads to the upper limit to the Arrhenius expression given.

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[6]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$7.80 \times 10^{-13} \exp[(241 \pm 61)/T]$	300–459	Kirchner *et al.*, 1990[1]	(a)
$(1.76 \pm 0.17) \times 10^{-12}$	300		
Reviews and Evaluations			
$5.0 \times 10^{-13} \exp(445/T)$	230–420	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
$5.63 \times 10^{-13} \exp(427/T)$	234–420	Atkinson, 1989[4]	(c)
$4.9 \times 10^{-13} \exp(450/T)$	234–420	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with MS detection of HO.
(b) See Comments on Preferred Values.
(c) Derived from the rate coefficient data of Howard[6] and Chang and Kaufman[7] and unpublished data of Davis *et al.* (cited in references 6 and 7).
(d) The 298 K value was derived from the mean of the values reported by Howard[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman[7] with the A-factor being reduced to yield the preferred value at 298 K.

Preferred Values

$k = 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.0 \times 10^{-13} \exp(445/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred 298 K rate coefficient is derived from the mean of the values of Howard[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman,[7] with the A-factor reduced to yield the preferred value at 298 K. The room temperature rate coefficients reported by Kirchner,[8] Edney *et al.*,[9] Klöpffer *et al.*[10] and Kirchner *et al.*,[1] which are not used in the derivation of the preferred values, are in general agreement with the preferred values.

References

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$HO + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.53 \times 10^{-12} \exp[-(1034 \pm 13)/T]$	301–433	Kirchner *et al.*, 1990[1]	(a)
1.73×10^{-13}	301		
Reviews and Evaluations			
$9.4 \times 10^{-12} \exp(-1200/T)$	300–420	CODATA, 1982[2]; IUPAC, 1989[3]	(b)
$9.64 \times 10^{-12} \exp(-1209/T)$	297–420	Atkinson, 1989[4]	(c)
$9.4 \times 10^{-12} \exp(-1200/T)$	297–420	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with MS detection of HO.
(b) See Comments on Preferred Values.
(c) Derived from the data of Howard[6] and Chang and Kaufman[7] and the unpublished 298 K rate coefficient of Davis *et al*. (cited in references 6 and 7).
(d) The 298 K value was derived from the mean of the values reported by Howard[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman.[7]

Preferred Values

$k = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.4 \times 10^{-12} \exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–420 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred 298 K value is derived from the mean of the values of Howard[6] and Chang and Kaufman.[7] The Arrhenius parameters are those of Chang and Kaufman.[7] The Arrhenius expression and 305 K rate coefficient reported by Kirchner[8] and Kirchner *et al.*,[1] which are not used in the derivation of the preferred values, are in reasonable agreement with the preferred values.

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$HO + CH_3CF_2Cl$ (HCFC–142b) → $H_2O + CH_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$9.8 \times 10^{-13} \exp[-(1660 \pm 200)/T]$	270–400	Liu, Huie and Kurylo, 1990[1]	(a)
$(4.02 \pm 1.0) \times 10^{-15}$	298		
$2.6 \times 10^{-13} \exp[-(1230 \pm 250)/T]$	231–423	Brown *et al.*, 1990[2]	(b)
$(3.7 \pm 1.4) \times 10^{-15}$	303		
$1.14 \times 10^{-12} \exp[-(1750 \pm 75)/T]$	223–374	Gierczak *et al.*, 1991[3]	(c)
$(2.95 \pm 0.25) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.6 \times 10^{-12} \exp(-1820/T)$	270–380	IUPAC, 1989[4]	(d)
$2.05 \times 10^{-18} T^2 \exp(-1171/T)$	273–375	Atkinson, 1989[5]	(e)
$9.6 \times 10^{-13} \exp(-1650/T)$	223–400	NASA, 1990[6]	(f)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.

(b) Discharge flow system with resonance fluorescence detection of HO.

(c) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used. GC analysis showed that the CH_3CF_2Cl sample used contained <0.0005% of reactive $CH_2=CCl_2$ impurity.

(d) Derived from a least-squares analysis of the rate coefficient data of Howard and Evenson,[7] Watson *et al.*,[8] Handwerk and Zellner[9] and Paraskevopoulos *et al.*[10] The data of Clyne and Holt[11] were not used in the evaluation.

(e) Derived from the absolute rate coefficient data of Howard and Evenson,[7] Watson *et al.*,[8] Handwerk and Zellner[9] and Paraskevouplous *et al.*,[10] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(f) Derived from the absolute rate coefficients of Howard and Evenson,[7] Watson *et al.*,[8] Handwerk and Zellner,[9] Paraskevopoulos *et al.*,[10] Liu *et al.*[1] and the as then unpublished data of Gierczak *et al.*[3]

Preferred Values

$k = 3.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

$k = 9.2 \times 10^{-13} \exp(-1705/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The rate coefficient data obtained[1-3,7-11] exhibit a large degree of scatter, especially at temperatures ≤300 K. In particular, the rate coefficients measured by Clyne and Holt,[11] Brown *et al.*[2] and, to a lesser extent, Handwerk and Zellner,[9] Paraskevopoulos *et al.*[10] and Liu *et al.*,[2] are higher than those of Howard and Evenson,[7] Watson *et al.*[8] and Gierczak *et al.*[3] Accordingly, the rate coefficient data of Howard and Evenson,[7] Watson *et al.*[8] and Gierczak *et al.*[3] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.77 \times 10^{-18} T^2 \exp(-1174/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–427 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

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$HO + CH_3CFCl_2$ (HCFC–141b) → $H_2O + CH_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.6 \times 10^{-13} \exp[-(1140 \pm 210)/T]$	243–400	Liu, Huie and Kurylo, 1990[1]	(a)
$(7.01 \pm 1.2) \times 10^{-15}$	298		
$5.8 \times 10^{-13} \exp[-(1100 \pm 250)/T]$	238–426	Brown *et al.*, 1990[2]	(b)
$(1.61 \pm 0.55) \times 10^{-14}$	297		
$1.47 \times 10^{-12} \exp[-(1640 \pm 100)/T]$	253–393	Talukdar *et al.*, 1991[3]	(c)
$(5.92 \pm 0.54) \times 10^{-15}$	298		
Reviews and Evaluations			
$4.2 \times 10^{-13} \exp(-1200/T)$	273–400	NASA, 1990[4]	(d)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO. Analysis of the CH_3CFCl_2 samples used showed the presence of $2.4 \times 10^{-3}\%$ and $3 \times 10^{-4}\%$ of reactive C_2 haloalkene impurities. However, Talukdar *et al.*[3] suggest that the $CH_2{=}CCl_2$ impurity levels may have been $\sim 1 \times 10^{-2}\%$ and have contributed significantly to the measured OH radical decay rates.

(b) Discharge flow system with resonance fluorescence detection of HO.

(c) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used. Two samples of CH_3CFCl_2 were used, analyzed to contain $<7 \times 10^{-4}\%$ and $<1 \times 10^{-4}\%$ of $CH_2{=}CCl_2$ impurity. The rate coefficients measured using these two samples were indistinguishable within the experimental errors. These observations are consistent with calculations in that the contributions of OH radical reactions with impurities were of negligible importance.

(d) Derived from the rate coefficient data of Liu *et al.*[1] and preliminary unpublished data of Gierczak *et al.*

Preferred Values

$k = 5.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.0 \times 10^{-13} \exp(-1425/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The measured rate coefficients of Liu *et al.*,[1] Brown *et al.*[2] and Talukdar *et al.*[3] are not in good agreement. In particular, the rate coefficients of Brown *et al.*[2] are higher than those of Liu *et al.*[1] and Talukdar *et al.*[3] over the entire temperature range studied, by a factor of 1.5–3.5, with the disagreement being more pronounced at lower temperatures. While the data of Liu *et al.*[1] and Talukdar *et al.*[3] are in good, or reasonably good, agreement over the temperature range 295–400 K, the rate coefficients of Liu *et al.*[1] at 243 K and 270 K are significantly higher than those of Talukdar *et al.*[2] These observations, together with the impurity analyses of the CH_3CFCl_2 samples used by Liu *et al.*[1] and Talukdar *et al.*,[3] suggest that the higher measured rate coefficients of Liu *et al.*[1] and Brown *et al.*[2] are due to the presence of reactive impurities in the CH_3CFCl_2 samples used.

Accordingly, the rate coefficients of Talukdar *et al.*[2] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.35 \times 10^{-18}\ T^2 \exp(-893/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–393 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$.

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[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.4 \times 10^{-12} \exp[-(1801 \pm 448)/T]$	359–402	Nelson *et al.*, 1990[1]	(a)
1.28×10^{-14}	298*		
$9.1 \times 10^{-13} \exp[-(1337 \pm 150)/T]$	278–378	Finlayson-Pitts *et al.*, 1992[2]	(b)
$(1.0 \pm 0.1) \times 10^{-14}$	298		
$1.75 \times 10^{-12} \exp[-(1550 \pm 60)/T]$	243–379	Talukdar *et al.*, 1992[3]	(c)
$(9.5 \pm 0.8) \times 10^{-15}$	298		
Relative Rate Coefficients			
$(1.08 \pm 0.35) \times 10^{-14}$	298 ± 3	Nelson *et al.*, 1990[1]	(d)
$2.0 \times 10^{-12} \exp[-(1531 \pm 75)/T]$	277–356	DeMore, 1992[4]	(e)
1.16×10^{-14}	298		
Reviews and Evaluations			
$5.1 \times 10^{-12} \exp(-1800/T)$	250–460	CODATA, 1980[5]; IUPAC, 1989[6]	(f)
$5.92 \times 10^{-18} T^2 \exp(-1129/T)$	253–457	Atkinson, 1989[7]	(g)
$5.0 \times 10^{-12} \exp(-1800/T)$	253–457	NASA, 1990[8]	(f)

Comments

(a) Pulsed radiolysis system with UV absorption detection of HO.

(b) Discharge flow system with resonance fluorescence detection of HO. Rate coefficients also measured for the HO radical reaction with CH_4, and results are in good agreement with the present evaluation for that reaction.

(c) Laser photolysis system with LIF detection of HO.

(d) Relative rate study. HO radicals generated by the photolysis of CH_3ONO in CH_3ONO–NO–CH_3CCl_3–CH_3Cl–air mixtures at atmospheric pressure. CH_3CCl_3 and CH_3Cl concentrations were monitored by GC, and the rate coefficient ratio $k(HO + CH_3CCl_3)/k(HO + CH_3Cl)$ placed on an absolute basis by use of $k(HO + CH_3Cl) = 4.3 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (this evaluation).

(e) Relative rate method. HO radicals generated by photolysis of O_3/H_2O mixtures in a slow-flow reactor. CH_4 and CH_3CCl_3 concentrations were measured by IR absorption spectroscopy. Rate coefficient ratio $k(HO + CH_3CCl_3)/k(HO + CH_4) = 0.51 \exp(354/T)$ placed on an absolute basis by use of $k(HO + CH_4) = 3.9 \times 10^{-12} \exp(-1885/T)$ cm³ molecule⁻¹ s⁻¹ (this evaluation).

(f) Derived from the absolute rate coefficients of Jeong and Kaufman[9] and Kurylo *et al.*[10]

(g) Derived from the absolute rate coefficients of Jeong and Kaufman[9,11] and Kurylo *et al.*,[10] using the three parameter equation $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 9.5 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 1.2 \times 10^{-12} \exp(-1440/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 240–300 K.

Reliability

$\Delta \log k = 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Finlayson-Pitts *et al.*[2] and Talukdar *et al.*[3] are significantly lower than those of Jeong and Kaufman[9,11], Kurylo *et al.*[10] and Nelson *et al.*[1]. It appears that the higher measured absolute rate coefficients of Jeong and Kaufman[9,11], Kurylo *et al.*[10] and Nelson *et al.*[1] at the higher temperatures were due to thermal decomposition of CH_3CCl_3 to reactive $CH_2{=}CCl_2$ on surfaces.[2,3] A unit-weighted least-squares analysis of the absolute rate coefficients of Finlayson-Pitts *et al.*[2] and Talukdar *et al.*[3], using the expression $k = CT^2 \exp(-D/T)$, leads to $k = 2.25 \times 10^{-18} T^2 \exp(-910/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 243–379 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

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HO + CH_2ClCF_3 (HCFC–133a) → H_2O + $CHClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.05 \pm 0.23) \times 10^{-14}$	296	Howard and Evenson, 1976[1]	(a)
$1.1 \times 10^{-12} \exp[-(1260 \pm 60)/T]$	263–373	Handwerk and Zellner, 1978[2]	(b)
$(1.5 \pm 0.3) \times 10^{-14}$	293		
$3.9 \times 10^{-11} \exp[-(2300 \pm 300)/T]$	294–427	Clyne and Holt, 1979[3]	(c)
$(1.03 \pm 0.30) \times 10^{-14}$	294		
Reviews and Evaluations			
$8.50 \times 10^{-19} T^2 \exp(-458/T)$	263–373	Atkinson, 1989[4]	(d)
$5.2 \times 10^{-13} \exp(-1100/T)$	263–373	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system with LMR detection of HO.

(b) Flash photolysis system with UV absorption detection of HO.

(c) Discharge flow system with resonance fluorescence detection of HO.

(d) Derived from the absolute rate coefficients of Howard and Evenson[1] and Handwerk and Zellner,[2] using the three parameter equation $k = CT^2 \exp(-D/T)$.

(e) The 298 K rate coefficient was the average of those of Howard and Evenson[1] and Handwerk and Zellner.[2] The temperature dependence was that determined by Handwerk and Zellner.[2]

Preferred Values

$k = 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.2 \times 10^{-13} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Howard and Evenson[1] and Handwerk and Zellner[2] (corrected to 298 K), and the temperature dependence is that obtained from a unit-weighted least squares analysis of the data of Handwerk and Zellner.[2] The rate coefficients of Clyne and Holt[3] are in serious disagreement with those of Handwerk and Zellner,[2] and are not used in the evaluation.

References

[1] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[2] V. Handwerk and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 1161 (1978).
[3] M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).
[4] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CH_2ClCF_2Cl$ (HCFC–132b) → $H_2O + CHClCF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3 \times 10^{-12} \exp[-(1578^{+400}_{-230})/T]$	250–350	Watson *et al.*, 1979[1]	(a)
$(1.6 \pm 0.3) \times 10^{-14}$	298		
$2.97 \times 10^{-13} T^{4.58} \exp[(252 \pm 377)/T]$	249–473	Jeong *et al.*, 1984[2]	(b)
$(2.42 \pm 0.16) \times 10^{-14}$	297		
Reviews and Evaluations			
$3.0 \times 10^{-12} \exp(-1580/T)$	250–350	IUPAC, 1989[3]	(c)
$2.80 \times 10^{-18} T^2 \exp(-672/T)$	249–473	Atkinson, 1989[4]	(d)
$3.6 \times 10^{-12} \exp(-1600/T)$	250–350	NASA, 1990[5]	(c)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO. Measured rate constants yielded the Arrhenius expression $k = 1.87 \times 10^{-12} \exp(-1351/T)$ cm^3 molecule^{-1} s^{-1}, with $k = (1.9 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K. However, chemical analysis showed the presence of reactive impurities, and the Arrhenius expression corrected to take into account the contributions of these impurities on the HO radical decay rates is given in the table.

(b) Discharge flow system with resonance fluorescence detection of HO.

(c) Derived from the corrected data of Watson *et al.*[1]

(d) Derived from the measured rate coefficients of Watson *et al.*[1] and Jeong *et al.*[2]

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.2 \times 10^{-12} \exp(-1580/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The corrected data of Watson *et al.*[2] are accepted, assuming that the observed C_2 haloalkene impurities present in the CH_2ClCF_2Cl sample react with the OH radical with a rate coefficient of 5×10^{-12} cm^3 molecule^{-1} s^{-1} independent of temperature. The rate coefficients of Jeong *et al.*[2] are higher, especially at <300 K, suggesting the presence of reactive impurities in the CH_2ClCF_2Cl sample used.

References

[1] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).

[2] K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. **88**, 1222 (1984).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

[5] NASA Evaluation No. 9, 1990 (see references in Introduction).

HO + $CHFClCF_3$ (HCFC–124) → H_2O + $CFClCF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
$4.45 \times 10^{-13} \exp[-(1150 \pm 60)/T]$	210–349	Gierczak *et al.*, 1991[1]	(a)
$(9.44 \pm 0.75) \times 10^{-15}$	298		
Reviews and Evaluations			
$6.4 \times 10^{-13} \exp(-1240/T)$	250–380	IUPAC, 1989[2]	(b)
$6.38 \times 10^{-13} \exp(-1233/T)$	250–375	Atkinson, 1989[3]	(b)
$6.6 \times 10^{-13} \exp(-1250/T)$	250–375	NASA, 1990[4]	(b)

Comments

(a) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.

(b) Derived from the rate coefficients of Howard and Evenson[5] and Watson *et al.*[6]

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.4 \times 10^{-13} \exp(-1205/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Relability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Watson *et al.*[6] and Gierczak *et al.*[1] are in excellent agreement over the common temperature range studied (250–375 K), but are ~30% lower at room temperature than the rate coefficient of Howard and Evenson.[5] The rate coefficients of Watson *et al.*[6] and Gierczak *et al.*[1] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.03 \times 10^{-18} T^2 \exp(-675/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–425 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C\, e^2\, T^2$ and $B = D + 2T$.

References

[1]T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).

[2]IUPAC, Supplement III, 1989 (see references in Introduction).

[3]R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 1, 1** (1989).

[4]NASA Evaluation No. 9, 1990 (see references in Introduction).

[5]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).

[6]R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).

$HO + CHCl_2CF_3$ (HCFC-123) $\rightarrow H_2O + CCl_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.1 \times 10^{-12} \exp[-(1040 \pm 140)/T]$	270–400	Liu, Huie and Kurylo, 1990[1]	(a)
$(3.52 \pm 0.28) \times 10^{-14}$	298		
$1.18 \times 10^{-12} \exp[-(900 \pm 150)/T$	232–426	Brown *et al.*, 1990[2]	(b)
$(5.9 \pm 0.6) \times 10^{-14}$	303		
$6.5 \times 10^{-13} \exp[-(840 \pm 40)/T]$	213–322	Gierczak *et al.*, 1991[3]	(c)
$(3.64 \pm 0.34) \times 10^{-14}$	298		
Reviews and Evaluations			
$1.2 \times 10^{-12} \exp(-1060/T)$	245–375	IUPAC, 1989[4]	(d)
$1.16 \times 10^{-12} \exp(-1056/T)$	245–375	Atkinson, 1989[5]	(d)
$6.4 \times 10^{-13} \exp(-850/T)$	245–380	NASA, 1990[6]	(e)

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.

(b) Discharge flow system with resonance fluorescence detection of HO.

(c) Flash photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used. The rate coefficient measured at 380 K, of $(7.20 \pm 0.58) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, was not included in the cited Arrhenius expression.

(d) Derived from least-squares analysis of the rate coefficients of Howard and Evenson[7] and Watson *et al.*[8] The data of Clyne and Holt[9] were not considered in evaluating this reaction.

(e) Derived from the rate coefficients of Howard and Evenson,[7] Watson *et al.*,[8] Liu *et al.*[1] and the as then unpublished data of Gierczak *et al.*[3]

Preferred Values

$k = 3.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.5 \times 10^{-13} \exp(-815/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The measured rate coefficients of Howard and Evenson,[7] Watson *et al.*,[8] Liu *et al.*[1] and Gierczak *et al.*[3] are in reasonable agreement, but are significantly lower than those of Brown *et al.*[2] These rate coefficients of Howard and Evenson,[7] Watson *et al.*,[8] Liu *et al.*[1] and Gierczak *et al.*[3] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.06 \times 10^{-18} T^2 \exp(-283/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213–400 K. The preferred Arrrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

[1] R. Liu, R. E. Huie and M. J. Kurylo, J. Phys. Chem. **94**, 3427 (1990).

[2] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

[3] T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, J. Geophys. Res. **96**, 5001 (1991).

[4] IUPAC, Supplement III, 1989 (see references in Introduction).

[5] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1, 1 (1989).

[6] NASA Evaluation No. 9, 1990 (see references in Introduction).

[7] C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 4303 (1976).

[8] R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. **11**, 187 (1979).

[9] M. A. A. Clyne and P. M. Holt, J. Chem. Soc., Faraday Trans. 2. **75**, 582 (1979).

HO + $CHCl_2CF_2CF_3$ (HCFC-225ca) → H_2O + $CCl_2CF_2CF_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.3 \times 10^{-13} \exp[-(550 \pm 750)/T]$	251–393	Brown *et al.*, 1990[1]	(a)
$(3.7 \pm 0.8) \times 10^{-14}$	300		
$1.92 \times 10^{-12} \exp[-(1290 \pm 90)/T]$	270–400	Zhang *et al.*, 1991[2]	(b)
$(2.60 \pm 0.29) \times 10^{-14}$	298		
$6.5 \times 10^{-13} \exp[-(970 \pm 115)/T]$	295–364	Nelson, Zahniser and Kolb, 1992[3]	(c)
$(2.41 \pm 0.24) \times 10^{-14}$	295		

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. The stated purity level of the $CHCl_2CF_2CF_3$ sample used was >99.5%.
(b) Flash photolysis system with resonance fluorescence detection of HO.
(c) Discharge flow system with LIF detection of HO.

Preferred Values

$k = 2.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12} \exp(-1130/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients measured by Zhang *et al.*[2] and Nelson *et al.*[3] over the temperature range 295–365 K are in good agreement within the experimental uncertainties. The rate coefficients measured by Brown *et al.*[1] at 251 K and 300 K are significantly higher, and are not used in the evaluation. The preferred 298 K rate coefficient is the average of those calculated from the Arrhenius expressions of Zhang *et al.*[2] and Nelson *et al.*,[3] and the preferred temperature dependence is the mean of those of Zhang *et al.*[2] and Nelson *et al.*[3] [a least-squares analysis of these data[2,3] yields $k = 1.56 \times 10^{-12} \exp(-1239/T)$ cm^3 molecule^{-1} s^{-1}, largely weighted by the 270 K and 400 K rate coefficients of Zhang *et al.*[2]].

References

[1] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).
[2] Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, Geophys. Res. Lett. **18**, 5 (1991).
[3] D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).

HO + $CHFClCF_2CF_2Cl$ (HCFC-225cb) → H_2O + $CFClCF_2CF_2Cl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.75 \times 10^{-13} \exp[-(1300 \pm 180)/T]$	298–400	Zhang *et al.*, 1991[1]	(a)
$(8.6 \pm 1.1) \times 10^{-15}$	298		
$3.9 \times 10^{-13} \exp[-(1120 \pm 125)/T]$	295–374	Nelson, Zahniser, and Kolb, 1992[2]	(b)
$(9.0 \pm 1.1) \times 10^{-15}$	295		

Comments

(a) Flash photolysis system with resonance fluorescence detection of HO.
(b) Discharge flow system with LIF detection of HO.

Preferred Values

$k = 8.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.5 \times 10^{-13} \exp(-1230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–400 K.

Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values
The preferred values are derived from a least-squares analysis of the rate coefficients of Zhang *et al.*[1] and Nelson *et al.*,[2] which are in excellent agreement.

References

[1]Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, Geophys. Res. Lett. **18**, 5 (1991).
[2]D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).

$HO + CH_3CF_2CFCl_2$ (HCFC–243cc) $\rightarrow H_2O + CH_2CF_2CFCl_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$7.1 \times 10^{-13} \exp[-(1690 \pm 230)/T]$	295–367	Nelson *et al.*, 1992[1]	(a)
$(2.1 \pm 0.2) \times 10^{-15}$	295		

Comments

(a) Discharge flow system with LIF detection of HO. Reliable data could not be obtained below 295 K owing to wall adsorption problems.

Preferred Values

$k = 2.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.0 \times 10^{-13} \exp(-1690/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–370 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values
The preferred values are based on the sole study of Nelson *et al.*[1]

References

[1]D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, J. Phys. Chem. **96**, 249 (1992).

HO + HCOCl → H_2O + ClCO

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$\leq 3.2 \times 10^{-13}$	299.2	Libuda *et al.*, 1990[1]	(a)

Comments

(a) Relative rate method. HO radicals generated by thermal decomposition of HO_2NO_2 after the addition of NO to HC(O)Cl–n-butane–O_2–N_2–HO_2NO_2 mixtures at 600 Torr total pressure. Upper limit derived from decay of n-butane (measured by GC) and lack of reaction of HC(O)Cl (as monitored by FTIR absorption spectroscopy).

Preferred Values

$k < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Based on the upper limit to the rate coefficient reported by Libuda *et al.*[1]

References

[1]H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. **94**, 5860 (1990).

HO + $COCl_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<1 \times 10^{-15}$	298 ± 3	Nelson *et al.*, 1990[1]	(a)

Comments

(a) Relative rate study. HO radicals generated from the photolysis of CH_3ONO in CH_3ONO–NO–$COCl_2$–reference compound-air mixtures at atmospheric pressure. No reaction of $COCl_2$ was observed. No details given concerning the identity of the reference compound or the amount of reference compound reacted.

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the sole reported study of Nelson *et al.*,[1] with the preferred upper limit being increased by a factor of 5 over that cited by Nelson *et al.*[1]

References

[1]L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

$HO + CH_2ClCHO \rightarrow H_2O + CH_2ClCO$ (1)
$\rightarrow H_2O + CHClCHO$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.6) \times 10^{-12}$	298	Balestra-Garcia, Le Bras and Mac Leod, 1992[1]	(a)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO.

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is that of Balestra-Garcia *et al.*[1] The reaction is expected to proceed essentially totally by channel (1) at 298 K.

Reference

[1]C. Balestra-Garcia, G. Le Bras and H. Mac Leod, J. Phys. Chem. **96**, 3312 (1992).

$HO + CHCl_2CHO \rightarrow H_2O + CHCl_2CO$ (1)
$\rightarrow H_2O + CCl_2CHO$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.5) \times 10^{-12}$	298	Balestra-Garcia, Le Bras and Mac Leod, 1992[1]	(a)

Comments

(a) Laser photolysis system with resonance fluorescence detection of HO.

Preferred Values

$k = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is that of Balestra-Garcia *et al.*[1] The reaction is expected to proceed essentially entirely by channel (1) at 298 K.

Reference

[1]C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, J. Phys. Chem. **96**, 3312 (1992).

$HO + CCl_3CHO \rightarrow H_2O + CCl_3CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.18 \times 10^{-11} \exp[-(600 \pm 90)/T]$	298–520	Dóbé, Khachatryan and Bérces, 1989[1]	(
1.61×10^{-12}	298		
$(8.6 \pm 1.7) \times 10^{-13}$	298	Balestra-Garcia, Le Bras and Mac Leod, 1992[2]	(
Relative Rate Coefficients			
$(1.63 \pm 0.29) \times 10^{-12}$	298 ± 3	Nelson *et al.*, 1990[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence or LIF detection of HO.

(b) Laser photolysis system with resonance fluorescence detection of HO.

(c) Relative rate method. HO radicals generated by photolysis of CH_3ONO–air mixtures at atmospheric pressure. Decay rates of CCl_3CHO and ethyl acetate measured by GC, and the rate coefficient ratio placed on an absolute basis by use of k(HO + ethyl acetate) $= 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[4]

Preferred Values

$k = 1.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

At 298 K, the absolute and relative rate coefficients Dóbé *et al.*[1] and Nelson *et al.*[2] are in good agreement, t are a factor of ~2 higher than the absolute rate coef cient of Balestra-Garcia *et al.*[1] The preferred 298 K ra coefficient is the average of the room temperature data Dóbé *et al.*,[1] Balestra-Garcia *et al.*[2] and Nelson *et al.*[3] N temperature dependence is recommended.

References

[1]S. Dóbé, L. A. Khachatryan, and T. Bérces, Ber. Bunsenges Phy Chem. **93**, 847 (1989).

[2]C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, J. Phys. Chem. 9 3312 (1992).

[3]L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

[4]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).

$HO + CH_3COCl \rightarrow H_2O + CH_2COCl$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(9.1 \pm 3.2) \times 10^{-15}$	298 ± 3	Nelson *et al.*, 1990[1]	(a)

Comments

(a) Relative rate method. HO radicals generated by the photolysis of CH_3ONO–air mixtures at atmospheric pressure. Decay rates of CH_3COCl and $CHCl_3$ measured by GC, and rate coefficient ratio placed on an absolute basis by use of $k(HO + CHCl_3) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

Preferred Values

$k = 9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the relative rate coefficient study of Nelson *et al.*[1] However, the data presented in Figure 5 of Nelson *et al.*[1] and in the earlier presentation of Nelson *et al.*[2] yields a rate coefficient for the reaction of HO radicals with $CH_3C(O)Cl$ of $k = 6.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 ± 3 K, a factor of ~7.5 higher than cited in Nelson *et al.*[1] This apparent discrepancy requires clarification.

References

[1]L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 577 (1990).

[2]L. Nelson, J. J. Treacy, and H. W. Sidebottom, Proceedings, 3rd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants, 1984; D. Riedel Pub. Co., Dordrecht, Holland, 1984, p. 258–263.

$HO + CHF_2OCHClCF_3 \rightarrow H_2O + CHF_2OCClCF_3$ (1)

$\rightarrow H_2O + CF_2OCHClCF_3$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.7) \times 10^{-14}$	298	Brown *et al.*, 1990[1]	(a)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. Stated purity level of the $CHF_2OCHClCF_3$ sample used was >99.5%.

Preferred Values

$k = 2.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Values

Based on the sole study of Brown *et al.*,[1] with expanded uncertainty limits.

References

[1]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$HO + CHF_2OCF_2CHFCl \rightarrow H_2O + CHF_2OCF_2CFCl$ (1)

$\rightarrow H_2O + CF_2OCF_2CHFCl$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.1 \times 10^{-13} \exp[-(1080 \pm 500)/T]$	302–422	Brown *et al.*, 1990[1]	(a)
$(1.7 \pm 0.5) \times 10^{-14}$	302		

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. The stated purity level of the CHF_2OCF_2CHFCl sample used was >99.5%.

Preferred Values

$k = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.1 \times 10^{-13} \exp(-1080/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–430 K.

Reliability

$\Delta \log k = \pm 0.5$.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the sole study of Brown *et al.*[1]

References

[1]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

$NO_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.9 \pm 0.2) \times 10^{-16}$	298	Atkinson, Aschmann and Goodman, 1987[1]	(a)
Reviews and Evaluations			
2.9×10^{-16}	298	IUPAC, 1989[2]	(b)

Comments

(a) Derived from a relative rate method, by monitoring the relative decay rates of C_2HCl_3 and C_2H_4 in N_2O_5–NO_2–organic–air mixtures at one atmosphere total pressure of air. The observed decay rates yielded $k(NO_3 + C_2HCl_3)/k(NO_3 + C_2H_4) = 1.37 \pm 0.08$. This rate coefficient ratio is placed on an absolute basis by use of $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) See Comments on Preferred Values.

Preferred Values

$k = 2.9 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*[1] as discussed in comment (a) above. The cited uncertainty limits have been increased.

References

[1]R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. 19, 299 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$NO_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<6 \times 10^{-17}$	298	Atkinson, Aschmann and Goodman, 1987[1]	(a)
Reviews and Evaluations			
$<1 \times 10^{-16}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Derived from a relative rate method, by monitoring the relative decay rates of C_2Cl_4 and C_2H_4 in N_2O_5–NO_2–organic–air mixtures at one atmosphere total pressure of air. The observations yielded $k(NO_3 + C_2Cl_4)/k(NO_3 + C_2H_4) < 0.25$. This upper limit to the rate coefficient ratio is placed on an absolute basis by use of $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) See Comments on Preferred Values.

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*[1] as discussed in comment (a) above. The upper limit to the rate coefficient has been increased over that derived from the relative rate coefficient data.[1]

References

[1]R. Atkinson, S. M. Aschmann, and M. A. Goodman, Int. J. Chem. Kinet. 19, 299 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).

$ClO + HO_2 \rightarrow HOCl + O_2$ (1)
$\rightarrow HCl + O_3$ (2)

$\Delta H°(1) = -195$ kJ·mol^{-1}
$\Delta H°(2) = -66$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.2 \pm 1.5) \times 10^{-12}$	308	Cattell and Cox, 1986[1]	(a)
Reviews and Evaluations			
4.6×10^{-13} exp(710/T)	200–300	IUPAC, 1989[2]	(b)
4.8×10^{-13} exp(700/T)	200–300	NASA, 1990[3]	(c)

Comments

(a) Molecular modulation with UV absorption study. ClO produced in presence of excess HO_2 from $Cl + HO_2$ reaction in photolysis of Cl_2–H_2–O_2–N_2 mixtures. $[HO_2]$ calculated using UV absorption cross-section of $\sigma = 3.5 \times 10^{-18}$ cm^2 molecule^{-1} at 220 nm. Rate coefficient was independent of pressure over the range 50–760 Torr at 308 K.
(b) See Comments on Preferred Values.
(c) Based on data of Reimann and Kaufman,[4] Stimpfle *et al*.,[5] Leck *et al*.,[6] Burrows and Cox[7] and Cattell and Cox.[1]

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.6 \times 10^{-13}$ exp(710/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The data of Cattell and Cox[1] are in good agreement with the earlier measurements,[4–7] and the absence of a pressure dependence excludes a possible addition channel. The lowest upper limit for HCl formation via channel (2) is $k_2 < 2.0 \times 10^{-14}$ cm^3 s^{-1} at 298 K.[7] The preferred value at room temperature is based on the results reported in references 1, 4–7, and the recommended temperature dependencies are from reference 5.

References

[1]F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **82**, 1413 (1986).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]B. Reimann and F. Kaufman, J. Chem. Phys. **69**, 2925 (1978).
[5]R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. **71**, 5183 (1979).
[6]T. J. Leck, J. E. Cook, and J. W. Birks, J. Chem. Phys. **72**, 2364 (1980).
[7]J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1, **77**, 2465 (1981).

$ClO + O_3 \rightarrow ClOO + O_2$ (1)
$\rightarrow OClO + O_2$ (2)

$\Delta H°(1) = -147$ kJ·mol^{-1}
$\Delta H°(2) = -144$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_2 < 5 \times 10^{-15}$	298	Clyne, *et al.*, 1975[1]	(a)
$k < 1 \times 10^{-18}$	298	DeMore *et al.*, 1975[2]	(b)
$k < 1 \times 10^{-18}$	296	Wongdontri-Stuper *et al.*, 1979[3]	(b)
$k_1 < 1.4 \times 10^{-17}$	233, 298	Stevens and Anderson, 1990[4]	(c)
$k_1 = (4.0 \pm 2.0) \times 10^{-16}$	413		
Reviews and Evaluations			
$k_1 < 1 \times 10^{-18}$	298	NASA, 1990[5]	(d)
$k_2 < 1 \times 10^{-18}$	298		

Comments

(a) Discharge flow system with MS detection.
(b) Steady state photolysis of Cl_2–O_3 mixtures.
(c) Discharge flow system. Reaction channel (1) was followed by monitoring the ClO produced from the thermal decomposition of the product ClOO in the presence of O_3. The product ClO was distinguished from reactant ClO through isotopic oxygen labelling. The authors combined the upper limit at 298 K with the value measured at 413 K to derive an A-factor of 2.4×10^{-12} cm^3 molecule^{-1} s^{-1} and a lower limit to E/R of 3600 K.
(d) Based on the results of DeMore *et al.*[2] and Wongdontri-Stuper *et al.*[3] The pre-exponential factor was estimated to be 1×10^{-12} cm^3 molecule^{-1} s^{-1}, resulting in a lower limit to E/R of 4000 K.

Preferred Values

$k_1 < 1.5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit for k_1 is based on the results of the recent study of Stevens and Anderson.[4] The preferred upper limit for k_2 is based on the data of DeMore *et al.*[2] and Wongdontri-Stuper *et al.*[3] Stevens and Anderson's upper limit at room temperature[4] can be combined with their measured rate coefficient at 413 K to derive $A = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $E/R > 3600$ K. For k_2 one can estimate $A = 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and derive $E/R > 4000$ K.

References

[1]M. A. A. Clyne, D. J. McKenney, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 322 (1975).
[2]W. B. DeMore, C. L. Lin, and S. Jaffe, presented at ACS National Meeting, Philadelphia, PA, 1975.
[3]W. Wongdontri-Stuper, R. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **10**, 163 (1979).
[4]P. S. Stevens and J. G. Anderson, Geophys. Res. Lett. **17**, 1287 (1990).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$ClO + NO \rightarrow Cl + NO_2$

$\Delta H^\circ = -38$ kJ·mol^{-1}

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.16) \times 10^{-11}$	295	Clyne and MacRobert, 1980[1]	(a)
$7.1 \times 10^{-12} \exp[(270 \pm 50)/T]$	202–393	Lee *et al.*, 1982[2]	(b)
Reviews and Evaluations			
$6.2 \times 10^{-12} \exp(294/T)$	202–415	CODATA, 1982[3]; IUPAC, 1989[4]	(c)
$6.4 \times 10^{-12} \exp(290/T)$	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with MS detection of ClO.
(b) Discharge flow system with LMR detection of ClO.
(c) See Comments on Preferred Values.
(d) Based on data of Clyne and MacRobert,[1] Lee *et al.*,[2] Clyne and Watson,[6] Leu and DeMore[7] and Ray and Watson.[8]

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.2 \times 10^{-12} \exp(294/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 202–415 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1982.[3] The room temperature rate coefficients reported by Clyne and MacRobert,[1] Lee *et al.*,[2] Clyne and Watson,[6] Leu and DeMore[7] and Ray and Watson[8] are in very good agreement and are averaged to yield the 298 K preferred value. The value reported by Zahniser and Kaufman[9] from a competitive study is about 30% higher. The Arrhenius expression is derived from a least squares fit to the data reported in Refs 1, 2 and 6–8.

References

[1]M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).
[2]Y. P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, Int. J. Chem. Kinet. **14**, 711 (1982).
[3]CODATA, Supplement I, 1982 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **70**, 2250 (1974).
[7]M. T. Leu and W. B. DeMore, J. Phys. Chem. **82**, 2049 (1978).
[8]G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[9]M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

$\Delta H^\circ = -112$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.2) \times 10^{-31}$ [N_2]	298	Dasch, Sternberg, and Schindler, 1981[1]	(a)
$(1.8 \pm 0.4) \times 10^{-31}$ [N_2]	270–295	Cox, Burrows and Coker, 1984[2]	(b)
$(1.6 \pm 0.2) \times 10^{-31}(T/300)^{-3.0}$ [N_2]	264–343	Handwerk and Zellner, 1984[3]	(c)
$(1.4 \pm 0.7) \times 10^{-31}$ [N_2]	298	Wallington and Cox, 1986[4]	(d)
Reviews and Evaluations			
$1.7 \times 10^{-31}(T/300)^{-3.4}$ [N_2]	250–420	CODATA, 1984[5]; IUPAC, 1989[6]	(e)
$1.8 \times 10^{-31}(T/300)^{-3.4}$ [air]	200–300	NASA, 1990[7]	(e)

Comments

(a) Laser flash photolysis generation of ClO radicals from Cl_2O. ClO radicals monitored by absorption at 285.2 nm using a Xe arc lamp or a Mg-hollow cathode lamp as a light source. Pressure range = 20–600 Torr. Results were in good agreement with falloff curve from earlier studies.

(b) Modulated photolysis of Cl_2–Cl_2O–NO_2–N_2 mixtures. $ClONO_2$ formation followed by diode laser spectroscopy. This study ruled out the formation of isomers other than $ClONO_2$.

(c) Flash photolyis generation of ClO from Cl_2O. Detection of ClO via absorption at 256 nm. Pressure range 17–790 Torr, with experiments conducted at 264, 298, and 343 K. Results were in good agreement with earlier data in the falloff range.[5]

(d) Modulated photolysis of OClO–NO_2–N_2 mixtures with ClO detection by UV absorption.

(e) Average of ten earlier measurements which all agreed very well.

Preferred Values

$k_0 = 1.6 \times 10^{-31}(T/300)^{-3.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

There is now excellent agreement between the various studies of the reaction in the falloff region close to the low-pressure limit. The preferred value is the average of eleven different studies evaluated earlier[5-7] and in the present evaluation. The formation of OClONO or ClOONO, suggested in order to explain earlier discrepancies between recombination and dissociation rate data, apparently does not occur (see reference 8). The discrepancies are now attributed to errors in the equilibrium constant and ΔH° of the reaction.[9] The falloff curve is evaluated with $F_c = 0.5$ at 298 K.

High-pressure rate coefficient

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3\text{–}6) \times 10^{-12}$	298	Dasch, Sternberg, and Schindler, 1983[1]	(a)
$(1.2^{+1.2}_{-0.6}) \times 10^{-11}$	264–343	Handwerk and Zellner, 1984[3]	(b)
Reviews and Evaluations			
2×10^{-11}	200–400	CODATA, 1984[5]; IUPAC, 1989[6]	(c)
$1.5 \times 10^{-11}(T/300)^{-1.9}$	200–300	NASA, 1990[7]	(d)

Comments

(a) See comment (a) for k_0. Extrapolation of k_∞ very uncertain. F_c unspecified.

(b) See comment (c) for k_0. Extrapolation of k_∞ very uncertain. Reported k_∞ value based on theoretical prediction. Using the reported k_0 and k_∞ values, and F_c = 0.55, 0.50, 0.45 for 264, 298, 343 K, respectively, falloff curves are obtained which are in good agreement with the majority of the available data.

(c) Based on a theoretical fit of various experimental falloff curves.

(d) k_∞ and its temperature coefficient are based on theoretical modeling by Smith and Golden.[10]

Preferred Values

$k_\infty = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

Since there are no direct measurements of k at pressures above 1 bar, k_∞ cannot be established with certainty, and theoretical predictions are no better than within a factor of 2. However, if the falloff curves below 1 atm are fitted with the given k_0, k_∞, and F_c values, this uncertainty does not influence the representation of the falloff curve in this range. For this reason, we suggest the preferred values with only a minor temperature dependence of k_∞. We prefer $F_c = 0.5$ at 298 K, and representation in the form $F_c = \exp(-T/T^*)$ yields $T^* = 430$ K.

Comment of Thermochemistry

The inconsistency between rate data for this reaction and the reverse dissociation $ClONO_2 + M \rightarrow ClO - NO_2 + M$ had been attributed earlier either to the formation of isomers in this reaction, to errors in the dissociation measurements,[11,12] or to errors in the equilibrium constant and thermochemistry. This discrepancy now has been resolved by the recent dissociation experiments,[9] which confirm the data of references 11 and 12, and by the exclusion of isomer formation.[8] Following Anderson and Fahey,[9] the heat of formation of $ClONO_2$ has been corrected by combining the recombination and dissociation rate data. These results are included in the present evaluation.

References

[1]W. Dasch, K. H. Sternberg, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **85**, 611 (1981).
[2]R. A. Cox, J. P. Burrows, and G. B. Coker, Int. J. Chem. Kinet. **16**, 445 (1984).
[3]V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. **88**, 405 (1984).
[4]T. J. Wallington and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **82**, 275 (1986).
[5]CODATA, Supplement II, 1984 (see references in Introduction).
[6]IUPAC, Supplement III, 1989 (see references in Introduction).
[7]NASA Evaluation No. 9, 1990 (see references in Introduction).
[8]J. P. Burrows, D. W. T. Griffiths, G. K. Moortgat, and G. S. Tyndall, J. Phys. Chem. **89**, 266 (1985).
[9]L. C. Anderson and D. W. Fahey, J. Phys. Chem. **94**, 644 (1990).
[10]G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).
[11]H. D. Knauth, Ber. Bunsenges. Phys. Chem. **82**, 212 (1978).
[12]G. Schoenle, H. D. Knauth, and R. N. Schindler, J. Phys. Chem. **83**, 3297 (1979).

$$ClO + NO_3 \rightarrow ClOO + NO_2 \quad (1)$$
$$\rightarrow OClO + NO_2 \quad (2)$$

$\Delta H°(1) = -36\ kJ{\cdot}mol^{-1}$
$\Delta H°(2) = -32\ kJ{\cdot}mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 1.7) \times 10^{-13}$	296	Cox *et al.*, 1984[1]	(a)
$1.6 \times 10^{-12} \exp[-(420 \pm 200)/T]$	278–338	Cox *et al.*, 1987[2]	(b)
Reviews and Evaluations			
4.0×10^{-13}	298	IUPAC, 1989[3]	(c)
4.0×10^{-13}	200–300	NASA, 1990[4]	(d)

Comments

(a) Time dependent measurements of NO_3 in the photolysis of $Cl_2-ClONO_2-N_2$ mixtures. ClO assumed to be produced in presence of excess NO_3 by the reaction Cl + NO_3. [NO_3] calculated using $\sigma = 1.7 \times 10^{-17}$ cm^2 molecule^{-1} at 662 nm.

(b) Molecular modulation system with UV absorption. Photolysis of $Cl_2-ClONO_2-N_2$ mixtures. ClO monitored in UV at 277.2 nm ($\sigma = 7.2 \times 10^{-18}$ cm^2) and NO_3 at 662 nm ($\sigma = 1.7 \times 10^{-17}$ cm^2 molecule^{-1}). Rate coefficients obtained by computer modeling of absorption-time profiles for ClO in the presence of excess NO_3. Upper limit of $k_2/k_1 < 0.4$ based on absence of observable OClO.

(c) See Comments on Preferred Values.

(d) Based on Cox *et al.*,[1,2] but with recommended zero temperature dependence.

Preferred Values

$k = 4.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The two studies[1,2] using a similar technique are in good agreement at 298 K. In view of the uncertainty in the data, the temperature dependence cannot be considered to be established and a temperature dependent expression for k is not recommended from this evaluation. The weight of evidence presented[2] suggests that channel (1) is the major pathway at $T <$ 300 K.

References

[1] R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, Chem. Phys. Lett. **108**, 228 (1984).
[2] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. Chem. **91**, 3361 (1987).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).
[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

$$ClO + ClO \rightarrow Cl + ClOO \quad (1)$$
$$\rightarrow Cl + OClO \quad (2)$$
$$\rightarrow Cl_2 + O_2 \quad (3)$$

$\Delta H°(1) = 15$ kJ·mol^{-1}
$\Delta H°(2) = 18$ kJ·mol^{-1}
$\Delta H°(3) = -204$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = (7.2 \pm 1.6) \times 10^{-15}$	300	Simon *et al.*, 1990[1]	(a)
$k_2 = (7.3 \pm 2.6) \times 10^{-15}$			
$k_3 = (7.3 \pm 1.8) \times 10^{-15}$			
Reviews and Evaluations			
$k_1 = 3.4 \times 10^{-15}$	298	IUPAC, 1989[2]	(b)
$k_2 = 1.7 \times 10^{-15}$			
$k_3 = 4.9 \times 10^{-15}$			
$k = 8.0 \times 10^{-13} \exp(-1250/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Photolysis of flowing Cl_2–Cl_2O–O_2 mixtures. Rate coefficients derived from computer simulation of time-resolved absorption at 240, 257.7, and 292 nm and between 281 and 362 nm using a chemical mechanism consisting of 12 reactions.

(b) Based on the data of Clyne *et al.*[4] and Cox and Derwent.[5]

(c) Based on the results of Clyne and co-workers,[4] as discussed in the reviews by Watson.[6,7]

Preferred Values

$k_1 = 3.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 4.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k_1 = \Delta\log k_2 = \Delta\log k_3 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred values are unchanged from the previous evaluation, IUPAC, 1989.[2] The preferred value for the overall rate constant at 298 K is a mean of the low pressure value of Clyne *et al.*[4] and Cox and Derwent.[5] The branching ratios at 298 K accept the results of Cox and Derwent.[5] The recent results of Simon *et al.*[1] are significantly different; the sum of the reported rate coefficients for the three reaction channels is twice as large as the overall rate coefficient established reliably by Clyne and co-workers,[4] indicating some complication with the chemistry in this new study.

References

[1]F. G. Simon, W. Schneider, G. K. Moortgat, and J. P. Burrows, J. Photochem. Photobiol. A 55, 1 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]M. A. A. Clyne, D. J. McKenney, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, 71, 322 (1975).
[5]R. A. Cox and R. G. Derwent, J. Chem. Soc. Faraday Trans. 1, 75, 1635 (1979).
[6]R. T. Watson, J. Phys. Chem. Ref. Data 6, 871 (1977).
[7]R. T. Watson, Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report FAA EE-80-20, FAA, Washington, DC (1980).

$ClO + ClO + M \rightarrow Cl_2O_2 + M$

$\Delta H° = -74\ kJ{\cdot}mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.5) \times 10^{-32}(T/300)^{-3.65}$ [N_2]	194–247	Sander, Friedl, and Yung, 1989[1]	(a)
$(1.64 \pm 0.09) \times 10^{-32}(T/300)^{-4.4}$ [N_2]	200–263	Trolier, Mauldin, and Ravishankara, 1990[2]	(b)
$(1.32 \pm 0.08) \times 10^{-32}(T/300)^{-4.4}$ [O_2]			
Reviews and Evaluations			
$4.0 \times 10^{-32}(T/300)^{-2.0}$ [N_2]	200–300	IUPAC, 1989[3]	(c)
$1.8 \times 10^{-32}(T/300)^{-3.6}$ [air]	200–300	NASA, 1990[4]	(d)

Comments

(a) ClO generated by flash photolysis of Cl_2-Cl_2O or Cl_2–O_3 mixtures and monitored by long-path UV detection. Bath gas densities N_2, Ar, or O_2 were in the range 10^{18} to 3×10^{19} molecule cm^{-3}. Falloff extrapolation to k_0 and k_∞ used $F_c = 0.6$.

(b) Flash photolysis of Cl_2–O_3 mixtures in the presence of 25–600 Torr of He, N_2, O_2, or SF_6. ClO and Cl_2O_2 were monitored by long-path UV absorption. Falloff curves were evaluated with $F_c = 0.6$; difficulties with the simple falloff expression (see Introduction) were encountered.

(c) The preferred values were averages of the data from references 5 and 6 for M = O_2 and references 7 and 8 for M = $N_2 + O_2$ and $Cl_2 + O_2$. The temperature dependence was based on the results from reference 8.

(d) Based on reference 1.

Preferred Values

$k_0 = 1.7 \times 10^{-32}(T/300)^{-4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–260 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 250 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred values are an average of the most recent results from references 1 and 2. Some minor inconsistencies between these data and earlier results,[7,8] obtained near 300 K and being slightly higher, remain unresolved. Difficulties[2] with fits based on the simple falloff expression (see Introduction) with a fixed value of $F_c = 0.6$ may be attributed to an oversimplified fitting procedure. As a next step, one may use theoretically modeled and temperature dependent values of F_c as well as F_c-dependent widths of the falloff curves.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6 \pm 2) \times 10^{-12}$	194–247	Sander, Friedl, and Yung, 1989[1]	(a)
$(4.8 \pm 1.3) \times 10^{-12}$	200–263	Trolier, Mauldin, and Ravishankara, 1990[2]	(b)
Reviews and Evaluations			
6×10^{-12}	200–300	NASA, 1990[4]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) Based on reference 1.

Preferred Values

$k_\infty = 5.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values
See comments on k_0.

References

[1]S. P. Sander, R. R. Friedl, and Y. L. Yung, Science **245**, 1095 (1989).
[2]M. Trolier, R. L. Mauldin III, and A. R. Ravishankara, J. Phys. Chem. **94**, 4896 (1990).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]H. S. Johnston, E. D. Morris Jr., and J. van den Bogaerde, J. Am. Chem. Soc. **91**, 7712 (1969).
[6]N. Basco and J. Hunt, Int. J. Chem. Kinet. **11**, 649 (1979).
[7]R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and H. J. Reid, J. Chem. Soc. Faraday Trans. 1, **75**, 1648 (1979).
[8]G. D. Hayman, J. M. Davies, and R. A. Cox, Geophys. Res. Lett. **13**, 1347 (1986).

$Cl_2O_2 + M \rightarrow ClO + ClO + M$

$\Delta H^\circ = 74$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$3.1 \times 10^{-5}(T/300)^{-3} \times \exp(-8720/T)$ [N$_2$]	230–300	IUPAC, 1989[1]	(a)
6.0×10^{-18} [N$_2$]	298		
$6.0 \times 10^{-6}(T/300)^{-3.6} \times \exp(-8450/T)$ [air]	200–300	NASA, 1990[2]	(b)
3.0×10^{-18} [air]	298		

Comments

(a) Based on $k_0 = 4.0 \times 10^{-32}(T/300)^{-2.0}$[N$_2$] cm^3 molecule^{-1} s^{-1} recommended for the reverse reaction ClO + ClO + M → Cl_2O_2 + M and an equilibrium constant $K_c = 4.2 \times 10^{-30}\, T \exp(8720/T)$ cm^3 molecule^{-1} from Cox and Hayman.[3]
(b) Based on $k_0 = 1.8 \times 10^{-32}(T/300)^{-3.6}$[air] cm^3 molecule^{-1} s^{-1} from Ref. 4 for the reverse reaction and $K_c = 3.0 \times 10^{-27} \exp(8450/T)$ cm^3 molecule^{-1} from Cox and Hayman.[3]

Preferred Values

$k_0 = 2.7 \times 10^{-18}$ [N$_2$] s^{-1} at 298 K.
$k_0 = 1.35 \times 10^{-5}(T/300)^{-5} \exp(-8720/T)$[N$_2$] s^{-1} over the temperature range 200–300 K.

Reliability
$\Delta \log k_0 = \pm 0.3$ at 300 K.
$\Delta(E/R) = \pm 900$ K.

Comments on Preferred Values
The preferred values are calculated from $k_0 = 1.7 \times 10^{-32}$ $(T/300)^{-4}$ [N$_2$] cm^3 molecule^{-1} s^{-1} for the reverse reaction (see this evaluation) and $K_c = 1.26 \times 10^{-27}(T/300) \exp(8720/T)$ cm^3 molecule^{-1} from Cox and Hayman.[3] The preferred values correspond to falloff curves with $F_c = 0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$2 \times 10^{15} \exp(-8450/T)$	200–300	NASA, 1990[2]	(a)

Comments

(a) Based on $k_\infty = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reverse reaction (see this evaluation) and $K_c = 3.0 \times 10^{-27} \exp(8450/T)$ cm^3 molecule^{-1} from Cox and Hayman.[3]

Preferred Values

$k_\infty = 8.7 \times 10^2$ s^{-1} at 298 K.

$k_\infty = 1.8 \times 10^{15} \exp(-8450/T)$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 300 K.

$\Delta(E/R) = \pm 900$ K.

Comments on Preferred Values

The preferred values are based on $k_\infty = 5.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the reverse reaction (see this evaluation) and $K_c = 3.0 \times 10^{-27} \exp(8450/T)$ cm^3 molecule^{-1} from Cox and Hayman.[3] Falloff curves with $F_c = 0.6$ were used for the extrapolation to k_∞.

References

[1]IUPAC, Supplement III, 1989 (see references in Introduction).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).
[3]R. A. Cox and G. D. Hayman, Nature 322, 796 (1988).
[4]S.P. Sander, R. R. Friedl, and Y. L. Yung, Science 245, 1095 (1989).

$ClO + OClO + M \rightarrow Cl_2O_3 + M$

$\Delta H^\circ = -62$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.8×10^{-31} [N_2]	226	Parr *et al.*, 1990[1]	(a)

Comments

(a) Molecular modulation technique with Cl_2–OClO–N_2 mixtures in the pressure range 4.8–29 Torr. ClO was monitored by UV absorption at 277.2 nm. The reaction was apparently close to the low pressure limit.

Preferred Values

$k_0 = 2.8 \times 10^{-31}[N_2]$ cm^3 molecule^{-1} s^{-1} at 226 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 226 K.

Comments on Preferred Values

Since this is the only rate measurement, large error limits are adopted. The thermochemical values were obtained from measurements of the equilibrium constant by Hayman and Cox.[2]

References

[1]A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. 17, 2357 (1990).
[2]G. D. Hayman and R. A. Cox, Chem. Phys. Lett. 155, 1 (1989).

$Cl_2O_3 + M \rightarrow ClO + OClO + M$

$\Delta H° = 62$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

No direct measurements.

Preferred Values

$k_0 = 2.8 \times 10^{-18}$ [N_2] s^{-1} at 226 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 226 K.

Comments on Preferred Values

This value is calculated from the rate coefficient of the reverse reaction $k_0 = 2.8 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1} at 226 K from reference 1 and the equilibrium constant $K_c = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} at 226 K from Ref. 2.

References

[1]A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. **17**, 2357 (1990).
[2]G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).

$ClO + CH_3O_2 \rightarrow ClOO + CH_3O$ (1)
$\rightarrow OClO + CH_3O$ (2)

$\Delta H°(1) = 3$ kJ·mol^{-1}
$\Delta H°(2) = 6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 < 4 \times 10^{-12}$	197–217	DeMore, 1991[1]	(a)
$k_2 < 1 \times 10^{-15}$	197–217		
$(3.1 \pm 1.7) \times 10^{-12}$	300	Simon *et al.*, 1989[2]	(b)
Branching Ratios			
$k_1/k = 0.85 \pm 0.15$	300	Simon *et al.*, 1989[2]	(b)
Reviews and Evaluations			
No recommended value		NASA, 1990[3]	(c)

Comments

(a) Photolysis of Cl_2–CH_4–O_3–O_2–N_2 mixtures at wavelengths >320 nm. The products were monitored by UV-visible and FTIR absorption spectroscopy. The experiments were sensitive to occurrence of reaction (1) because it produces an enhanced rate of ozone loss. The sensitivity declines rapidly with lower values of k_1, and a value of 1×10^{-12} cm^3 molecule^{-1} s^{-1} could not be excluded.

(b) Modulated photolysis of Cl_2–CH_4–Cl_2O–O_2 mixtures using UV-visible and FTIR absorption spectroscopy. ClO was monitored at 292 nm and CH_3O_2 at 240 nm. The authors state that the observations were best explained by postulating a fast biomolecular reaction between ClO and CH_3O_2. They derived the stated value of k at 300 K and 240 Torr total pressure. Based on an estimated value of $E/R = -200$ K, they estimate that at 190 K, the rate coefficient k would be $\sim(4\text{–}5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Results of Simon *et al.*[2] cited, but no recommended value given.

Preferred Values

$k_1 < 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 200 K.
$k_2 < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 200 K.

Comments on Preferred Values

The preferred values are the upper limits at 200 K reported by DeMore.[1] These results are preferred over the estimated low-temperature value suggested by Simon *et al.*[2] because they appear to provide more direct information as to the rate coefficient for this reaction. They do not support the low temperature value suggested by Simon *et al.*[2] on the basis of the room temperature results reported by those authors.

References

[1]W. B. DeMore, J. Geophys. Res. **96**, 4995 (1991).
[2]F. G. Simon, J. P. Burrows, W. Schneider, G. K. Moortgat, and P. J. Crutzen, J. Phys. Chem. **93**, 7807 (1989).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$OClO + O_3 \rightarrow ClO_3 + O_2$

$\Delta H° = -11$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.20 \pm 0.15) \times 10^{-19}$	298	Birks *et al.*, 1977[1]	(a)
$2.3 \times 10^{-12} \exp[-(4730 \pm 630)/T]$	262–298	Wongdontri-Stuper *et al.*, 1979[2]	(b)
3.0×10^{-19}	298		
Reviews and Evaluations			
$2.1 \times 10^{-12} \exp(-4700/T)$	262–298	NASA, 1990[3]	(c)

Comments

(a) Static system used. Rate coefficient was determined by monitoring the loss of O_3 in excess OClO and also the loss of OClO in excess O_3. Both species were measured by UV absorption; O_3 at 254 nm and OClO at 366 nm.
(b) The decay of OClO in excess O_3 was monitored by UV absorption at 400 nm. The reaction rate was also determined by the photolysis of Cl_2–O_3 mixtures at 366 nm to produce OClO, followed by monitoring OClO decay in the dark.
(c) Based on the results of Wongdontri-Stuper *et al.*[2]

Preferred Values

$k = 3.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1 \times 10^{-12} \exp(-4700/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 262–298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred value is based on the results reported in the study of Wongdontri-Stuper *et al.*[2] Within the indicated uncertainty limits it encompasses the lower room temperature value reported by Birks *et al.*[1]

References

[1]J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. **66**, 4591 (1977).
[2]W. Wongdontri-Stuper, R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **10**, 163 (1979).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$OClO + NO \rightarrow NO_2 + ClO$

$\Delta H° = -56$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.4 \pm 0.5) \times 10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	(a)
Reviews and Evaluations			
3.4×10^{-13}	298	IUPAC, 1989[2]	(b)
$2.5 \times 10^{-12} \exp(-600/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with MS determination of OClO decay in presence of excess NO. Secondary reactions as a result of Cl generation from $ClO + NO \rightarrow NO_2 + Cl$ suppressed by addition of NOCl or Br_2.

(b) See Comments on Preferred Values.

(c) Arrhenius parameters estimated using 298 K value of Bemand *et al.*[1]

Preferred Values

$k = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The preferred value is based on the only direct study of this reaction reported by Bemand *et al.*[1] In the absence of experimental data no recommendation is given for the temperature dependence.

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **69**, 1356 (1973).

[2] IUPAC, Supplement III, 1989 (see references in Introduction).

[3] NASA Evaluation No. 9, 1990 (see references in Introduction).

$Cl_2O_2 + O_3 \rightarrow ClO + ClOO + O_2$

$\Delta H° = -73$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 1 \times 10^{-19}$	195–217	DeMore and Tschuikow-Roux, 1990[1]	(a)
Reviews and Evaluations			
$< 1 \times 10^{-19}$	200	NASA, 1990[2]	(b)

Comments

(a) Photolysis ($\lambda > 300$ nm) of Cl_2–O_3 or Cl_2–Cl_2O mixtures, both in the gas phase and in the cryogenic solvents CF_4, CO_2, and N_2O. The quantum yield of O_3 loss was measured.

(b) Based on the results of DeMore and Tschuikow-Roux.[1]

Preferred Values

$k < 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 200 K.

Comments on Preferred Values

The recommended upper limit is that determined by DeMore and Tschuikow-Roux[1] from measurement of the quantum yield of O_3 loss in the photolysis of Cl_2–O_3 mixutes at $\lambda > 300$ nm. The experiments were very sensitive to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quantum yield on the ozone concentration; however, neither effect was observed. These measurements refer to a temperature of about 200 K – the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl_2O_2 dimer.

References

[1]W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$

$\Delta H° = -147$ kJ·mol^{-1}

Low-pressure rate coefficient

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.2) \times 10^{-29}(T/300)^{-4.7}$ [N_2]	233–373	Caralp, Lesclaux, and Dognon, 1986[1]	(a)
Reviews and Evaluations			
$1.9 \times 10^{-29}(T/300)^{-4.7}$ [N_2]	200–400	IUPAC, 1989[2]	(b)
$1.5 \times 10^{-29}(T/300)^{-4.7}$ [air]	200–300	NASA, 1990[3]	(c)
$1.55 \times 10^{-29}(T/300)^{-4.8}$ [N_2]	233–295	Forst and Caralp, 1991[4]	(d)

Comments

(a) Pulsed laser photolysis-MS system used. The pressure range was 0.2–12 Torr. Falloff extrapolation using $F_c = 0.6$.
(b) Based on Ref. 1.
(c) Based on Ref. 1 and earlier work from the same laboratory.
(d) Based on reference 1 and a new falloff extrapolation using theoretical modelling.

Preferred Values

$k_0 = 1.9 \times 10^{-29}(T/300)^{-4.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

There is good agreement between Refs. 1 and 5 for M = He. Falloff extrapolation with $F_c = 0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.0×10^{-11}	298	Cooper *et al.*, 1980[6]	(a)
8.0×10^{-12}	295	Ryan and Plumb, 1982[5]	(b)
9.0×10^{-12}	233–373	Caralp, Lesclaux, and Dognon, 1986[1]	(c)
Reviews and Evaluations			
1×10^{-11}	200–400	IUPAC, 1989[2]	(d)
$8.5 \times 10^{-12}(T/300)^{-1}$	200–300	NASA, 1990[3]	(e)
$6.3 \times 10^{-12}(T/300)^{-0.27}$	233–295	Forst and Caralp, 1991[4]	(f)

Comments

(a) Pulsed radiolysis of CF_3Cl. CF_3O_2 radicals were detected by UV absorption spectroscopy. Measurements made at 700 Torr of Ar.
(b) Microwave discharge-flow system coupled to quadrupole MS. CF_3 radicals were monitored by MS. Falloff curve measured over the range 0.5–8.3 Torr, and extrapolated using $F_c = 0.38$.
(c) See comment (a) for k_0.
(d) Based on Ref. 6.
(e) See comment (c) for k_0.
(f) See comment (d) for k_0.

Preferred Values

$k_\infty = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are from Ref. 6 because those measurements were relatively close to the high-pressure limit, in contrast to other work.

References

[1] F. Caralp, R. Lesclaux, and A. M. Dognon, Chem. Phys. Lett. **129**, 433 (1986).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] NASA Evaluation No. 9, 1990 (see references in Introduction).
[4] W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).
[5] K. R. Ryan and I. C. Plumb, J. Phys. Chem. **86**, 4678 (1982).
[6] R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).

$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$

$\Delta H^\circ = -137.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$1.44 \times 10^{-29}(T/298)^{-5.19}$ [N_2]	230–370	Forst and Caralp, 1991[1]	(a)

Comments

(a) Theoretical prediction based on modeling of the complete series $CX_3 + O_2 + M$ (with X = F, Cl).

Preferred Values

$k_0 = 1.4 \times 10^{-29}(T/300)^{-5}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

There are no measurements for this reaction, but the theoretical modeling of the complete series $CX_3 + O_2 + M$ (X = F, Cl) provides a reliable basis for interpolating rate data between members of this series.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$7.1 \times 10^{-12}(T/298)^{-0.56}$	230–370	Forst and Caralp, 1991[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

We prefer a slightly higher value than estimated in Ref. 1. These preferred values are chosen as for the related reaction $CFCl_2 + O_2 + M$ (see this evaluation, based on data from Ref. 2). $F_c = 0.6$ is recommended as for $CFCl_2 + O_2 + M$. $\Delta H°$ is estimated following Ref. 1.

References

[1]W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).

[2]F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in reference 1.

$CFCl_2 + O_2 + M \rightarrow CFCl_2O_2 + M$

$\Delta H° = -124.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 0.8) \times 10^{-30}$ [N_2]	298	Caralp and Lesclaux, 1983[1]	(a)
$5.5 \times 10^{-30}(T/298)^{-6}$ [N_2]	233–373	Danis, 1991[2]	(b)
Reviews and Evaluations			
$5 \times 10^{-30}(T/300)^{-4}$ [N_2]	200–300	IUPAC, 1989[3]	(c)
$5 \times 10^{-30}(T/300)^{-2}$ [air]	200–300	NASA, 1990[4]	(d)
$6 \times 10^{-30}(T/298)^{-5.6}$ [N_2]	233–373	Forst and Caralp, 1991[5]	(e)

Comments

(a) Pulsed laser photolysis-MS system used. Falloff curve measured over the range 0.2–12 Torr, and extrapolated using $F_c = 0.6$.

(b) New measurements reported in Ref. 5.

(c) Based on Ref. 1, with the temperature-dependence from the analogous reaction $CF_3 + O_2 + M$.

(d) Based on Ref. 1, with an estimated temperature-dependence.

(e) Based on Ref. 1 and a theoretical evaluation with estimated value of $\Delta H_0° = -121$ kJ·mol^{-1}.

Preferred Values

$k_0 = 5.5 \times 10^{-30}(T/300)^{-6}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on Ref. 2. The data appear consistent with other results for the series $CX_3 + O_2 + M$ (X = Cl, F) (see this evaluation).

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6 \pm 1) \times 10^{-12}$	298	Caralp and Lesclaux, 1983[1]	(a)
$(9 \pm 3) \times 10^{-12}$	233–373	Danis, 1991[2]	(b)
Reviews and Evaluations			
6×10^{-12}	200–300	IUPAC, 1989[3]	(c)
$6 \times 10^{-12}(T/300)^{-1}$	200–300	NASA, 1990[4]	(d)
$7 \times 10^{-12}(T/298)^{-0.77}$	233–373	Forst and Caralp, 1991[5]	(e)

Comments

(a)– (e) See comment (a)– (e) for k_0.

Preferred Values

$k_\infty = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.5$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

Experiments have been limited to the lower part of the falloff curve. Therefore, the extrapolation to the high pressure limit remains relatively uncertain. The more recent value from Ref. 2 is preferred because it is close to the k_∞ value for the reaction $CF_3 + O_2 + M$ (see this evaluation).

References

[1]F. Caralp and R. Lesclaux, Chem. Phys. Lett. **102**, 54 (1983).
[2]F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in reference 5.
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).

$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$

$\Delta H^\circ = -82.4$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.8 \pm 0.6) \times 10^{-31}$ [He]	295	Ryan and Plumb, 1984[1]	(a)
$(1.6 \pm 0.3) \times 10^{-30}(T/298)^{-6.3}$ [N_2]	233–333	Danis *et al.*, 1991[2]	(b)
Reviews and Evaluations			
$1.5 \times 10^{-30}(T/300)^{-4}$ [N_2]	200–300	IUPAC, 1989[3]	(c)
$1.0 \times 10^{-30}(T/300)^{-2}$ [air]	200–300	NASA, 1990[4]	(c)
$1.78 \times 10^{-30}(T/300)^{-6.4}$ [N_2]	233–333	Forst and Caralp, 1991[5]	(d)

Comments

(a) Microwave discharge flow system study using quadrupole MS. CCl_3 radicals were generated by the reaction $F + CHCl_3 \rightarrow CCl_3 + HF$. Falloff curve was studied between 1.7 and 5.4 Torr of He, and extrapolated with $F_c = 0.25$.
(b) New measurements over the pressure range 1–760 Torr, cited in Refs. 5 and 6.
(c) Estimated on the basis of the data from Ref. 1 with $F_c = 0.6$.
(d) Based on Ref. 2 together with theoretical modeling.

Preferred Values

$k_0 = 1.6 \times 10^{-30}(T/300)^{-6}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on Ref. 2, and are consistent with the data for M = He from Ref. 1. The falloff curves are extrapolated with $F_c = 0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.1×10^{-12}	300	Cooper *et al.*, 1980[7]	(a)
2.5×10^{-12}	295	Ryan and Plumb, 1984[1]	(b)
$3.2 \times 10^{-12}(T/298)^{-1.2}$	233–333	Danis *et al.*, 1991[2]	(c)
Reviews and Evaluations			
5×10^{-12}	200–300	IUPAC, 1989[3]	(d)
$2.5 \times 10^{-12}(T/300)^{-2.5}$	200–300	NASA, 1990[4]	(e)
$2.95 \times 10^{-12}(T/298)^{-0.63}$	233–333	Forst and Caralp, 1991[5]	(e)

Comments

(a) CCl_3 radicals were generated by pulsed radiolysis of CCl_4 at 700 Torr of He. CCl_3O_2 radicals were detected by UV absorption.
(b) See comment (a) for k_0.
(c) See comment (b) for k_0.
(d) See comment (c) for k_0.
(e) Based on Ref. 7.
(f) See comment (d) for k_0.

Preferred Values

$k_\infty = 3.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

Because the available measurements are in the lower part of the falloff curve, the extrapolation to k_∞ remains fairly uncertain. The preferred values are an average of the data from Refs. 1, 2, and 7. They probably present a lower limit for k_∞. $\Delta H°$ of the reaction was determined from measurements of the equilibrium.

References

[1]K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. **16**, 591 (1984).
[2]F. Danis, F. Caralp, M. T. Rayez, and R. Lesclaux, J. Phys. Chem., **95**, 7300 (1991).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).
[6]J. J. Russell, J. A. Seetula, D. Gutman, F. Danis, F. Caralp, P. D. Lightfoot, R. Leslaux, C. F. Melius, and S. M. Senkan, J. Phys. Chem. **94**, 3277 (1990).
[7]R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).

$CF_3O \rightarrow COF_2 + F$ and

$CF_xCl_{3-x}O \rightarrow COF_xCl_{2-x} + Cl$

k/s^{-1}	Temp./K	Reference	Comments
CF_3O			
$5 \times 10^{13} \exp(-14300/T)$	509–545	Batt *et al.*, 1986[1]	(a)
7×10^{-8}	298*		
CF_2ClO			
$\geq 7 \times 10^5$	~298	Carr, Peterson, and Smith, 1986[2]	(b)
$3 \times 10^{13} \exp(-6240/T)$	220–300	Rayez *et al.*, 1987[3]	(c)
2×10^4	298		
$CFCl_2O$			
$>3 \times 10^4$ (6.7 Torr)	253	Lesclaux, Dognon, and Caralp, 1987[4]	(d)
$3 \times 10^{13} \exp(-5335/T)$	220–300	Rayez *et al.*, 1987[3]	(c)
2×10^4	253		
CCl_3O			
$>1 \times 10^5$ (7.5 Torr)	233	Lesclaux, Dognon, and Caralp, 1987[3]	(d)
$4 \times 10^{13} \exp(-4880/T)$	220–300	Rayez *et al.*, 1987[3]	(c)
3×10^4	233		

Comments

(a) Reanalysis of previous data concerning the thermal decomposition of CF_3OOCF_3,[5] using RRKM theory. The cited values are those at the high-pressure limit.

(b) Derived from a numerical analysis, using a 33-step mechanism, of the reactions following the flash photolysis of $CF_2ClCOCF_2Cl$ in the presence of O_2. ClO radical time-concentration profiles were measured by UV absorption and fitted with CF_2ClO decomposition rate constants $>5 \times 10^5$ s^{-1}.

(c) Calculated using the MNDO/CI method. These are the high-pressure limiting values.

(d) Photolysis of Cl_2–O_2–$CHCl_3$ (or $CHFCl_2$)–NO mixtures with MS detection of NO_2 and, for the $CHCl_3$ system, $COCl_2$. The number of NO_2 molecules produced per Cl atom formed from the photolysis of Cl_2 was measured as a function of the NO concentration. The $CFCl_2O$ and CCl_3O radical decompositon rates were then derived relative to the rate constants for their reactions with NO. Use of rate constants of $k(CF_2ClO + NO) = k(CCl_3O + NO) = 1.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [3] lead to the cited lower limits to the $CFCl_2$ and CCl_3O decomposition rate constants.

Preferred Values

CF_3O
$k < 10^{-5}$ s^{-1} at 298 K.
CF_2ClO and $CFCl_2O$
$k = 7 \times 10^5$ s^{-1} at 298 K.
$k = 3 \times 10^{13} \exp(-5250/T)$ s^{-1} over the temperature range 220–300 K.
CCl_3O
$k = 8 \times 10^6$ s^{-1} at 298 K.
$k = 4 \times 10^{13} \exp(-4600/T)$ s^{-1} over the temperature range 220–330 K.

Reliability
CF_2ClO, $CFCl_2O$ and CCl_3O
$\Delta \log k = \pm 1.0$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The tentatively preferred values for the CF_2ClO, $CFCl_2O$ and CCl_3O radicals are based on a combination of the experimental data[2,4] and the calculations of Rayez *et al.*,[3] with wide uncertainty limits. The upper limit to the decomposition rate for the CF_3O radical at 298 K is based on the data of Batt *et al.*[1] The experimental observations that F atom elimination from $CF_xCl_{3-x}O$ (x = 1–3) radicals is slow and that Cl atom elimination from $CF_xCl_{3-x}O$ (x = 0–2) radicals is rapid is supported by the molecular orbital calculations of Rayez *et al.*[3,6] and Li and Francisco.[7] Thus, the Cl atom eliminations of CF_2ClO, $CFCl_2O$ and CCl_3O radicals are expected to occur rapidly even at stratospheric temperatures and competing pathways need not be considered in the atmospheric oxidation of chlorofluoromethanes.

References

[1]L. Batt, M. MacKay, I. A. B. Reid, and P. Steward, Presented at 9th International Symposium on Gas Kinetics, University of Bordeaux, Bordeaux, France, July 20–25, 1986.

[2]R. W. Carr, Jr., D. G. Peterson, and F. K. Smith, J. Phys. Chem. **90**, 607 (1986).

[3]J. C. Rayez, M. T. Rayez, P. Halvick, B. Duguay, R. Lesclaux, and J. J. Dannenberg, Chem. Phys. **116**, 203 (1987).

[4]R. Lesclaux, A. M. Dognon, and F. Caralp, J. Photochem. Photobiol., A: Chemistry **41**, 1 (1987).

[5]L. Batt and R. Walsh, Int. J. Chem. Kinet. **14**, 933 (1982).

[6]J. C. Rayez, M. T. Rayez, P. Halvick, B. Duguay, and J. J. Dannenberg, Chem. Phys. **118**, 265 (1987).

[7]Z. Li and J. S. Francisco, J. Am. Chem. Soc. **111**, 5660 (1989).

$RO_2 + NO \rightarrow RO + NO_2$

(R = CF_3, CF_2Cl, $CFCl_2$, CCl_3)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
R = CF₃			
$(1.78 \pm 0.36) \times 10^{-11}$	295	Plumb and Ryan, 1982[1]	(a)
$1.45 \times 10^{-11} (T/298)^{-(1.2 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
R = CF₂Cl			
$1.6 \times 10^{-11} (T/298)^{-(1.5 \pm 0.4)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
R = CFCl₂			
$(1.6 \pm 0.2) \times 10^{-11}$	298	Lesclaux and Caralp, 1984[3]	(c)
$1.45 \times 10^{-11} (T/298)^{-(1.3 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985[2]	(b)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
R = CCl₃			
$(1.86 \pm 0.28) \times 10^{-11}$	295	Ryan and Plumb, 1984[4]	(d)
$1.7 \times 10^{-11} (T/298)^{-(1.0 \pm 0.2)}$	230–430	Dognon, Caralp, and Lexclaux, 1985[2]	(b)
$(1.7 \pm 0.2) \times 10^{-11}$	298		
Reviews and Evaluations			
R = CF₃			
$1.6 \times 10^{-11} (T/300)^{-1.2}$	230–430	IUPAC, 1989[5]	(e)
$3.9 \times 10^{-12} \exp[(400 \pm 200)/T]$	230–430	NASA, 1990[6]	(f)
R = CF₂Cl			
$1.6 \times 10^{-11} (T/300)^{-1.5}$	230–430	IUPAC, 1989[5]	(e)
$3.1 \times 10^{-12} \exp[(500 \pm 200)/T]$	230–430	NASA, 1990[6]	(f)
R = CFCl₂			
$1.5 \times 10^{-11} (T/300)^{-1.3}$	230–430	IUPAC, 1989[5]	(e)
$3.5 \times 10^{-12} \exp[(430 \pm 200)/T]$	230–430	NASA, 1990[6]	(f)
R = CCl₃			
$1.8 \times 10^{-11} (T/300)^{-1.0}$	230–430	IUPAC, 1989[5]	(e)
$5.7 \times 10^{-12} \exp[(330 \pm 200)/T]$	230–430	NASA, 1990[6]	(f)

Comments

(a) Discharge flow – mass spectrometry system used. Rate coefficient independent of pressure over the range 1.9–5.1 Torr.
(b) Pulsed laser photolysis – mass spectrometry system used. No significant pressure dependence of the rate coefficient over the range 1–10 Torr.
(c) Pulsed laser photolysis – mass spectrometry system used. Measurement made at 2 Torr total pressure.
(d) Discharge flow – mass spectrometry system used. Rate coefficient independent of pressure over the range 1.7–5.4 Torr.
(e) See Comments on Preferred Values.
(f) Recommendation based on the results of Dognon *et al.*[2]

Preferred Values

$R = CF_3$

$k = 1.6 \times 10^{-11} (T/300)^{-1.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.

$\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

$R = CF_2Cl$

$k = 1.6 \times 10^{-11} (T/300)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.

$\Delta \log k = \pm 0.3$ over the temperature range 230–430 K.

$R = CFCl_2$

$k = 1.5 \times 10^{-11} (T/300)^{-1.3}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.

$\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

$R = CCl_3$

$k = 1.8 \times 10^{-11} (T/300)^{-1.0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–430 K.

$\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[5]

$R = CF_3$

The preferred values are based on the temperature dependent data of Dognon *et al.*[2] and the 298 K value of Plumb and Ryan.[1]

$R = CF_2Cl$

The preferred values are given by the expression of Dognon *et al.*[2]

$R = CFCl_2$

The preferred values are based on the temperature dependent data of Dognon *et al.*[2] These data supersede the previous result of Lesclaux and Caralp.[3]

$R = CCl_3$

The preferred values are based on the temperature dependent data of Dognon *et al.*,[2] and the 298 K value of Ryan and Plumb.[4]

The temperature dependence expressions are given in the form favored by Dognon *et al.*,[2] which best describe the measured data. If Arrhenius expressions are required, then the expressions recommended in NASA 1990[6] should be employed. In view of the consistent observation of pressure independence, it seems unlikely that $RONO_2$ is produced as a product. Dognon *et al.*[2] measured quantum yields for NO_2 greater than unity for all the RO_2 radicals suggesting that the $RO_2 + NO$ reactions form RO and NO_2 exclusively, with additional NO_2 produced from secondary chemistry.

References

[1]I. C. Plumb and K. R. Ryan, Chem. Phys. Lett. **92**, 236 (1982).
[2]A. M. Dognon, F. Caralp and R. Lesclaux, J. Chim. Phys. **82**, 349 (1985).
[3]R. Lesclaux and F. Caralp, Int. J. Chem. Kinet. **16**, 1117 (1984).
[4]K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet. **16**, 591 (1984).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).

$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M$

$\Delta H° = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.8) \times 10^{-29}(T/298)^{-4.7}$ [O_2]	233–373	Caralp *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$2.7 \times 10^{-29}(T/300)^{-5}$ [N_2]	200–300	IUPAC, 1989[2]	(b)
$2.2 \times 10^{-29}(T/300)^{-5}$ [air]	200–300	NASA, 1990[3]	(c)
$3.0 \times 10^{-29}(T/298)^{-6.4}$ [N_2]	233–373	Destriau and Troe, 1990[4]	(d)

Comments

(a) Pulsed laser photolysis with time-resolved MS. Falloff curves measured over the pressure range 1–10 Torr and extrapolated using $F_c = \exp(-T/416)$. Increasing width of falloff curve was included via the use of N from reference 5.
(b) Based on data of Ref. 1.
(c) Based on data of Ref. 1 using $F_c = 0.6$.
(d) Theoretical analysis of the falloff curve of Ref. 1. The fit was based on $k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, similar to the value for the reactions $CCl_3O_2 + NO_2 \rightarrow CCl_3O_2NO_2$ and $CCl_2FO_2 + NO_2 \rightarrow CCl_2FO_2NO_2$. A value of $F_c = 0.28$ at 298 K was calculated and used for the falloff extrapolation.

Preferred Values

$k_0 = 4.5 \times 10^{-29}(T/300)^{-6.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 220–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values correspond to the theoretical analysis of Ref. 4, which was based on the experiments of Ref. 1. A value of $F_c = 0.28$ at 300 K was calculated and used. In contrast to Ref. 4, however, an adjustment of $\Delta H_0°$ to the value of 103.6 kJ·mol^{-1} was made in order to meet the trend for other $CX_3O_2NO_2$ (X = Cl, F) which were investigated in Ref. 6. This modifies the k_0 values in the indicated way. The falloff curves correspond to F_c = 0.28 at 220–300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.9 \times 10^{-12}(T/300)^{-(0.72 \pm 0.3)}$	233–373	Caralp *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$9.2 \times 10^{-12}(T/300)^{-0.7}$	200–300	IUPAC, 1989[3]	(b)
$6.0 \times 10^{-12}(T/300)^{-2.5}$	200–300	NASA, 1990[4]	(c)
7.5×10^{-12}	233–373	Destriau and Troe, 1990[5]	(d)

Comments

(a) – (d) See comment (a) – (d) for k_0.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

See comment to k_0. Because the measurements were made at low pressures only, the extrapolation to k_∞ remains fairly uncertain. F_c was calculated[4] to be close to 0.28 over the temperature range 220–300 K.

References

[1] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] NASA Evaluation No. 9. 1990 (see references in Introduction).
[4] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5] J. Troe, J. Phys. Chem. **83**, 114 (1979).
[6] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M$

$\Delta H° = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$5 \times 10^{-1}(T/300)^{-6} \times \exp(-12460/T)$ [N_2]	233–373	Destriau and Troe, 1990[1]	(a)

Comments

(a) Based on measurements of the reverse reaction[2] and calculated equilibrium constants with $\Delta H_0° = 103.6$ kJ·mol^{-1}, adjusted to meet the extrapolated value of Ref. 3. $F_c = 0.28$ calculated[1] for 220–300 K.

Preferred Values

$k_0 = 3.6 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 5 \times 10^{-1}(T/300)^{-6} \exp(-12460/T)$[$N_2$] s^{-1} over the temperature range 233–373 K.

Reliability
$\Delta \log k_0 = \pm 0.4$ at 300 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
See Comment (a) for k_0. Direct measurements of the dissociation rate are required together with measurements over a wider pressure range. $F_c = 0.28$ is used for falloff curves over the range 220–300 K.

High-pressure rate coefficients

Rate coefficients data

k_∞/s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$8.3 \times 10^{16}(T/300)^{0.4} \times \exp(-12460/T)$	233–373	Destriau and Troe, 1990[1]	(a)

Comments

(a) See comment (a) for k_0.

Preferred Values

$k_\infty = 5.6 \times 10^{-2}$ s^{-1} at 298 K.
$k_\infty = 1.2 \times 10^{17} \exp(-12580/T)$ s^{-1} over the temperature range 233–373 K.

Reliability
$\Delta \log k_\infty = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
See comments on k_0.

References

[1]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[2]F. Caralp, R. Lesclaux, M. T. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[3]D. Koppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

$CF_2ClO_2 + NO_2 + M \rightarrow CF_2ClO_2NO_2 + M$

$\Delta H^\circ = -98$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 1.8) \times 10^{-29}$ [O_2]	298	Moore and Carr, 1990[1]	(a)
$(5 \pm 1) \times 10^{-29}(T/298)^{-6.2}$ [O_2]	248–324	Wu and Carr, 1991[2]	(b)
Reviews and Evaluations			
$4.0 \times 10^{-29}(T/298)^{-5.1}$ [O_2]	233–373	Caralp *et al.*, 1988[3]	(c)
$4.0 \times 10^{-29}(T/300)^{-5}$ [N_2]	200–300	IUPAC, 1989[4]	(d)
$1.4 \times 10^{-28}(T/300)^{-6.4}$ [N_2]	200–300	Destriau and Troe, 1990[5]	(e)

Comments

(a) CF_2ClO_2 radicals were generated by flash photolysis of CF_2ClBr in the presence of O_2 and detected by MS. k_0 values were measured over the pressure range 1–10 Torr and extrapolated with $F_c = 0.6$.

(b) See comment (a). The analysis includes dissociation data from reference 6. $F_c = 0.78 \exp(-T/569)$ was used for extrapolation.

(c) Interpolated values from measurements in the series of $CX_3O_2 + NO_2 + M$ with X = Cl, F.

(d) Based on Ref. 3.

(e) Theoretical analysis of dissociation data from Köppenkastrop and Zabel,[6] converted by calculated equilibrium constants. Falloff extrapolations based on an estimated value of $k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $F_c = 0.26$ (independent of temperature over the range 220–300 K).

Preferred Values

$k_0 = 1.4 \times 10^{-28}(T/300)^{-6.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are from Ref. 5. They are consistent with data for the reactions $CCl_3O_2 + NO_2$ and $CCl_2FO_2 + NO_2$. These values are sensitive to the chosen value of F_c, for which a value of 0.26 was calculated[5] over the range 220–300 K. The values from Ref. 2 are lower in part because of a larger value of F_c.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
5.2×10^{-12}	298	Moore and Carr, 1990[1]	(a)
$4.5 \times 10^{-12}(T/298)^{-2.5}$	248–324	Wu and Carr, 1991[2]	(b)
Reviews and Evaluations			
$1.0 \times 10^{-11}(T/300)^{-0.66}$	233–373	Caralp *et al.*, 1988[3]	(c)
$1.0 \times 10^{-11}(T/300)^{-0.7}$	200–300	IUPAC, 1989[4]	(d)
7.5×10^{-12}	200–300	Destriau and Troe, 1990[5]	(e)

Comments

(a) – (e) See comments (a) – (e) for k_0.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are from the fit in Ref. 5 using identical k_∞ values for all $CX_3O_2 + NO_2$ reactions (X = F, Cl) independent of the temperature. The large negative temperature coefficient of k_∞ reported in Ref. 2 appears to be an artifact from the falloff extrapolations used.

References

[1]S. M. Moore and R. W. Carr, J. Phys. Chem. **94**, 1393 (1990).
[2]F. Wu and R. W. Carr, Int. J. Chem. Kinet. **23**, 701 (1991).
[3]F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[6]D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

$CF_2ClO_2NO_2 + M \rightarrow CF_2ClO_2 + NO_2 + M$

$\Delta H° = 98$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.8 \times 10^{-3} \exp(-10500/T)$ [N_2]	260–300	Köppenkastrop and Zabel, 1991[1]	(a)
9.0×10^{-19} [N_2]	298		
Reviews and Evaluations			
$5.6 \times 10^{-4} \exp(-9310/T)$ [N_2]	260–290	IUPAC, 1990[2]	(b)
1.5×10^{-17} [N_2]	298		

Comments

(a) Thermal decomposition of $CF_2ClO_2NO_2$ in a temperature controlled 420 liter reaction chamber. The reactant was monitored *in situ* by long-path IR absorption. N_2 pressures from 10 to 800 mbar were employed. Falloff extrapolations were made with theoretical values of $F_c = 0.30$ at 280 K.

(b) Based on preliminary data from Ref. 1, apparently quoted erroneously and to be disregarded.

Preferred Values

$k_0 = 9.0 \times 10^{-19}$ [N_2] s^{-1} at 298 K.

$k_0 = 1.8 \times 10^{-3} \exp(-10500/T)$ [N_2] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 300 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The experiments of Ref. 1 are preferred here. The calculations of F_c (0.3 at 280 K from Ref. 1 and 0.26 over the range 250–300 K from Ref. 2) agree.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.6 \times 10^{16} \exp(-11990/T)$	260–300	Köppenkastrop and Zabel, 1991[1]	(a)
Reviews and Evaluations			
$1.0 \times 10^{16} \exp(-11880/T)$	260–290	IUPAC, 1989[3]	(b)
4.9×10^{-2}	298		

Comments

(a) See comment (a) for k_0.
(b) Based on preliminary data from Ref. 1.

Preferred Values

$k_\infty = 5.4 \times 10^{-2}\ s^{-1}$ at 298 K.
$k_\infty = 1.6 \times 10^{16} \exp(-11990/T)\ s^{-1}$ over the temperature range 260–300 K.

Reliability
$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
See comments on k_0.

References

[1]D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
[2]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).

$CFCl_2O_2 + NO_2 + M \rightarrow CFCl_2O_2NO_2 + M$

$\Delta H^\circ = -96\ kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k_0/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.5) \times 10^{-29}\ [O_2]$	298	Lesclaux and Caralp, 1984[1]	(a)
$(3.5 \pm 0.5) \times 10^{-29}(T/298)^{-4 1}\ [O_2]$	233–373	Lesclaux, Caralp, and Dognon, 1986[2]	(b)
$(5.5 \pm 1.6) \times 10^{-29}(T/298)^{-5 5}\ [O_2]$	233–373	Caralp *et al.*, 1988[3]	(c)
Reviews and Evaluations			
$5.5 \times 10^{-29}(T/300)^{-5}\ [N_2]$	200–300	IUPAC, 1989[4]	(d)
$3.5 \times 10^{-29}(T/300)^{-5}$ [air]	200–300	NASA, 1990[5]	(e)
$1.7 \times 10^{-28}(T/298)^{-6.7}\ [N_2]$	233–373	Destriau and Troe, 1990[6]	(f)

Comments

(a) Pulsed laser photolysis system with MS detection of $CFCl_2O_2$ over the pressure range 1–10 Torr.
(b) Falloff extrapolation using $F_c = 0.6$.
(c) Falloff extrapolation using $F_c = \exp(-T/342)$.
(d) Based on results from Refs. 1–3.
(e) Based on the data of Ref. 3 using $F_c = 0.6$.
(f) Theoretical analysis of the recombination data at 298 K from Ref. 3 and the dissociation data at 273 K from Ref. 7. Falloff curves constructed with F_c = 0.23 over the range 230–300 K.

Preferred Values

$k_0 = 1.7 \times 10^{-28}(T/300)^{-6.7}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 300 K.
$\Delta n = \pm 2$.

Comments from Preferred Values

The preferred values are from the analysis of Ref. 6 on the basis of $F_c = 0.23$. The falloff data from Ref. 3 show some anomalies for T = 233 K. The best fit is obtained for 298 K.

High-pressure rate coefficients

Rate coefficients data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 1.0) \times 10^{-12}$	298	Lesclaux and Caralp, 1984[1]	(a)
$(5.9 \pm 1.0) \times 10^{-12}(T/298)^{-0.72}$	233–373	Lesclaux, Caralp, and Dognon, 1986[2]	(b)
$(8.3 \pm 1) \times 10^{-12}(T/298)^{-0.66}$	233–373	Caralp *et al.*, 1988[3]	(a,c)
Reviews and Evaluations			
$8.3 \times 10^{-12}(T/300)^{-0.7}$	200–300	IUPAC, 1989[4]	(d)
$6.0 \times 10^{-12}(T/300)^{-2.5}$	200–300	NASA, 1990[5]	(e)
7.5×10^{-12}	233–373	Destriau and Troe, 1990[6]	(f)

Comments

(a) – (c) See comments (a) – (c) for k_0.
(d) Based on Refs. 1–3.
(e) See comment (e) for k_0.
(f) See comment (f) for k_0. Identical values of k_∞ were chosen for all of the $CX_3O_2 + NO_2$ reaction systems (X = F, Cl).

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

See comments on k_0.

References

[1] R. Lesclaux and F. Caralp, Int. J. Chem. Kinet. **16**, 1117 (1984).
[2] R. Lesclaux, F. Caralp, and A. M. Dognon, Geophys. Res. Lett. **13**, 933 (1986).
[3] F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[4] IUPAC, Supplement III, 1989 (see references in Introduction).
[5] NASA Evaluation No. 9, 1990 (see references in Introduction).
[6] M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[7] D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

$CFCl_2O_2NO_2 + M \rightarrow CFCl_2O_2 + NO_2 + M$

$\Delta H° = 96$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.01 \times 10^{-2} \exp(-10860/T)$ [N_2]	260–300	Köppenkastrop and Zabel, 1991[1]	(a)
1.5×10^{-18} [N_2]	298		
Reviews and Evaluations			
$3.0 \times 10^{-3} \exp(-10570/T)$ [N_2]	270–290	IUPAC, 1989[2]	(b)
1.2×10^{-18} [N_2]	298		

Comments

(a) Thermal decomposition of $CFCl_2O_2NO_2$ in a temperature-controlled 420 liter reaction chamber. The reactant was monitored *in situ* by long-path IR absorption. N_2 pressures from 10 to 800 mbar were employed. The data were extrapolated to the low- and high-pressure limits using $F_c = 0.28$.

(b) Based on preliminary results from Ref. 3.

Preferred Values

$k_0 = 1.5 \times 10^{-18}$ [N_2] s^{-1} at 298 K.

$k_0 = 1.0 \times 10^{-2} \exp(-10860/T)$ [N_2] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The experiments of Ref. 1 are recommended. The calculation of $F_c = 0.28$ is consistent with the analysis of Ref. 4 leading to $F_c = 0.23$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.0 \times 10^{16} \exp(-12300/T)$	274–305	Simonaitis, Glavas, and Heicklen, 1979[5]	(a)
4.7×10^{-2}	298		
$6.6 \times 10^{16} \exp(-12240/T)$	260–300	Köppenkastrop and Zabel, 1991[1]	(b)
9.6×10^{-2}	298		
Reviews and Evaluations			
$2.1 \times 10^{16} \exp(-11980/T)$	270–290	IUPAC, 1989[9]	(c)
7.3×10^{-2}	298		

Comments

(a) Steady-state photolysis of Cl_2–$CHFCl_2$–O_2–NO–NO_2 mixtures at 1 atm. Simulation of the mechanism was dependent on various Cl-consuming reactions, and k was assumed to be close to k_∞.
(b) See comment (a) for k_0.
(c) See comment (b) for k_0.

Preferred Values

$k_\infty = 9.6 \times 10^{-2}$ s^{-1} at 298 K.
$k_\infty = 6.6 \times 10^{16} \exp(-12240/T)$ s^{-1} over the temperature range 250–300 K.

Reliability
$\Delta\log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
See comments on k_0. The agreement between Refs. 1 and 5 at 1 atm total pressure ($\Delta\log k = 0.17$) appears satisfactory.

References

[1]D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]F. Zabel, in Proceedings of the International Conference on Photochemistry, Budapest, August 1987.
[4]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5]R. Simonaitis, S. Glavas, and J. Heicklen, Geophys. Res. Lett. **6**, 385 (1979).

$CCl_3O_2 + NO_2 + M \rightarrow CCl_3O_2NO_2 + M$

$\Delta H° = -108$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.2 \pm 3) \times 10^{-29}(T/298)^{-6.0}$ [O_2]	233–373	Caralp *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$9.2 \times 10^{-29}(T/300)^{-6}$ [N_2]	200–300	IUPAC, 1989[2]	(b)
$5.0 \times 10^{-29}(T/300)^{-5}$ [air]	200–300	NASA, 1990[3]	(c)
$3.2 \times 10^{-28}(T/298)^{-7.7}$ [N_2]	230–373	Destriau and Troe, 1990[4]	(d)

Comments

(a) Pulsed laser photolysis system used with time-resolved MS. The falloff curve was measured over the pressure range 1–10 Torr, and extrapolated using $F_c = \exp(-T/260)$.
(b) Based on reference 1 using $F_c = 0.32$ at 300 K.
(c) Based on reference 1 using $F_c = 0.6$.
(d) Theoretical analysis of recombination experiments at 298 and 373 K from reference 1 and dissociation rate data at 273 K from reference 5. Falloff curves were constructed using $F_c = 0.21$.

Preferred Values

$k_0 = 3.2 \times 10^{-28}(T/300)^{-7.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230–300 K.

Reliability
$\Delta\log k_0 = \pm 0.5$ at 300 K.
$\Delta n = \pm 3$.

Comments on Preferred Values
The preferred values are from the theoretical analysis of reference 4. The experimental data from reference 1 for $T = 233$ K are apparently inconsistent with this analysis. $F_c = 0.21$ is used for falloff extrapolations.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.49 \times 10^{-11}(T/298)^{-0.3}$	233–373	Caralp *et al.*, 1988[1]	(a)
Reviews and Evaluations			
$1.5 \times 10^{-11}(T/300)^{-0.3}$	200–300	IUPAC, 1989[2]	(b)
$6.0 \times 10^{-12}(T/300)^{-2.5}$	200–300	NASA, 1990[3]	(c)
7.5×10^{-12}	233–373	Destriau and Troe, 1990[4]	(d)

Comments

(a) – (d) See comments (a) – (d) for k_0.

Preferred Values

$k_\infty = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_\infty = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The value of k_∞ in Ref. 4 was chosen to be identical for all reactions $CX_3O_2 + NO_2 + M$ (X = F, Cl), which leads to a consistent set of falloff curves.

References

[1]F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5]D. Koppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

$CCl_3O_2NO_2 + M \rightarrow CCl_3O_2 + NO_2$

$\Delta H° = 108$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.3 \times 10^{-3}\exp(-10235/T)$ [N$_2$]	260–300	Köppenkastrop and Zabel, 1991[1]	(a)
7.6×10^{-18} [N$_2$]	298		
Reviews and Evaluations			
$5.6 \times 10^{-4}\exp(-9310/T)$ [N$_2$]	260–300	IUPAC, 1989[2]	(b)
1.5×10^{-17} [N$_2$]	298		

Comments

(a) Thermal decomposition of $CCl_3O_2NO_2$ in a temperature-controlled 420 liter reaction chamber. The reactant was monitored *in situ* by long-path IR absorption. N_2 pressures from 10 to 800 mbar were employed. The data were extrapolated to the low and high-pressure limits using $F_c = 0.22$.

(b) Based on preliminary experiments from Ref. 3. $F_c = 0.20$ was employed in the falloff extrapolation.

Preferred Values

$k_0 = 7.6 \times 10^{-18}$ [N$_2$] s^{-1} at 298 K.

$k_0 = 6.3 \times 10^{-3}\exp(-10235/T)$ [N$_2$] s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The experimental data of Ref. 1 are recommended. The calculation of $F_c = 0.22$ is consistent with the analysis of Ref. 4, which gave $F_c = 0.20$ with only a weak temperature dependence.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.42 \times 10^{16} \exp(-11500/T)$	268–298	Simonaitis and Heicklen, 1979[5]	(a)
0.24	298		
$4.8 \times 10^{16} \exp(-11820/T)$	260–300	Köppenkastrop and Zabel, 1991[1]	(b)
0.29	298		
Reviews and Evaluations			
$9.1 \times 10^{14} \exp(-10820/T)$	260–300	IUPAC, 1989[2]	(c)
0.16	298		

Comments

(a) Steady-state photolysis of Cl_2–$CHCl_3$–O_2–N_2–NO–NO_2 mixtures at 1 atm. NO was monitored continuously using the chemiluminescent reaction between NO and O_3. In the same experiments, product formation was monitored by IR spectroscopy. A value of 2.5 was employed for the ratio of the rate coefficients for the reactions Cl + NO_2 + M → $ClNO_2$ + M and Cl + NO + M → ClNO + M. The measured rate coefficients were assumed to be close to k_∞.

(b) See comment (a) for k_0.

(c) See comment (b) for k_0.

Preferred Values

$k_\infty = 0.29\ s^{-1}$ at 298 K.

$k_\infty = 4.8 \times 10^{16} \exp(-11820/T)\ s^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on k_0. The agreement between Refs. 1 and 5 for 1 atm total pressure ($\Delta \log k = 0.11$) appears satisfactory.

References

[1]D. Köppenkastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]F. Zabel, in Proceedings of the International Conference on Photochemistry, Budapest, August 1987.
[4]M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
[5]R. Simonaitis and J. Heicklen, Chem. Phys. Lett. **62**, 473 (1979); **68**, 245 (1979).

$O_3 + C_2HCl_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3 \times 10^{-20}$	296	Atkinson *et al.*, 1982[1]	(a)
Reviews and Evaluations			
$<5 \times 10^{-20}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Decay of O_3 (at initial concentrations of $\leq 2.4 \times 10^{13}$ molecule cm^{-3}) measured in the presence of excess C_2HCl_3 in one atmosphere of air, using a chemiluminescence analyzer to monitor O_3.
(b) See Comments on Preferred Values.

Preferred Values

$k < 5 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The upper limit to the preferred value is taken from the data of Atkinson *et al.*,[1] with the upper limit being increased by a factor of ~2 to take into account additional uncertainties in the study of Atkinson *et al.*[1] This upper limit is consistent with the reported data for the reactions of O_3 with the chloroethenes,[3] which show that Cl atom substitution markedly decreases the rate coefficients at room temperature, relative to that for ethene.

References

[1]R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., Int. J. Chem. Kinet. **14**, 13 (1982).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

$O_3 + C_2Cl_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<2 \times 10^{-23}$	297	Mathias *et al.*, 1974[1]	(a)
Reviews and Evaluations			
$<10^{-21}$	298	IUPAC, 1989[2]	(b)

Comments

(a) Derived from experiments carried out at initial O_3 and C_2Cl_4 concentrations of $\gtrsim 10^{17}$ molecule cm^{-3} in the presence of excess O_2, using an assumed mechanism and monitoring the formation rate of $COCl_2$. From the data given in Mathias *et al.*,[1] a more conservative upper limit of $k \leq 8 \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} can be derived by assuming that only one $COCl_2$ molecule is formed per C_2Cl_4 reacting.
(b) See Comments on Preferred Values.

Preferred Values

$k < 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The upper limit to the preferred value is derived from the very limited amount of data reported by Mathias *et al.*,[1] with the upper limit to the rate coefficient being increased by a factor of 50 over that reported [see also comment (a) above]. This upper limit to the rate coefficient for C_2Cl_4 is consistent with the kinetic data for the other chloroethenes,[3] which show that Cl atom substitution markedly decreases the reactivity of the chloroethenes towards O_3, compared to that for ethene.

References

[1]E. Mathias, E. Sanhueza, I. C. Hisatsune, and J. Heicklen, Can. J. Chem. **52**, 3852 (1974).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]R. Atkinson and W. P. L. Carter, Chem. Rev. **84**, 437 (1984).

$HCl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HCl + h\nu \rightarrow H + Cl$	432	277

Preferred Values

Absorption cross-sections for HCl photolysis at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
140	211	180	58.8
145	281	185	31.3
150	345	190	14.5
155	382	195	6.18
160	332	200	2.56
165	248	205	0.983
170	163	210	0.395
175	109	215	0.137
		220	0.048

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Inn.[1] Photolysis is expected to occur with unit quantum efficiency.

Reference

[1]E. C. Y. Inn, J. Atmos. Sci. **32**, 2375 (1975).

$HOCl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HOCl + h\nu \rightarrow HO + Cl$	(1)	239	500
$\rightarrow HCl + O$	(2)	235	510

Preferred Values

Absorption cross-sections for HOCl photolysis at 298 K

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\ \sigma/cm^2$
215	8.71	295	16.12
220	13.26	300	14.55
225	18.95	305	12.30
230	25.33	310	10.43
235	31.48	315	8.60
240	36.48	320	6.95
245	38.89	325	5.54
250	40.49	330	4.35
255	38.54	335	3.32
260	34.11	340	2.48
265	28.34	345	1.83
270	23.61	350	1.34
275	20.63	355	0.92
280	19.18	360	0.61
285	18.26	365	0.42
290	17.38	370	0.27
		375	0.15

Quantum Yields for HOCl Photolysis at 298 K

$\phi_1 = 1.0$ for $\lambda > 200$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported recently by Permien *et al.*[1] Earlier results are discussed in our previous evaluation, IUPAC, 1989.[2] The preferred quantum yield values are based on the results of Molina *et al.*[3]

References

[1]T. Permien, R. Vogt, and R. N. Schindler, in *Mechanisms of Gas Phase and Liquid Phase Chemical Transformations in Tropospheric Chemistry*, R. A. Cox, Ed., Air Pollution Research Report No. 17, Environmental Research Program of the CEC, EUR 12035 EN, Brussels, Belgium.
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]M. J. Molina, T. Ishiwata, and L. T. Molina, J. Phys. Chem. **84**, 821 (1980).

OClO + $h\nu$ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
OClO + $h\nu$ → ClO + O(^{3}P)	(1)	250	478
→ ClO + O(^{1}D)	(2)	440	272

Preferred Values

Absorption cross-sections of OClO at the band peaks at 204 K, 296 K and 378 K

	10^{20} σ/cm^2		
λ/nm	204 K	296 K	378 K
475.53	–	13	–
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
291.77	138	114	130
287.80	105	86	105
283.51	89	72	90
279.64	73	60	79
275.74	59	46	–
272.93	53	33	–

Quantum Yields for OClO Photolysis at 298 K

ϕ_1 = 1.0 throughout the wavelength range 270–480 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 204 K, 296 K and 378 K are the values reported by Wahner *et al.*[1] The bands became appreciably sharper with decreasing temperature. However, the integrated band intensities remained constant for all bands between 204 K and 296 K, and therefore the solar photolysis rate is not expected to have a significant temperature dependence. Earlier cross-section studies have been discussed in our previous evaluation.[2] The recommended quantum yield is based on results reported by Colussi[3] and results of results of earlier studies discussed in the review by Watson.[4] Colussi[3] in a laser flash photolysis study at 308 nm determined the quantum yield for O atom production to be 1.02 ± 0.05 and the quantum yield for Cl atom production to be < 0.01. Vaida and co-workers[5,6] reported the detection of Cl atoms by resonance-enhanced multiphoton ionization (REMPI) in the photodecomposition of OClO in the region 360–363 nm. They interpreted this as resulting from the photoisomerization of OClO to ClOO followed by dissociation to Cl + O_2, but did not report quantum yields. Lawrence *et al.*,[7] using a technique involving charge transfer excitation of Cl–Xe collision pairs as a sensitive probe of Cl atoms, established that the quantum yield for Cl atom production in the 359–368 nm region is $< 5 \times 10^{-4}$, and that therefore this process would not significantly perturb the stratospheric ozone budget. However, in a very recent study, Bishenden *et al.*[8] report that the quantum yield for Cl atom formation near 362 nm is 0.15 ± 0.10; these results are in conflict with those reported by Lawrence *et al.*[7] Further studies are required to resolve this issue.

References

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8E. Bishenden, J. Haddock, and D. J. Donaldson, J. Phys. Chem. **95**, 2113 (1991).

$Cl_2O + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2O + h\nu \rightarrow Cl + ClO$	(1)	142	840
$\rightarrow O + Cl_2$	(2)	168	710
$\rightarrow O + 2\ Cl$	(3)	410	292

Preferred Values

Absorption cross-sections for Cl_2O photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	71.0	330	8.40
210	23.8	340	3.58
220	8.6	350	1.54
230	28.1	360	0.73
240	103	370	0.40
250	191	380	0.36
260	195	390	0.51
270	151	400	0.79
280	126	420	1.26
290	103	440	1.11
300	71.0	460	0.63
310	40.3	480	0.32
320	19.5	500	0.22

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Knauth *et al.*[1] They are in excellent agreement with the values reported by Molina and Molina,[2] except for the 330–400 nm range where the values in reference 2 are higher, and they are in reasonable agreement with the values reported by Lin.[3] Values for the 150–200 nm wavelength region have recently been reported by Nee.[4]

Photolysis proceeds predominantly by breaking of the Cl–O bond to yield Cl + ClO. However in the most recent study of the products of Cl_2O photolysis, Sander and Friedl[5] determined the quantum yield for formation of oxygen atoms from Cl_2O photolysis to be 0.25 ± 0.05. In these experiments a broad-band photolysis source with a spectral distribution extending from the visible down to 180 nm was used, so that it was not possible to determine the wavelength dependence of the quantum yield.

References

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[3]C. L. Lin, J. Chem. Eng. Data **21**, 411 (1976).
[4]J. B. Nee, J. Quant. Spectrosc. Radiat. Transfer **46**, 55 (1991).
[5]S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).

$Cl_2O_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2O_2 + h\nu \rightarrow ClO + ClO$	(1)	74	1620
$\rightarrow Cl + ClOO$	(2)	89	1340

Preferred Values

Absorption cross-sections for Cl_2O_2 photolysis at 200–250 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
200	383.5	240	600.3	280	172.5	320	25.6
2	352.9	2	625.7	2	159.6	2	23.4
4	325.3	4	639.4	4	147.3	4	21.4
6	298.6	6	642.6	6	136.1	6	19.2
8	274.6	8	631.5	8	125.2	8	17.8
210	251.3	250	609.3	290	114.6	330	16.7
2	231.7	2	580.1	2	104.6	2	15.6
4	217.0	4	544.5	4	95.4	4	14.4
6	207.6	6	505.4	6	87.1	6	13.3
8	206.1	8	463.1	8	79.0	8	13.1
220	212.1	260	422.0	300	72.2	340	12.1
2	227.1	2	381.4	2	65.8	2	11.5
4	249.4	4	344.6	4	59.9	4	10.9
6	280.2	6	311.6	6	54.1	6	10.1
8	319.5	8	283.3	8	48.6	8	9.0
230	365.0	270	258.4	310	43.3	350	8.2
2	415.4	2	237.3	2	38.5	2	7.9
4	467.5	4	218.3	4	34.6	4	6.8
6	517.5	6	201.6	6	30.7	6	6.1
8	563.0	8	186.4	8	28.0	8	5.8
						360	5.5

Quantum Yields

$\phi_2 = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values given in the NASA, 1990, evaluation.[1] They are the smoothed average of the results reported by Cox and Hayman,[2] DeMore and Tschuikow-Roux,[3] Permien *et al.*[4] and Burkholder *et al.*[5] These studies indicate that in the recombination reaction, ClO + ClO → products, the only stable species produced is ClOOCl. The structure of the recombination product has been established to be ClOOCl by the study of Birk *et al.*[6] using submillimeter wave spectroscopy. Theoretical studies[7–9] of thermochemical stabilities of Cl_2O_2 isomers are in agreement with these observations. The preferred quantum yield values are based on results of the study by Molina *et al.*[10] in which the production of Cl atoms in the laser flash photolysis of ClOOCl at 308 nm was directly determined by time-resolved atomic resonance fluorescence. These results are in agreement with the interpretation of the steady-state photolysis experiments of Cox and Hayman.[2]

It should be noted that absorption cross section values for the longer wavelength region from 360 nm to 400 nm are reported in Refs. 3 and 5. However these values, which continue to decrease with increasing wavelength, are in poor agreement (factor of 2–3), and no recommended absorption cross section values are given for the wavelength range 360–400 nm.

References

[1]NASA Evaluation No. 9, 1990 (see references in Introduction).

[2]R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).

[3]W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).

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$Cl_2O_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2O_3 + h\nu \rightarrow ClO + OClO$	(1)	62	1930
$\rightarrow Cl + ClO_3$	(2)	212	564

Preferred Values

Absorption cross-sections for Cl_2O_3 photolysis at 233 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
220	1400	280	1380
225	1420	285	1130
230	1370	290	890
235	1370	295	690
240	1390	300	550
245	1460	305	390
250	1590	310	280
255	1720	315	220
260	1840	320	190
265	1860	325	170
270	1790	330	150
275	1620	335	130

Comments on Preferred Values

The preferred values of the absorption cross-sections at 233 K are the values reported by Hayman and Cox.[1] The mechanism and quantum yield for photodissociation have not been determined.

Reference

[1]G. D. Hayman and R. A. Cox, Chem. Phys. Lett. 155, 1 (1989).

ClNO + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$ClNO + h\nu \rightarrow Cl + NO$	160	750

Preferred Values

Absorption cross-sections for ClNO photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	4320	230	266	270	12.9	310	11.5
192	5340	232	212	272	12.3	312	11.9
194	6150	234	164	274	11.8	314	12.2
196	6480	236	128	276	11.3	316	12.5
198	6310	238	101	278	10.7	318	13.0
200	5860	240	82.5	280	10.6	320	13.4
202	5250	242	67.2	282	10.2	322	13.6
204	4540	244	55.1	284	9.99	324	14.0
206	3840	246	45.2	286	9.84	326	14.3
208	3210	248	37.7	288	9.71	328	14.6
210	2630	250	31.7	290	9.64	330	14.7
212	2180	252	27.4	292	9.63	332	14.9
214	1760	254	23.7	294	9.69	334	15.1
216	1400	256	21.3	296	9.71	336	15.3
218	1110	258	19.0	298	9.89	338	15.3
220	896	260	17.5	300	10.0	340	15.2
222	707	262	16.5	302	10.3	342	15.3
224	552	264	15.3	304	10.5	344	15.1
226	436	266	14.4	306	10.8	346	15.1
228	339	268	13.6	308	11.1	348	14.9
						350	14.5

Quantum Yields for ClNO Photolysis at 298 K
ϕ = 1.0 over the entire wavelength range.

Comments on Preferred Values
The preferred values of the absorption cross-sections at 298 K are the values reported by Tyndall *et al.*[1] Earlier results are discussed in NASA, 1990.[2] The preferred quantum yield values are taken from the review by Calvert and Pitts.[3]

References

[1]G. S. Tyndall, K. M. Stedman, W. Schneider, J. P. Burrows, and G. K. Moortgat, J. Photochem. **36**, 133 (1987).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).
[3]J. G. Calvert and J. N. Pitts, *Photochemistry* (John Wiley & Sons, Inc., New York, 1966) p. 230.

ClONO + $h\nu$ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
ClONO + $h\nu$ → Cl + NO_2	(1)	98	1220
→ ClO + NO	(2)	136	880

Preferred Values

Absorption cross-sections for ClONO photolysis at 231 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

Comments on Preferred Values
The preferred values of the absorption cross-sections at 231 K are the values reported by Molina and Molina.[1] Photolysis is expected to occur with unit quantum efficiency by breaking of the Cl–O bond to yield Cl + NO_2. The lifetime against photodissociation for ClONO in the atmosphere was calculated to 2 to 3 minutes.[1]

Reference

[1]L. T. Molina and M. J. Molina, Geophys. Res. Lett. **4**, 83 (1977).

$ClNO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$ClNO_2 + h\nu \rightarrow Cl + NO_2$	(1)	142	840
$\rightarrow ClNO + O$	(2)	288	415

Preferred Values

Absorption cross-sections for $ClNO_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	2690	290	18.1
200	455	300	15.5
210	339	310	12.5
220	342	320	8.70
230	236	330	5.58
240	140	340	3.33
250	98.5	350	1.78
260	63.7	360	1.14
270	37.2	370	0.72
280	22.3		

Comments on Preferred Values

The preferred values of the absorption cross-sections for 190–270 nm are those reported by Illies and Takacs,[1] and for 270–370 nm are those reported by Nelson and Johnston.[2] The latter authors showed that the higher values above 300 nm reported in reference 1 could be accounted for by a 6% Cl_2 impurity in the $ClNO_2$ sample used. Nelson and Johnston[2] determined that photolysis occurs with a quantum yield of unity (within experimental error) to produce $Cl + NO_2$ ($\phi_1 = 0.93 \pm 0.15$). They also report a negligible production of oxygen atoms ($\phi_2 < 0.02$).

References

[1] A. J. Illies and G. A. Takacs, J. Photochem. **6**, 35 (1976/77).
[2] H. H. Nelson and H. S. Johnston, J. Phys. Chem. **85**, 3891 (1981).

$ClONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	(1)	112	1065
$\rightarrow Cl + NO_3$	(2)	163	735
$\rightarrow ClONO + O(^3P)$	(3)	282	425

Preferred Values

Absorption cross-sections for $ClONO_2$ photolysis at 296 K, 243 K and 227 K

	10^{20} σ/cm²				10^{20} σ/cm²		
λ/nm	296 K	243 K	227 K	λ/nm	296 K	243 K	227 K
190	589		555	325	0.655	0.502	0.463
195	381		358	330	0.514	0.381	0.353
200	307		293	335	0.397	0.307	0.283
205	299		293	340	0.323	0.255	0.246
210	329		330	345	0.285	0.223	0.214
215	360		362	350	0.246	0.205	0.198
220	344		348	355	0.218	0.183	0.182
225	286		282	360	0.208	0.173	0.170
230	210		206	365	0.179	0.159	0.155
235	149		141	370	0.162	0.140	0.142
240	106		98.5	375	0.139	0.130	0.128
245	77.0		70.6	380	0.122	0.114	0.113
250	57.7	50.9	52.6	385	0.108	0.100	0.098
255	44.7	39.1	39.8	390	0.090	0.083	0.082
260	34.6	30.1	30.7	395	0.077	0.070	0.069
265	26.9	23.1	23.3	400	0.064	0.058	0.056
270	21.5	18.0	18.3	405	0.055		
275	16.1	13.5	13.9	410	0.044		
280	11.9	9.98	10.4	415	0.035		
285	8.80	7.73	7.50	420	0.027		
290	6.36	5.36	5.45	425	0.020		
295	4.56	3.83	3.74	430	0.016		
300	3.30	2.61	2.51	435	0.013		
305	2.38	1.89	1.80	440	0.009		
310	1.69	1.35	1.28	445	0.007		
315	1.23	0.954	0.892	450	0.005		
320	0.895	0.681	0.630				

Quantum Yields for $ClONO_2$ Photolysis

$\phi_2 = 0.90$ for $\lambda > 260$ nm.

$\phi_3 = 0.10$ for $\lambda > 260$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Molina and Molina.[1] The preferred quantum yield values are based on the direct results of Margitan.[2] They are confirmed by the results of Knauth and Schindler[3] based on final product analysis, and also by the results of Chang *et al.*[4] Burrows *et al.*[5] report Cl + NO_3 as the photolysis products at 254 nm, with a quantum yield of unity. Earlier results are discussed in our previous evaluation.[6]

References

[1]L. T. Molina and M. J. Molina, J. Photochem. **11**, 139 (1979).
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[5]J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **92**, 4340 (1988).
[6]CODATA, Supplement II, 1984 (see references in Introduction).

$Cl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$Cl_2 + h\nu \rightarrow Cl + Cl$	242	495

Preferred Values

Absorption cross-sections for Cl_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
240	0.08	350	18.9
250	0.12	360	13.1
260	0.23	370	8.3
270	0.88	380	4.9
280	2.7	390	3.3
290	6.5	400	1.9
300	12.0	410	1.3
310	18.5	420	0.99
320	23.6	430	0.73
330	25.6	440	0.53
340	23.6	450	0.34

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Seery and Britton.[1] They are in good agreement with results reported by Gibson and Bayliss[2] and Burkholder and Bair.[3] Photolysis is expected to occur with unit quantum efficiency.

References

[1]D. J. Seery and D. Britton, J. Phys. Chem. **68**, 2263 (1964).
[2]G. E. Gibson and N. S. Bayliss, Phys. Rev. **44**, 188 (1933).
[3]J. B. Burkholder and E. J. Bair, J. Phys. Chem. **87**, 1859 (1983).

$CH_3Cl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Cl + h\nu \rightarrow CH_3 + Cl$ (1)	349	343

Preferred Values

Absorption cross-sections for CH_3Cl photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	111	111	200	1.76	1.51
6	93.8	93.8	2	1.13	0.93
8	76.6	76.6	4	0.750	0.573
180	60.7	60.7	6	0.483	0.345
2	46.7	46.7	8	0.318	0.212
4	35.0	35.0	210	0.206	0.130
6	25.5	25.5	2	0.132	0.080
8	18.2	18.2	4	0.086	0.047
190	12.7	12.7	6	0.055	0.027
2	8.72	8.72			
4	5.88	5.88			
6	4.01	4.01			
8	2.66	2.43			

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*[1] This publication[1] reports the results of the most comprehensive study of the temperature dependence. These values are in very good agreement with the room temperature values reported by Robbins,[2] and are in reasonable agreement with the results of Hubrich *et al.*[3] who also made low temperature measurements. In this wavelength region, photolysis occurs with unit quantum efficiency by breaking of the C–Cl bond to yield CH_3 + Cl. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert.[4]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] D. E. Robbins, Geophys. Res. Lett. **3**, 213 (1976); erratum op. cit. **3**, 757 (1976).
[3] C. Hubrich, C. Zetzsch, and F. Stuhl, Ber. Bunsenges Phys. Chem. **81**, 437 (1977).
[4] D. M. Shold and R. E. Rebbert, J. Photochem. **9**, 499 (1978).

CHF_2Cl (HCFC–22) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ{\cdot}mol^{-1}$	$\lambda_{threshold}$/nm
$CHF_2Cl + h\nu \rightarrow CHF_2 + Cl$	362	330

Preferred Values

Absorption cross-sections for CHF_2Cl photolysis at 298 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
174	5.72	190	0.245
176	4.04	192	0.156
178	2.76	194	0.103
180	1.91	196	0.072
182	1.28	198	0.048
184	0.842	200	0.032
186	0.576	202	0.022
188	0.372	204	0.014

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Simon *et al.*[1] In the same study the temperature dependence down to 210 K has been reported, with the values at the shorter wavelengths being temperature-independent while the values at longer wavelengths show a decrease as the temperature is lowered. For values at low temperatures the reader is referred to the original reference. These results are in reasonable agreement with the results of earlier studies cited in NASA, 1990.[2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CHF_2 + Cl.

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] NASA Evaluation No. 9, 1990 (see references in Introduction).

CF_2Cl_2 (CFC–12) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	(1)	346	346
$\rightarrow CF_2 + 2\ Cl$	(2)	542	221

Preferred Values

Absorption cross-sections for CF_2Cl_2 photolysis at 295 K and 210 K

	$10^{20}\ \sigma/cm^2$			$10^{20}\ \sigma/cm^2$	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	162	162	200	8.89	5.11
6	181	181	2	5.51	2.97
8	187	187	4	3.44	1.69
180	179	179	6	2.09	0.99
2	160	160	8	1.27	0.56
4	134	134	210	0.76	0.32
6	107	107	2	0.45	0.18
8	82.8	79.3	4	0.27	0.10
190	63.2	52.9	6	0.16	0.058
2	45.5	35.8	8	0.10	0.033
4	31.5	22.8	220	0.060	0.018
6	21.1	14.4	2	0.036	0.010
8	13.9	8.8	4	0.022	0.006
			6	0.013	0.003

Quantum Yields for CF_2Cl_2 Photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.59	0.41	210	0.85	0.15
180	0.62	0.38	220	0.96	0.04
190	0.67	0.33	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence. The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980,[2] where a detailed discussion of earlier work can be found. The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[3]

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).
[2] CODATA, 1980 (see references in Introduction).
[3] R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).

$CFCl_3$ (CFC–11) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$	(1)	317	380
$\rightarrow CFCl + 2\ Cl$	(2)	507	236

Preferred Values

Absorption cross-sections for $CFCl_3$ photolysis at 295 K and 210 K

	$10^{20}\ \sigma/cm^2$			$10^{20}\ \sigma/cm^2$	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	313	313	210	14.8	9.9
6	324	324	2	10.5	6.63
8	323	323	4	7.56	4.31
180	314	314	6	5.38	2.78
2	296	296	8	3.79	1.77
4	272	272	220	2.64	1.13
6	243	230	2	1.82	0.71
8	213	202	4	1.24	0.45
190	179	170	6	0.84	0.29
2	154	141	8	0.56	0.19
4	124	115	230	0.37	0.12
6	99.1	90.5	235	0.126	
8	78.0	71.8	240	0.046	
200	64.5	55.8	245	0.017	
2	50.0	42.0	250	0.0066	
4	37.4	30.0	255	0.0034	
6	28.0	21.6	260	0.0015	
8	19.7	14.9			

Quantum Yields for $CFCl_3$ Photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.57	0.43	210	0.84	0.16
180	0.66	0.34	220	0.94	0.06
190	0.66	0.34	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174–230 nm at 295 K and at 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence. The values are in good agreement with those recommended in our previous evaluation, CODATA, 1982,[2] where a detailed discussion of earlier work can be found. For λ > 230 nm, the values are those reported by Hubrich and Stuhl[3]. The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[4]

References

[1]P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).

[2]CODATA, Supplement I, 1982 (see references in Introduction).

[3]C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

[4]R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).

$CCl_4 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CCl_4 + h\nu \rightarrow CCl_3 + Cl$	(1)	288	415
$\rightarrow CCl_2 + 2\ Cl$	(2)	577	207

Preferred Values

Absorption cross-sections for CCl_4 photolysis at 295 K and 210 K

	$10^{20}\ \sigma/cm^2$			$10^{20}\ \sigma/cm^2$	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	990	990	8	22.1	16.3
6	1010	1010	220	17.5	12.5
8	975	975	2	13.6	9.0
180	720	720	4	10.2	6.4
2	590	590	6	7.6	4.4
4	440	440	8	5.6	3.16
6	310	310	230	4.28	2.27
8	198	198	2	3.04	1.52
190	147	147	4	2.20	1.05
2	99.2	99.2	6	1.60	0.72
4	76.7	76.7	8	1.16	0.50
6	69.5	69.5	240	0.830	0.342
8	68.0	68.0	2	0.590	0.234
200	66.0	66.0	4	0.413	0.158
2	63.8	63.8	6	0.290	0.108
4	61.0	60.1	8	0.210	0.076
6	57.0	54.4	250	0.148	0.053
8	52.5	48.3	255	0.066	
210	46.9	41.5	260	0.025	
2	41.0	34.8	265	0.013	
4	34.5	27.9	270	0.006	
6	27.8	21.7	275	0.002	

Quantum Yields for CCl_4 Photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.30	0.70	210	0.83	0.17
180	0.36	0.64	220	0.96	0.04
190	0.46	0.54	230	1.0	
200	0.63	0.37	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence. The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1982,[2] where a detailed discussion of earlier work can be found. For λ > 250 nm, the values are those reported by Hubrich and Stuhl.[3] The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[4]

References

[1]P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. 7, 107 (1988).

[2]CODATA, Supplement I, 1982 (see references in Introduction).

[3]C. Hubrich and F. Stuhl, J. Photochem. 12, 93 (1980).

[4]R. E. Rebbert and P. J. Ausloos, J. Photochem. 6, 265 (1976/77).

CH_3CF_2Cl (HCFC–142b) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CF_2Cl + h\nu \rightarrow CH_3CF_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CF_2Cl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	0.94	210	0.017
2	0.66	2	0.010
4	0.46	4	0.007
6	0.31	6	0.004
8	0.21	8	0.003
200	0.14	220	0.002
2	0.09	2	0.0009
4	0.061	4	0.0005
6	0.039	6	0.0003
8	0.026	8	0.0002

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Orlando *et al.*[2] The agreement between these studies over the wavelength range of preferred values is good. The results of Hubrich and Stuhl[3] are in reasonable agreement. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. They are in fair agreement at the shorter wavelengths, both studies reporting a significant decrease in absorption as the temperature is lowered. At the longer wavelengths they are in disagreement at low temperatures. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CH_3CF_2 + Cl.

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. **12**, 269 (1991).
[2]J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. **96**, 5013 (1991).
[3]C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

CH_3CFCl_2 (HCFC–141b) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CFCl_2 + h\nu \rightarrow CH_3CFCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CFCl_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	75.3	210	2.2
2	58.8	2	1.4
4	44.3	4	0.94
6	32.2	6	0.61
8	22.8	8	0.41
200	15.8	220	0.27
2	10.8	2	0.18
4	7.3	4	0.12
6	4.9	6	0.08
8	3.2	8	0.06

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Talukdar *et al.*[2] The agreement between results of these studies at 298 K over the wavelength range of preferred values is only fair. The ratio of the value in Ref. 1 to that in Ref. 2 decreases monotonically from 1.20 at 190 nm to 0.86 at 220 nm and to 0.60 at 230 nm. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. They are in fair agreement at the longer wavelengths, both studies reporting a significant decrease in absorption as the temperature is lowered. At the shorter wavelengths they are in disagreement at low temperatures. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CH_3CFCl + Cl.

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. **12**, 269 (1991).
[2]R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Phys. Chem. **95**, 5815 (1991).

$CH_3CCl_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$	(1)	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
182	315	315	210	24.0	19.8
4	280	280	2	16.8	13.2
6	250	250	4	12.0	8.8
8	220	220	6	8.6	6.1
190	192	192	8	6.0	4.2
2	163	163	220	4.1	2.9
4	140	140	2	2.9	1.2
6	118	118	4	2.0	1.2
8	99	99	6	1.5	0.76
200	81	81	8	1.0	0.51
2	66	64	230	0.70	0.33
4	52	49	2	0.49	0.18
6	40	36	4	0.33	0.11
8	31	26	6	0.23	0.064
			8	0.15	0.036
			240	0.10	0.024

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Vanlaethem-Meuree *et al.*[1] These values are preferred over the substantially higher values reported by Hubrich and Stuhl,[2] in which study a correction was required for the presence of the UV-absorbing stabilizer 1,4-dioxane. In Ref. 1, absorption cross-section values are given for 295 K, 270 K, 250 K, 230 K and 210 K. Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CH_3CCl_2 + Cl.

References

[1]N. Vanlaethem-Meuree, J. Wisemberg, and P. C. Simon, Geophys. Res. Lett. **6**, 451 (1979).
[2]C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

CF_3CHFCl (HCFC–124) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHFCl + h\nu \rightarrow CF_3CHF + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHFCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	0.73	210	0.018
2	0.53	2	0.012
4	0.38	4	0.008
6	0.26	6	0.006
8	0.18	8	0.004
200	0.13	220	0.003
2	0.086	2	0.003
4	0.059	4	0.002
6	0.040	6	0.002
8	0.026	8	0.001

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Orlando *et al.*[1] In the same study the temperature dependence down to 203 K has been reported, with the values showing a significant decrease in absorption as the temperature is lowered. For values at low temperatures the reader is referred to the original reference. Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CF_3CHF + Cl.

References

[1]J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. 96, 5013 (1991).

CF_3CHCl_2 (HCFC–123) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CHCl_2 + h\nu \rightarrow CF_3CHCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHCl_2 photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	59.0	210	1.8
2	44.5	2	1.3
4	32.9	4	0.87
6	23.6	6	0.61
8	16.9	8	0.40
200	11.9	220	0.28
2	8.3	2	0.20
4	5.7	4	0.14
6	4.0	6	0.10
8	2.7	8	0.07

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Orlando *et al.*[2] The agreement between these studies over the wavelength range of preferred values is very good. The results of Green and Wayne[3] are in reasonable agreement. The temperature dependence down to 210 K has been reported in references 1 and 2. They are in fair agreement at the shorter wavelengths, both studies reporting a significant decrease in absorption as the temperature is lowered. At the longer wavelengths they are in disagreement at low temperatures. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CF_3CHCl + Cl.

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. 12, 269 (1991).
[2]J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, J. Geophys. Res. 96, 5013 (1991).
[3]R. G. Green and R. P. Wayne, J. Photochem. 6, 375 (1976/77).

$CF_2ClCFCl_2$ (CFC–113) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCFCl_2 + h\nu \rightarrow CF_2ClCFCl + Cl$	(1)	346 (est)	346
$\rightarrow CFCl_2CF_2 + Cl$	(2)	346 (est)	346

Preferred Values

Absorption cross-sections for $CF_2ClCFCl_2$ photolysis at 295 K and 210 K

	10^{20} σ/cm^2			10^{20} σ/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
184	118	118	210	1.80	1.12
6	104	104	2	1.15	0.696
8	83.5	83.5	4	0.760	0.452
190	64.5	64.5	6	0.505	0.298
2	48.8	48.8	8	0.318	0.184
4	36.0	36.0	220	0.220	0.125
6	26.0	24.3	2	0.145	0.081
8	18.3	15.9	4	0.095	0.053
200	12.5	10.1	6	0.063	0.034
2	8.60	6.54	8	0.041	0.022
4	5.80	4.09	230	0.027	0.014
6	4.00	2.66			
8	2.65	1.68			

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Simon *et al.*[1] They are in very good agreement with the room temperature results of Chou *et al.*[2] They are in good agreement with those of Hubrich and Stuhl,[3] who also made low temperature measurements. Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield $CF_2ClCFCl + Cl$ or $CFCl_2CF_2 + Cl$.

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae **6**, 239 (1988).

[2] C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **82**, 1 (1978).

[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

CF_2ClCF_2Cl (CFC–114) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_2ClCF_2Cl + h\nu \rightarrow CF_2ClCF_2 + Cl$	346 (est)	346

Preferred Values

Absorption cross-sections for CF_2ClCF_2Cl photolysis at 295 K and 210 K

	$10^{20}\ \sigma/cm^2$			$10^{20}\ \sigma/cm^2$	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
172	69	69	200	0.80	0.55
4	55	55	2	0.54	0.34
6	43	43	4	0.37	0.22
8	34	34	6	0.24	0.13
180	26	26	8	0.16	0.084
2	19.8	19.8	210	0.104	0.051
4	15.0	15.0	2	0.068	0.031
6	11.0	11.0	4	0.044	0.020
8	7.80	7.72	6	0.029	0.012
190	5.35	5.03	8	0.019	0.007
2	3.70	3.28	220	0.012	0.004
4	2.56	2.13			
6	1.75	1.39			
8	1.20	0.88			

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Simon *et al.*[1] They are in very good agreement with the room temperature results of Chou *et al.*[2] Hubrich and Stuhl[3] reported higher values and a smaller temperature dependence. Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CF_2ClCF_2 + Cl.

References

[1] P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae **6**, 239 (1988).

[2] C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **82**, 1 (1978).

[3] C. Hubrich and F. Stuhl, J. Photochem. **12**, 93 (1980).

CF_3CF_2Cl (CFC–115) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$CF_3CF_2Cl + h\nu \rightarrow CF_3CF_2 + Cl$	346	346

Preferred Values

Absorption cross-sections for CF_3CF_2Cl photolysis

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
172	5.65	190	0.27
4	4.05	2	0.19
6	2.85	4	0.13
8	2.05	6	0.090
180	1.45	8	0.063
2	1.05	200	0.044
4	0.75	2	0.031
6	0.53	4	0.021
8	0.38		

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Simon *et al.*[1] In this study measurements were made down to 225 K, and the absorption cross-section values were found to be independent of temperature. They are in good agreement with the results of Hubrich and Stuhl[2] who also made low temperature measurements. Earlier measurements of Chou *et al.*[3] are 50% higher. Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CF_3CF_2 + Cl.

References

[1]P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, Ann. Geophysicae 6, 239 (1988).
[2]C. Hubrich and F. Stuhl, J. Photochem. 12, 93 (1980).
[3]C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, J. Phys. Chem. 82, 1 (1978).

$CF_3CF_2CHCl_2$ (HCFC–225ca) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3CF_2CHCl_2 + h\nu \rightarrow CF_3CF_2CHCl + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for $CH_3CF_2CHCl_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
160	269	200	16
165	197	205	6.9
170	183	210	2.9
175	191	215	1.2
180	177	220	0.46
185	129	225	0.17
190	74	230	0.065
195	37	235	0.025
		239	0.011

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*[1] In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–270 nm. Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–270 nm were fitted with the expression:

$$\log_{10}\sigma = -17.966 + 4.542 \times 10^{-2}X - 2.036 \times 10^{-3}X^2 + 1.042 \times 10^{-5} X^3 \text{ where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield CF_3CF_2CHCl + Cl.

References

[1]W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. 96, 13009 (1991).

CF_2ClCF_2CHFCl (HCFC–225cb) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2ClCF_2CHFCl + h\nu \rightarrow CF_2ClCF_2CHF + Cl$	335 (est)	360
$\rightarrow CHFClCF_2CF_2 + Cl$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_2ClCF_2CHFCl photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
160	188	185	9.1
165	145	190	3.5
170	91	195	1.4
175	47	200	0.63
180	21	205	0.33
		210	0.25

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*[1] In the same study absorption cross-section measurements in the liquid phase were made over the wavelength range 205–250 nm. Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–250 nm were fitted with the expression:

$$\log_{10}\sigma = -17.714 - 2.175 \times 10^{-2}X - 1.484 \times 10^{-3}X^2 + 1.147 \times 10^{-5}X^3 \text{ where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Cl bond to yield $CF_2ClCF_2CHF + Cl$ or $CHFClCF_2CF_2 + Cl$.

Reference

[1]W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. 96, 13009 (1991).

HCOCl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HCOCl + h\nu \rightarrow HCO + Cl$	340 (est)	350

Preferred Values

Absorption cross-sections of HCOCl at the band maxima (298 K, 1013 mbar of N_2, spectral resolution 0.7 nm)

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
236.1	3.8	280.2	2.4
241.5	4.9	282.7	2.3
247.3	5.6	285.3	1.64
251.4	5.4	286.8	1.04
253.7	6.0	288.0	0.86
256.1	5.6	289.4	0.97
258.2	5.8	292.2	0.81
260.2	6.0	294.9	0.46
263.5	5.1	296.7	0.32
265.7	5.3	298.1	0.22
267.9	5.2	299.5	0.25
269.1	3.9	302.3	0.172
270.2	3.5	305.2	0.080
271.4	4.0	308.1	0.027
273.8	4.1	309.3	0.021
276.3	3.4	311.1	0.020
277.7	2.4	314.1	0.013
278.9	2.1	316.7	0.008
		318.7	0.007

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Libuda *et al.*[1] These are the values of the absorption cross-sections at the absorption maxima and were measured at a spectral resolution of 0.7 nm. The absorption bands for $\lambda > 265$ nm became distinctly sharper when the spectral resolution was improved to 0.4 nm. The spectrum of HCOCl is similar to that of HCHO but is shifted to shorter wavelengths by 45 nm. Although there have been no quantum yield studies of HCOCl photolysis, it is reasonable to assume by analogy with the photolysis of $COCl_2$ that the primary photolysis pathway proceeds by breaking of the C–Cl bond to yield HCO + Cl.

References

[1]H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, J. Phys. Chem. **94**, 5860 (1990).

COFCl + $h\nu$ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
COFCl + $h\nu$ → FCO + Cl	(1)	377	317
→ ClCO + F	(2)	489	244
→ CO + F + Cl	(3)	517	231
→ CFCl + O(^{3}P)	(4)	656	182

Preferred Values

Absorption cross-sections for COFCl photolysis at 298 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
186.0	15.6	205.1	11.2
187.8	14.0	207.3	10.5
189.6	13.4	209.4	9.7
191.4	12.9	211.6	9.0
193.2	12.7	213.9	7.9
195.1	12.5	216.2	6.9
197.0	12.4	218.6	5.8
199.0	12.3	221.0	4.8
201.0	12.0	223.5	4.0
203.0	11.7	226.0	3.1

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou *et al.*[1] The spectrum shows some structure, and the values listed are averages over 500 cm^{-1} intervals. Although there have been no quantum yield studies of COFCl photolysis, it is reasonable to assume by analogy with the photolysis of $COCl_2$ that process (1) is the primary photolysis pathway.

References

[1]G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.

$COCl_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$COCl_2 + h\nu \rightarrow ClCO + Cl$	(1)	324	369
$\rightarrow CO + 2Cl$	(2)	352	340
$\rightarrow CCl_2 + O(^3P)$	(3)	707	169

Preferred Values

Absorption cross-sections for $COCl_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
184.9	204	211.6	12.2
186.0	189	213.6	11.7
187.8	137	216.3	11.6
189.6	117	218.6	11.9
191.4	93.7	221.0	12.3
193.2	69.7	223.5	12.8
195.1	52.5	226.0	13.2
197.0	41.0	240.0	12.2
199.0	31.8	250.0	8.36
201.0	25.0	253.7	6.74
203.0	20.4	260.0	4.43
205.1	16.9	270.0	1.58
207.3	15.1	280.0	0.53
209.4	13.4		

Quantum Yields for $COCl_2$ Photolysis at 298 K

$\phi_1 = 1$ for $\lambda > 184.9$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou *et al.*[1] for 185–226 nm and by Okabe[2] for 240–280 nm. The spectrum is a continuum, and the values listed are averaged over 500 cm^{-1} intervals. The observations of Wijnen,[3] Heicklen[4] and earlier investigators[5] show that process (1) is the primary photolysis pathway.

References

[1] G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.

[2] H. Okabe, J. Chem. Phys. **66**, 2058 (1977).

[3] W. H. Wijnen, J. Am. Chem. Soc. **83**, 3014 (1961).

[4] J. Heicklen, J. Am. Chem. Soc. **87**, 445 (1965).

[5] J. G. Calvert and J. N. Pitts, *Photochemistry* (John Wiley and Sons, Inc., New York, 1966), p. 231.

$CCl_3CHO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CCl_3CHO + h\nu \rightarrow CCl_3 + HCO$	(1)		
$\rightarrow CCl_3CO + H$	(2)		
$\rightarrow CHCl_3 + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–340	Rattigan, Jones and Cox, 1991[1]	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

(a) Absolute absorption cross-sections measured using a dual beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of CCl_3CHO shows a broad band centered at 290 nm and extending out to 360 nm. Values of σ were given at 5 nm intervals at 298 K. A second absorption band appears at wavelengths <230 nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
200	115	255	2.80	310	6.07
205	86.1	260	3.98	315	4.57
210	48.2	265	5.36	320	3.06
215	23.9	270	6.72	325	1.90
220	10.9	275	8.01	330	1.12
225	4.76	280	9.32	335	0.498
230	2.03	285	10.08	340	0.193
235	0.944	290	10.32	345	0.086
240	0.774	295	9.89	350	0.019
245	1.13	300	9.02	355	0.002
250	1.83	305	7.67	360	0.0

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan *et al*.[1] There are no data concerning the quantum yields, but by analogy with acetaldehyde, which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

[1]O. Rattigan, R. L. Jones, and R. A. Cox, J. Photochem., submitted for publication.

$CF_3COCl + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		ΔH°/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3COCl + h\nu \rightarrow CF_3 + ClCO$	(1)		
$\rightarrow CF_3CO + Cl$	(2)		
$\rightarrow CF_3Cl + CO$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–335	Rattigan, Jones and Cox, 1991[1]	(a)
230 300	Jemi-Alade, Lightfoot and Lesclaux, 1991[2]	(b)

Quantum yield data

There are no reported data for ϕ_1 or ϕ_2.

Comments

(a) Absolute absorption cross-sections measured using a dual beam diode array spectrometer over the temperature range 233–300 K. The UV spectrum of CF_3COCl shows two overlapping bands, the first having a maximum at 255 nm ($\sigma = 6.78 \times 10^{-20}$ cm^2 molecule^{-1}) and the second at <200 nm. There is significant absorption at wavelengths >300 nm, where the cross-sections become increasingly temperature dependent. Values of σ were given at 5 nm intervals at 298 K and 240 K as well as temperature coefficients in the long wavelength tail at >270 nm. Photolysis was observed at 254 nm, but no quantum yield data were reported.

(b) Absorption cross-sections determined by conventional method at room temperature. σ(250 nm) = 6.72×10^{-20} cm^2 molecule^{-1}.

Preferred Values

Absorption cross-sections at 296 K and 233 K

λ/nm	10^{20} σ/cm²		λ/nm	10^{20} σ/cm²	
	296 K	233 K		296 K	233 K
200	32.5	27.4	270	5.13	4.79
205	14.8	12.0	275	4.22	3.88
210	3.53	2.56	280	3.11	2.82
215	1.04	0.786	285	2.17	1.91
220	0.972	0.921	290	1.39	1.20
225	1.61	1.58	295	0.809	0.667
230	2.68	2.66	300	0.425	0.334
235	3.89	3.87	305	0.198	0.144
240	5.01	4.97	310	0.077	0.048
245	5.94	5.84	315	0.024	0.012
250	6.54	6.39	320	0.0069	0.0038
255	6.78	6.55	325	0.0016	0.0008
260	6.60	6.32	330	0.0	0.0
265	5.97	5.62			

Quantum Yields

No recommendation.

Comments on Preferred Values

The cross-sections at 255 nm reported from the two studies[1,2] are in good agreement. The preferred values for the cross-sections are based on the more extensive data reported by Rattigan *et al.*,[1] which also provide the temperature dependence.

References

[1] O. Rattigan, R. L. Jones, and R. A. Cox, J. Photochem., submitted for publication.

[2] A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, Chem. Phys. Lett. **179**, 119 (1991).

4.8. Bromine Species

$O + BrO \rightarrow O_2 + Br$

$\Delta H^\circ = -262$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.5×10^{-11}	298	Clyne, Monkhouse, and Townsend, 1976[1]	(a)
Reviews and Evaluations			
3×10^{-11}	298	CODATA, 1980[2]; IUPAC, 1989[3]	(b)
3×10^{-11}	200–300	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of Br and O(^{3}P) atoms. The value shown was derived from two independent methods of determining the rate constant: (a) monitoring Br atom formation in the absence of NO, and (b) monitoring O(^{3}P) atom decay in the absence of NO.
(b) See Comments on Preferred Values.
(c) Based on results of Clyne *et al.*[1]

Preferred Values

$k = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[2] The preferred value is based on the results of Clyne *et al.*[1] The value appears to be reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for such an atom-radical process, as for the analogous ClO reaction.

References

[1] M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem. Kinet. **8**, 425 (1976).
[2] CODATA, 1980 (see references in Introduction).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).
[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H^\circ = -163$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.2) \times 10^{-12}$	298	Laverdet *et al.*, 1990[1]	(a)
Reviews and Evaluations			
$1.4 \times 10^{-11} \exp(-590/T)$	260–390	IUPAC, 1989[2]	(b)
$1.5 \times 10^{-11} \exp(-600/T)$	200–300	NASA, 1990[3]	(b)

Comments

(a) Discharge flow system with EPR detection of Br and of HO_2 by conversion to HO by reaction with excess NO. Previous indirect results of Poulet *et al.*[4] were reinterpreted to yield values of k in the range $(1.0–2.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
(b) Based on the results of Toohey *et al.*[5]

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-11} \exp(-590/T)$ molecule^{-1} s^{-1} over the temperature range 260–390 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
This recommendation is unchanged from our previous evaluation, IUPAC, 1989.[2] It is based on results obtained over the 260–390 K temperature range by Toohey *et al.*[5] using a discharge flow system with LMR detection of HO_2 decay in excess Br. The value determined by Laverdet *et al.*[1] is in good agreement with this recommendation. Laverdet *et al.*[1] have reinterpreted previous indirect measurements conducted in the same laboratory (by Poulet *et al.*[4]) to give a range of values higher than had been reported[4] and in agreement with the present recommendation.

References

[1]G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **172**, 430 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).
[4]G. Poulet, G. Laverdet, and G. Le Bras, J. Chem. Phys. **80**, 1922 (1984).
[5]D. W. Toohey, W. M. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).

$Br + H_2O_2 \rightarrow HBr + HO_2$ (1)
$\rightarrow HOBr + HO$ (2)

$\Delta H°(1) = 2.7$ kJ·mol^{-1}
$\Delta H°(2) = -16$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5 \times 10^{-16}$	298	Toohey, Brune, and Anderson, 1987[1]	(a)
$<5 \times 10^{-16}$	378		
Reviews and Evaluations			
$<5 \times 10^{-16}$	298	IUPAC, 1989[2]	(b)
$<1 \times 10^{-11} \exp(-3000/T)$	200–300	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of Br atoms. Decays of Br atoms monitored in the presence of excess H_2O_2. Attempted measurement of HO_2 and OH products by LMR allowed upper limits of 5×10^{-16} cm^3 molecule^{-1} s^{-1} to be quoted for either channel (1) or (2).
(b) See Comments on Preferred Values.
(c) Based on the data of Toohey *et al.*[1]

Preferred Values

$k = <5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[2] The upper limit to the preferred value is based on the data of Toohey *et al.*,[1] who also obtained the same upper limit at 378 K.

References

[1]D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Br + O_3 \rightarrow BrO + O_2$

$\Delta H^\circ = -130$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.28 \times 10^{-11} \exp[-(944 \pm 30)/T]$	248–418	Toohey, Brune, and Anderson, 1988[1]	(a)
$(1.42 \pm 0.03) \times 10^{-12}$	298		
$1.50 \times 10^{-11} \exp[-(775 \pm 30)/T]$	195–392	Nicovich, Kreutter, and Wine, 1990[2]	(b)
$(1.11 \pm 0.07) \times 10^{-12}$	298		
Reviews and Evaluations			
$1.7 \times 10^{-11} \exp(-800/T)$	220–360	IUPAC, 1989[3]	(c)
$1.7 \times 10^{-11} \exp(-800/T)$	220–360	NASA, 1990[4]	(d)

Comments

(a) Discharge flow system. First-order decay of Br atoms in the presence of excess O_3 monitored by resonance fluorescence.

(b) Laser flash photolysis system with resonance fluorescence detection of Br atoms used. Br atoms were produced by the 355 nm photolysis of Br_2.

(c) Based on the results of Toohey *et al.*,[1] Clyne and Watson,[5] Leu and DeMore,[6] Michael *et al.*[7] and Michael and Payne.[8]

(d) Based on the results of Refs. 1, 2, and 5–8.

Preferred Values

$k = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-11} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 195–392 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommended Arrhenius expression is unchanged from that given in the previous evaluation, IUPAC, 1989.[3] It is based on a fit to the results of Toohey *et al.*,[1] Clyne and Watson,[5] Leu and DeMore,[6] Michael *et al.*,[7] Michael and Payne[8] and the recent results of Nicovich *et al.*,[2] which are in excellent agreement with the average of all earlier studies.

References

[1]D. W. Toohey, W. H. Brune, and J. G. Anderson, Int. J. Chem. Kinet. **20**, 131 (1988).
[2]J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet. **22**, 399 (1990).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 336 (1975).
[6]M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **48**, 317 (1977).
[7]J. V. Michael, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **68**, 4093 (1978).
[8]J. V. Michael and W. A. Payne, Int. J. Chem. Kinet. **11**, 799 (1979).

$Br + NO_2 + M \rightarrow BrNO_2 + M$

$\Delta H° = -82$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.7) \times 10^{-31}$ [He]	298	Mellouki *et al.*, 1989[1]	(a)
$(2.75 \pm 0.55) \times 10^{-31}$ [He]	298	Kreutter, Nicovich, and Wine, 1991[2]	(b)
$4.24 \times 10^{-31}(T/300)^{-2.4}$ [N_2]	259–346		

Comments

(a) Discharge flow study with EPR and MS detection. Pressure range = 0.6–2.1 Torr.

(b) Laser flash photolysis-resonance fluorescence study over the pressure range 12.5–700 Torr. Bath gases He, Ar, H_2, N_2, CO_2, CF_4, and SF_6. Falloff curves were analyzed with a theoretically modeled value of $F_c = 0.59$ at 259 K, 0.55 at 298 K, and 0.50 at 346 K. Approach of equililbrium was observed at higher temperatures, leading to the reaction enthalpy given above.

Preferred Values

$k_0 = 4.2 \times 10^{-31}(T/300)^{-2.4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The recommended values of Ref. 2 are consistent with theoretical predictions. The falloff curves are represented with $F_c = 0.55$ at 298 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.66×10^{-11}	259–346	Kreutter, Nicovich, and Wine, 1991[2]	(a)

Comments

(a) See comment (b) for k_0.

Preferred Values

$k_\infty = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ over the temperature range 200–300 K.

Comments on Preferred Values

See comments on k_0. There is only a single determination of k_∞, but the measured falloff curve looks well behaved with a rate coefficient close to those of the reactions I + NO + M and I + NO_2 + M (see this evaluation).

References

[1]A. Mellouki, G. Laverdet, J. L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).

[2]K. D. Kreutter, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **95**, 4010 (1991).

$Br + OClO \rightarrow BrO + ClO$

$\Delta H° = 14$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.5) \times 10^{-14}$	300	Clyne and Coxon, 1967[1]	(a)
4.2×10^{-13}	298	Clyne and Watson, 1975[2]	(b)
$2.4 \times 10^{-11} \exp(-1320/T)$	267–423	Toohey, 1988[3]	(c)
2.82×10^{-13}	299		
Reviews and Evaluations			
$2.6 \times 10^{-11} \exp(-1300/T)$	200–450	IUPAC, 1989[4]	(d)
$2.6 \times 10^{-11} \exp(-1300/T)$	200–300	NASA, 1990[5]	(e)

Comments

(a) Discharge flow system with UV absorption detection of OClO. High concentrations of Br and OClO were employed under second order kinetic conditions.
(b) Discharge flow system with MS detection of OClO decay in excess Br. Decays were first order and computer fitting was used to compensate for the reverse reaction.
(c) Discharge flow system with resonance fluorescence detection of Br decay in excess OClO.
(d) See Comments on Preferred Values.
(e) Based on the data of Toohey[3] and Clyne and Watson.[2]

Preferred Values

$k = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-11} \exp(-1300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–450 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The preferred value at 298 K is the mean of the values reported by Toohey[3] and Clyne and Watson.[2] The latter study required correction for the effect of the reverse reaction on the decay, which was not taken into account in the earlier study of Clyne and Coxon[1] and which is therefore disregarded. The temperature dependence of Toohey[3] is accepted.

References

[1]M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. **A298**, 424 (1967).
[2]M. A. A. Clyne and R. T. Watson J. Chem. Soc. Faraday Trans. 1, **73**, 1169 (1977).
[3]D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Br + Cl_2O \rightarrow BrCl + ClO$

$\Delta H^\circ = -77$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-11} \exp[-(520 \pm 260)/T]$	220–298	Sander and Friedl, 1989[1]	(a)
$(3.79 \pm 0.38) \times 10^{-12}$	298		
Reviews and Evaluations			
$2.0 \times 10^{-11} \exp(-500/T)$	220–300	NASA, 1990[2]	(b)

Comments

(a) Flash photolysis ($\lambda > 300$ nm) of Br_2-Cl_2O mixtures in 100 Torr Ar. Rate of formation of ClO radicals in presence of excess $[Cl_2O]$ monitored by long-path UV absorption at 275.2 nm.
(b) Based on results of Sander and Friedl.[1]

Preferred Values

$k = 3.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1 \times 10^{-11} \exp(-520/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred value accepts the results of the study by Sander and Friedl[1] in which the rate of formation of ClO radicals was measured by long-path UV absorption following the flash photolysis of Br_2-Cl_2O mixtures. The significantly lower (by a factor of 4) value reported earlier by Basco and Dogra[3] has been rejected. In that same study Basco and Dogra[3] reported a value of $k(Cl + Cl_2O)$ more than two orders of magnitude less than that recommended in this evaluation, suggesting the possibility of a systematic error in their method of determination of [ClO].

References

[1]S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).
[3]N. Basco and S. K. Dogra, Proc. Roy. Soc. London A, **323**, 401 (1971).

$Br + Cl_2O_2 \rightarrow BrCl + ClOO$

$\Delta H^\circ = -130$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3 \pm 2) \times 10^{-12}$	298	Friedl, 1991[1]	(a)
Reviews and Evaluations			
3.0×10^{-12}	298	NASA, 1990[2]	(b)

Comments

(a) Discharge flow – mass spectrometric study.
(b) Based on results of the absolute rate study of Friedl.[1]

Preferred Values

$k = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on results of the discharge flow – mass spectrometric study of Friedl.[1]

References

[1]R. R. Friedl, manuscript in preparation (1991).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$Br + HCHO \rightarrow HBr + HCO$

$\Delta H^\circ = -2.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.97 \times 10^{-11} \exp[-(1015 \pm 70)/T]$	295–480	Poulet, Laverdet, and Le Bras, 1981[1]	(a)
$(9.4 \pm 0.8) \times 10^{-13}$	295		
Reviews and Evaluations			
$1.7 \times 10^{-11} \exp(-800/T)$	223–480	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
$1.7 \times 10^{-11} \exp(-800/T)$	223–480	NASA, 1990[4]	(c)

Comments

(a) Discharge flow system with MS detection of HCHO, with the Br atom concentration in excess. The earlier data of Le Bras *et al.*[5] were shown to be in error due to secondary reactions of Br atoms with HCO.
(b) See Comments on Preferred Values.
(c) Based on a least-squares analysis of the absolute rate coefficient data of Nava *et al.*[6] and Poulet *et al.*[1]

Preferred Values

$k = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-11} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–480 K.

Reliability
$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1984.[2] The preferred rate expression is obtained from a least-squares analysis of the absolute rate coefficient data of Nava *et al.*[6] and Poulet *et al.*,[1] which are in reasonably good agreement.

References

[1]G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]G. Le Bras, R. Foon, and J. Combourieu, Chem. Phys. Lett. **73**, 357 (1980).
[6]D. F. Nava, J. V. Michael, and L. J. Stief, J. Phys. Chem. **85**, 1896 (1981).

$Br + CH_3CHO \rightarrow HBr + CH_3CO$

$\Delta H^\circ = -6.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.51 \times 10^{-11} \exp[-(364 \pm 41)/T]$	255–400	Nicovich *et al.*, 1990[1]	(a)
4.45×10^{-12}	298		
Reviews and Evaluations			
3.6×10^{-12}	298	IUPAC, 1989[2]	(b)

Comments

(a) Pulsed laser photolysis system with resonance fluorescence detection of Br atoms. Bromine atoms generated by photolysis of Br_2 at 355 nm, and experiments carried out with initial Br atom concentrations $\leq 3.5 \times 10^{10}$ molecule cm^{-3}.
(b) Derived from the absolute and relative rate coefficient studies of Islam *et al.*[3] and Niki *et al.*,[4] respectively.

Preferred Values

$k = 3.9 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 1.3 \times 10^{-11} \exp(-360/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250–400 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of absolute rate coefficients of Nicovich *et al.*[1] and Islam *et al.*[3] and the relative rate coefficient of Niki *et al.*[4] The temperature dependence is that measured by Nicovich *et al.*,[1] with the *A* factor being adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the recent relative rate studies of Barnes *et al.*[5] and Wallington *et al.*[6] [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH_3CHO].

References

[1]J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Photochem. Photobiol., A: Chemistry, **51**, 141 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]T. S. A. Islam, R. M. Marshall, and S. W. Benson, Int. J. Chem. Kinet. **16**, 1161 (1984).
[4]H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Int. J. Chem. Kinet. **17**, 525 (1985).
[5]I. Barnes, V. Bastian, K. H. Becker, R. Overath, and Z. Tong, Int. J. Chem. Kinet. **21**, 499 (1989).
[6]T. J. Wallington, L. M. Skewes, W. O. Siegl, and S. M. Japar, Int. J. Chem. Kinet. **21**, 1069 (1989).

$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.9$ $kJ{\cdot}mol^{-1}$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.12 \pm 0.045) \times 10^{-11}$	298	Cannon *et al.*, 1984[1]	(a)
$(1.1 \pm 0.1) \times 10^{-11}$	298	Ravishankara, Wine and Wells, 1985[2]	(b)
Reviews and Evaluations			
1.1×10^{-11}	249–416	IUPAC, 1989[3]	(c)
1.1×10^{-11}	200–300	NASA, 1990[4]	(d)

Comments

(a) Flash photolysis system with LIF detection of HO radicals.
(b) Laser flash photolysis system with resonance fluorescence detection and laser flash photolysis system with LIF detection used, resulting in rate coefficients of $(1.14 \pm 0.03) \times 10^{-11}$ and $(1.07 \pm 0.03) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.
(c) See Comments on Preferred Values.
(d) Based on the results of Ravishankara *et al.*,[2,5] Jourdain *et al.*[6] and Cannon *et al.*[1]

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 249–416 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The preferred 298 K rate coefficient is based on the results of Ravishankara *et al.*,[2,5] Jourdain *et al.*[6] and Cannon *et al.*[1] with the temperature independence being based on the results of Ravishankara *et al.*[5] Ravishankara *et al.*[2] monitored HBr in the UV and have suggested that HBr adsorption on surfaces might be source of error in the lower determinations.

References

[1]B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).
[2]A. R. Ravishankara, P. H. Wine, and J. R. Wells, J. Chem. Phys. **83**, 447 (1985).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).
[6]J. L. Jourdain, G. Le Bras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).

$HO + Br_2 \rightarrow HOBr + Br$

$\Delta H° = -38$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.28 \pm 0.5) \times 10^{-11}$	298	Lowenstein and Anderson, 1984[1]	(a)
$(2.8 \pm 1.2) \times 10^{-11}$	262–303	Boodaghians *et al.*, 1987[2]	(a)
$1.35 \times 10^{-11} \exp(400/T)$	260–360	Toohey, 1988[3]	(b)
5.2×10^{-11}	298		
Reviews and Evaluations			
$1.2 \times 10^{-11} \exp(400/T)$	260–360	IUPAC, 1989[4]	(c)
4.2×10^{-11}	200–300	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) Discharge flow system with LMR detection of HO radicals.
(c) See Comments on Preferred Values.
(d) Based on results of Loewenstein and Anderson,[1] Boodaghians *et al.*[2] and Poulet *et al.*[6]

Preferred Values

$k = 4.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.2 \times 10^{-11} \exp(400/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–360 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[4] The rate constant is reasonably well determined at room temperature – the recommended value is the mean of the values reported in Refs. 1–3 and 6. Boodaghians *et al.*[2] found a near zero temperature dependence for 262–303 K. In contrast, the recent data of Toohey[3] display a significant negative temperature dependence in the range 260–360 K. The latter result is preferred, and the recommendation for E/R is based on this study. Loewenstein and Anderson[1] determined that the exclusive products are Br + HOBr.

References

[1]L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **88**, 6277 (1984).
[2]R. B. Boodaghians, I. W. Hall, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **83**, 529 (1987).
[3]D. W. Toohey, private communication (1988).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).
[6]G. Poulet, G. Laverdet, and G. Le Bras, Chem. Phys. Lett. **94**, 129 (1983).

$HO + CH_3Br \rightarrow H_2O + CH_2Br$

$\Delta H^\circ = -74.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.35 \times 10^{-12} \exp[-(1300 \pm 150)/T]$	233–379	Mellouki *et al.*, 1992[1]	(a)
$(2.96 \pm 0.36) \times 10^{-14}$	298		
$5.79 \times 10^{-12} \exp[-(1560 \pm 150)/T]$	250–400	Zhang *et al.*, 1992[2]	(b)
$(2.96 \pm 0.83) \times 10^{-14}$	298		
Reviews and Evaluations			
$7.6 \times 10^{-13} \exp(-890/T)$	244–350	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$2.60 \times 10^{-18} T^2 \exp(-521/T)$	244–2000	Atkinson, 1989[5]	(d)
$6.8 \times 10^{-13} \exp(-850/T)$	244–350	NASA, 1990[6]	(c)

Comments

(a) Laser photolysis system with LIF detection of HO.
(b) Flash photolysis system with resonance fluorescence detection of HO.
(c) Derived from the rate coefficients of Howard and Evenson[7] and Davis *et al.*[8].
(d) Derived from the rate coefficients of Howard and Evenson[7], Davis *et al.*[8] and Wilson[9].

Preferred Values

$k = 3.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.9 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recent absolute rate coefficient measurements of Mellouki *et al.*[1] and Zhang *et al.*[2], are significantly lower than those previously determined by Howard and Evenson[7] and Davis *et al.*[8]. The rate coefficients of Mellouki *et al.*[1] and Zhang *et al.*[2] are in good agreement, and a unit-weighted least-squares analysis of the rate coefficients of Mellouki *et al.*[1] and Zhang *et al.*[2], using the three parameter expression $k = CT^2 \exp(-D/T)$, leads to $k = 3.62 \times 10^{-18} T^2 \exp(-711/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–400 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

References

[1]A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon and A. R. Ravishankara, Geophys. Res. Lett. **19**, 2059 (1992).
[2]Z. Zhang, R. D. Saini, M. J. Kurylo and R. E. Huie, Geophys. Res. Lett., in press (1992).
[3]CODATA, 1980 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]R. Atkinson, J. Phys. Chem. Ref. Data, Monograph **1**, 1 (1989).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).
[7]C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
[8]D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, J. Chem. Phys. **65**, 1268 (1976).
[9]W. E. Wilson, Jr., 10th Int. Symposium on Combustion, 1964; The Combustion Institute, Pittsburgh, PA, 1965, p. 47.

$HO + CHF_2Br$ (Halon 1201) $\rightarrow H_2O + CF_2Br$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.4 \times 10^{-13} \exp[-(1050 \pm 400)/T]$	275–420	Brown *et al.*, 1990[1]	(a)
$(1.3 \pm 0.3) \times 10^{-14}$	298		
$7.4 \times 10^{-13} \exp[-(1300 \pm 100)/T]$	233–352	Talukdar *et al.*, 1991[2]	(b)
$(1.06 \pm 0.08) \times 10^{-14}$	298		

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. The stated purity level of the CHF_2Br sample used was 94.23%, with the major impurities being CHF_2Cl, $C_3F_6H_2$, CHF_2CF_2Cl, C_3F_6, C_4F_6 and C_3F_5H.
(b) Laser photolysis system with LIF detection of HO and a discharge flow system with LMR detection of HO used.

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.7 \times 10^{-13} \exp(-1310/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–300 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The rate coefficients measured by Talukdar *et al.*[2] are consistently lower, by up to a factor of 2 at 275 K, than those of Brown *et al.*,[1] possibly because of the presence of reactive impurities in the CHF_2Br sample used by Brown *et al.*[1] The rate coefficients of Talukdar *et al.*[2] have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.48 \times 10^{-18} T^2 \exp(-779/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–432 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C\,e^2 T^2$ and $B = D + 2T$.

References

[1]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).
[2]R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen and A. R. Ravishankara, Science **252**, 693 (1991).

HO + CF_3Br (Halon 1301) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 1 \times 10^{-15}$	298	Le Bras and Combourieu, 1978[1]	(a)
$<1 \times 10^{-16}$	294	Burkholder *et al.*, 1991[2]	(b)
$<1.7 \times 10^{-16}$	297		
$<1 \times 10^{-16}$	373		
$<2 \times 10^{-16}$	424		
Reviews and Evaluations			
$<1.2 \times 10^{-16}$	298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with EPR detection of HO.
(b) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.
(c) Based on the data of Burkholder *et al.*[2]

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values
The preferred upper limit to the rate coefficient at 298 K is based on the upper limits to the rate coefficients of $<1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} determined by Burkholder *et al.*[2] at 294 and 373 K.

References

[1]G. Le Bras and J. Combourieu, Int. J. Chem. Kinet. **10**, 1205 (1978).
[2]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

HO + CF_2ClBr (Halon 1211) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1 \times 10^{-15}$	293	Clyne and Holt, 1979[1]	(a)
$<2 \times 10^{-16}$	293	Burkholder *et al.*, 1991[2]	(b)
$<9 \times 10^{-17}$	297		
$<7 \times 10^{-17}$	373		
$<2 \times 10^{-16}$	424		
Reviews and Evaluations			
$<1.5 \times 10^{-16}$	298	NASA, 1990[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.
(b) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.
(c) Based on the study of Burkholder *et al.*,[2] which is consistent with that of Clyne and Holt.[1]

Preferred Values

$k < 1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Based on the upper limits to the rate coefficients of $<1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} determined by Burkholder *et al.*[2] at 297 and 373 K. The preferred value is consistent with the earlier study of Clyne and Holt.[1]

References

[1]M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 569 (1979).
[2]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[3]NASA Evaluation No. 9, 1990 (see references in Introduction).

HO + CF_2Br_2 (Halon 1202) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<4.5 \times 10^{-16}$	293	Burkholder *et al.*, 1991[1]	(a)
$<5.9 \times 10^{-16}$	297		
$<7.2 \times 10^{-16}$	325		
$<9.2 \times 10^{-16}$	373		
$<3.7 \times 10^{-16}$	384		
$<4.2 \times 10^{-16}$	424		
Reviews and Evaluations			
$<5 \times 10^{-16}$	298	NASA, 1990[2]	(b)

Comments

(a) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.
(b) Based on the study of Burkholder *et al.*[1]

Preferred Values

$k < 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

Based on the sole study of Burkholder *et al.*[1] The preferred upper limit to the rate coefficient at 298 K is confirmed by the values of $k \leq 4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} measured at 384 and 424 K.

References

[1]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

$HO + CF_3CHFBr$ (Halon 2401) → $H_2O + CF_3CFBr$

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.13 \times 10^{-12} \exp[-(1250 \pm 350)/T]$	279–423	Brown *et al.*, 1990[1]	(a)
$(1.7 \pm 0.3) \times 10^{-14}$	298		

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. The stated purity level of the CF_3CHFBr sample used was >99.5%, with CF_3CH_2F and CHF_2Br being the major impurities.

Preferred Values

$k = 1.7 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 298 K.
$k = 1.1 \times 10^{-12} \exp(-1250/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 270–430 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values
Based on the sole study of Brown *et al.*,[1] with expanded uncertainty limits.

Reference

[1]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature 347, 541 (1990).

$HO + CF_3CHClBr$ (Halon 2311) → $H_2O + CF_3CClBr$

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 0.4) \times 10^{-14}$	303	Brown *et al.*, 1990[1]	(a)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. Stated purity level of the $CF_3CHClBr$ sample used was >99%.

Preferred Values

$k = 5.8 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
The preferred 298 K rate coefficient is based on the sole study of Brown *et al.*,[1] extrapolated from 303 K to 298 K by use of an Arrhenius equation and assuming an A factor of 1×10^{-12} cm³ molecule⁻¹ s⁻¹.

Reference

[1]A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. 24A, 2499 (1990).

HO + CF_2BrCF_2Br (Halon 2402) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1.9 \times 10^{-15}$	295	Burkholder *et al.*, 1991[1]	(a)
$<1.3 \times 10^{-16}$	296		
$<1.4 \times 10^{-16}$	374		
$<4 \times 10^{-16}$	424		
Reviews and Evaluations			
$<1.5 \times 10^{-16}$	298	NASA, 1990[2]	(b)

Comments

(a) Laser photolysis system with LIF detection of HO and discharge flow system with LMR detection of HO used.

(b) Based upon the rate coefficient data of Burkholder *et al.*[1]

Preferred Values

$k < 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Burkholder *et al.*[1] The upper limit to the rate coefficient at 374 K of $<1.4 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} confirms the upper limit observed at 298 K.

References

[1]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[2]NASA Evaluation No. 9, 1990 (see references in Introduction).

BrO + HO_2 → HOBr + O_2 (1)
→ HBr + O_3 (2)

$\Delta H°(1) = -220$ kJ·mol^{-1}
$\Delta H°(2) = -33$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.3 \pm 0.5) \times 10^{-11}$	298	Poulet *et al.* 1992[1]	(a)
Reviews and Evaluations			
5×10^{-12}	298	CODATA, 1984[2]; IUPAC, 1989[3]	(b)
5×10^{-12}	298	NASA, 1990[4]	(b)

Comments

(a) Discharge flow system in which pseudo-first order decay of BrO in excess HO_2 was monitored by mass spectrometry.

(b) Based on data of Cox and Sheppard[5] and analogy with the ClO + HO_2 reaction.

Preferred Values

$k = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 6.2 \times 10^{-12}\exp(500/T)$ cm^3 molecule^{-1}s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the recent study of Poulet *et al.*[1] in which BrO decay in excess HO_2 was monitored by DF/MS. The only product observed was HOBr; however, the possible production of HBr requires further study. These new results are preferred over those reported in the earlier study of Cox and Sheppard[5] by molecular modulation –UV absorption in which a much lower value (factor of 6) was reported. The temperature dependence is our estimate, based on analogy with the ClO + HO_2 reaction.

References

[1]G. Poulet, M. Pirre, F. Maguin, R. Ramaroson, and G. Le Bras, Geophys. Res. Lett. **19**, 2305 (1992).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]R. A. Cox and D. W. Sheppard, J. Chem. Soc. Faraday Trans. 2, **78**, 1383 (1982).

$BrO + O_3 \rightarrow Br + 2O_2$

$\Delta H° = -156$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<8 \times 10^{-14}$	293	Clyne and Cruse, 1970[1]	(a)
$<4 \times 10^{-15}$	298	Sander and Watson, 1981[2]	(b)
Reviews and Evaluations			
$<5 \times 10^{-15}$	298	CODATA, 1980[3]; IUPAC, 1989[4]	(c)
$<5 \times 10^{-15}$	298	NASA, 1990[5]	(d)

Comments

(a) Discharge flow system with UV absorption detection of BrO and O_3.
(b) Flash photolysis system with UV absorption detection of BrO and O_3. Upper limit was placed on k by monitoring $\Delta[O_3]$ as a function of $[BrO]_0$ in presence of a large excess concentration of O_3.
(c) See Comments on Preferred Values.
(d) Based on data of Sander and Watson.[2]

Preferred Values

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[3] The upper limit is based on results reported by Sander and Watson.[2] There is no evidence for this reaction. The analogous ClO reaction has a rate constant of $<10^{-18}$ cm^3 molecule^{-1} s^{-1}.

References

[1]M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2214 (1970).
[2]S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).
[3]CODATA, 1980 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]NASA Evaluation No. 9, 1990 (see references in Introduction).

$BrO + NO \rightarrow Br + NO_2$

$\Delta H° = -70$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.8) \times 10^{-12}$	293	Clyne and Cruse, 1970[1]	(a)
$(2.2 \pm 0.4) \times 10^{-11}$	298	Clyne and Watson, 1975[2]	(b)
$(2.2 \pm 0.2) \times 10^{-11}$	298	Ray and Watson, 1981[3]	(b)
$1.28 \times 10^{-11} \exp(181/T)$	224–398	Watson, Sander, and Yung, 1979[4]	(c)
$(2.15 \pm 0.25) \times 10^{-11}$	298		
$7.11 \times 10^{-12} \exp(296/T)$	230–425	Leu, 1979[5]	(b)
$(1.89 \pm 0.16) \times 10^{-11}$	298		
Reviews and Evaluations			
$8.7 \times 10^{-12} \exp(260/T)$	224–425	CODATA, 1980[6]; IUPAC, 1989[7]	(d)
$8.8 \times 10^{-12} \exp(260/T)$	200–300	NASA, 1990[8]	(e)

Comments

(a) Discharge flow system with UV absorption detection of BrO.
(b) Discharge flow system with MS detection of BrO.
(c) Flash photolysis system with UV absorption detection of BrO.
(d) See Comments on Preferred Values.
(e) Based on data of Clyne and Watson,[2] Ray and Watson,[3] Watson et al.[4] and Leu.[5]

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.7 \times 10^{-12} \exp(260/T)$ cm^3 molecule^{-1} s^{-1} over the range 224–425 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1980.[6] The results of the three low pressure mass spectrometric studies[2,3,5] and the high pressure UV absorption study,[4] which all used pseudo-first-order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse.[1] The results of the two temperature dependence studies[4,5] are in good agreement. The preferred Arrhenius expression was derived from a least-squares fit to all the data in Refs. 2–5. By combining the data reported in the high pressure UV absorption study[4] with those from the mass spectrometric studies,[2,3,5] it can be shown that this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependences of the rate coefficient for the analogous ClO and HO_2 reactions are also negative and similar in magnitude.

References

[1]M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **66**, 2227 (1970).
[2]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **71**, 336 (1975).
[3]G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[4]R. T. Watson, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **83**, 2936 (1979).
[5]M. T. Leu, Chem. Phys. Lett. **61**, 275 (1979).
[6]CODATA, 1980 (see references in Introduction).
[7]IUPAC, Supplement III, 1989 (see references in Introduction).
[8]NASA Evaluation No. 9, 1990 (see references in Introduction).

$BrO + NO_2 + M \rightarrow BrONO_2 + M$

$\Delta H^\circ = -111$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.0) \times 10^{-31}$ [N_2]	298	Sander, Ray, and Watson, 1981[1]	(a)
$(4.2 \pm 0.8) \times 10^{-31}(T/298)^{-2.0}$ [O_2]	263–343	Danis *et al.*, 1990[2]	(b)
$5.7 \times 10^{-31}(T/298)^{-3.1}$ [N_2]	251–346	Thorn, Daykin, and Wine, 1991[3]	(c)
Reviews and Evaluations			
$5.0 \times 10^{-31}(T/300)^{-3.0}$ [N_2]	200–300	CODATA, 1982[4]; IUPAC, 1989[5]	(d)
$5.2 \times 10^{-31}(T/300)^{-3.8}$ [air]	200–300	NASA, 1990[6]	(e)

Comments

(a) Two independent studies conducted, one using a discharge flow MS technique for pressures 1–6 Torr, the other using a flash photolysis-UV absorption technique for pressures 50–700 Torr. BrO was formed by the reaction $Br + O_3 \rightarrow BrO + O_2$. A major part of the falloff curve was observed and analyzed with $F_c = 0.4$ at 298 K.
(b) BrO was generated by laser photolysis of O_3 at 248 nm in the presence of Br_2 and monitored by time-resolved MS. Rate coefficients were measured at total pressures below 12 Torr. Falloff curves were extrapolated using $F_c = \exp(-T/325)$.
(c) BrO produced by laser flash photolysis at 351 nm of NO_2–Br_2–N_2 mixtures and monitored by long-path (550 cm) absorption at 338 nm. Pressure range = 16–800 Torr.
(d) Based on Ref. 1. The temperature coefficient was estimated by analogy with the $ClO + NO_2$ reaction.
(e) Mainly based on Ref. 1.

Preferred Values

$k_0 = 4.7 \times 10^{-31}(T/300)^{-3.1}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values represent an average[3] of the data from Refs. 1–3, with falloff extrapolations based on $F_c = \exp(-T/327)$.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2^{+0.5}_{-1.0}) \times 10^{-11}$	298	Sander, Ray, and Watson, 1981[1]	(a)
$(2.0 \pm 1.0) \times 10^{-11}(T/298)^{-1}$	263–343	Danis *et al.*, 1990[2]	(b)
$1.8 \times 10^{-11}(T/298)^{-0.6}$	251–346	Thorn, Daykin, and Wine, 1991[3]	(c)
Reviews and Evaluations			
2×10^{-11}	200–300	CODATA, 1982[4]; IUPAC, 1989[5]	(d)
$9.0 \times 10^{-12}(T/300)^{-2.5}$	200–300	NASA, 1990[6]	(e)

Comments

(a)– (c) See Comments (a)– (c) for k_0.
(d) Estimated by analogy with the $ClO + NO_2$ reaction.
(e) Based on Refs. 1 and 3.

Preferred Values

$k_\infty = 1.7 \times 10^{-11}(T/298)^{-0.6}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See comment on k_0. A temperature independent value of k_∞, such as generally adopted in this evaluation, would also be compatible with the available data.

References

[1]S. P. Sander, G. W. Ray, and R. T. Watson, J. Phys. Chem. **85**, 199 (1981).
[2]F. Danis, F. Caralp, J. Masanet, and R. Lesclaux, Chem. Phys. Lett. **167**, 450 (1990).
[3]R. P. Thorn, E. P. Daykin, and P. H. Wine, Int. J. Chem. Kinet., in press.
[4]CODATA, Supplement I, 1982 (see references in Introduction).
[5]IUPAC. Supplement III, 1989 (see references in Introduction).
[6]NASA Evaluation No. 9, 1990 (see references in Introduction).

$$BrO + ClO \rightarrow Br + OClO \quad (1)$$
$$\rightarrow Br + ClOO \quad (2)$$
$$\rightarrow BrCl + O_2 \quad (3)$$

$\Delta H°(1) = -14$ kJ·mol^{-1}
$\Delta H°(2) = -18$ kJ·mol^{-1}
$\Delta H°(3) = -212$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.13 \pm 0.15) \times 10^{-11}$	298	Poulet *et al.*, 1990[1]	(a)
$2.59 \times 10^{-12} \exp[(445 \pm 50)/T]$	234–406	Turnipseed, Birks, and Calvert, 1991[2]	(b)
$(1.08 \pm 0.20) \times 10^{-11}$	304		
Branching Ratios			
$k_1/k = 0.43 \pm 0.10$	298	Poulet *et al.*, 1990[1]	(a)
$k_3/k = 0.12 \pm 0.05$	298		
$k_1/k = 0.51 \pm 0.09$	250	Turnipseed, Birks, and Calvert, 1991[2]	(b)
$k_2/k = 0.36 \pm 0.07$	250		
$k_3/k = 0.10 \pm 0.02$	250		
$k_1/k = 0.48 \pm 0.07$	304		
$k_2/k = 0.46 \pm 0.09$	304		
$k_3/k = 0.09 \pm 0.02$	304		
$k_1/k = 0.39 \pm 0.07$	406		
$k_2/k = 0.52 \pm 0.11$	406		
$k_3/k = 0.09 \pm 0.02$	406		
Reviews and Evaluations			
$k_1 = 1.9 \times 10^{-12} \exp(390/T)$	200–400	IUPAC, 1989[3]	(c)
$(k_2 + k_3) = 3.9 \times 10^{-12} \exp(140/T)$	200–400		
$k_1 = 1.6 \times 10^{-12} \exp(430/T)$	220–400	NASA, 1990[4]	(d)
$k_2 = 2.9 \times 10^{-12} \exp(220/T)$	220–400		
$k_3 = 5.8 \times 10^{-13} \exp(170/T)$	220–400		

Comments

(a) Discharge flow system with MS detection of BrO, ClO, OClO, and BrCl. Pseudo-first-order decays of BrO were monitored in the presence of excess ClO. ClO was produced by Cl + OClO; BrO by Br + O_3.

(b) Discharge flow system with MS detection of BrO, ClO, OClO, and BrCl. Pseudo-first-order decays of BrO were monitored in the presence of excess ClO. ClO produced by Cl + O_3 or Cl + Cl_2O; BrO by O + Br_2 or Br + O_3.

(c) Based on the room temperature results of Clyne and Watson[5] and Toohey and Anderson[6] and the temperature dependent data of Sander and Friedl[7] and Friedl and Sander.[8]

(d) Accepted the Arrhenius expressions reported by Friedl and Sander[8] for the individual reaction channels, as supported by the data of Clyne and Watson,[5] Toohey and Anderson,[6] Sander and Friedl[7] and Poulet *et al.*[1]

Preferred Values

$k_1 = 6.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 6.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 1.6 \times 10^{-12} \exp(430/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.
$k_2 = 2.9 \times 10^{-12} \exp(220/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.
$k_3 = 5.8 \times 10^{-13} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.1$ at 298 K.
$\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200$ K.

Comments on Preferred Values

In recent years there has been a substantial improvement in the data-base for this rate coefficient. Friedl and Sander,[8] using discharge flow-mass spectrometry techniques, measured the overall rate constant over the temperature range 220–400 K and also over this temperature range determined directly the branching ratios for the reaction channels producing BrCl and OClO. In a separate study the same authors, using flash photolysis-ultraviolet absorption techniques,[7] determined the overall rate constant over the temperature range 220–400 K and pressure range 50–750 Torr and also determined the branching ratio for OClO production at 220 K and 298 K. The results by these two independent techniques[7,8] are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Toohey and Anderson,[6] using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate constant and the branching ratio for OClO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state.[6] Poulet *et al.*,[1] using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate constant and branching ratios for OClO and BrCl production.

All the above-mentioned results[1,6–8] are in reasonably good agreement. Hills *et al.*,[9] using a discharge flow-mass spectrometry technique, obtained an overall rate constant which was independent of temperature over the range 241–308 K and substantially lower than the room temperature average of the above mentioned studies; they also reported no BrCl production. Room temperature overall rate constant values reported also include that from the discharge flow-mass spectrometry study of Clyne and Watson[5] and the very low value derived in the flash photolysis study of Basco and Dogra[10] using a different interpretation of the reaction mechanism.

The recommended Arrhenius expressions for the individual reaction channels are taken from the study of Friedl and Sander.[8] This study and the recent study of Turnipseed *et al.*[2] contain the most comprehensive sets of rate coefficient and branching ratio data. The overall rate coefficients reported in these two studies are in good agreement (within 20%) at room temperature and are in excellent agreement at stratospheric temperatures. Both of these studies, as well as that of Sander and Friedl,[7] show that OClO production by channel (1) becomes dominant at very low temperature. Both studies show an ~8% yield of BrCl by channel (3). The recommended expressions are consistent with the body of data from all studies, except those of Refs. 9 and 10.

References

[1] G. Poulet, I. T. Lancar, G. Laverdet, and G. Le Bras, J. Phys. Chem. **94**, 278 (1990).

[2] A. A. Turnipseed, J. W. Birks, and J. G. Calvert, J. Phys. Chem. **95**, 4356 (1991).

[3] IUPAC, Supplement III, 1989 (see references in Introduction).

[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

[5] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, **73**, 1169 (1977).

[6] D. W. Toohey and J. G. Anderson, J. Phys. Chem. **92**, 1705 (1988).

[7] S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).

[8] R. R. Friedl and S. P. Sander, J. Phys. Chem. **93**, 4756 (1989).

[9] A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, J. Phys. Chem. **92**, 1853 (1988).

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$$BrO + BrO \rightarrow 2Br + O_2 \quad (1)$$
$$\rightarrow Br_2 + O_2 \quad (2)$$

$\Delta H°(1) = -26$ kJ·mol^{-1}
$\Delta H°(2) = -219$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.06 \times 10^{-12} \exp[(251 \pm 56)/T]$	253–400	Turnipseed, Birks, and Calvert, 1990[1]	(a)
$(2.45 \pm 0.26) \times 10^{-12}$	304		
$k_2 = (2.9 \pm 1.0) \times 10^{-13}$	304		
$(3.2 \pm 0.5) \times 10^{-12}$	298	Lancar *et al.*, 1991[2]	(b)
$k_2 = (4.7 \pm 1.5) \times 10^{-13}$	298		
Reviews and Evaluations			
$1.1 \times 10^{-12} \exp(255/T)$	223–398	IUPAC, 1989[3]	(c)
$k_1 = 2.2 \times 10^{-12}$	298		
$k_2 = 4.5 \times 10^{-13}$	298		
$k_1 = 1.4 \times 10^{-12} \exp(150/T)$	200–300	NASA, 1990[4]	(d)
$k_2 = 6.0 \times 10^{-14} \exp(600/T)$	200–300		

Comments

(a) Discharge flow system with MS detection of BrO. Two sources of BrO were used: O + Br_2 and Br + O_3. The Arrhenius expression given above is a fit to results using the first source. Results using the second source of BrO were in good agreement at 304 K and at 400 K but were significantly higher at 253 K; interpreted by authors as possibly due to BrO·O_3 adduct formation or to vibrationally or spin-orbit excited BrO radicals which were not quenched efficiently at low temperatures. A branching ratio of $k_2/k = 0.12 \pm 0.04$ was derived using the second source with excess ozone.

(b) Discharge flow system with MS detection of BrO. For measurement of k, BrO was generated by O + Br_2 reaction; for measurement of k_2, BrO was generated by Br + O_3 reaction in excess O_3.

(c) Overall rate constant based on room temperature results of Sander and Watson[5] and Clyne and Watson[6] and the temperature dependence reported by Sander and Watson.[5] Branching ratio k_1/k at room temperature based on results of Sander and Watson,[5] Cox *et al.*[7] and Jaffe and Mainquist.[8]

(d) Based on results of Sander and Watson[5] and Clyne and Watson.[6] Branching ratio as a function of temperature was derived on basis of results of Cox *et al.*[7] and Jaffe and Mainquist.[8] These data were used to derive temperature dependent expressions for the individual reaction channels. The uncertainties in E/R cover possible temperature-independent rate coefficients for either or both channels.

Preferred Values

$k_1 = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 4.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-12} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 223–400 K.

Reliability

$\Delta \log k_1 = \pm 0.1$ at 298 K.
$\Delta \log k_2 = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The data base for this reaction has been improved since the previous evaluation.[3] The temperature dependence of k reported in the new study of Turnipseed *et al.*[1] is in very good agreement with that reported by Sander and Watson.[5] The value of the branching ratio at room temperature is well established with $k_1/k = 0.84 \pm 0.03$ based on results of Refs. 1, 2, 5, 6 and 7. However, the temperature dependence of the branching ratio has been investigated in only two studies (Refs. 7 and 8), both quantum yield studies, and the temperature dependence was not in good agreement.

The preferred Arrhenius expression for the overall rate coefficient is based on a fit to the temperature dependent data of Turnipseed *et al.*[1] and Sander and Watson[5] and the room temperature data of Clyne and Watson[6] and Lancar *et al.*[2] The uncertainty in (E/R) is reduced from our previous evaluation[3] on the basis of the very good agreement of the two temperature dependent studies.[1,5] The preferred values for the two channels at 298 K are based on the preferred value of k at 298 K and the ratio $k_1/k = 0.84$. In view of the uncertainties noted above, no recommendation is given for the temperature dependence of the individual channels.

References

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[2]I. T. Lancar, G. Laverdet, G. Le Bras, and G. Poulet, Int. J. Chem. Kinet. 23, 37 (1991).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]NASA Evaluation No. 9, 1990 (see references in Introduction).
[5]S. P. Sander and R. T. Watson, J. Phys. Chem. 85, 4000 (1981).
[6]M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1, 71, 336 (1975).
[7]R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. 19, 189 (1982).
[8]S. Jaffe and W. K. Mainquist, J. Phys. Chem. 84, 3277 (1980).

HOBr + $h\nu$ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HOBr + $h\nu$ → HO + Br	(1)	231	518
→ HBr + O(^{3}P)	(2)	293	409
→ BrO + H	(3)	423	283

Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[1] In the absence of experimental data for HOBr in the gas phase, it is suggested that the modelers use the absorption cross-section data for HOCl (see table of preferred values) red-shifted by 30 nm. Anbar and Dostrovski[2] reported aqueous phase spectra for both HOBr and HOCl. From those data, the values of σ_{max} were comparable, but the absorption maxima [HOCl (230 nm), HOBr (260 nm)] were displaced by 30 nm. By analogy with HOCl it is probable that ϕ_1 is unity for all wavelengths > 200 nm.

References

[1]CODATA, Supplement I, 1982 (see references in Introduction).
[2]M. Anbar and I. Dostrovski, J. Chem. Soc., London, Part I, 1105 (1954).

BrO + $h\nu$ → products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
BrO + $h\nu$ → Br + O(^{3}P)	(1)	232	515
→ Br + O(^{1}D)	(2)	422	283

Preferred Values

Absorption cross-sections of BrO averaged over 5 nm intervals

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
300–305	200	340–345	515
305–310	259	345–350	399
310–315	454	350–355	228
315–320	391	355–360	172
320–325	600	360–365	161
325–330	753	365–370	92
330–335	628	370–375	51
335–340	589		

Comments on Preferred Values

The BrO radical has a banded absorption spectrum in the 290–380 nm range. The absorption cross-section values at the band peaks are dependent on temperature and spectral resolution. The band locations, vibrational level assignments, and absorption cross-section values at 0.4 nm resolution are reported by Wahner *et al.*[1] The strongest absorption feature is the (7,0) band at 338.5 nm; the cross-section for 0.18 nm resolution was determined to be $(1.71 \pm 0.14) \times 10^{-17}$ cm^2 at 298 K and $(2.21 \pm 0.16) \times 10^{-17}$ cm^2 at 223 K.[1]

The preferred values given here are the averaged values over 5 nm intervals reported by Cox *et al.*[2]; in that paper the authors used these data to calculate a lifetime against solar photodissociation of 30 seconds for a solar zenith angle of 30 degrees. Earlier studies are discussed in previous evaluations.[3,4]

References

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[2]R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).
[3]CODATA, 1980 (see references in Introduction).
[4]CODATA, Supplement II, 1984 (see references in Introduction).

$BrONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$BrONO_2 + h\nu \rightarrow BrO + NO_2$ (1)	111	1080
$\rightarrow Br + NO_3$ (2)	129	930
$\rightarrow BrONO + O(^3P)$ (3)	306	390
$\rightarrow BrONO + O(^1D)$ (4)	496	240

Preferred Values

Absorption cross-sections for $BrONO_2$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.8

Quantum Yields

No recommendation is given for the relative importance of the possible pathways since there are no data which provide a basis for a recommendation.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[1] The recommended values are taken from Spencer and Rowland.[2] They are unchanged from those given in CODATA, 1980,[3] where a detailed discussion can be found.

References

[1]CODATA, Supplement I, 1982 (see references in Introduction).
[2]J. E. Spencer and F. S. Rowland, J. Phys. Chem. **82**, 7 (1978).
[3]CODATA, 1980 (see references in Introduction).

$CH_3Br + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3Br + h\nu \rightarrow CH_3 + Br$	295	405

Preferred Values

Absorption cross-sections for CH_3Br photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	44	230	15
2	53	2	12
4	62	4	9.9
6	69	6	7.6
8	76	8	5.9
200	79	240	4.5
2	80	2	3.3
4	79	4	2.5
6	77	6	1.8
8	73	8	1.3
210	67	250	0.96
2	61	2	0.69
4	56	4	0.49
6	49	6	0.34
8	44	8	0.23
220	38	260	0.16
2	32		
4	28		
6	23		
8	19		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Gillotay and Simon.[1] Molina *et al*.[2] reported values at 5 nm intervals, and Robbins[3] reported values at 2 nm intervals. The agreement among these three studies over the wavelength range of preferred values is very good. The temperature dependence down to 210 K has been reported in Ref. 1. At shorter wavelengths the cross-sections are independent of temperature, while at $\lambda > 210$ nm there is a decrease in absorption as the temperature is lowered. For values at low temperatures the reader is referred to the original reference.[1] Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield CH_3 + Br.

References

[1]D. Gillotay and P. C. Simon, Annales Geophysicae. **6**, 211 (1988).
[2]L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).
[3]D. E. Robbins, Geophys. Res. Lett. **3**, 213 (1976).

CF_3Br (Halon-1301) $+ h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_3Br + h\nu \rightarrow CF_3 + Br$	295	405

Preferred Values

Absorption cross-sections for CF_3Br photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	6.4	230	3.1
2	7.5	2	2.4
4	8.5	4	1.9
6	9.5	6	1.4
8	10.4	8	1.1
200	11.2	240	0.81
2	11.8	2	0.59
4	12.2	4	0.43
6	12.4	6	0.31
8	12.4	8	0.22
210	12.0	250	0.16
2	11.4	2	0.11
4	10.7	4	0.076
6	9.8	6	0.053
8	8.8	8	0.037
220	7.7	260	0.026
2	6.7	2	0.018
4	5.7	4	0.012
6	4.7	6	0.009
8	3.8	8	0.006

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] have also reported values at 5 nm intervals. The agreement among these three studies over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At λ > 220 nm both studies reported a decrease in absorption as the temperature is lowered. Near the absorption peak (~205 nm), Burkholder *et al.*[2] reported the cross-section to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature. For values at low temperatures, the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C−Br bond to yield CF_3 + Br. CF_3Br has no apparent tropospheric loss mechanism,[2] and is estimated to have a tropospheric lifetime against direct solar photoexcitation of greater than 1000 years.[3]

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).
[2]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[3]L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

CF_2ClBr (Halon–1211) + *hν* → products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
CF_2ClBr + *hν* → CF_2Cl + Br	281	426

Preferred Values

Absorption cross-sections for CF_2ClBr photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	47	240	18
2	58	2	15
4	70	4	12
6	83	6	10
8	96	8	8
200	112	250	6.5
2	118	2	5.1
4	121	4	4.0
6	122	6	3.2
8	121	8	2.4
210	117	260	1.9
2	112	2	1.4
4	106	4	1.1
6	98	6	0.84
8	90	8	0.63
220	81	270	0.48
2	72	2	0.36
4	64	4	0.27
6	56	6	0.20
8	49	8	0.15
230	42	280	0.11
2	36	2	0.079
4	31	4	0.058
6	26	6	0.043
8	22	8	0.031

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] have also reported values at 5 nm intervals, and Giolando *et al.*[4] reported values at 10 nm intervals. The agreement among these four studies over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At λ > 230 nm both studies reported a decrease in absorption as the temperature is lowered. Near the absorption peak (~205 nm), Burkholder *et al.*[2] reported the cross-section to be independent of temperature, while Gillotay and Simon[1] found the absorption to increase with decreasing temperature, reaching nearly a 20% increase at the lowest temperature. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Br bond to yield CF_2Cl + Br, and CF_2ClBr has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 15 to 20 years.[2]

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).
[2]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).
[3]L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).
[4]D. M. Giolando, G. B. Fazekas, W. D. Taylor, and G. A. Takacs, J. Photochem. **14**, 335 (1980).

CF_2Br_2 (Halon–1202) + $h\nu$ → products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Br_2 + h\nu \rightarrow CF_2Br + Br$	280 (est.)	430

Preferred Valu

Absorption cross-sections for CF_2Br_2 phot

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
190	114	250	59
2	109	2	47
4	100	4	37
6	91	6	29
8	82	8	23
200	75	260	18
2	72	2	13
4	74	4	10
6	81	6	7.6
8	93	8	5.7
210	110	270	4.2
2	136	2	3.1
4	155	4	2.2
6	180	6	1.6
8	203	8	1.2
220	224	280	0.89
2	242	2	0.65
4	251	4	0.48
6	253	6	0.34
8	250	8	0.24
230	241	290	0.18
2	227	2	0.13
4	209	4	0.096
6	189	6	0.068
8	168	8	0.050
240	147	300	0.036
2	125	2	0.026
4	106	4	0.019
6	88	6	0.014
8	73	8	0.010

Quantum Yields

ϕ = 1.0 throughout this wavelength rar

Comments on Preferred Values

The preferred values of the absorption cross-sectio at 298 K are the mean of the values reported by Gillot and Simon[1] and Burkholder *et al.*[2] Molina *et al.*[3] ha also reported values at 5 nm intervals. The agreeme among these three studies over the wavelength range preferred values is very good. The temperature depe dence down to 210 K has been reported in Refs. 1 and with fair agreement between the studies. At λ > 250 n both studies reported a decrease in absorption as t temperature is lowered. Near the absorption peak (~2 nm) both studies report an 11% increase in absorption the lowest temperature. For values at low temperatur the reader is referred to the original references.[1,2] It h been shown by Molina and Molina[4] that CF_2B photodissociates with unit quantum efficiency over t 200–300 nm region by breaking of the C–Br bond to yie CF_2Br + Br. Because its absorption extends into the 29 310 nm wavelength range, CF_2Br_2 has a short trop spheric lifetime against direct solar photoexcitation, a this has been estimated to be about 3 years.[2]

References

[1]D. Gillotay and P. C. Simon, J. Atmos. Chem. **8**, 41 (1989).

[2]J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McK een, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J Geophys. Res. **96**, 5025 (1991).

[3]L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 267 (1982).

[4]L. T. Molina and M. J. Molina, J. Phys. Chem. **87**, 1306 (1983).

$CHBr_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol⁻¹	$\lambda_{threshold}$/nm
$CHBr_3 + h\nu \rightarrow CHBr_2 + Br$	276	433

Preferred Values

Absorption cross-sections for $CHBr_3$ photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	399	250	174
2	360	2	158
4	351	4	136
6	366	6	116
8	393	8	99
200	416	260	83
2	433	2	69
4	440	4	57
6	445	6	47
8	451	8	38
210	468	270	31
2	493	2	25
4	524	4	20
6	553	6	16
8	574	8	12
220	582	280	9.9
2	578	2	7.8
4	558	4	6.1
6	527	6	4.8
8	487	8	3.7
230	441	290	2.9
2	397	2	2.2
4	362	4	1.7
6	324	6	1.3
8	295	8	0.96
240	273	300	0.72
2	253	2	0.54
4	234	4	0.40
6	214	6	0.30
8	194	8	0.22
		310	0.16

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Gillotay *et al.*,[1] which are the only published values. The temperature dependence down to 240 K was measured and values extrapolated to 210 K are given.[1] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Br bond to yield $CHBr_2$ + Br.

Reference

[1]D. Gillotay, A. Jenouvrier, B. Coquart, M. F. Merrienne, and P. C. Simon, Planet. Space Sci. **37**, 1127 (1989).

CF_2BrCF_2Br (Halon–2402) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CF_2BrCF_2Br + h\nu \rightarrow CF_2BrCF_2 + Br$	280 (est)	430

Preferred Values

Absorption cross-sections for CF_2BrCF_2Br photolysis at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	109	240	13
2	114	2	11
4	119	4	8.4
6	122	6	6.7
8	124	8	5.2
200	124	250	4.1
2	124	2	3.1
4	120	4	2.3
6	117	6	1.8
8	112	8	1.3
210	106	260	0.95
2	100	2	0.71
4	92	4	0.53
6	85	6	0.39
8	77	8	0.28
220	69	270	0.21
2	61	2	0.16
4	54	4	0.11
6	47	6	0.082
8	40	8	0.060
230	35	280	0.044
2	29		
4	24		
6	20		
8	16		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay *et al.*[1] and Burkholder *et al.*[2] Molina *et al.*[3] have also reported values at 5 nm intervals. The agreement among these three studies over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in references 1 and 2. The results differ qualitatively. For values at low temperatures the reader is referred to the original references.[1,2] Photolysis is expected to occur with unit quantum efficiency by breaking of the C–Br bond to yield CF_2BrCF_2 + Br, and CF_2BrCF_2Br has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 34 years.[2]

References

[1] D. Gillotay, P. C. Simon, and L. Dierickx, Aeronomica Acta **335**, 1 (1988).

[2] J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, J. Geophys. Res. **96**, 5025 (1991).

[3] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

4.9. Iodine Species

$O + I_2 \rightarrow IO + I$

$\Delta H^\circ = -98$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.38 \pm 0.44) \times 10^{-10}$	298	Ray and Watson, 1982[1]	(a)
Reviews and Evaluations			
1.4×10^{-10}	200–400	CODATA, 1984[2]; IUPAC, 1989[3]	(b)

Comments

(a) Discharge flow system with MS detection of I_2 in the presence of a large excess of O atoms. O(^{3}P) atom concentrations were determined by titration with NO_2. Total pressure = 2.0 Torr.

(b) See Comments on Preferred Values.

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

This data sheet is reproduced fron our previous evaluation, CODATA, 1984.[2] The recommended rate coefficient is consistent with the trend observed in the rate coefficients for the O + X_2 reaction, which increase steadily: $< 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} for X = F,[4] 4.2×10^{-14} cm^3 molecule^{-1} s^{-1} for X = Cl[5] and 1.4×10^{-11} cm^3 molecule^{-1} s^{-1} for X = Br (Ref. 3) at 298 K. The molecular beam study of Parrish and Herschbach[6] suggests a zero activation energy, consistent with the near gas kinetic value of k at 298 K.

References

[1]G. W. Ray and R. T. Watson, J. Phys. Chem. 85, 2955 (1981).
[2]CODATA, Supplement II, 1984 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).
[4]R. H. Krech, G. J. Diebold, and D. L. McFadden, J. Am. Chem. Soc. 99, 4605 (1977).
[5]R. T. Watson, J. Phys. Chem. Ref. Data 6, 871 (1977).
[6]D. D. Parrish and D. R. Herschbach, J. Am. Chem. Soc. 95, 6133 (1973).

$O + IO \rightarrow O_2 + I$

$\Delta H^\circ = -249$ kJ·mol^{-1}

Rate coefficient data

No experimental data available.

Preferred Value

$k = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of IO is similar to that of ClO and BrO (this is true in the case of XO + NO where X = F, Cl, Br and I). The recommended rate constants for ClO and BrO at ~298 K are 5×10^{-11} cm^3 molecule^{-1} s^{-1} and 3.8×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively.[1] The temperature dependence of the rate constant is expected to be small.

Reference

[1]IUPAC, Supplement III, 1989 (see references in Introduction).

$I + HO_2 \rightarrow HI + O_2$

$\Delta H^\circ = -95.6\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.47 \times 10^{-11} \exp(-1090/T)$	283–353	Jenkin *et al.*, 1990[1]	(a)
$(3.8 \pm 1.0) \times 10^{-13}$	298		

Comments

(a) Results using two techniques reported: discharge flow-EPR measurement of I(directly) and HO_2 after conversion to OH by reaction with NO. First order decay of HO_2 in excess I measured. This method gave $k = (3.1 \pm 1.2) \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K. The second method, which provided the temperature dependence, employed the molecular modulation technique with UV absorption detection of HO_2, and [I] determined from modulation of I_2 absorption at 500 nm. Excess I employed, but HO_2 self-reaction competed with I + HO_2. The best analysis gave $k = (4.17 \pm 0.4) \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K. The Arrhenius expression was obtained from the mean of the discharge flow and molecular modulation determinations at 298 K and the E/R from a least-squares fit to the temperature dependence data.

Preferred Values

$k = 3.8 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$ at 298 K.

$k = 1.5 \times 10^{-11} \exp(-1090/T)$ over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value is based on the two experimental studies reported by Jenkin *et al.*,[1] which are the only reported measurements for this reaction. The rate coefficients k at 298 K agree quite well although both studies exhibited significant experimental error. The Arrhenius expression suggested by Jenkin *et al.*[1] is accepted for the temperature dependence.

Reference

[1] M. E. Jenkin, R. A. Cox, A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **94**, 2927 (1990).

$I + O_3 \rightarrow IO + O_2$

$\Delta H^\circ = -142\ kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}\ s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.3 \times 10^{-11} \exp[-(886 \pm 15)/T]$	231–337	Buben *et al.*, 1990[1]	(a)
$(1.2 \pm 0.1) \times 10^{-12}$	298		
Reviews and Evaluations			
9.5×10^{-13}	298	IUPAC, 1989[2]	(b)

Comments

(a) Discharge flow system with resonance fluorescence detection of I.
(b) Based on the direct measurements of Jenkin and Cox[3] and Sander.[4]

Preferred Values

$k = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-11} \exp(-890/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The new data of Buben *et al.*[1] agree well with the two previous measurements of k at 298 K and provide the first measurement of the temperature dependence of this reaction. The preferred Arrhenius expression uses the activation energy from Buben *et al.*[1] with an A factor adjusted to give the mean value at 298 K from the three studies.[1,3,4]

References

[1]S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Khim. Fiz. **9**, 116 (1990).
[2]IUPAC, Supplement III, 1989 (see references in Introduction).
[3]M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[4]S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).

$I + NO + M \rightarrow INO + M$

$\Delta H° = -75.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 2.5) \times 10^{-33}(T/300)^{-1.0}$ [He]	320–450	Van den Bergh and Troe, 1976[1]	(a)
$(1.6 \pm 0.5) \times 10^{-32}$ [N_2]	330	Van den Bergh, Benoit-Guyot, and Troe, 1977[2]	(b)
$(9.5 \pm 3) \times 10^{-33}$ [Ar]	330		
$(10.3 \pm 0.6) \times 10^{-33}(T/300)^{-1.1}$ [Ar]	298–328	Basco and Hunt, 1978[3]	(c)
Reviews and Evaluations			
$1.8 \times 10^{-32}(T/300)^{-1.0}$ [N_2]	200–400	CODATA, 1982[4]	(d)

Comments

(a) Laser flash photolysis of I_2 at 694 nm in the presence of NO and He. He pressures were varied between 1 and 200 atm. I_2 and INO spectra observed.
(b) As in comment (a). The effect of 14 different bath gases was studied. The rate coefficient for M = Ar at 298 K was calculated from the measured rate coefficient at 330 K and the temperature coefficient reported by Ref. 1.
(c) Flash photolysis of I_2 in the presence of NO and Ar.
(d) Based on Refs. 1–3.

Preferred Values

$k_0 = 1.8 \times 10^{-32}(T/300)^{-1.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta \log k_0 = \pm 0.1$ at 300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, CODATA, 1982.[4] The rate coefficients for M = Ar determined in references 2 and 3 agree remarkably well. The collision efficiencies for He, Ar, and N_2 follow the usual trends. The transition to the high pressure limit is of no importance for pressures below 1 bar ($k_\infty = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K, $F_c = 0.75$ at 298 K, see Ref. 4).

References

[1]H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2]H. Van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 233 (1977).
[3]N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).
[4]CODATA, Supplement I, 1982 (see references in Introduction)

$I + NO_2 + M \rightarrow INO_2 + M$

$\Delta H^\circ = -79.8$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.52 \times 10^{-31}(T/300)^{-1}$ [He]	320–450	Van den Bergh and Troe, 1976[1]	(a)
2.60×10^{-31} [N_2]	330	Van den Bergh, Benoit-Guyot and Troe, 1977[2]	(b)
$(9.5 \pm 3.5) \times 10^{-32}$ [He]	298	Mellouki *et al.*, 1989[3]	(c)
3.1×10^{-31} [N_2]	298	Buben *et al.*, 1990[4]	(d)
Reviews and Evaluations			
$2.9 \times 10^{-31}(T/300)^{-1.0}$ [N_2]	200–300	CODATA, 1982[5]	(e)

Comments

(a) Derived from the NO_2 catalyzed recombination of iodine atoms, with iodine atoms being produced by laser flash photolysis at 694 nm. The falloff curve was measured from 1 to 200 atm of He, and only a short extrapolation to k_0 was required.

(b) As in comment (a). The efficiencies of 26 bath gases were studied.

(c) Discharge-flow system coupled to an EPR spectrometer to monitor I atom concentrations. Measurements were performed over the total pressure range 0.6–2.2 Torr.

(d) UV photolysis of CH_3I in a flow system with NO_2–N_2 mixtures, and I atoms were monitored by resonance fluorescence. The bath gases N_2, O_2, Ar, and He were studied at total pressures between 0.5 and 10 Torr.

(e) Based on the data of Refs. 1 and 2. The value for M = N_2 at 298 K was derived from the measurements at 330 K[2] and the temperature-dependence for M = He.[1] The value of n is assumed to be identical for He and N_2.

Preferred Values

$k_0 = 3.0 \times 10^{-31}(T/300)^{-1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from Refs. 1, 2 and 4. The data of Ref. 3 for M = He are also consistent with the data of Refs. 1, 2, and 4. Falloff extrapolations are made with a fitted[1] value of $F_c = 0.63$ near 300 K.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
6.6×10^{-11}	320–450	Van den Bergh and Troe, 1976[1]	(a)
Reviews and Evaluations			
6.6×10^{-11}	300–400	CODATA, 1982[5]	(b)

Comments

(a) See comment (a) for k_0. Only a short extrapolation of the falloff curve to the high pressure limit was required.
(b) See comment (e) for k_0.

Preferred Values

$k_\infty = 6.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability
$\Delta \log k = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values
See comments on k_0.

References

[1]H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2]H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 223 (1977).
[3]A. Mellouki, G. Laverdet, L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).
[4]S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Kinetika i Kataliz **31**, 973 (1990).
[5]CODATA, Supplement I, 1982 (see references in Introduction).

$HO + HI \rightarrow H_2O + I$

$\Delta H^\circ = -200$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.2) \times 10^{-11}$	298	Mac Leod *et al.*, 1990[1]	(a)
$(3.3 \pm 0.2) \times 10^{-11}$	298	Lancar, Mellouki, and Poulet, 1981[2]	(b)
Reviews and Evaluations			
1.3×10^{-11}	298	CODATA, 1982[3]; IUPAC, 1989[3]	(c)

Comments

(a) Laser photolysis of HNO_3 at 248 nm; HO detected by LIF.
(b) Discharge flow system used. HO radicals produced from the $H + NO_2$ reaction and detected by EPR.
(c) Based on the results of Takacs and Glass.[4]

Preferred Values

$k = 3.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values
The preferred value is based on the new results of Mac Leod *et al.*[1] and Lancar *et al.*[2], which are more than a factor of two higher than the earlier results of Takacs and Glass[4] on which the previous recommendation was based. The reliability of the latter study has been questioned since the rate coefficient for the HO + HBr reaction measured in the same system was a factor of 2.5 lower than other reliable literature values.

References

[1]H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **22**, 1167 (1990).
[2]I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).
[3]CODATA, Supplement I, 1982 (see references in Introduction).
[4]IUPAC, Supplement III, 1989 (see references in Introduction).
[5]G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).

$HO + I_2 \rightarrow HOI + I$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6^{+1.6}_{-0.8}) \times 10^{-10}$	298	Loewenstein and Anderson, 1985[1]	(a)
Relative Rate Coefficients			
$(2.1 \pm 1.0) \times 10^{-10}$	294	Jenkin, Clemitshaw, and Cox, 1984[2]	(b)
Reviews and Evaluations			
1.8×10^{-10}	298	IUPAC, 1989[3]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of HO. Reaction studied as a function of pressure and surface/volume. Interference from heterogeneous reactions experienced, but cited value of $k(I_2 + HO)$ represents homogeneous reaction and was independent of pressure over the ranges 0.56–5.9 Torr He and 0.51–7.75 Torr Ar.

(b) Steady state photolysis system. HO concentrations inferred from the rate of disappearance of C_2H_4, and determined as a function of I_2 concentration. The rate coefficient $k(I_2 + HO)$ was therefore measured relative to k(HO + ethene) and placed on an absolute basis by use of k(HO + ethene) = 8×10^{-12} cm^3 molecule^{-1} s^{-1}. Measurements made at 760 Torr.

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1989.[3] The two reported values agree well considering the quoted error limits. The preferred value is the mean of the two studies.

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **89**, 5371 (1985).
[2] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2, **80**, 1633 (1984).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).

$HO + CH_3I \rightarrow H_2O + CH_2I$

$\Delta H° = -65.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.1 \times 10^{-12} \exp[-(1119 \pm 204)/T]$	271–423	Brown, Canosa-Mas and Wayne, 1990[1]	(a)
$(7.2 \pm 0.7) \times 10^{-14}$	298		

Comments

(a) Discharge flow system with resonance fluorescence detection of HO.

Preferred Values

$k = 7.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.1 \times 10^{-12} \exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–430 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficients are based on the sole study of Brown *et al.*[1] The uncertainty limits in the preferred values take into account the significant error limits (30–50% except at 298 K) cited by Brown *et al.*[1]

Reference

[1] A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, Atmos. Environ. **24A**, 361 (1990).

$NO_3 + HI \rightarrow HNO_3 + I$

$\Delta H° = -119.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp[(-1830 \pm 300)/T]$	298–373	Lancar, Mellouki and Poulet, 1991[2]	(a)
$(2.5 \pm 0.8) \times 10^{-15}$	298		
Reviews and Evaluations			
2.5×10^{-15}	298	Wayne *et al.*, 1991[2]	(b)

Comments

(a) Discharge flow system used. NO_3 radicals were produced from the $F + HNO_3$ reaction and detected by MS after correction for interference at m/e = 62 due to HNO_3. Reaction was also followed by observation of I atom production using EPR spectrometry. Psuedo-first-order kinetics in the presence of excess HI, with an assessment of the effect of NO_2 production from secondary processes.

(b) Based on the results of Ref. 1.

Preferred Values

No recommendation.

Comments on Preferred Values

Although the rate coefficients measured in the single study[1] of this reaction from the decay of NO_3 using MS and I atom production using EPR spectrometry were in agreement, there is a serious potential for secondary chemistry occuring in the system leading to an overestimation of the rate coefficient for the elementary process. The authors state that the reaction of $I + NO_3 \rightarrow IO + NO_2$ does not occur,[1] while Chambers *et al.*[3] have established that this $I + NO_3$ reaction is extremely rapid, with a rate coefficient of $k(I + NO_3) = 4.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and that I atoms are regenerated from subsequent reactions of IO. While this uncertainty exists, no recommendation can be made.

References

[1]I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

[2]R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom, Atmos. Environ. **25A**, 1 (1991).

[3]R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem., **96**, 3321 (1992).

$IO + HO_2 \rightarrow HOI + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.4 \pm 0.7) \times 10^{-11}$	298	Jenkin *et al.*, 1990[1]	(a)

Comments

(a) Molecular modulation technique with UV absorption detection of HO_2 at 220 nm, and visible absorption detection of IO at 427 nm. Radicals produced by photolysis of O_3–CH_3OH–I_2–O_2–Ar mixtures at 254 nm with HO_2 in excess over IO. The rate coefficient k was derived from non-linear least-squares analysis of absorption waveforms.

Preferred Values

$k = 6.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the only experimental study of this reaction, in which the value of k seems reasonably well determined, although the chemical system was rather complex. The value of k at 298 K is a factor of 10 higher than that for the equivalent reaction with ClO and the single reported value for $BrO + HO_2$ but is consistent with the emerging reactivity pattern for the halogen oxide radicals. The temperature dependence is expected to be small.

Reference

[1]M. E. Jenkin and R. A. Cox, Chem. Phys Lett. **177**, 272 (1991).

$$IO + IO \rightarrow I_2 + O_2 \quad (1)$$
$$\rightarrow 2I + O_2 \quad (2)$$
$$\rightarrow I + OIO \quad (3)$$
$$IO + IO + M \rightarrow I_2O_2 + M \quad (4)$$

$\Delta H°(1) = -152$ kJ·mol^{-1}
$\Delta H°(2) = 0$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$[M])

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.8) \times 10^{-11}$	298	Barnes *et al.*, 1991[1]	(a)
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(1020/T)$	250–373	IUPAC, 1989[2]	(b)

Comments

(a) Discharge flow system with MS detection of IO using parent peak. Calibration by titration with NO and detection of NO_2 at $m/z = 46$. O + I_2 reaction used to produce IO. Pressure 0.5 − 6.8 mbar of He.
(b) Based on the measurements of Sander.[3]

Preferred Values

$k = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.7 \times 10^{-12} \exp(1020/T)$ over the temperature range 250–373 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value is unchanged from the previous evaluation.[2] The new data confirm that the pressure independence of the rate of this reaction, observed by Sander,[3] extends to low pressures as indicated by the less reliable results of Martin *et al.*[4] No new data relating to the branching ratios have been reported and therefore no recommendation can be made, as discussed in the previous evaluation.[2]

References

[1] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).
[2] IUPAC, Supplement III, 1989 (see references in Introduction).
[3] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
[4] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).

$$IO + NO \rightarrow I + NO_2$$

$\Delta H° = -57$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.8 \pm 0.2) \times 10^{-11}$	298	Inoue *et al.*, 1983[1]	(a)
$6.9 \times 10^{-12} \exp[(328 \pm 71)/T]$	242–359	Daykin and Wine, 1990[2]	(b)
$(2.17 \pm 0.22) \times 10^{-11}$	298		
$(2.15 \pm 0.30) \times 10^{-11}$	298	Buben *et al.*, 1991[3]	(c)
Reviews and Evaluations			
1.7×10^{-11}	298	CODATA, 1982[4]; IUPAC, 1989[5]	(d)

Comments

(a) Pulsed laser photolysis system with LIF detection of IO decay in the presence of excess NO. IO produced by the $O(^1D)$ + HI reaction.
(b) IO generated in 351 nm laser flash photolysis of NO_2–I_2–NO–N_2 mixtures and detected by longpath absorption spectroscopy. Pseudo-first order kinetics with a small correction for the contribution by the reaction IO + NO_2 + M → $IONO_2$ + M to the IO decay. No pressure dependence observed over the range 40–200 Torr N_2.
(c) Discharge flow system with resonance fluorescence detection of I.
(d) Based on the work of Ray and Watson.[6]

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.3 \times 10^{-12}\exp(330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability
$\Delta\log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values
The recent studies[2,3] give values of k at 298 K midway between those reported in earlier studies.[1,6] The work of Inoue *et al.*[1] was not included in previous evaluations,[4,5] which gave recommendations based on the data of Ray and Watson[6] only. The preferred value at 298 K is the mean of the values reported in Refs. 1, 2, 3 and 6. The temperature dependence measurements of Daykin and Wine[2] appear to be of excellent quality and provide the basis for the recommendation, which uses the preferred 298 K value with the E/R from Daykin and Wine.[2]

References

[1]G. Inoue, M. Suzuki, and N. Washida, J. Chem. Phys. **79**, 4730 (1983).
[2]E. P. Daykin and P. H. Wine, J. Phys. Chem. **94**, 4528 (1990).
[3]S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, in press (1991).
[4]CODATA, Supplement I, 1982 (see references in Introduction).
[5]IUPAC, Supplement III, 1989 (see references in Introduction).
[6]G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).

IO + NO_2 + M → $IONO_2$ + M

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3 \pm 2.0) \times 10^{-31}$ [N_2]	277	Jenkin and Cox, 1984[1]	(a)
$7.7 \times 10^{-31}(T/300)^{-5.0}$ [N_2]	254–354	Daykin and Wine, 1990[2]	(b)
Reviews and Evaluations			
$3.4 \times 10^{-31}(T/300)^{-3}$ [N_2]	200–400	CODATA, 1984[3]	(c)

Comments

(a) Molecular modulation system used. I_2 photolysis in the presence of O_3 was used to produce IO radicals. IO radicals were monitored by absorption at 427 nm in the presence of an excess of NO_2. The total pressure range was varied over the 35–404 Torr of N_2. The falloff curve was analyzed using $F_c = 0.4$ by analogy to the BrO + NO_2 reaction. A small correction was made for a second-order component in the IO kinetics at higher pressures.
(b) IO radicals were generated by the 351 nm laser flash photolysis of I_2–NO_2–N_2 mixtures and monitored by absorption at 427 nm. The association reaction was in the falloff regime over the temperature and pressure ranges (40–750 Torr of N_2) investigated. The data were extrapolated to the low- and high-pressure rate coefficients using $F_c = 0.4$.
(c) Based on Ref. 1 and assuming a temperature dependence of T^{-3} by analogy to the ClO + NO reaction.

Preferred Values

$k_0 = 7.7 \times 10^{-31}(T/300)^{-5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability
$\Delta\log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 2$.

Comments on Preferred Values
The data from Ref. 2 are recommended because perturbations from wall reactions and other processes were less of a problem than was the case in Ref. 1. Falloff extrapolations are made with $F_c = 0.4$.

High-pressure rate coefficients

Rate coefficients data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.6) \times 10^{-11}$	277	Jenkin and Cox, 1989[1]	(a)
1.55×10^{-11}	254–354	Daykin and Wine, 1990[2]	(b)
Reviews and Evaluations			
1.6×10^{-11}	200–400	CODATA, 1984[3]	(c)

Comments

(a) See comment (a) for k_0. The rate coefficient k_∞ was obtained from a fit of the falloff curve using $F_c = 0.4$.
(b) See comment (b) for k_0.
(c) Based on Ref. 1.

Preferred Values

$k_\infty = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–350 K.

Comments on Preferred Values

The preferred values are based on the data of Refs. 1 and 2. Falloff extrapolations are made with $F_c = 0.4$ at 300 K.

References

[1]M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).
[2]E. P. Daykin and P. H. Wine, J. Phys. Chem. **94**, 4528 (1990).
[3]CODATA Supplement II, 1984 (see references in Introduction).

$IO + CH_3SCH_3 \rightarrow I + CH_3SOCH_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3.5 \times 10^{-14}$	298	Daykin and Wine, 1990[1]	(a)
$(1.5 \pm 0.2) \times 10^{-14}$	298	Maguin *et al.*, 1991[2]	(b)
$(8.8 \pm 2.1) \times 10^{-15}$	296	Barnes *et al.*, 1991[3]	(c)

Comments

(a) IO generated in 351 nm laser flash photolysis of NO_2–I_2–CH_3SCH_3–N_2–O_2 mixtures and detected by long path absorption spectroscopy. Only a weak dependence of first-order decay rate on [DMS] observed, allowing only an upper limit for k to be determined.
(b) Discharge flow system with MS technique at <2 Torr total pressure. IO generated from microwave discharge of O_2 in the presence of I_2. Pseudo-first order conditions with DMS in excess over IO. Small correction applied for the IO self-reaction using a value of $k(IO + IO) = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. DMSO observed as product; <5% HOI formed.
(c) Same technique as (b); correction for IO self reaction using a value of $k(IO + IO) = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} as determined in the same apparatus. CH_3SOCH_3 yield was 84 ± 40%.

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Value

The new studies[1-3] all show that the rate of this reaction is at least 2 orders of magnitude slower than suggested by earlier studies,[4,5] which were clearly in error due to experimental difficulties associated with high radical concentrations and surface reactions. The preferred value is based on the results of Maguin *et al.*[2] and Barnes *et al.*[3] The large uncertainty limit reflects the need to correct the kinetic decays for minor competing processes.

References

[1]E. P. Daykin and P. H. Wine, J. Geophys. Res. 95, 18547 (1990).
[2]F. Maguin, A. Mellouki, G. Laverdet, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. 23, 237 (1991).
[3]I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. 23, 579 (1991).
[4]I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, Int. J. Chem. Kinet. 19, 489 (1987).
[5]D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. 19, 503 (1987).

$INO + INO \rightarrow I_2 + 2NO$

$\Delta H^\circ = 0.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<6.7 \times 10^{-14}$	333	Porter, Szabo and Townsend, 1962[1]	(a)
$8.4 \times 10^{-11} \exp(-2620/T)$	320–450	Van den Bergh and Troe, 1976[2]	(b)
1.3×10^{-14}	298*		
$2.9 \times 10^{-12} \exp(-1320/T)$	298–328	Basco and Hunt, 1978[3]	(c)
3.4×10^{-14}	298		
Reviews and Evaluations			
$8.4 \times 10^{-11} \exp(-2620/T)$	300–450	CODATA, 1982[4]; IUPAC, 1989[5]	(d)

Comments

(a) Flash photolysis of I_2 in the presence of NO. Although the observations were interpreted with inadequate assumptions about the mechanism, the results on the reaction INO + INO are consistent with later work (see Ref. 3).
(b) Laser flash photolysis of I_2 in the presence of NO. Analysis of the time-resolved I_2 absorption signals after the flash.
(c) Flash photolysis of I_2 in the presence of NO. Measurements of the UV spectrum of INO.
(d) See Comments on Preferred Values.

Preferred Value

$k = 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.4 \times 10^{-11} \exp(-2620/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–450 K.

Reliability
$\Delta \log k = \pm 0.4$ at 298 K.
$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values
This data sheet is reproduced from our previous evaluation, CODATA, 1982.[4] The results from Ref. 2 are preferred over those from Ref. 3 because of a much wider range of conditions studied.

References

[1]G. Porter, Z. G. Szabo, and M. G. Townsend, Proc. Roy. Soc. A270, 493 (1962).
[2]H. Van den Bergh and J. Troe, J. Chem. Phys. 64, 736 (1976).
[3]N. Basco and J. E. Hunt, Int. J. Chem. Kinet. 10, 733 (1978).
[4]CODATA, Supplement I, 1982 (see referencess in Introduction).
[5]IUPAC, Supplement III, 1989 (see referencess in Introduction).

$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$

$\Delta H° = 8.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.7×10^{-14}	350	Van den Bergh and Troe, 1976[1]	(a)
Reviews and Evaluations			
$2.9 \times 10^{-11} \exp(-2600/T)$	298–400	CODATA, 1982[2]; IUPAC, 1989[3]	(b)

Comments

(a) From the NO_2 catalyzed recombination of iodine atoms, with I atoms being produced by laser flash photolysis of I_2. Temperature dependence probably similar to that for the INO + INO reaction.

Preferred Values

$k = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.9 \times 10^{-11} \exp(-2600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 298–400 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values
This data sheet is reproduced from our earlier evaluation, CODATA, 1982.[2] The preferred value is based on the measured rate constant at 350 K and an assumed value for E/R equal to that for the reaction INO + INO $\rightarrow I_2$ + 2NO. In the analogous reactions for other halogens this behavior appears to apply (see Ref. 1).

References

[1]H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2]CODATA, Supplement I, 1982 (see references in Introduction).
[3]IUPAC, Supplement III, 1989 (see references in Introduction).

HOI + $h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HOI + $h\nu \rightarrow$ HO + I	(1)		
$\rightarrow$ HI + O(^{3}P)	(2)		
$\rightarrow$ IO + H	(3)		
$\rightarrow$ HI + O(^{1}D)	(4)		

Note: There are no thermodynamic data for HOI.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
300–475	Jenkin, 1991[1]	(a)

Quantum Yield Data
There are no reported quantum yield data.

Comments

(a) The absorption spectrum of a short-lived product of the 254 nm modulated photolysis of H_2O_2–I_2–N_2 mixtures was assigned to HOI. The spectrum showed maxima at 335 nm and 410 nm. Absolute cross-sections were based on the loss of I_2, measured by absorption at 500 nm and assuming quantitative conversion to HOI. Evidence was found to support this assumption. Table of cross-sections averaged over 5 nm intervals was given.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm²	λ/nm	10^{20} σ/cm²
300–305	0.02	385–390	11.8
305–310	3.29	390–395	14.0
310–315	5.80	395–400	16.7
315–320	9.10	400–405	20.0
320–325	12.9	405–410	22.8
325–330	17.0	410–415	23.3
330–335	20.6	415–420	21.9
335–340	21.4	420–425	19.2
340–345	19.5	425–430	16.2
345–350	16.7	430–435	13.5
350–355	14.3	435–440	11.0
355–360	12.4	440–445	9.10
360–365	11.0	445–450	7.50
365–370	10.2	450–455	5.80
370–375	9.90	455–460	4.11
375–380	9.90	460–465	2.47
380–385	10.4	465–470	1.10
		470–475	0.28

Quantum Yields

No recommendation. Reaction (1) is the most likely pathway for photolysis in the lower atmosphere.

Comments on Preferred Values

The recommended values for the cross-sections are those given by Jenkin,[1] which are the only available data for the gas phase. Confirmation of these data are required.

Reference

[1]M. E. Jenkin, Ph.D Thesis, University of East Anglia (1991).

IO + $h\nu$ → products

Primary photochemical processes

Reactions		ΔH°_{298}/kJ·mol⁻¹	$\lambda_{threshold}$/nm
IO + $h\nu$ → I + O(^{3}P)	(1)	249	480
→ I + O(^{1}D)	(2)	439	270

Preferred Values

Absorption cross-sections

λ/nm	10^{18} σ/cm²	λ/nm	10^{18} σ/cm²
415–420	8.4	445–450	14.1
420–425	9.3	450–455	4.0
425–430	16.4	455–460	10.0
430–435	2.9	460–465	4.2
435–440	10.2	465–470	2.8
440–445	3.1		

Temperature dependence of the IO absorption cross-section at 427.2 nm

Temp./K	10^{17} σ/cm²
250	5.3 ± 0.5
273	4.3 ± 0.4
298	3.1 ± 0.3
317	2.3 ± 0.2
341	2.3 ± 0.2
373	2.1 ± 0.2

Comments on Prefered Values

Sander,[1] Stickel *et al.*[2] and Cox and Coker[3] all report the same value of $\sigma = 3.1 \times 10^{-17}$ cm^2 molecule^{-1} for the 4–0 band at a resolution of 0.27 nm or less. The preferred absorption cross-sections at 298 K are based on this value.

The preferred values, which are averaged over 5 nm intervals, are based on the data reported by Cox and Coker.[3] Stickel *et al.*[2] pointed out an error in Table II of Ref. 3 where the listed σ values averaged over 5 nm are a factor of 10 higher than the true values based on the data plotted in Figure 1 of that work. The atmospheric photolysis rate calculated from the tabulated data for a solar zenith angle of 40° (i.e., 0.3 s^{-1}) is consequently a factor of 10 too high. Stickel *et al.*[2] do not present averaged cross-section data, so it is not possible to utilize their measurements over the whole spectral range.

Sander[1] reported cross-sections at the head of the 4–0 band measured at six temperatures in the range 250–373 K. A strong temperature dependence is apparent at temperatures < 317 K, with σ increasing with decreasing temperature.

No recommendation is given for the quantum yield. Durie and Ramsay[4] report extensive predissociation in the A–X progression of IO; therefore the quantum yield for process (1) is probably unity throughout the wavelength region of the preferred σ values.

The preferred values are unchanged from our previous evaluation.[5]

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[5]IUPAC, Supplement III, 1989 (see referencess in Introduction).

INO + $h\nu$ → products

Primary photochemical transitions

Reactions	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
INO + $h\nu$ → I + NO	72	1650

Absorption cross-section data

Wavelength range/nm	Reference	Comments
360–460	Porter, Szabo and Townsend, 1962[1]	(a)
360–460, 220–320	Van den Bergh and Troe, 1976[2]	(b)
360–400, 220–320	Basco and Hunt, 1978[3]	(c)
360–460, 220–320	Forte, Hippler, and Van den Bergh, 1981[4]	(d)

Quantum Yield Data

No data are available.

Comments

(a) Flash photolysis of I_2 in the presence of NO. Inadequate interpretation of the mechanism, and the cited values are therefore uncertain.

(b) Laser flash photolysis of I_2 in the presence of NO. Values have been confirmed by later work of Refs. 3 and 4.

(c) Flash photolysis of I_2 in the presence of NO. Values derived from an analysis of the mechanism.

(d) Spectroscopic investigation of the I_2 + 2NO → 2INO equilibrium. The results are in very good agreement with Refs. 2 and 3.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{17} σ/cm^2	λ/nm	10^{17} σ/cm^2
230	1.4	380	0.065
235	5.3	390	0.078
238	7.0	400	0.92
245	6.5	410	1.10
251	5.9	420	0.10
260	2.4	430	0.094
270	1.0	440	0.080
300	0.09	450	0.060
360	0.045	460	0.040
370	0.059		

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[5] The values are the averages from the data of Refs. 2–4. The deviations between the results of these studies are only small. No quantum yield data are available. Presumably the photolysis quantum yield is unity over the whole wavelength range.

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[5]CODATA, Supplement I, 1982 (see references in Introduction).

$INO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$INO_2 + h\nu \rightarrow I + NO_2$	77	1560

Absorption cross-section data

No absorption spectrum has been detected to date, although the spectrum has been searched for in the NO_2-catalyzed recombination of iodine atoms.[1] It is presumed that $\sigma(INO_2) < \sigma(NO_2)$ over the wavelength range 250–600 nm.

References

[1]H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

$IONO_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$IONO_2 + h\nu \rightarrow IO + NO_2$	(1)		
$\rightarrow I + NO_3$	(2)		
$\rightarrow IONO + O(^3P)$	(3)		
$\rightarrow IONO + O(^1D)$	(4)		

Note: There are no thermodynamic data for $IONO_2$.

Absorption cross-section data

No experimental data are available.

Quantum yield data
No experimental data are available.

Preferred Values

Neither qualitative absorption spectra or absolute cross-sections have been measured for $IONO_2$. It is suggested that in the absence of experimental data the absorption cross-section data for $BrONO_2$ be used (this will probably lead to an underestimate of the $IONO_2$ photolysis rate J as the $IONO_2$ spectrum is expected to be red-shifted relative to the $BrONO_2$ spectrum by ~50 nm).

5. Appendix 1

Enthalpy Data*

Species	$\Delta H_f^\circ(298)$ kJ·mol^{-1}	$\Delta H_f^\circ(0)$ kJ·mol^{-1}	Reference
H	217.997	216.024	1
H_2	0	0	1
O	249.17	246.78	1
$O(^1D)$	438.9	436.6	2
O_2	0	0	1
$O_2(^1\Delta)$	94.3	94.3	2
$O_2(^1\Sigma)$	156.9	156.9	2
O_3	142.7	145.4	3
HO	39.3	39.0	4
HO_2	14.6		4
H_2O	−241.81	−238.92	1
H_2O_2	−136.32	−130.04	3
N	472.68	470.82	1
N_2	0	0	1
NH	352		55
NH_2	185.4	188.4	4
NH_3	−45.94	−38.95	1
NO	90.25	89.75	3
NO_2	33.2	36	3
NO_3	64.4		34
N_2O	82.05	85.50	3
N_2O_4	9.1	18.7	6
N_2O_5	5.0		34
HNO	99.6	102.5	6
HNO_2	−79.5	−74	3
HNO_3	−135.06	−125.27	3
HO_2NO_2	−57		10
CH	596.35		4
$CH_2(^3B_1)$	392.5		4
$CH_2(^1A_1)$	430.1		4
CH_3	146.0		51
CH_4	−74.81	−66.82	3
CN	435		4,6
HCN	135		6
HCO	37.2		4
CH_2O	−108.6	−104.7	2
CH_3O	17.6		4
CH_2OH	−25.9		4
CH_3OH	−201.6		7
CO	−110.53	−113.81	1
NCO	159		6
COOH	−223		4
HCOOH	−378.8	−371.6	7
CH_3O_2	10.4		38
CH_3OOH	−131		6
$HOCH_2O_2$	−162.1		38
CH_3ONO	−65.3		5
CH_3ONO_2	−119.7		5
$CH_3O_2NO_2$	−44		10
CO_2	−393.51	−393.14	1
C_2H	565		4
C_2H_2	228.0		7
C_2H_3	279.9		33
C_2H_4	52.2		7
C_2H_5	118.5		51
C_2H_6	−84.0		7
CH_2CN	244.8		4
CH_3CN	64.3		8
CH_2CO	−47.7		56
CH_3CO	−24.3		4
CH_2CHO	12.6		4
CH=CHOH	115		43

Enthalpy Data* – Continued

Species	$\Delta H_f^\circ(298)$ kJ·mol^{-1}	$\Delta H_f^\circ(0)$ kJ·mol^{-1}	Reference
CH_3CHO	−165.8		7,8
C_2H_5O	−17.2		4
C_2H_4OH	−34		5
CH_3CHOH	−63.6		4
C_2H_5OH	−234.8		7,8
$(CHO)_2$	−211.9		7,8
CH_3CO_2	−207.5		4
CH_3CO_2H	−432.04		7,8
$C_2H_5O_2$	−28.7		38
CH_3OOCH_3	−125.7		7,8
$CH_3C(O)O_2$	−172		38
C_2H_5ONO	−103.8		7,8
$C_2H_5ONO_2$	−154.0		7,8
$C_2H_5O_2NO_2$	−63.2		45
$CH_2{=}CHCH_2$	163.6		4
C_3H_6	20.2		7,8
n-C_3H_7	100.7		54
i-C_3H_7	89.0		51
C_3H_8	−104.5		7,8
CH_3COCH_2	−23.9		4
C_2H_5CHO	−187.4		7,8
CH_3COCH_3	−217.2		7,8
C_3H_6OH	−74		5
n-C_3H_7O	−41.4		4
i-C_3H_7O	−52.3		4
i-C_3H_7OH	−272.5		7,8
CH_3COCHO	−271.1		7,8
$C_3H_5O_2$	87.9		38
i-$C_3H_7O_2$	−68.9		38
n-$C_3H_7ONO_2$	−174.1		7,8
i-$C_3H_7ONO_2$	−190.8		7,8
$CH_3C(O)O_2NO_2$	−258		47
S	276.98	274.72	1
HS	143.0		29
H_2S	−20.63	−17.70	3
HSO	−4		23
SO	5.0	5.0	6
HSO_2	−222		25
SO_2	−296.81	−294.26	1
$HOSO_2$	−385		26
SO_3	−395.7	−390	3
HSNO	94		48
CH_3S	124.6		29
CH_3SH	−22.9		41
CH_3SCH_2	135.1		30
CH_3SCH_3	−38.1		30
CS	272	268	9
CH_3SO	−67		42
OCS	−142	142	3
S_2	128.49	128.20	1
CH_3SS	68		9
CH_3SSCH_3	−24.3		9
CS_2	117.2	116.6	3
$HOCS_2$	110.5		49
F	79.39	77.28	1
HF	−273.30	−273.26	1
HOF	−98	−95	6
FO	109	109	5
FO_2	26.1		28
FONO	67		57
FNO_2	−108.8		10
$FONO_2$	10	18	6
CH_2F	−31.8		4

Enthalpy Data* — Continued

Species	$\Delta H_f^\circ(298)$ kJ·mol^{-1}	$\Delta H_f^\circ(0)$ kJ·mol^{-1}	Reference
CH_3F	−232.6		37
CH_3CH_2F	−263		16
HCOF		−392.5	31
FCO	−171.5	−172.1	6
F_2	0	0	1
CHF_2	−238.9		4
CH_2F_2	−453		16
CH_3CHF_2	−501		16
CF_2	−194.1		4
COF_2	−634.7	−631.6	3
CHF_3	−697.6		16
CF_3	−467.4		4
CH_2CF_3	−517.1		4
CH_3CF_3	−748.7		18
CH_2FCHF_2	−691		18
CF_3COF	−785		16
CF_3O_2	−614		38
$CF_3O_2NO_2$	−686		45
CF_4	−933	−927	11
Cl	121.30	119.62	1
HCl	−92.31	−92.13	1
HOCl	−78	−75	2,14
ClO	102	102	2,12
ClOO	97.5		15
OClO	101	104	27
sym-ClO_3	232.6		35
ClNO	51.7	53.6	6
$ClNO_2$	12.5	18.0	3
ClONO	56		10
$ClONO_2$	22.9		36
CH_2Cl	121.8		24
CH_3Cl	−82.0	−74.0	11
CHF_2Cl	−483.7		17
CH_3CHFCl	−313.4		18
CH_3CF_2Cl	−536.2		18
ClCO	−17		5
COFCl	−427	−423	6
CFCl	−20		16
CF_2Cl	−269.0		4
CF_2ClO_2	−406.5		38
$CF_2ClO_2NO_2$	−471		53
CF_3Cl	−707.9	−702.9	17
Cl_2	0	0	1
Cl_2O	81.4	83.2	13
Cl_2O_2	130		22
Cl_2O_3	142		39
CCl_2	239		4
$CHCl_2$	98.3		24
CH_2Cl_2	−95.4	−88.5	11
$CHFCl_2$	−284.9		17
$COCl_2$	−220.1	−218.4	2
$CFCl_2$	−89.1		24
$CFCl_2O_2$	−213.7		38
$CFCl_2O_2NO_2$	−277		53
CF_2Cl_2	−493.3	−489.1	17
CH_2ClCF_2Cl	−543		16
CF_3CHCl_2	−740		16
$CF_2ClCHFCl$	−724		16
CF_2ClCF_2Cl	−925.5		18
CCl_3	71.1	69.9	32
CCl_3O_2	−11.3		38
$CCl_3O_2NO_2$	−86.2		53
$CHCl_3$	−103.3		6
C_2HCl_3	−7.8	−4.3	3

Enthalpy Data* — Continued

Species	$\Delta H_f^\circ(298)$ kJ·mol^{-1}	$\Delta H_f^\circ(0)$ kJ·mol^{-1}	Reference
CH_3CCl_3	−144.6		18
$CFCl_3$	−284.9	−281.1	17
$CF_2ClCFCl_2$	−726.8		18
CCl_4	−95.8	−93.6	11
C_2Cl_4	−12.4	−11.9	6
Br	111.86	117.90	1
HBr	−36.38	−28.54	1
HOBr	−80		5
BrO	125	133	3
BrNO	82.2	91.5	3
BrONO	103		40
$BrNO_2$	63		44
$BrONO_2$	47		10
CH_2Br	169.0		24
CH_3Br	−38.1		19
CF_3Br	−650		16
CF_2ClBr	−438		16
BrCl	14.6	22.1	6
$Br_2(g)$	30.91	45.69	1
$CHBr_2$	188		24
CF_2Br_2	−379		16
CF_2BrCF_2Br	−789.9		18
$CHBr_3$	23.8		19
I	106.762		1
HI	26.36		1
IO	107		50
INO	121.3	124.3	20
INO_2	60.2	66.5	20
CH_2I	230.1		4
CH_3I	14.2		7
$I_2(g)$	62.421		1

*Most of the thermochemical data have been taken from evaluations or from reviews. In some cases, we have selected more recent experimental data which appear to be reliable.

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