Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement I CODATA Task Group on Chemical Kinetics

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Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement I

CODATA Task Group on Chemical Kinetics

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This paper updates and extends a previous critical evaluation of the kinetics and photochemistry of gas phase chemical reactions of neutral species involved in middle atmosphere chemistry (10–55 km altitude) [J. Phys. Chem. Ref. Data 9, 295 (1980)]. The work has been carried out by the authors under the auspices of the CODATA Task Group on Chemical Kinetics. Data sheets have been prepared for 228 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; photo-absorption cross section; photochemistry; quantum yield; rate coefficient.

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1. Preface

This paper is the first supplement to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Chemical Kinetics in 1980 [1].[1] At the present rate of publication of experimental laboratory data on the rates of elementary atmospheric reactions, we estimate that Supplements to the Evaluation are required at approximately two-year intervals.

The approach to the present supplement has been to prepare data sheets for reactions for which results have been published since December 1978, i.e., new data since the original evaluation. At the same time we have widened the scope of the data base by including two further types of reaction, (i) reactions involving C_2 organic molecules and radicals and (ii) reactions of iodine containing species. In addition we have included selected information on the reactions of vibrationally excited species such as HO^*, O_3^* and vibrationally excited singlet O_2.

It should be emphasised that in preparing the updated data sheets we have not listed all the previous data contained in the original evaluation [1]. Consequently, to obtain the overall picture and background to the preferred rate parameters it is essential that the present supplement should be read in conjunction with the original evaluation [1]. For photochemical data sheets, in cases where no new data have been published since the previous evaluation, we have repeated here a summary of the recommended values of the cross sections and quantum yields.

The cut-off point for literature searching for this supplement was December 1980. As in our previous evaluation, however, we also include data which, at the time of our final Task Group Meeting (May 1981), was available to us in preprint form.

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[1] Figures in brackets indicate literature references.

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
	<u>O_x Reactions</u>						
349	$O + O_2 + M \rightarrow O_3 + M$	$6.9 \times 10^{-34}[O_2]$	(k_0)	± 0.1	$6.9 \times 10^{-34}(T/300)^{-1.25}[O_2]$	220–370	$\Delta n = \pm 0.5$
		$6.2 \times 10^{-34}[N_2]$	(k_0)	± 0.1	$6.2 \times 10^{-34}(T/300)^{-2.0}[N_2]$	220–370	$\Delta n = \pm 0.5$
		2.8×10^{-12}	(k_∞)	± 0.3	2.8×10^{-12}	200–300	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$\exp(-T/1800) + \exp(-7200/T)$	200–300	$\Delta T^* = \pm 800$
350	$O_3^* + M \rightarrow O_3 + M$	See data sheets for $O + O_2 + M \rightarrow O_3 + M$					
351	$O + O_3 \rightarrow 2O_2$	8.4×10^{-15}		$+0.1$	$1.8 \times 10^{-11} \exp(-2300/T)$	220–400	± 200
351	$O + O_3^* \rightarrow O + O_3$ $\rightarrow 2O_2$	1.5×10^{-11}		± 0.5			
352	$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$ $\rightarrow O(^3P) + O_2(^1\Delta_g)$ $\rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	4.0×10^{-11}		± 0.05	$3.2 \times 10^{-11} \exp(+67/T)$	200–350	± 100
353	$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$ $\rightarrow O(^3P) + O_3$ $\rightarrow 2O_2(^1\Delta_g)$ $\rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$ $\rightarrow 2O_2(^3\Sigma_g^-)$	2.4×10^{-10}		± 0.05	2.4×10^{-10}	100–400	± 100
354	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	$< 1.4 \times 10^{-19}$	($M = N_2$)				
		2.2×10^{-18}	($M = O_2$)	± 0.3			
		5×10^{-18}	($M = H_2O$)	± 0.3			
		$< 8 \times 10^{-20}$	($M = CO_2$)				
355	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	3.8×10^{-15}		± 0.1	$5.2 \times 10^{-11} \exp(-2840/T)$	280–360	± 500
356	$O_2(^1\Delta_g)^* + M \rightarrow O_2(^1\Delta_g) + M$	See data sheets					
356	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	2.0×10^{-15}	($M = N_2$)	± 0.1			
		8.0×10^{-14}	($M = O$)	± 0.3			
		4.0×10^{-17}	($M = O_2$)	± 0.3			
		4.0×10^{-12}	($M = H_2O$)	± 0.3			
357	$O_2(^1\Sigma_g^+) + O_3 \rightarrow O + 2O_2$	1.5×10^{-11}		± 0.06			
	$\rightarrow O_2(^1\Delta_g) + O_3$ $\rightarrow O_2(^3\Sigma_g^-) + O_3$	6.6×10^{-12}		± 0.06			
358	$O_2(^1\Sigma_g^-)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$	See data sheets					
358	$O_2 + h\nu \rightarrow 2O$	See data sheets					
360	$O_3 + h\nu \rightarrow O + O_2$	See data sheets					
	<u>HO_x Reactions</u>						
•	$H + HO_2 \rightarrow H_2 + O_2$	1.4×10^{-11}		± 0.4			
	$\rightarrow 2HO$	3.2×10^{-11}		± 0.4			
	$\rightarrow H_2O - O$	$\leq 9.4 \times 10^{-13}$		$^{+0.3}_{-?}$			

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
*	$H + O_2 + M \rightarrow HO_2 + M$	$5.9\times10^{-32}[O_2]$	(k_0)	± 0.2	$5.9\times10^{-32}(T/300)^{-1.0}[O_2]$	200–400	$\Delta n = \pm 0.5$
		$5.9\times10^{-32}[N_2]$	(k_0)	± 0.2	$5.9\times10^{-32}(T/300)^{-1.0}[N_2]$	200–400	$\Delta n = \pm 0.5$
		2.5×10^{-10}	(k_∞)	± 0.5	2.5×10^{-10}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$\exp(-T/1800) + \exp(-7200/T)$	200–300	$\Delta T^* = \pm 800$
362	$H + O_3 \rightarrow HO + O_2$	2.8×10^{-11}		± 0.2	$1.4\times10^{-10}\exp(-480/T)$	220–360	± 100
363	$H + O_3 \rightarrow HO^* + O_2$	See data sheets					
364	$O + H_2 \rightarrow HO + H$	3.5×10^{-18}		± 0.3	$1.6\times10^{-11}\exp(-4570/T)$	298–830	± 500
364	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		± 0.15	$2.3\times10^{-11}\exp(+110/T)$	220–500	± 100
365	$O + HO_2 \rightarrow HO + O_2$	3.7×10^{-11}		± 0.3			
366	$O + H_2O_2 \rightarrow HO + HO_2$	2.3×10^{-15}		± 0.3	$1.0\times10^{-11}\exp(-2500/T)$	250–370	± 1000
367	$O(^1D) + H_2 \rightarrow HO + H$ $\rightarrow O(^3P) + H_2$	1.1×10^{-10}		$+ 0.15$	1.1×10^{-10}	200–350	± 100
368	$O(^1D) + H_2O \rightarrow 2HO$ $\rightarrow H_2 + O_2$ $\rightarrow O(^3P) + H_2O$	2.3×10^{-10}		± 0.1	2.3×10^{-10}	200–350	± 100
369	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		± 0.1	$7.7\times10^{-12}\exp(-2100/T)$	200–450	± 200
369	$HO + HO \rightarrow H_2O + O$	1.8×10^{-12}		± 0.15			
	$HO + HO + M \rightarrow H_2O_2 + M$	$6.5\times10^{-31}[O_2]$	(k_0)	± 0.3	$6.5\times10^{-31}(T/300)^{-0.7}[O_2]$	200–400	$\Delta n = \pm 1.0$
		$6.5\times10^{-31}[N_2]$	(k_0)	± 0.3	$6.5\times10^{-31}(T/300)^{-0.7}[N_2]$	200–400	$\Delta n = \pm 1.0$
		3×10^{-11}	(k_∞)	± 0.5	3×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.8$		$\Delta F_c = \pm 0.1$	$\exp(-T/1300) + \exp(-5200/T)$	200–400	$\Delta T^* = \pm 500$
370	$HO + HO_2 \rightarrow H_2O + O_2$	8×10^{-11}		± 0.3			
371	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}		± 0.1	$2.9\times10^{-12}\exp(-160/T)$	240–460	± 100
372	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}		± 0.15	$1.9\times10^{-12}\exp(-1000/T)$	220–450	± 300
373	$HO^* + M \rightarrow$ products	See data sheets					
374	$HO^* + O_3 \rightarrow$ products	See data sheets					
375	$HO_2 + HO_2(+M) \rightarrow H_2O_2 + O_2(+M)$	2.5×10^{-12}		± 0.3	$4.5\times10^{-14}\exp(+1200/T)$	275–400	± 300
376	$HO_2 + O_3 \rightarrow HO + 2O_2$	2.0×10^{-15}		± 0.2	$1.4\times10^{-14}\exp(-600/T)$	250–400	$^{+500}_{-100}$
377	$H_2O + h\nu \rightarrow HO + H$	See data sheets					
377	$H_2O_2 + h\nu \rightarrow 2HO$	See data sheets					
	NO_x Reactions						
378	$N + HO \rightarrow NO + H$	4.9×10^{-11}		± 0.15	$3.8\times10^{-11}\exp(+85/T)$	250–500	± 100
379	$N + NO \rightarrow N_2 + O$	3.1×10^{-11}		± 0.15	3.1×10^{-11}	200–400	± 100
380	$N + NO_2 \rightarrow N_2O + O$	1.4×10^{-12}		± 0.2			
	$N + O_2 \rightarrow NO + O$	8.9×10^{-17}		± 0.1	$4.4\times10^{-12}\exp(-3220/T)$	280–333	± 350
381	$N + O_2(^1\Delta) \rightarrow NO + O$	$<1\times10^{-16}$			$\leqslant 1\times10^{-16}$	200–300	
	$N + O_3 \rightarrow NO + O_2$	$\leqslant 1.0\times10^{-15}$					
381	$O + NO + M \rightarrow NO_2 + M$	$8.6\times10^{-32}[O_2]$	(k_0)	± 0.2	$8.6\times10^{-32}(T/300)^{-1.8}[O_2]$	200–300	$\Delta n = \pm 0.5$
		$1.2\times10^{-31}[N_2]$	(k_0)	± 0.1	$1.2\times10^{-31}(T/300)^{-1.8}[N_2]$	200–300	$\Delta n = \pm 0.5$
		3.0×10^{-11}	(k_∞)	± 0.2	$3.0\times10^{-11}(T/300)^{+0.3}$	300–1500	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$\exp(-T/1800) + \exp(-7200/T)$	200–300	$\Delta T^* = \pm 800$
*	$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}		± 0.06	9.3×10^{-12}	230–340	$^{+0}_{-150}$

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
*	$O + NO_2 + M \rightarrow NO_3 + M$	$9\times10^{-32}[O_2]$	(k_0)	±0.3	$9\times10^{-32}(T/300)^{-2.0}[O_2]$	200–400	$\Delta n = \pm1.0$
		$9\times10^{-32}[N_2]$	(k_0)	±0.1	$9\times10^{-32}(T/300)^{-2.0}[N_2]$	200–400	$\Delta n = \pm1.0$
		2.2×10^{-11}	(k_∞)	±0.1	2.2×10^{-11}	200–400	$\Delta n = \pm0.5$
		$F_c = 0.8$		$\Delta F_c = \pm0.1$	$\exp(-T/1300) + \exp(-5200/T)$	200–400	$\Delta T^* = \pm500$
*	$O + NO_3 \rightarrow O_2 + NO_2$	1×10^{-11}		±0.5			
*	$O + N_2O_5 \rightarrow$ products	$\leqslant 3\times10^{-16}$			$\leqslant 3\times10^{-16}$	220–300	
382	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}		±0.1	$1.8\times10^{-11}\exp(+107/T)$	200–350	±100
383	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}		±0.15	4.4×10^{-11}	200–350	±100
	$\rightarrow 2NO$	7.2×10^{-11}		±0.15	7.2×10^{-11}	200–350	±100
	$\rightarrow O(^3P) + N_2O$	$< 0.1\times10^{-11}$					
384	$NH_2 + HO \rightarrow NH + H_2O$	No recommendation					
	$\rightarrow NH_3 + O$	No recommendation					
385	$NH_2 + HO_2 \rightarrow$ products	3.4×10^{-11}		±0.4			
386	$NH_2 + NO \rightarrow$ products	1.7×10^{-11}		$+0.3$	$1.7\times10^{-11}(T/298)^{-1.6}$	210–500	$\Delta n = +0.5$
387	$NH_2 + NO_2 \rightarrow$ products	1.7×10^{-11}		±0.5	$1.7\times10^{-11}(T/298)^{-2.2}$	250–500	$\Delta n = \pm1.5$
387	$NH_2 + O_2 \rightarrow$ products	$< 3\times10^{-18}$					
388	$NH_2 + O_3 \rightarrow$ products	1.2×10^{-13}		±0.5	$3.4\times10^{-12}\exp(-1000/T)$	250–380	±500
389	$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}		±0.08	$3.6\times10^{-12}\exp(-1560/T)$	200–400	±150
*	$NO + NO_3 \rightarrow 2NO_2$	2×10^{-11}		±0.5			
390	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$3.7\times10^{-30}[O_2]$	(k_0)	±0.3	$3.7\times10^{-30}(T/300)^{-4.1}[O_2]$	220–300	$\Delta n = \pm1.0$
		$3.7\times10^{-30}[N_2]$	(k_0)	±0.2	$3.7\times10^{-30}(T/300)^{-4.1}[N_2]$	220–300	$\Delta n = \pm0.5$
		1.6×10^{-12}	(k_∞)	±0.2	$1.6\times10^{-12}(T/300)^{+0.2}$	220–520	$\Delta n = \pm0.5$
		$F_c = 0.34$		$\Delta F_c = \pm0.05$	$\exp(-T/250) + \exp(-1050/T)$	220–520	$\Delta T^* = \pm20$
391	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$1.6\times10^{-19}[O_2]$	(k_0/s^{-1})	$+0.3$	$2.2\times10^{-3}(T/300)^{-4.4}\exp$ $(-11080/T)[O_2]s^{-1}$	220–330	±500
		$1.6\times10^{-19}[N_2]$	(k_0/s^{-1})	±0.2	$2.2\times10^{-3}(T/300)^{-4.4}\exp$ $(-11080/T)[N_2]s^{-1}$	220–300	±500
		6.9×10^{-2}	(k_∞/s^{-1})	±0.3	$9.7\times10^{14}(T/300)^{+0.1}\exp$ $(-11080/T)s^{-1}$	220–300	±500
		$F_c = 0.34$		$\Delta F_c = \pm0.05$	$\exp(-T/250) + \exp(-1050/T)$	220–300	$\Delta T^* = \pm20$
*	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}		±0.06	$1.2\times10^{-13}\exp(-2450/T)$	230–360	±150
393	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}		±0.15	$3.3\times10^{-12}\exp(-900/T)$	230–450	±200
*	$HO + NO + M \rightarrow HONO + M$	$6.5\times10^{-31}[O_2]$	(k_0)	±0.2	$6.5\times10^{-31}(T/300)^{-2.4}[O_2]$	220–440	$\Delta n = \pm1.0$
		$6.5\times10^{-31}[N_2]$	(k_0)	±0.1	$6.5\times10^{-31}(T/300)^{-2.4}[N_2]$	220–440	$\Delta n = \pm0.5$
		1.0×10^{-11}	(k_∞)	±0.2	1.0×10^{-11}	220–400	$\Delta n = \pm0.5$
		$F_c = 0.8$		$\Delta F_c = \pm0.1$	$\exp(-T/1300) + \exp(-5200/T)$	200–400	$\Delta T^* = \pm500$
394	$HO + NO_2 + M \rightarrow HONO_2 + M$	$1.8\times10^{-30}[O_2]$	(k_0)	±0.2	$1.8\times10^{-30}(T/300)^{-2.9}[O_2]$	200–300	$\Delta n = \pm1.0$
		$2.6\times10^{-30}[N_2]$	(k_0)	±0.1	$2.6\times10^{-30}(T/300)^{-2.9}[N_2]$	200–300	$\Delta n = \pm0.5$
		3.5×10^{-11}	(k_∞)	±0.2	3.5×10^{-11}	200–300	$\Delta n = \pm0.5$
		$F_c = 0.7$		$\Delta F_c = \pm0.1$	$\exp(-T/840) + \exp(-3360/T)$	200–300	$\Delta T^* = \pm500$
395	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.3×10^{-13}		±0.2	$1.5\times10^{-14}\exp(+650/T)$	220–360	±300
396	$HO + HO_2NO_2 \rightarrow$ products	4.0×10^{-12}		±0.3	4.0×10^{-12}	246–324	±400
397	$HO_2 + NO \rightarrow HO + NO_2$	8.3×10^{-12}		±0.1	$3.7\times10^{-12}\exp(+240/T)$	230–500	±100

2. Summary of Reactions and Preferred Rate Data—Continued

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		Δ log k_{298}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}		Temp. range/K	$\Delta(E/R)$/K
398	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	1.5×10^{-31} [O_2]	(k_0)	± 0.3	$1.5\times10^{-31}(T/300)^{-5.0}$ [O_2]		200–300	$\Delta n = \pm 2.0$
		2.1×10^{-31} [N_2]	(k_0)	± 0.3	$2.1\times10^{-31}(T/300)^{-5.0}$ [N_2]		200–300	$\Delta n = +2.0$
		5×10^{-12}	(k_∞)	± 0.4	5×10^{-12}		200–300	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$\exp(-T/320) + \exp(-1280/T)$		200–300	$\Delta T^* = \pm 50$
399	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	9.3×10^{-21} [O_2]	(k_0/s^{-1})	± 0.3	$3.6\times10^{-6} \exp(-10000/T)$ [O_2] s^{-1}		260–300	± 500
		1.3×10^{-20} [N_2]	(k_0/s^{-1})	± 0.3	$5\times10^{-6} \exp(-10000/T)$ [N_2] s^{-1}		260–300	± 500
		0.23	(k_∞/s^{-1})	± 0.6	$3.4\times10^{14} \exp(-10420/T)$ s^{-1}		250–300	± 500
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$\exp(-T/320) + \exp(-1280/T)$		200–300	$\Delta T^* = \pm 50$
400	$NO + h\nu \rightarrow$ products	See data sheets						
400	$NO_2 + h\nu \rightarrow$ products	See data sheets						
401	$NO_3 + h\nu \rightarrow$ products	See data sheets						
403	$N_2O + h\nu \rightarrow$ products	See data sheets						
404	$N_2O_5 + h\nu \rightarrow$ products	See data sheets						
404	$HONO + h\nu \rightarrow$ products	See data sheets						
405	$HONO_2 + h\nu \rightarrow$ products	See data sheets						
406	$HO_2NO_2 + h\nu \rightarrow$ products	See data sheets						
	Organic Reactions							
407	$O + CH_3 \rightarrow H + HCHO$	1.3×10^{-10}		± 0.2	1.3×10^{-10}		200–300	± 200
408	$O(^1D) + CH_4 \rightarrow HO + CH_3$	1.4×10^{-10}		± 0.1	1.4×10^{-10}		200–300	± 100
	$\rightarrow HCHO + H_2$	1.5×10^{-11}			1.5×10^{-11}		200–300	± 100
409	$HO + CH_4 \rightarrow H_2O + CH_3$	8.0×10^{-15}		± 0.1	$2.4\times10^{-12} \exp(-1710/T)$		200–300	± 200
410	$HO + C_2H_2(+M) \rightarrow$ products	7.3×10^{-13}	(1 atm)	± 0.2	$6.5\times10^{-12} \exp(-650/T)$	(1 atm)	220–410	± 200
411	$HO + C_2H_4(+M) \rightarrow C_2H_4OH(+M)$	8.0×10^{-12}	(1 atm)	± 0.2	$2.2\times10^{-12} \exp(+400/T)$	(1 atm)	250–500	± 200
413	$HO + C_2H_6 \rightarrow H_2O + C_2H_5$	2.9×10^{-13}		± 0.1	$1.9\times10^{-11} \exp(-1230/T)$		290–500	± 150
*	$HO + CO \rightarrow H + CO_2$	1.5×10^{-13}	($\leqslant$100 Torr)	± 0.05	1.5×10^{-13}		200–300	
*	$HO + CO \rightarrow$ products	2.8×10^{-13}	(1 atm air)	± 0.10				
414	$HO + HCHO \rightarrow H_2O + HCO$ $\rightarrow H_2O + H + CO$	1.1×10^{-11}		± 0.10	1.1×10^{-11}		200–425	± 150
415	$HO + CH_3OH \rightarrow H_2O + CH_2OH$ $\rightarrow H_2O + CH_3O$	1.0×10^{-12}		± 0.10				
416	$HO + CH_3CHO \rightarrow H_2O + CH_3CO$	1.6×10^{-11}		± 0.1	$6.9\times10^{-12} \exp(+260/T)$		298–450	± 300
417	$HO + CH_3CO_3NO_2 \rightarrow$ products	$\leqslant 2\times10^{-13}$						
417	$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$	6.5×10^{-12}	(1 atm)	± 0.7	$7.7\times10^{-14} \exp(+1300/T)$		275–338	± 700
418	$CH_3 + O_2 \rightarrow HCHO + HO$	$< 5\times10^{-17}$						
*	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	2.6×10^{-31} [O_2]	(k_0)	± 0.3	$2.6\times10^{-31}(T/300)^{-3.0}$ [O_2]		260–340	$\Delta n = \pm 1.0$
		2.6×10^{-31} [N_2]	(k_0)	± 0.3	$2.6\times10^{-31}(T/300)^{-3.0}$ [N_2]		260–300	$\Delta n = \pm 1.0$
		2×10^{-12}	(k_∞)	± 0.3	2×10^{-12}		200–400	$\Delta n = \pm 0.5$
		$F_c = 0.45$		± 0.1	$\exp(-T/360) + \exp(-1440/T)$		200–400	$\Delta T^* = \pm 100$
419	$HCO + O_2 \rightarrow CO + HO_2$	5.1×10^{-12}		± 0.1				
419	$HCO + O_2 + M \rightarrow HCO_3 + M$	$< 5.1\times10^{-12}$	(1 atm)					
419	$CH_3O + NO(+M) \rightarrow CH_3ONO(+M)$	2×10^{-11}		± 0.5	2×10^{-11}		200–400	
420	$CH_3O + O_2 \rightarrow HCHO \rightarrow HO_2$	1.5×10^{-15}		± 1.0	$1.3\times10^{-13} \exp(-1350/T)$		298–450	$^{+1100}_{-500}$
421	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	2×10^{-12}		± 0.5				
421	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.4×10^{-12}		± 0.1	7.4×10^{-12}		200–300	± 250
422	$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	2.3×10^{-30} [O_2]	(k_0)	± 0.2	$2.3\times10^{-30}(T/300)^{-4.0}$ [O_2]		200–300	$\Delta n = \pm 2.0$
		2.3×10^{-30} [N_2]	(k_0)	± 0.1	$2.3\times10^{-30}(T/300)^{-4.0}$ [N_2]		200–300	$\Delta n = \pm 2.0$
		8×10^{-12}	(k_∞)	± 0.2	8×10^{-12}		200–400	$\Delta n = \pm 0.5$
		$F_c = 0.4$		± 0.1	[illegible]		[illegible]	[illegible]

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
423	$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$	No recommendation						
424	$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2$	$< 2\times10^{-17}$						
425	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$	2.2×10^{-13}		± 0.1				
	$\rightarrow 2CH_3O + O_2$	1.5×10^{-13}		± 0.15				
	$\rightarrow CH_3OOCH_3 + O_2$	$\leqslant 3\times10^{-14}$		± 0.3				
426	$C_2H_5 + O_2(+M) \rightarrow C_2H_5O_2 (+M)$	6.9×10^{-12}	(k_∞)	± 0.5				
427	$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	No recommendation						
427	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	7.4×10^{-12}		± 0.5				
428	$C_2H_5O_2 + NO_2(+M) \rightarrow C_2H_5O_2NO_2 (+M)$	5.0×10^{-12}	(1 atm)	± 0.7				
428	$C_2H_5O_2NO_2 + M \rightarrow C_2H_5O_2 + NO_2 + M$	No recommendation						
429	$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$	1.4×10^{-11}		± 0.7				
429	$CH_3CO_3 + NO_2 + M \rightarrow CH_3CO_3NO_2 + M$	6×10^{-12}	(1 atm)	± 0.5				
430	$CH_3CO_3NO_2 + M \rightarrow CH_3CO_3 + NO_2 + M$	4.2×10^{-4} s^{-1}	(1 atm)	± 0.1	$1.12\times10^{16}\exp(-13330/T)$	(1 atm)	295–330	± 1000
431	$HCHO + h\nu \rightarrow$ products	See data sheets						
433	$CH_3OOH + h\nu \rightarrow$ products	See data sheets						
434	$CH_3OONO_2 + h\nu \rightarrow$ products	See data sheets						
436	$CH_3CHO + h\nu +$ products	See data sheets						
437	$CH_3CO_3NO_2 + h\nu \rightarrow$ products	See data sheets						
	<u>SO_x Reactions</u>							
438	$O + H_2S \rightarrow HO + HS$	2.2×10^{-14}		± 0.3	$1.4\times10^{-11}\exp(-1920/T)$		290–500	± 750
	$O + CS \rightarrow CO + S$	2.1×10^{-11}		± 0.1	$2.7\times10^{-10}\exp(-760/T)$		150–300	± 250
439	$O + CH_3SCH_3 \rightarrow CH_3SOCH_3 \rightarrow$ products	4.8×10^{-11}		± 0.15	$1.3\times10^{-11}\exp(+390/T)$		270–500	± 100
440	$O + CS_2 \rightarrow SO + CS$	3.0×10^{-12}		± 0.2	$1.8\times10^{-11}\exp(-530/T)$		200–500	± 100
	$\rightarrow CO + S_2$	5.8×10^{-14}		± 0.2				
	$\rightarrow OCS + S$	3.3×10^{-13}		± 0.25	$1.8\times10^{-12}\exp(-530/T)$		200–500	± 100
441	$O + CH_3SSCH_3 \rightarrow$ products	2.1×10^{-10}		± 0.3	2.1×10^{-10}		270–330	
•	$O + OCS \rightarrow SO + CO$	1.4×10^{-14}		± 0.2	$2.6\times10^{-11}\exp(-2250/T)$		220–600	± 150
•	$O + SO_2 + M \rightarrow SO_3 + M$	$1.4\times10^{-33}[O_2]$	(k_0)	± 0.3	$4.0\times10^{-32}\exp(-1000/T)[O_2]$		200–400	$^{+200}_{-100}$
		$1.4\times10^{-33}[N_2]$	(k_0)	± 0.3	$4.0\times10^{-32}\exp(-1000/T)[N_2]$		200–400	$^{+200}_{-100}$
441	$S + O_2 \rightarrow SO + O$	2.3×10^{-12}		± 0.2	2.3×10^{-12}		230–400	± 200
•	$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}		± 0.3				
442	$HO + H_2S \rightarrow H_2O + HS$	5.3×10^{-12}		± 0.1	$1.1\times10^{-11}\exp(-225/T)$		250–400	± 225
442	$HO + CH_3SCH_3 \rightarrow$ products	9.1×10^{-12}		± 0.1	$5.5\times10^{-12}\exp(+150/T)$		200–500	± 200
443	$HO + CS_2 \rightarrow$ products	$\leqslant 1.5\times10^{-15}$						
444	$HO + CH_3SSCH_3 \rightarrow$ products	2.2×10^{-10}		± 0.3				
444	$HO + OCS \rightarrow$ products	$\leqslant 9\times10^{-15}$						

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
445	$HO + SO_2 + M \rightarrow HOSO_2 + M$	3.0×10^{-31} [O_2]	(k_0)	± 0.3	$3.0\times10^{-31}(T/300)^{-2.9}$ [O_2]	200–400	$\Delta n = \pm 1$
		3.0×10^{-31} [N_2]	(k_0)	± 0.3	$3.0\times10^{-31}(T/300)^{-2.9}$ [N_2]	200–400	$\Delta n = \pm 1$
		2.5×10^{-12}	(k_∞)	± 0.3	2.5×10^{-12}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.55$		$\Delta F_c = \pm 0.15$	$\exp(-T/500) + \exp(-2000/T)$	200–400	$\Delta T^* = \pm 200$
446	$HO_2 + SO_2 \rightarrow$ products	$\leqslant 1\times10^{-18}$					
447	$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ $\rightarrow CH_3O_2SO_2$	$\leqslant 5\times10^{-17}$					
*	$HS + O_2 \rightarrow HO + SO$	No recommendation (see data sheets)					
*	$CS + O_2 \rightarrow CO + SO \rightarrow OCS + O$	No recommendation (see data sheets)					
*	$SO + O_2 \rightarrow SO_2 + O$	9×10^{-18}		± 0.5	$6\times10^{-13} \exp(-3300/T)$	300–1000	± 500
447	$SO + O_3 \rightarrow SO_2 + O_2$	7.9×10^{-14}		± 0.2	$3.2\times10^{-12} \exp(-1100/T)$	220–300	$+400$
448	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}		± 0.2			
*	$SO_3 + H_2O \rightarrow$ products	No recommendation (see data sheets)					
448	$CS_2 + h\nu \rightarrow$ products	See data sheets					
449	$CH_3SSCH_3 + h\nu \rightarrow$ products	See data sheets					
450	$OCS + h\nu \rightarrow$ products	See data sheets					
	<u>FO_x Reactions</u>						
*	$O + FO \rightarrow O_2 + F$	5×10^{-11}		± 0.5			
*	$O + FO_2 \rightarrow O_2 + FO$	5×10^{-11}		± 0.7			
*	$O(^1D) + HF \rightarrow HO + F$ $\rightarrow O(^3P) + HF$	1×10^{-10}		± 0.5			
451	$F + H_2 \rightarrow HF + H$	2.8×10^{-11}		± 0.1	$1.9\times10^{-10} \exp(-570/T)$	190–770	± 150
452	$F + O_2 + M \rightarrow FO_2 + M$	1.6×10^{-32} [O_2]	(k_0)	± 0.3	$1.6\times10^{-32}(T/300)^{-2.5}$ [O_2]	223–360	$\Delta n = \pm 1.0$
		1.6×10^{-32} [N_2]	(k_0)	± 0.3	$1.6\times10^{-32}(T/300)^{-2.5}$ [N_2]	223–360	$\Delta n = \pm 1.0$
		3×10^{-11}	(k_∞)	± 0.5	3×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.85$		$\Delta F_c = \pm 0.1$	$\exp(-T/1800) + \exp(-7200/T)$	200–300	$\Delta T^* = \pm 800$
*	$F + O_3 \rightarrow FO + O_2$	1.3×10^{-11}		± 0.3	$2.8\times10^{-11} \exp(-226/T)$	250–365	± 200
*	$F + H_2O \rightarrow HF + HO$	1.1×10^{-11}		± 0.5	$2.2\times10^{-11} \exp(-200/T)$	240–360	± 200
*	$F + CH_4 \rightarrow HF + CH_3$	8×10^{-11}		± 0.2	$3.0\times10^{-10} \exp(-400/T)$	250–450	± 150
*	$FO + O_3 \rightarrow F + 2O_2$ $\rightarrow FO_2 + O_2$	No recommendation					
453	$FO + NO \rightarrow F + NO_2$	2.6×10^{-11}		± 0.3			
*	$FO + NO_2 + M \rightarrow FONO_2 + M$	1.6×10^{-31} [O_2]	(k_0)	± 0.7	$1.6\times10^{-31}(T/300)^{-3.4}$ [O_2]	200–400	$\Delta n = \pm 1.0$
		1.6×10^{-31} [N_2]	(k_0)	± 0.7	$1.6\times10^{-31}(T/300)^{-3.4}$ [N_2]	200–400	$\Delta n = \pm 1.0$
		2×10^{-11}	(k_∞)	± 0.5	2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$\Delta F_c = \pm 0.1$	$\exp(-T/430) + \exp(-1720/T)$	200–400	$\Delta T^* = \pm 100$
*	$FO + FO \rightarrow 2F + O_2$ $\rightarrow FO_2 + F$ $\rightarrow F_2 + O_2$	1.5×10^{-11}		± 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
453	$HF + h\nu \rightarrow$ products	See data sheets				
453	$COF_2 + h\nu \rightarrow$ products	See data sheets				
454	$FONO_2 + h\nu \rightarrow$ products	See data sheets				
	ClO$_x$ Reactions					
	$O + HCl \rightarrow HO + Cl$	1.4×10^{-16}	± 0.3	$1.1\times10^{-11}\exp(-3370/T)$	293–718	± 550
454	$O + HOCl \rightarrow HO + ClO$	6×10^{-15}	± 1.0	$1\times10^{-11}\exp(-2200/T)$	200–300	± 1000
*	$O + ClO \rightarrow O_2 + Cl$	5.0×10^{-11}	± 0.1	$7.5\times10^{-11}\exp(-120/T)$	220–425	± 120
*	$O + ClONO_2 \rightarrow ClO + NO_3$ $\rightarrow OClO + NO_2$ $\rightarrow O_2 + ClONO$	1.9×10^{-13}	± 0.1	$3.0\times10^{-12}\exp(-808/T)$	213–295	± 200
455	$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl$ $\rightarrow O(^3P) + CF_2Cl_2$ $\rightarrow COF_2 + Cl_2$ $\rightarrow COFCl + FCl$	1.4×10^{-10}	± 0.1			
456	$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2$ $\rightarrow O(^3P) + CFCl_3$ $\rightarrow COFCl + Cl_2$ $\rightarrow COCl_2 + FCl$	2.3×10^{-10}	± 0.1			
457	$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ $\rightarrow O(^3P) + CCl_4$ $\rightarrow COCl_2 + Cl_2$	3.3×10^{-10}	± 0.1			
*	$Cl + H_2 \rightarrow HCl + H$	1.8×10^{-14}	± 0.2	$4.7\times10^{-11}\exp(-2340/T)$	210–1070	± 200
458	$Cl + HO_2 \rightarrow HCl + O_2$	4.8×10^{-11}	$^{+0.3}_{-0.5}$	4.8×10^{-11}	274–338	± 200
*	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.3×10^{-13}	± 0.2	$1.1\times10^{-11}\exp(-980/T)$	265–424	± 500
*	$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}	± 0.06	$2.7\times10^{-11}\exp(-257/T)$	205–298	± 100
459	$Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}	± 0.1	$9.6\times10^{-12}\exp(-1350/T)$	200–300	± 250
*	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.7×10^{-11}	± 0.06	$7.7\times10^{-11}\exp(-90/T)$	220–350	± 100
460	$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}	± 0.06	$7.9\times10^{-11}\exp(-34/T)$	200–500	± 100
*	$Cl + HONO_2 \rightarrow HCl + NO_3$	$\leqslant 7\times10^{-15}$	$^{+0.3}_{-2.5}$			
*	$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}	± 0.1	$3.4\times10^{-11}\exp(-1260/T)$	233–350	± 200
*	$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$ $\rightarrow ClONO + ClO$	2.2×10^{-13}	± 0.3	$1.7\times10^{-12}\exp(-610/T)$	224–273	± 400
*	$HO + HCl \rightarrow H_2O + Cl$	6.6×10^{-13}	± 0.06	$3.0\times10^{-12}\exp(-425/T)$	210–460	± 100
461	$HO + HOCl \rightarrow H_2O + ClO$	1.8×10^{-12}	± 1.0	$3\times10^{-12}\exp(-150/T)$	200–300	$^{+850}_{-150}$
461	$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$ $\rightarrow HOClO$	9.1×10^{-12}	± 0.3			
*	$HO + ClONO_2 \rightarrow HOCl + NO_3$ $\rightarrow HO_2 + ClONO$ $\rightarrow HNO_3 + ClO$	3.9×10^{-13}	± 0.2	$1.2\times10^{-12}\exp(-330/T)$	246–387	± 200
462	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.2×10^{-14}	± 0.1	$1.9\times10^{-12}\exp(-1120/T)$	247–350	± 200
463	$HO + CH_2FCl \rightarrow H_2O + CHFCl$	4.4×10^{-14}	± 0.1	$2.6\times10^{-12}\exp(-1210/T)$	245–350	± 100

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
464	$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.7×10^{-15}		± 0.1	$1.1\times10^{-12}\exp(-1620/T)$	250–360	± 100
465	$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	3.0×10^{-14}		± 0.1	$1.1\times10^{-12}\exp(-1070/T)$	240–350	± 100
466	$HO + C_2HCl_3 \rightarrow$ products	2.2×10^{-12}		± 0.1	$5.0\times10^{-13}\exp(+445/T)$	234–420	± 445
466	$HO + C_2Cl_4 \rightarrow$ products	1.7×10^{-13}		± 0.1	$9.4\times10^{-12}\exp(-1200/T)$	297–420	± 200
*	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	1.2×10^{-14}		± 0.15	$5.1\times10^{-12}\exp(-1800/T)$	250–460	± 200
467	$ClO + HO_2 \rightarrow HOCl + O_2$	5.0×10^{-12}		± 0.15	$4.6\times10^{-13}\exp(+710/T)$	235–298	$^{+250}_{-700}$
	$\rightarrow HCl + O_3$						
*	$ClO + HO_2 + (M) \rightarrow HOOClO + (M)$						
468	$ClO + H_2CO \rightarrow$ products	$< 10^{-15}$					
469	$ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}		± 0.1	$6.2\times10^{-12}\exp(+294/T)$	202–415	± 100
470	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$1.6\times10^{-31}[O_2]$	(k_0)	± 0.2	$1.6\times10^{-31}(T/300)^{-3.4}[O_2]$	250–420	$\Delta n = \pm 1.0$
		$1.6\times10^{-31}[N_2]$	(k_0)	± 0.1	$1.6\times10^{-31}(T/300)^{-3.4}[N_2]$	250–420	$\Delta n = \pm 1.0$
		2×10^{-11}	(k_∞)	± 0.3	2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.5$		$\Delta F_c = \pm 0.1$	$\exp(-T/430) + \exp(-1720/T)$	200–400	$\Delta T^* = \pm 100$
471	$HOCl + h\nu \rightarrow$ products	See data sheets					
472	$COFCl + h\nu \rightarrow$ products	See data sheets					
472	$ClONO_2 + h\nu \rightarrow$ products	See data sheets					
473	$COCl_2 + h\nu \rightarrow$ products	See data sheets					
474	$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheets					
476	$CFCl_3 + h\nu \rightarrow$ products	See data sheets					
478	$CCl_4 + h\nu \rightarrow$ products	See data sheets					
	BrO_x Reactions						
*	$O + HBr \rightarrow HO + Br$	3.9×10^{-14}		± 0.2	$7.0\times10^{-12}\exp(-1560/T)$	250–400	± 300
*	$O + BrO \rightarrow O_2 + Br$	3×10^{-11}		± 0.5			
480	$Br + HO_2 \rightarrow HBr + O_2$	No recommendation (see data sheets)					
481	$Br + H_2O_2 \rightarrow HBr + HO_2$	$\leqslant 2\times10^{-15}$					
481	$Br + H_2CO \rightarrow HBr + HCO$	1.1×10^{-12}		± 0.2	$1.4\times10^{-11}\exp(-750/T)$	223–480	± 250
*	$Br + O_3 \rightarrow BrO + O_2$	1.1×10^{-12}		± 0.1	$1.4\times10^{-11}\exp(-760/T)$	220–360	± 200
*	$HO + HBr \rightarrow H_2O + Br$	8.5×10^{-12}		± 0.3	8.5×10^{-12}	249–416	± 250
*	$HO + CH_3Br \rightarrow H_2O + CH_2Br$	3.8×10^{-14}		± 0.1	$7.6\times10^{-12}\exp(-890/T)$	244–350	± 200
*	$BrO + HO_2 \rightarrow HOBr + O_2$	5×10^{-12}		± 0.5			
	$\rightarrow HBr + O_3$						
*	$BrO + NO \rightarrow Br + NO_2$	2.1×10^{-11}		± 0.1	$8.7\times10^{-12}\exp(+260/T)$	224–425	± 100
482	$BrO + NO_2 + M \rightarrow BrONO_2 + M$	$5.0\times10^{-31}[O_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.0}[N_2]$	200–400	$\Delta n = \pm 1$
		$5.0\times10^{-31}[N_2]$	(k_0)	± 0.3	$5.0\times10^{-31}(T/300)^{-3.0}[N_2]$	200–400	$\Delta n = \pm 1$
		2×10^{-11}	(k_∞)	± 0.3	2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$\exp(-T/320) + \exp(-1280/T)$	200–400	$\Delta T^* = \pm 50$
*	$BrO + O_3 \rightarrow Br + 2O_2$	$< 5\times10^{-15}$		$^{+0.5}_{-?}$			
	$BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}		± 0.3			
	$\rightarrow Br + Cl + O_2$	6.7×10^{-12}		± 0.3			
	$\rightarrow BrCl + O_2$						

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
*	$BrO + BrO \rightarrow 2Br + O_2$ $\rightarrow Br_2 + O_2$	2.8×10^{-12}		± 0.1	2.8×10^{-12}	220–440	± 500
483	$BrO + h\nu \rightarrow$ products	See data sheets					
483	$HOBr + h\nu \rightarrow$ products	See data sheets					
484	$BrONO_2 + h\nu \rightarrow$ products	See data sheets					
	<u>IO_x Reactions</u>						
484	$O + IO \rightarrow O_2 + I$	5×10^{-11}		± 0.5			
485	$HO + HI \rightarrow H_2O + I$	1.3×10^{-11}		± 0.5			
485	$I + HO_2 \rightarrow HI + O_2$	No recommendation					
486	$I + O_3 \rightarrow IO + O_2$	1.0×10^{-12}		± 1.0			
486	$I + NO + M \rightarrow INO + M$	$1.8\times10^{-32}\,[O_2]$	(k_0)	± 0.2	$1.8\times10^{-32}(T/300)^{-1.0}\,[O_2]$	200–400	$\Delta n = \pm 0.5$
		$1.8\times10^{-32}\,[N_2]$	(k_0)	± 0.1	$1.8\times10^{-32}(T/300)^{-1.0}\,[N_2]$	200–400	$\Delta n = \pm 0.5$
		1.7×10^{-11}	(k_∞)	± 0.3	1.7×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.75$		$\Delta F_c = \pm 0.15$	$\exp(-T/1040) + \exp(-4160/T)$	200–400	$\Delta T^* = \pm 500$
487	$I + NO_2 + M \rightarrow INO_2 + M$	$2.9\times10^{-31}\,[O_2]$	(k_0)	± 0.3	$2.9\times10^{-31}(T/300)^{-1.0}\,[O_2]$	298–450	$\Delta n = +0.5$
		$2.9\times10^{-31}\,[N_2]$	(k_0)	± 0.3	$2.9\times10^{-31}(T/300)^{-1.0}\,[N_2]$	298–450	$\Delta n = \pm 0.5$
		6.6×10^{-11}	(k_∞)	± 0.3	6.6×10^{-11}	300–400	$\Delta n = \pm 0.5$
		$F_c = 0.63$		$\Delta F_c = \pm 0.1$	$\exp(-T/650) + \exp(-2600/T)$	200–400	$\Delta T^* = \pm 200$
480	$IO + HO_2 \rightarrow$ products	No recommendation					
488	$IO + NO \rightarrow I + NO_2$	1.7×10^{-11}		± 0.3			
489	$IO + NO_2 + M \rightarrow IONO_2 + M$	$5.0\times10^{-31}\,[O_2]$	(k_0)	± 0.5	$5.0\times10^{-31}(T/300)^{-3.0}\,[O_2]$	200–400	$\Delta n = \pm 1$
		$5.0\times10^{-31}\,[N_2]$	(k_0)	± 0.5	$5.0\times10^{-31}(T/300)^{-3.0}\,[N_2]$	200–400	$\Delta n = \pm 1$
		2×10^{-11}	(k_∞)	± 0.5	2×10^{-11}	200–400	$\Delta n = \pm 0.5$
		$F_c = 0.4$		$\Delta F_c = \pm 0.1$	$\exp(-T/320) + \exp(-1280/T)$	200–400	$\Delta T^* = \pm 100$
489	$IO + IO \rightarrow 2I + O_2$ $\rightarrow I_2 + O_2$	3.0×10^{-12}		± 1.0			
489	$INO + INO \rightarrow I_2 + 2NO$	1.3×10^{-14}		± 0.4	$8.4\times10^{-11}\exp(-2620/T)$	298–450	± 600
490	$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	4.7×10^{-15}		± 0.5	$2.9\times10^{-11}\exp(-2600/T)$	298–400	± 1000
490	$IO + h\nu \rightarrow$ products	See data sheets					
491	$HOI + h\nu \rightarrow$ products	See data sheets					
491	$INO + h\nu \rightarrow$ products	See data sheets					
492	$INO_2 + h\nu \rightarrow$ products	See data sheets					
492	$IONO_2 + h\nu \rightarrow$ products	See data sheets					

*Data sheet for this reaction appears in earlier evaluation, J. Phys. Chem. Ref. Data 9, 295 (1980).

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 I.

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 here only data which have been published since the previous CODATA evaluation [1] and under heading (iii) are listed the preferred rate data from the most recent NASA evaluations [2,3], from our own CODATA evaluation [1] and from any new review or evaluation sources. 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, $k = A\ \exp(-C/T)$ where $C = E/R$. For a few bimolecular reactions we have listed temperature dependences in the alternative form, $k = A'T^{-n}$, where the original authors have found this to give a better fit to their data. For pressure-dependent combintion and dissociation reactions the non-Arrhenius temperature dependence is used. This is discussed more fully in subsequent section of the introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at 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. For measurements of relative rate coefficients, 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 is that 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 the preferred values describe how the selection was made and given 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 tables are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.

$$\mathrm{A} + \mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$$

$$-(\tfrac{1}{2})d[\mathrm{A}]/dt = d[\mathrm{B}]/dt = d[\mathrm{C}]/dt = k[\mathrm{A}]^2.$$

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 $2k[\mathrm{A}]^2$) 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

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightleftarrows \mathrm{AB} + \mathrm{M},$$

depend on the temperature T, the nature and the 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

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

in which the second-order rate constant depends on [M]. The low pressure third-order limit is characterized by k_0,

$$k_0 = \lim_{[\mathrm{M}]\rightarrow 0} k([\mathrm{M}])$$

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

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

which is independent of [M]. For a combination reaction in the low pressure range, the summary table gives a second-order rate constant expressed as the product of a third-order rate constant and the third body concentration. The transition between the third-order and the second-order range is represented by a reduced fall-off expression of k/k_∞ as a function of $k_0/k_\infty = [\mathrm{M}]/[\mathrm{M}]_c$ where the "center of the fall-off curve" $[\mathrm{M}]_c$ indicates the third body concentration for which the extrapolated k_0 would be equal to k_∞. This is illustrated in figure 1. 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:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0\left(\frac{1}{1 + [\mathrm{M}]/[\mathrm{M}]_c}\right)F$$

$$= k_\infty\left(\frac{[\mathrm{M}]/[\mathrm{M}]_c}{1 + [\mathrm{M}]/[\mathrm{M}]_c}\right)F$$

where the first factors at the r.h.s. represent the Lindemann-Hinshelwood expression, and the additional broadening factor F is approximately given by

$$\log F \cong \frac{\log F_c}{1 + [\log([\mathrm{M}]/[\mathrm{M}]_c)]^2}$$

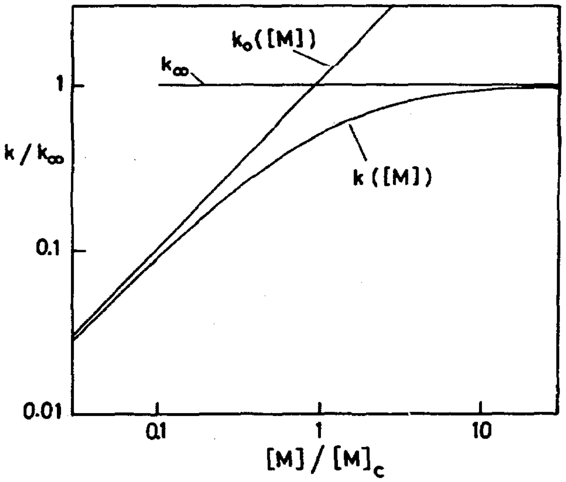

FIGURE 1. Reduced fall-off curve of k/k_∞ as a function of $[M]/[M]_c$.

In this way the three quantities k_0, k_∞, and F_c with

$$[M]_c = \frac{k_\infty}{k_0/[M]}$$

characterize the fall-off curve for the present application. Alternatively the three quantities k_∞, $[M]_c$ and F_c (or k_0, $[M]_c$ and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe [4]. The results can usually be represented approximately by an experimental equation $F_c = \exp(-T/T^*) + \exp(-T^{**}/T)$. If F_c values are available for one temperature only, we have derived data at other temperatures from the expression $F_c \simeq \exp(-T/T^*) + \exp(-4T^*/T)$, where T^* is chosen to reproduce the one available value of F_c. This approach was developed for the $NO_2 + NO_3 \rightarrow N_2O_5$ reaction (see this evaluation). In the absence of better data the above treatment serves as a first approximation.

The dependence of k_0 and k_∞ on the temperature T is represented in a T-exponent n

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

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_0 on the nature of the third body M generally is represented by the relative efficiencies of M_1 and M_2

$$k_0(M_1)/[M_1] : k_0(M_2)/[M_2].$$

The few thermal dissociation reactions of interest in the present application are treated analogously to the combination reactions with pseudo first-order rate constants $k([M])$. The rate constants expressed in units of second^{-1} are denoted in the tables by the symbols (k_0/s^{-1}) and (k_∞/s^{-1}).

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 calculated from the data in appendix I. 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 wavelength intervals of 5 nm where possible. The preferred data are often amplified by diagrams of absorption cross sections versus wavelength and, where appropriate, by diagrams of quantum yield versus wavelength.

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

For photochemical reactions where no new data have been published since 1978, we have listed summaries of preferred cross sections and quantum yields from our previous evaluation [1].

3.5. Convention 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 in 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 1 standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19}. For other conversion factors see appendix II.

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 $E/R = H \pm G$.

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 measurements, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90 percent confidence limits, of ± 10 percent 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 two 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 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 two are appropriate.

We do not feel justified now in assigning error limits to the parameters reported for the photochemical reactions.

4. Atmospheric Chemistry

4.1. Introduction

During the past decade considerable attention has been directed towards research in atmospheric chemistry with emphasis on the gas phase reactions of ozone and important hydrogen, nitrogen, carbon, halogen, and sulfur species. The critical evaluation of kinetic and photochemical data of key atmospheric processes has been an integral part of this research effort. Indeed the present CODATA Task Group on Chemical Kinetics was reconstituted in 1977 to prepare comprehensive critical evaluations of kinetic and photochemical data for atmospheric chemistry.

The composition of the natural atmosphere is to a considerable degree determined by biological and microbiological processes in soils, vegetation and waters. A typical life cycle of an element consists of release at the earth's surface in the form of a reduced gas (often bonded to hydrogen), photochemical oxidation in the atmosphere, and removal from the atmosphere by precipitation scavenging (for water soluble compounds) and/or by direct uptake at ground and water surfaces and vegetation. Important examples of reduced gases of biological origin include CH_4, C_5H_8 (isoprene), $C_{10}H_{16}$ (terpenes), CO, NH_3, H_2S, CH_3SH and $(CH_3)_2S$. These gases are photochemically oxidized in the atmosphere to compounds such as aldehydes, peroxides, alcohols, CO, CO_2, and SO_2, and possibly NO_x (i.e., NO and NO_2) but all the details of the oxidation mechanisms are not known.

The increased interest in atmospheric chemistry over the past decade has been stimulated by a recognition that man's activities could lead to significant changes in the chemical composition of the atmosphere on a significant changes in the chemical composition of the atmosphere on global scale. Such a danger has been recognized for the stratosphere (the 17–50 km altitude region in the tropics, 10–15 km in the middle and high latitudes) due to the input of NO_x and halogen containing compounds, but global effects on the troposphere (the lowest 10–17 km of the atmosphere) due to man's activities can likewise be identified.

Increasing amounts of oxidized gases are being directly emitted into the atmosphere through man's activities. The total global sources of NO_x and SO_2 to the atmosphere due to man's activities are now comparable to or larger than the natural atmospheric sources of these gases. Although these emissions occur mainly in highly industrialized regions photochemical pollution has been observed over distances of a few thousand kilometers adjacent to industrial centers. Because of the vastly increased sources of pollutants and other reaction products to the atmosphere, there is much concern about the effects not only on humans, but also on large scale ecological systems. In particular, attention has been directed to the effects of the increased acidity of precipitation from H_2SO_4 and HNO_3.

In the following we present a review of the most important reactions in the atmosphere (troposphere and stratosphere) emphasizing their role in the cycling of oxygen, hydrogen, nitrogen, carbon, halogen, and sulfur compounds. Particular attention is given to those chemical processes which control the atmospheric distribution of ozone. In this discussion we treat stratospheric and tropospheric chemistry separately. Although there are meteorological and chemical connections between these regions they have the following quite distinct properties:

(a) Temperature decreases with altitude in the troposphere and increases with altitude in the stratosphere, resulting in much more rapid vertical mixing in the troposphere than in the stratosphere.

(b) There are marked differences in the chemical composition of these regions. For instance the stratosphere contains much larger concentrations of ozone, but much less water vapour than the troposphere. The large differences in water vapour concentrations mean that clouds form only rarely in the stratosphere but more commonly in the troposphere. This influences the residence time and distribution of many water soluble chemical compounds in the troposphere.

(c) Only solar radiation at wavelengths longer than about 300 nm penetrates into the troposphere because O_2 and O_3 absorb shorter wavelength radiation in the stratosphere. Photochemical dissociation of many molecules therefore does not occur in the troposphere, e.g., N_2O, and the fluorocarbons. As a consequence those molecules which do not react with HO radicals and are not removed by heterogeneous processes are transported into the stratosphere.

4.2. The Stratosphere

Until the 1960's most studies of stratospheric ozone only considered the Chapman [5] reactions in order to explain its distribution. The Chapman mechanism can be written:

$$O_2 + h\nu \rightarrow O + O \quad (\lambda \leqslant 242 \text{ nm}) \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{3}$$

$$O + O_3 \rightarrow 2O_2 \tag{4}$$

In this set of reactions the production and loss of odd oxygen (O and O_3) is controlled by reactions (1) and (4), respectively, while reactions (2) and (3) partition the odd oxygen species between O and O_3. It was subsequently recognized that other ozone destruction mechanisms had to be introduced in order to explain the observations of stratospheric ozone. Since the early 1960's it has been suggested that HO_x [6], NO_x [7], ClO_x [8], and BrO_x [9] species can all, with varying degrees of efficiency, control the ozone abundance and distribution in the stratosphere. The natural sources of inorganic HO_x, NO_x, ClO_x, and BrO_x radicals in the stratosphere result from reactions of H_2O and N_2O with electronically excited oxygen atoms (O^1D):

$$H_2O + O(^1D) \rightarrow 2HO$$

$$N_2O + O(^1D) \rightarrow 2NO$$

and from reactions of CH_3Cl and CH_3Br with hydroxyl radicals:

$$CH_3Cl + HO \rightarrow CH_2Cl + H_2O$$

$$CH_3Br + HO \rightarrow CH_2Br + H_2O$$

The CH_2Cl and CH_2Br radicals undergo subsequent reactions to yield Cl and ClO, and Br, and BrO, respectively. The excited oxygen atom $O(^1D)$ is produced by photolysis of ozone by ultraviolet solar radiation at wavelengths shorter than 320 nm:

$$O_3 + h\nu \rightarrow O(^1D) + O_2.$$

Interest in the fate of NO_x increased when it was suggested [7] that a substantial reduction in the stratospheric ozone content might occur due to the direct injection of nitric oxide into the stratosphere from the exhaust gases of supersonic aircraft. In addition, it has been suggested that man's agricultural practices may lead to enhanced levels of N_2O [10]. Similarly the potential for significant destruction of ozone by ClO_x radicals was recognized when it was suggested [11] that an important anthropogenic source of Cl and ClO would result from the photolysis of $CFCl_3$ (CFC-11) and CF_2Cl_2 (CFC-12) in the stratosphere. CFC-11 and CFC-12 are only known to have man-made sources (used as aerosol propellents, refrigerants, etc.). It has recently been noted that other industrially used chlorine containing chemicals, e.g., CCl_4, CH_3CCl_3, CHF_2Cl (CFC-22) and $C_2F_3Cl_3$ (CFC-113) add significantly to the stratospheric chlorine content. It should be noted that fully halogenated species, e.g., $CFCl_3$ and CF_2Cl_2 have no identified loss mechanisms in the troposphere, whereas those species which contain H atoms (e.g., CH_3Cl, CH_3CCl_3) or C=C linkages (e.g., C_2HCl_3) react with HO radicals in the troposphere to limit the fraction of them which can be transported into the stratosphere where their degradation products then participate in ozone destruction cycles.

The chemistry of the upper and lower regions of the stratosphere are distinctly different. The chemistry of the upper stratosphere, i.e., 30–35 km, is reasonably well defined. In this region the chemical composition is predominantly photochemically controlled, particularly in summer, and the lifetime of predicted temoporary reservoir species such as HOCl, HO_2NO_2, $ClONO_2$, N_2O_5, and H_2O_2 are short and hence they play only a minor role. Thus the important processes above 30 km predominantly involve atoms and small molecules. In contrast the chemistry of the lower stratosphere, 15–30 km, is quite complex with significant coupling between the HO_x, NO_x, and ClO_x families. It is within this region of the atmosphere where both dynamics and photochemistry play key roles in controlling the trace gas distributions. It is also within this region of the stratosphere that the question of pressure and temperature dependences of the rate coefficients is most critical arising from the low temperatures (210–225 K) and the high total pressure (30–200 Torr). The question of the pressure and temperature dependences of HO and HO_2 reactions is highly pertinent considering the unexpected pressure dependences observed in certain reactions (e.g., HO + CO, $HO_2 + HO_2$) and the unusual temperature dependences observed in other reactions, (e.g., $HO_2 + HO_2$, $HO + HNO_3$, $HO_2 + O_3$, $HO_2 + ClO$).

Ozone is photochemically controlled by HO_x, NO_x, ClO_x, and BrO_x through the following simple catalytic cycle:

$$\left.\begin{array}{l} X + O_3 \rightarrow XO + O_2 \\ XO + O \rightarrow X + O_2 \\ \hline \text{net: } O + O_3 \rightarrow 2O_2 \end{array}\right\} \qquad \text{(I)}$$

where X = HO, NO, Cl, or Br. The catalyst X is constantly regenerated in this simple cycle. In the case of ClO_x two other catalytic cycles have also been considered:

$$\left.\begin{array}{r} Cl + O_3 \rightarrow ClO + O_2 \\ HO + O_3 \rightarrow HO_2 + O_2 \\ ClO + HO_2 \rightarrow HOCl + O_2 \\ HOCl + h\nu \rightarrow HO + Cl \\ \hline \text{net: } 2O_3 \rightarrow 3O_2 \end{array}\right\} \qquad \text{(II)}$$

$$\left.\begin{array}{r} Cl + O_3 \rightarrow ClO + O_2 \\ NO + O_3 \rightarrow NO_2 + O_2 \\ ClO + NO_2 + M \rightarrow ClONO_2 + M \\ ClONO_2 + h\nu \rightarrow Cl + NO_3 \\ NO_3 + h\nu \rightarrow NO + O_2 \\ \hline \text{net: } 2O_3 \rightarrow 3O_2 \end{array}\right\} \qquad \text{(III)}$$

The latter two cycles, which have been recognized to be potentially important in the lower stratosphere, illustrate the highly coupled nature of the HO_x, NO_x, and ClO_x families, and involve species normally thought of as temporary reservoirs, i.e., HOCl and $ClONO_2$. Recent photochemical modelling calculations which use these CODATA evaluated rate coefficients for key HO_x reactions (discussed latter) have shown that these two cycles are relatively unimportant due to the low predicted values of ClO below 30 km (in fair agreement with observations).

In each chemical family there is normally one species which participates in the rate limiting step of the catalytic cycles. These are HO_2, NO_2, and ClO for the HO_x, NO_x, and ClO_x families, respectively. Consequently the efficiency of HO_x, NO_x, and ClO_x to catalytically destroy stratospheric odd oxygen ($O + O_3$) is dependent upon how these families are partitioned between their active (radical) and inactive (reservoir/sink) constituents, e.g., $ClO_x = HCl + ClONO_2 + HOCl + ClO + Cl$, where HCl is a reservoir, HOCl and $ClONO_2$ are temporary reservoirs, and Cl and ClO are active radicals. Reservoir species do not directly participate in odd oxygen destruction catalytic cycles in contrast to the radical species. Temporary species, e.g., HOCl, can either inhibit or enhance the catalytic destruction of ozone depending upon how they reduce the active radical concentration, e.g., ClO.

The efficiency of NO_x and ClO_x in destroying odd oxygen is highly dependent upon the concentration of HO in the stratosphere. High levels of HO radicals enhance the catalytic efficiency of ClO_x and decrease the catalytic efficiency of NO_x in destroying odd oxygen because HO converts HCl to Cl and NO_2 to HNO_3:

$$HO + HCl \rightarrow H_2O + Cl \qquad \text{(inactive}\rightarrow\text{active)}$$

$$HO + NO_2 + M \rightarrow HNO_3 + M \qquad \text{(active}\rightarrow\text{inactive)}$$

The odd hydrogen budget is controlled by the following termination reactions:

$$HO + HO_2 \rightarrow H_2O + O_2$$

$$HO + HNO_3 \rightarrow H_2O + NO_3$$

$$HO + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

The $HO + HNO_3$, $HO + HO_2NO_2$ and $HO + HO_2$ reactions all contribute significantly to the termination of HO_x radicals below 30 km, but the $HO + HO_2$ reaction dominates the termination of HO_x radicals above 30 km. The partitioning between HO and HO_2 is controlled by:

$$HO + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O_3 \rightarrow HO + 2O_2$$

$$HO_2 + NO \rightarrow HO + NO_2$$

in the lower and mid-stratosphere, and by

$$HO_2 + O \rightarrow HO + O_2$$

$$HO + O \rightarrow H + O_2$$

$$H + HO_2 \rightarrow 2HO$$

in the upper stratosphere and mesosphere. Also in the upper stratosphere and mesosphere an additional termination reaction for HO_x radicals becomes important:

$$H + HO_2 \rightarrow H_2 + O_2$$

As stated earlier, processes which directly convert radical species into reservoir/sink species inhibit the catalytic efficiency of that cycle, e.g.,

$$Cl + CH_4 \rightarrow HCl + CH_3$$

$$Cl + HO_2 \rightarrow HCl + O_2$$

In addition there are reactions which modify the partitioning between radical and reservoir species indirectly, e.g.,

$$NO + ClO \rightarrow NO_2 + Cl$$

$$NO + HO_2 \rightarrow NO_2 + HO$$

In each of these cases the normal catalytic cycles (I) have to compete with

$$\left.\begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ HO + NO \rightarrow X + NO_2 \\ \\ NO_2 + h\nu \rightarrow NO + O \\ O + O_2 + M \rightarrow O_3 + M \\ \hline \text{no net chemical change} \end{array}\right\} \qquad \text{(IV)}$$

where $X = HO$ or Cl. The $XO + NO$ reactions effectively modify the radical to reservoir ratios thus limiting the catalytic efficiencies of these families.

It was stated earlier that BrO_x has been postulated to catalytically destroy oxygen [9]. While BrO_x can destroy odd oxygen through cycles analogous to those of ClO_x the cycle of most probable importance involving BrO_x (for low BrO_x mixing ratios, i.e., 20 pptv) is one where there is synergism between ClO_x and BrO_x via the following reaction sequence:

$$\begin{array}{c} Cl + O_3 \rightarrow ClO + O_2 \\ Br + O_3 \rightarrow BrO + O_2 \\ ClO + BrO \rightarrow Cl + Br + O_2 \\ \hline \text{net: } 2O_3 \rightarrow 3O_2 \end{array}$$

The importance of this cycle is not only dependent upon the atmospheric mixing ratio of BrO_x but also upon the concentration of ClO in the lower stratosphere.

Fluorine is not thought to catalytically destroy odd oxygen in a manner analogous to chlorine, as all of the inorganic fluorine is tied up in the inactive form of HF. Atomic fluorine rapidly reacts with all hydrogen containing species, i.e., H_2O, CH_4, H_2, etc., to form HF, but is only slowly regenerated owing to the unreactivity of HF towards HO radicals and $O(^3P)$ atoms, thus leaving only reaction with $O(^1D)$ atoms and photolysis at wavelengths below 165 nm as regeneration processes.

As shown earlier methane plays an important role in stratospheric photochemistry because it limits the efficiency of ClO_x in destroying odd oxygen by converting Cl to HCl. Methane is of further importance as its oxidation leads to the production of water vapour.

The complex interactions between the many species involved in stratospheric photochemistry have been summarized in figure 2. Our view of the importance of these interactions changes as our knowledge of the rate coefficients, absorption cross-sections, etc., improves. As our understanding of stratospheric chemistry has evolved, the ozone depletion predictions due to increases in stratospheric NO_x and ClO_x have changed significantly. A brief historical overview of this is presented in figure 3.

The lower stratosphere contains a small number of aerosol particles which form the Junge layer. Around 20 km altitude, there is about one particle per cubic centimetre which is larger

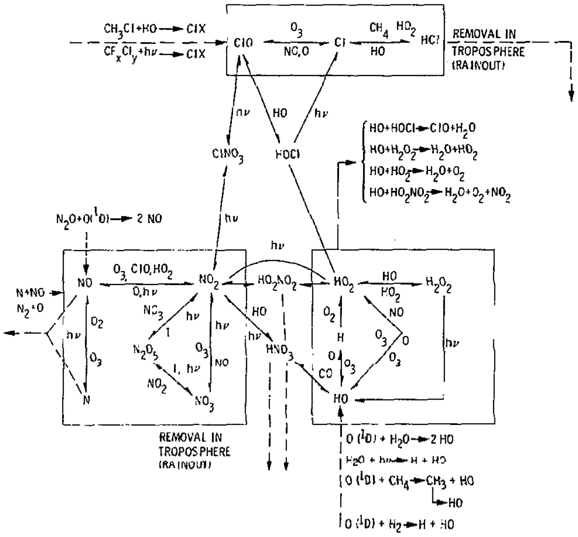

Figure 2. Interactions between the hydrogen, nitrogen, and chlorine families of reactants.

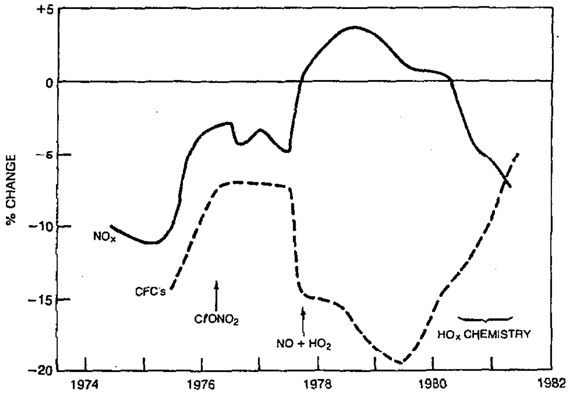

FIGURE 3. Predictions of ozone depletion in steady state resulting from nitrogen oxides (NO_x) and from chlorofluorocarbons (CFC's); changes since 1974 based on improved understanding of stratospheric chemistry.

than 0.3 μm. These particles are believed to consist of sulphuric acid, ammonium sulphate and related species. Laboratory experiments suggest that reactions on the surface of such particles would be too slow to provide a significant sink or source of the trace species important in ozone chemistry although more studies are needed. However, because of backscattering of incoming solar radiation, this layer has climatic significance. The particulate loading of the stratosphere is clearly influenced by volcanic activity. As stated, the main chemical component of this aerosol is sulfuric acid, the formation of which occurs almost certainly through the oxidation of volcanic SO_2 which is initiated by the reaction:

$$HO + SO_2 + M \rightarrow HSO_3 + M$$

However, during extended periods without significant volcanic activity, this sulfate layer persists. Under these circumstances it is likely that the production of SO_2 occurs through the photolysis of COS

$$COS + h\nu \rightarrow CO + S$$

and further oxidation of S to SO_2. Carbonyl sulfide is sufficiently photochemically stable in the troposphere so that it can be transported into the stratosphere. The processes at the earth's surface which produce COS are unknown, and it may be that this gas has been affected by human activities.

Altitude profiles, of the concentrations of some important stratospheric (and tropospheric) gaseous species, calculated using a one-dimensional photochemical model, are presented in figures 4a–4g. It is beyond the scope of this short review to describe the comparison of experimental observations with theoretical predictions. It should be noted that there have been numerous field measurements of source and sink molecules (e.g., CFC's, N_2O, H_2O, HCl, HNO_3, HF, etc.), more limited field data on radicals (e.g., $O(^3P)$, Cl, NO, NO_2, HO, HO_2, etc.) and almost no field data on temporary reservoirs (e.g., HOCl, $ClONO_2$, H_2O_2, HO_2NO_2, and N_2O_5).

4.3. The Troposphere

Although only about 10% of all atmospheric ozone is located in the troposphere, this small fraction is nevertheless of fundamental importance for the composition of the earth's atmosphere. The reason for this is the production of the hydroxyl radical by the two reactions:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2HO$$

It is attack by HO that initiates the oxidation of many gases in the atmosphere [12, 13, 14] including hydrocarbons (e.g., CH_4, C_5H_8, $C_{10}H_{16}$), halogen-containing organics (e.g., CH_3Cl, CH_3CCl_3, C_2Cl_4, C_2HCl_3, CH_3Br), sulfur-containing organics (e.g., CH_3SCH_3, CH_3SH) and many inorganic gases such as CO, NO_2, H_2S, SO_2. In this way HO acts as a scavenging agent, preventing the build up of these "pollutant" gases in the atmos-

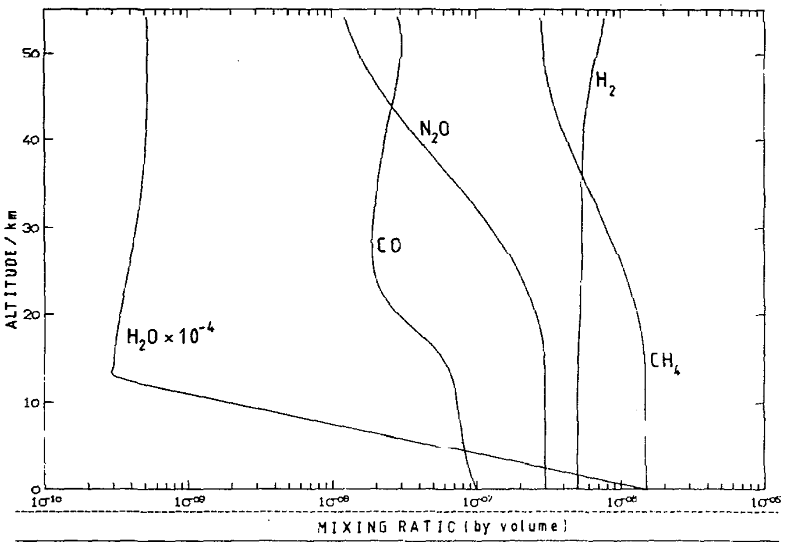

FIGURE 4a. Altitude profiles of mixing ratio of some important stratospheric and tropospheric gaseous species.

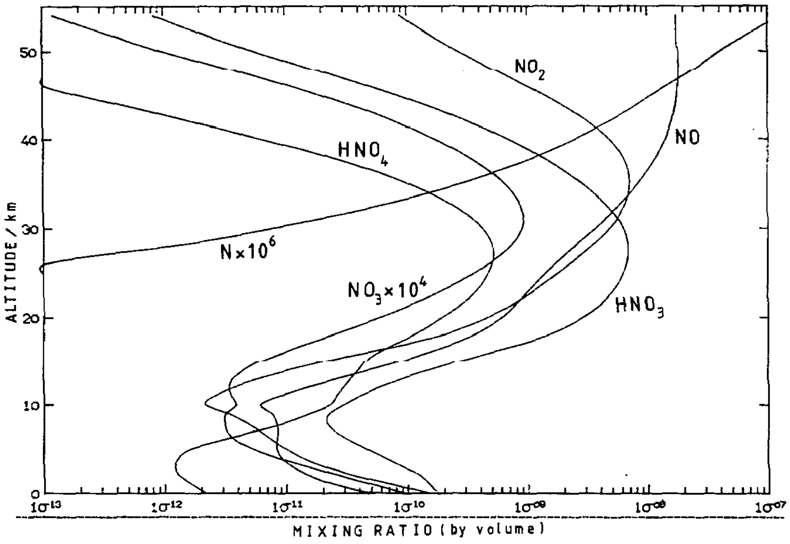

FIGURE 4b. Altitude profiles of mixing ratio of some important nitrogen species.

phere. In the unpolluted troposphere about 70% of the HO radicals react with carbon monoxide and 30% with methane:

$$HO + CO \rightarrow H + CO_2$$

$$HO + CH_4 \rightarrow H_2O + CH_3$$

The subsequent reactions of H and CH_3 can either regenerate HO, e.g., by the reactions:

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

$$HO_2 + NO \rightarrow HO + NO_2$$

or lead to removal of radicals, e.g.,

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

The resultant steady state concentration of hydroxyl depends on the relative importance of the chain carrying reactions involving NO and the radical termination reactions. The important role of NO in tropospheric chemistry is therefore apparent.

Oxidation of CH_3O_2 via the reaction with NO subsequently leads to formaldehyde formation:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

Photodissociation of HCHO can lead to further production of radicals from CH_4 oxidation:

$$HCHO + h\nu \rightarrow CHO + H \quad (\lesssim 350\ \text{nm})$$

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

$$HCO + O_2 \rightarrow HO_2 + CO$$

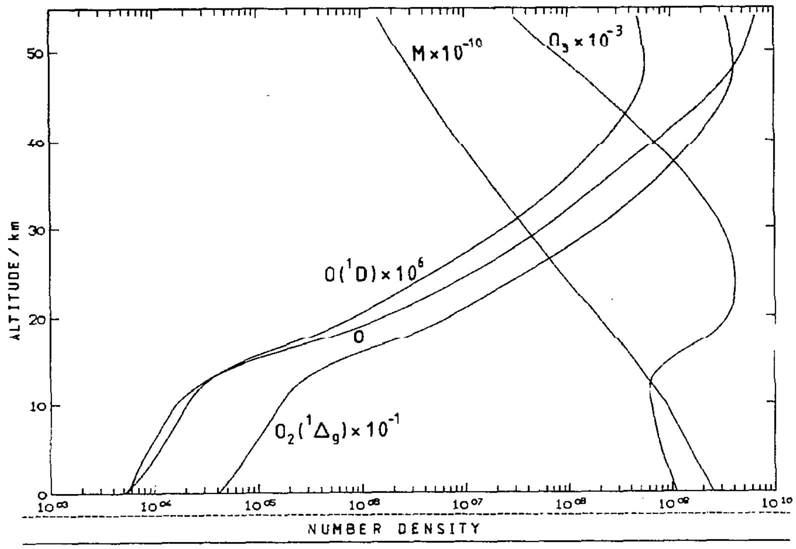

FIGURE 4c. Altitude profiles of number density of some important oxygen species.

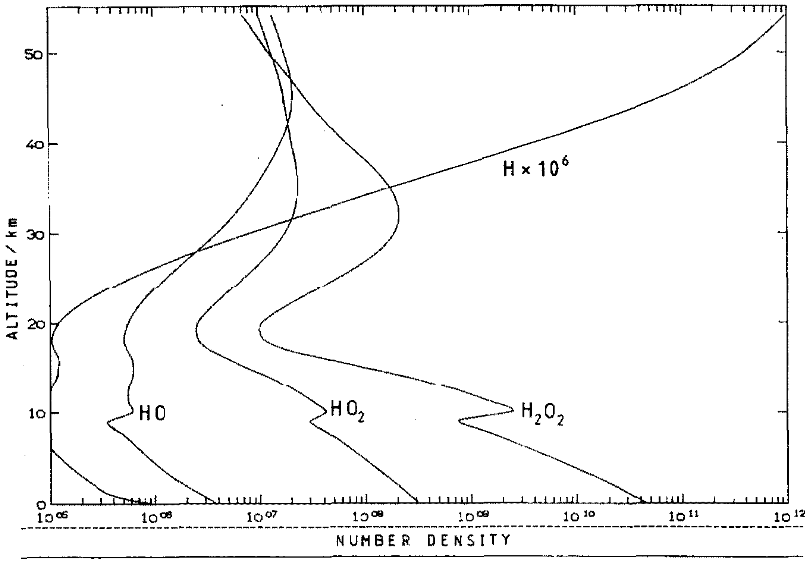

FIGURE 4d. Altitude profiles of number density of some important hydrogen species.

The other two possible reaction paths:

$$HCHO + h\nu \rightarrow CO + H_2 \quad (\lesssim 350\ nm)$$

and

$$HO + HCHO \rightarrow H_2O + CHO$$
$$CHO + O_2 \rightarrow CO + HO_2$$

do not lead to any net gain of HO_x (HO or HO_2) radicals in the methane oxidation chain.

The RO_2 + NO reactions, in which NO is oxidized to NO_2, are additionally important in that they provide a net source of ozone [15] through NO_2 photodissociation:

$$RO_2 + NO \rightarrow RO + NO_2$$
$$NO_2 + h\nu \rightarrow O + NO$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net production of O_3 from this route occurs at all altitudes below ~15 km but is particularly important in the lower troposphere where, in polluted air, it leads to photochemical smog formation.

The oxidation of carbon monoxide, methane and other hydrocarbons does not always lead to ozone production. For example, if HO_2 reacts with ozone, i.e., when insufficient NO is present, ozone is then lost via the reaction sequence:

$$HO + CO \rightarrow H + CO_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$\underline{HO_2 + O_3 \rightarrow HO + 2O_2}$$
$$\text{net: } CO + O_3 \rightarrow CO_2 + O_2$$

Applying the available kinetic information, one may roughly determine that nitric oxide volume mixing ratios larger than

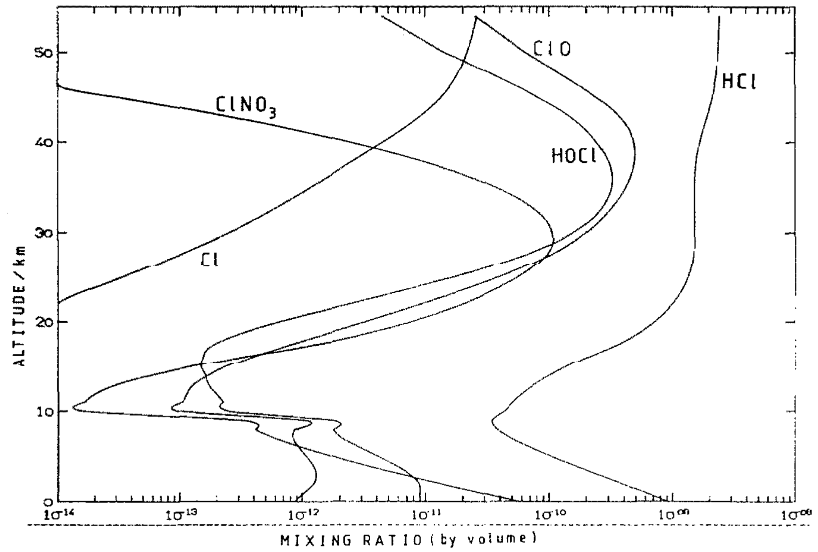

FIGURE 4e. Altitude profiles of mixing ratio of some important chlorine species.

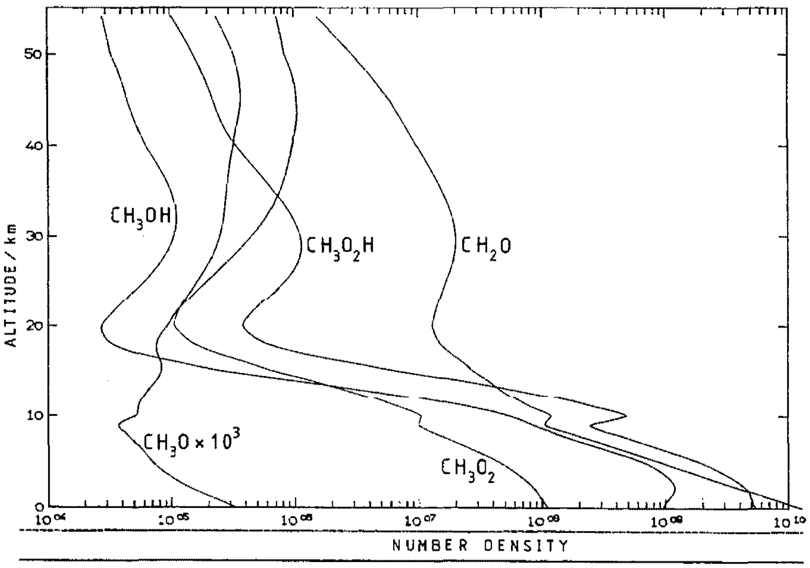

FIGURE 4f. Altitude profiles of number density of some important organic species.

about 10^{-11} are required for the atmospheric oxidation chains to follow those reactions involving NO. This condition may not be reached in extensive regions of the troposphere because of the very short residence times of NO and NO_2 through the reactions

$$NO + O_3 \rightarrow NO_2 + O_2$$

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

followed by rain-out of HNO_3. Recent measurements [16] have shown that NO volume mixing ratios may indeed be very low in the marine boundary layer, less than 10 ppt (10×10^{-12}) in the tropical Pacific. There are, unfortunately, too few observations of NO available now to derive a typical tropospheric distribution of this gas, so that at present it is not possible to make good estimates of the photochemical production of tropospheric ozone. As indicated above, the role of methane oxidation reactions in controlling the HO_x (HO and HO_2) concentrations in the background atmosphere is likewise dependent on the global NO distribution.

In the absence of NO the fate of CH_3OOH and H_2O_2 must be considered. These molecules may be removed by photolysis, e.g.,

$$CH_3OOH + h\nu \rightarrow CH_3O + HO$$

or by reaction with HO. Furthermore, since CH_3OOH and H_2O_2 are water soluble, they are readily removed by precipitation

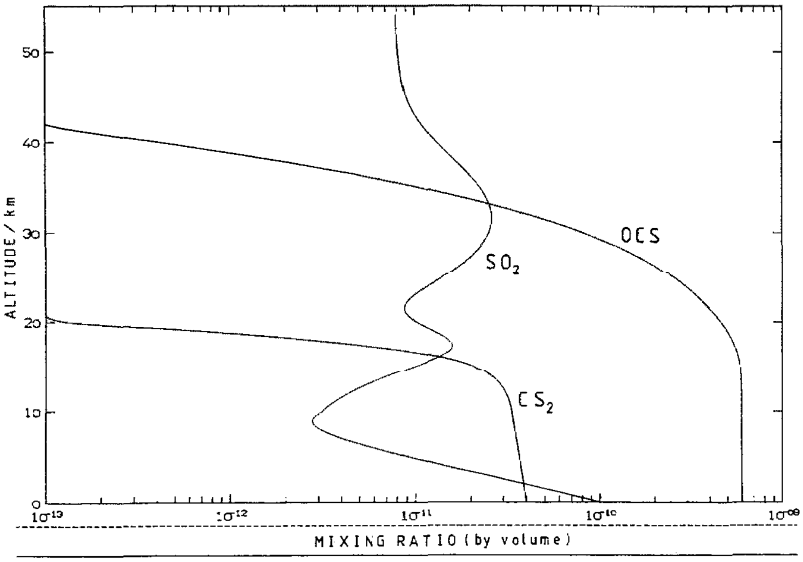

FIGURE 4g. Altitude profiles of mixing ratio of some important sulfur species.

scavenging, which has an average time constant of 1 week and which is competitive with the gas phase removal routes.

The total turnover of carbon in the atmospheric CH_4 cycle is augmented by other hydrocarbons from both natural and man-made sources. Of particular importance are emissions from vegetation of terpenes which are oxidized to CO by analogous reactions to those outlined above for CH_4. A summary of the atmospheric budgets of the species involved in the tropospheric carbon cycle is given in table 1.

The atmospheric cycles of many trace gases are determined by the HO distribution. For instance, the removal of the natural sulfur compounds H_2S, $(CH_3)_2S$, and CH_3SH takes place by HO attack. It is commonly assumed that the subsequent reactions lead rapidly to the formation of SO_2, although the detailed oxidation mechanisms are not well known [17]. A fraction of the SO_2 in the atmosphere is converted to H_2SO_4 by gas phase oxidation, the first step again being accomplished by reaction with HO. Oxidation of SO_2 in atmospheric raindrops is also important [18].

NO_x molecules are mainly removed from the troposphere by reactions with hydroxyl leading to the formation of nitric acid which is very soluble in water. The photochemical lifetime of HNO_3 in the troposphere is more than a month, i.e., much longer than the average precipitation time constant of about one week. Nitric acid is, therefore, mainly removed by precipitation in the troposphere. In this way the transport of NO_x from the troposphere to the stratosphere is inhibited.

Ammonia plays an important role in tropospheric chemistry since it can combine with acid species such as HNO_3, H_2SO_4, and HCl to form ammonium salts, which are a major constituent of the atmosphere aerosol. NH_3 also reacts with HO and subsequent reactions of the NH_2 radical may lead to NO_x production in the troposphere by reactions such as

$$NH_3 + HO \rightarrow NH_2 + H_2O$$

$$NH_2 + O_3 \rightarrow NH_2O + O_2$$

$$NH_2O + O_2 \rightarrow HNO + HO_2$$

$$HNO + h\nu \rightarrow H + NO$$

However, competing reactions of NH_2 can lead to destruction of NO_x

$$NH_2 + NO_x \rightarrow N_2O_{x-1} + H_2O$$

Furthermore, NH_2 reacts rapidly with HO_2

$$NH_2 + HO_2 \rightarrow NH_3 + O_2$$

to yield ammonia again. Since NH_3 is removed by precipitation with a characteristic time scale of about one week while the time constant for attack by HO is of the order of a few months, the production and destruction of NO_x through NH_3 oxidation is probably of minor importance.

A summary of atmospheric budgets of some nitrogen species is given in table 2.

Chlorine chemistry in the troposphere is largely governed by HO attack followed by conversion of the Cl constituent of the resultant radical to HCl or $COCl_2$, which are removed mainly by precipitation. The detailed mechanisms of the photo-oxidation of chloro-organics is not well known, however. The tropospheric chemistry of bromine and iodine is even less well understood. Since HBr and HI are more reactive than HCl with HO and are also less readily formed from atomic Br and I, it seems probable that the chemical behaviour of iodine and bromine differs from that of chlorine species.

TABLE 1. Budgets of carbon species

Gas	Direct source/year Source identification	Secondary source/year Source identification	Removal by	Atmospheric lifetimes[a]	Transport distances[b] Δx, Δy, Δz (km)
CO	$4\text{–}16\times10^{14}$ g CO biomass burning 6.4×10^{14} g CO industry	6×10^{14} g CO methane oxidation $4\text{–}13\times10^{14}$ g CO C_5H_8, $C_{10}H_{16}$ oxidation	HO	2 months	4000,2500,10
CH_4	$0.7\text{–}1.2\times10^{14}$ g CH_4 rice paddy fields $0.3\text{–}2.2\times10^{14}$ g CH_4 natural wetlands 0.6×10^{14} g CH_4 ruminants $0.3\text{–}1.1\times10^{14}$ g CH_4 biomass burning 0.5×10^{14} g CH_4 gas leakage		HO	7 years	complete
C_5H_8 $C_{10}H_{16}$	8.3×10^{14} g C trees		HO	10 hours	400.200.1

[a] Atmospheric lifetimes in hours, months or years.

[b] Diffusion distances in E-W, S-N and vertical directions (in km) over which concentrations are reduced to 30% by chemical reactions; calculated with $[HO] \approx 7\times10^5$ molecule cm^{-3}.

TABLE 2. Budgets of nitrogen species

Gas	Direct source/year Source identification	Secondary source/year Source identification	Removal by	Atmospheric lifetimes[a]	Transport distances[b] $\Delta x, \Delta y, \Delta z$ (km)
NO_x $(NO + NO_2)$	$8.2\text{–}18.5 \times 10^{12}$ g N industry $10\text{–}40 \times 10^{12}$ g N biomass burning $3\text{–}4 \times 10^{12}$ g N lightning $0\text{–}15 \times 10^{12}$ g N soils 0.25×10^{12} g N jet aircraft	$0.5\text{–}1.5 \times 10^{12}$ g N oxidation of N_2O	HO	1.5 days	1500,400,1.0
HNO_3		$22\text{–}77 \times 10^{12}$ g N $HO + NO_2$	rain	3 days	3000,600,1.5
N_2O	1.8×10^{12} g N fossil fuel burning $1\text{–}2 \times 10^{12}$ g N biomass burning $4\text{–}10 \times 10^{12}$ g N oceans $2\text{–}6 \times 10^{12}$ g N loss organic matter $< 3 \times 10^{12}$ g N fertilized fields		Stratospheric photolysis	100 years	global
NH_3	$10\text{–}20 \times 10^{12}$ g N domestic animals $2\text{–}6 \times 10^{12}$ g N wild animals $< 3 \times 10^{12}$ g N fertilized fields $< 30 \times 10^{12}$ g N natural fields $4\text{–}12 \times 10^{12}$ g N coal burning $< 60 \times 10^{12}$ g N biomass burning		rain	<9 days	<9000,1000,3

[a] Atmospheric lifetimes in hours, months or years.

[b] Diffusion distances in E-W, S-N and vertical directions (in km) over which concentrations are reduced to 30% by chemical reactions; calculated with $[HO] = 7 \times 10^5$ molecule cm^{-3}.

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5. Data Sheets

5.1. Oxygen Compounds

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

$\Delta H^\circ = -106.5$ kJ mol^{-1}

Low pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1}s^{-1}	Temp./K	References	Comments
Absolute Rate Coefficients			
$(6.75 \pm 0.43)\times 10^{-35} \exp((635 \pm 18)/T)$ [O$_2$]	262–319	Arnold and Comes, 1979 [1]	(a)
5.69×10^{-34} [O$_2$]	298		
$(1.82 \pm 0.23)\times 10^{-35} \exp((995 \pm 37)/T)$ [N$_2$]	262–309		
5.13×10^{-34} [N$_2$]	298		
$(6.24 \pm 1.53\times 10^{-35} \exp((525 \pm 70)/T)$ [Ar]	263–298		
3.63×10^{-34} [Ar]	298		
5.91×10^{-34} [N$_2$]	298	Lin and Leu, 1980 [2]	(b)
3.75×10^{-34} [Ar]	298		
3.48×10^{-34} [He]	298		
$(6.9 \pm 1.0)\times 10^{-34}(T/300)^{-1.25\pm 0.2}$ [O$_2$]	219–368	Klais, Anderson, and Kurylo, 1980 [3]	(c)
$2.15\times 10^{-34} \exp(345/T)$ [O$_2$]			
$(6.2 \pm 0.9)\times 10^{-34}(T/300)^{-2.0\pm 0.5}$ [N$_2$]	219–368		
$8.82\times 10^{-35} \exp(575/T)$ [N$_2$]			
$(3.9 \pm 0.5)\times 10^{-34}(T/300)^{-1.9\pm 0.3}$ [Ar]	219–368		
$6.3\times 10^{-35} \exp(535/T)$ [Ar]			
Reviews and Evaluations			
$6.2\times 10^{-34}(T/300)^{-2.0}$ [N$_2$]	220–300	NASA, 1979 [4]; NASA, 1981 [6]	(d)
$5.6\times 10^{-34}(T/300)^{-2.36}$ [N$_2$]	218–298	CODATA, 1980 [5]	(e)
$3.6\times 10^{-34}(T/300)^{-1.96}$ [Ar]	200–346		

Comments

(a) O_3 flash photolysis-O resonance absorption. Corrections for the reactions $O + O_3 \rightarrow 2O_2$ and $O + O_2 + O_3 \rightarrow 2O_3$ are necessary.

(b) Preliminary data from O_2 flash photolysis-O resonance fluorescence.

(c) O_2 flash photolysis-O resonance fluorescence technique. Most extensive available data in agreement with the earlier results from [5]. Smaller temperature coefficient for $M = O_2$, compared to $M = N_2$ or Ar, attributed to $O_3 + O_2 \rightarrow O_2 + O_3$ exchange energy transfer.

(d) Based on data of ref. [3].

(e) Based on results from ref. [7] essentially in agreement with the present preferred values.

Preferred Values

$k_0 = 6.9\times 10^{-34}(T/300)^{-1.25}$ [O$_2$] cm^3 molecule^{-1} s^{-1} over range 219–368 K.

$k_0 = 6.2\times 10^{-34}(T/300)^{-2.0}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over range 219–368 K.

$k_0 = 3.9\times 10^{-34}(T/300)^{-1.9}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 219–368 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 200–370 K.
$\Delta n = \pm 0.5$ over range 200–370 K.

Comments on Preferred Values

Good agreement between various studies in the overlapping ranges of conditions. Preferred values based on ref. [3]. Differing temperature coefficients in other studies are partly due to too narrow temperature ranges. No new data on high pressure rate coefficients and intermediate fall-off range, for older data see CODATA, 1980 [5].

Vibrational Deactivation of O_3^* formed by combination $O + O_2 \rightarrow O_3^*$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
6.6×10^{-15}	O_2	298	Hochanadel, Ghormley, and Boyle, 1968 [8]	(a)
1.0×10^{-14}	O_2	298	Bevan and Johnson, 1973 [9]	(a,b)
7×10^{-14}	O_2	298	Bevan and Johnson, 1973 [9]	(a,c)
2.0×10^{-14}	N_2, O_2	298	von Rosenberg, and Trainor, 1974 [10]	(d)
2.3×10^{-14}	O_2	298	Kleindienst, Burkholder, and Bair, 1980 [12]	(e)
Reviews and Evaluations				
3×10^{-12}	O_2	300	Troe, 1979 [13]	(f)

Comments

(a) Pulse radiolysis of O_2; time resolved observation of changes in the O_3 uv absorption spectrum during the $O + O_2 \rightarrow O_3$ recombination reaction.

(b) Rate coefficient corresponding to low energy levels of O_3^*.

(c) Rate coefficient corresponding to high energy levels of O_3^*.

(d) Flash photolysis of O_2; time resolved IR emission measurements of the O_3^* (101) mode during the $O + O_2 \rightarrow O_3$ recombination reaction. Rate coefficient corresponding probably to low excitation of O_3^* because of good agreement with deactivation of laser excited O_3^* (101) molecules, see Rosen and Cool, 1973 [11].

(e) Flash photolysis of O_2; time resolved observation of O_3 uv absorption spectrum during $O + O_2 \rightarrow O_3$ recombination. Rate coefficient probably corresponding to slowest step, i.e., deactivation of low energy levels of O_3.

(f) Analysis of collision efficiencies of steady state rate constants for recombination of $O + O_2 \rightarrow O_3$. This rate coefficient is estimated from an average energy of 1 kJ mol^{-1} transferred per collision of highly excited O_3^* formed during the initial association $O + O_2 \rightarrow O_3^*$.

Preferred Values

$k^{**} = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K for M = O_2, N_2 (O_3^* energies near 100 kJ mol^{-1}).

$k^{*} = 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K for M = O_2, N_2 (O_3^* energies near 20 kJ mol^{-1}).

Reliability

$\Delta \log k^{**} = \pm 0.5$.

$\Delta \log k^{*} = \pm 0.3$.

Comments on Preferred Values

The deexcitation of O_3^* during the recombination $O + O_2 \rightarrow O_3$ presents a complex time dependence involving elementary steps of quite different rates. Presumably the effective relaxation rate slows down with decreasing energy as indicated by the preferred rate coefficients. Preferred values of k^{**} are taken from ref. [13], values of k^{*} from refs [10] and [12].

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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			
$(8.3 \pm 0.6) \times 10^{-15}$	298	West, Weston, and Flynn, 1978 [1]	(a)
$(2.12 \pm 0.18) \times 10^{-11} \exp(-(2337 \pm 26)/T)$	262–335	Arnold and Comes, 1980 [2]	(b)
$(8.33 \pm 0.18) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.5 \times 10^{-11} \exp(-2218/T)$	200–300	NASA, 1979 [3]	(c)
$2.0 \times 10^{-11} \exp(-2280/T)$	220–1000	CODATA, 1980 [4]	(d)
$1.5 \times 10^{-11} \exp(-2218/T)$	200–300	NASA, 1981 [5]	(c)

Comments

(a) O_3 photolysis in dye laser pulses at 600 nm, O_3 vibrational excitation produced in CO_2 laser pulses, O detection by resonance fluorescence.

(b) O_3-flash photolysis-O resonance absorption technique.

(c) Value based on the data by Davis, Wong, and Lephardt [6], which agreed within error limits with the slightly lower value by McCrumb and Kaufman [7].

(d) Value based on ref. [6], in agreement also with earlier high temperature data.

Preferred Values

$k = 8.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(-2300/T)$ cm^3 molecule^{-1} s^{-1} over range 220–400 K.

Reliability

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

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

Comments on Preferred Values

The preferred value is an averaged value of the data from refs. [1], [2], [6], and [7].

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$O + O_3^* \rightarrow O + O_3 \quad (1)$
$\rightarrow 2O_2 \quad (2)$

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comment
Absolute Rate Coefficients			
1.5×10^{-11}	298	West, Weston, and Flynn, 1976 [1]	(a)
Branching ratios			
$k_2/k < 0.3$	298	West, Weston, and Flynn, 1978 [2]	(b)

Comments

(a) Discharge flow system, O_3 vibrationally excited by CO_2 laser pulses. O_3^* (vibrational excitation mainly O_3^* (100), O_3^* (001)) monitored by IR fluorescence, O monitored by $O + NO_2$ titration.

(b) O_3 photolysis with dye laser pulses, O_3 vibrational excitation in CO_2 laser pulses, O detection by resonance fluorescence.

Preferred Value

$k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

More measurements with other selectively excited O_3 molecules are needed. This preferred value applies to O_3^* (100) and O_3^* (001) molecules.

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

$\Delta H°(1) = -32.8$ kJ mol^{-1}

$\Delta H°(2) = -95.4$ kJ mol^{-1}

$\Delta G°(3) = -189.7$ 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)
$k_2/k \leqslant 0.05$	300	Gauthier and Snelling, 1971 [4]	(d)
Reviews and Evaluations			
$2.9\times 10^{-11}\exp(67/T)$	200–300	NASA, 1979 [5]	(e)
$3.7\times 10^{-11}\exp(67/T)$	200–350	CODATA, 1980 [6]	(f)
$3.2\times 10^{-11}\exp(67/T)$	200–300	NASA, 1981 [7]	(g)

Comments

(a) $O(^1D)$ production by laser flash photolysis of O_3 at 248 nm, $O(^3P)$ detection by resonance absorption at 130 nm.

(b) $O(^1D)$ production by laser flash photolysis of O_3 at 266 nm. $O(^3P)$ detection by resonance fluorescence at 130 nm.

(c) $O(^1D)$ detection from $O(^1D)\rightarrow O(^3P)$ emission at 630 nm. $O_2(^1\Sigma_g^+)$ 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 $v = 0$ and 1 levels with $k(1)/k(0) = 0.7$.

(d) $O(^1D)$ production by photolysis of O_3.

(e) Based on $O(^1D)$ emission measurements only (ref. [8]).

(f) Average from $O(^1D)$ measurements by 630 nm emission and 115 nm absorption and $O(^3P)$ measurements by 130 nm absorption and fluorescence.

(g) Based on ref. [1] and earlier references excluding $O(^1D)$ absorption measurements.

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 range 200–350 K.

$k_1/k = 0.8$

$k_2/k \leqslant 0.05$.

Reliability

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

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

$\Delta \log (k_1/k) = \pm 0.1$.

Comments on Preferred Values

The earlier controversy between measurements using $O(^1D)$ emission at 630 nm and absorption at 115 nm appears to be resolved now, since $O(^3P)$ detection by absorption at 130 nm and fluorescence support the $O(^1D)$ emission results. Apparently the γ-value in the Lambert-Beer law used in the $O(^1D)$ absorption results was too small. The preferred value for k averages the results from refs. [1], [2], [3], and [8] which all agree very well. The temperature coefficients are accepted from ref. [8], the branching ratios from refs. [3] and [4].

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$$
\begin{aligned}
\mathrm{O(^1D) + O_3} &\rightarrow \mathrm{O_2 + 2O(^3P)} && (1)\\
&\rightarrow \mathrm{O(^3P) + O_3} && (2)\\
&\rightarrow \mathrm{2O_2(^1\Delta_g)} && (3)\\
&\rightarrow \mathrm{O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)} && (4)\\
&\rightarrow \mathrm{2O_2(^3\Sigma_g^-)} && (5)
\end{aligned}
$$

$\Delta H°(1) = -83.2\ \mathrm{kJ\ mol^{-1}}$

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

$\Delta H°(3) = -393.0\ \mathrm{kJ\ mol^{-1}}$

$\Delta H°(4) = -424.7\ \mathrm{kJ\ mol^{-1}}$

$\Delta H°(5) = -581.6\ \mathrm{kJ\ mol^{-1}}$

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			
$(2.7 \pm 0.2)\times 10^{-10}$	300	Heidner, Husain, and Wiesenfeld, 1973 [1]	(a)
$(2.4 \pm 0.5)\times 10^{-10}$	103–393	Streit et al., 1976 [2]	(b)
$(2.41 \pm 0.11)\times 10^{-10}$	300	Amimoto, Force, and Wiesenfeld, 1978 [3]	(c)
$(2.5 \pm 0.5)\times 10^{-10}$	300	Amimoto et al., 1980 [5]	(c)
$(2.28 \pm 0.23)\times 10^{-10}$	298	Ravishankara and Wine, 1981 [6]	(d)
Branching ratios			
$k_4/k \leqslant 0.15$	300	Klais, Laufer, and Kurylo, 1980 [7]	(e)
$k_5/k \simeq k_1/k \simeq 0.5$	300	Davenport, Schiff, and Welge, 1974 [9]	(f)
$k_2/k \simeq 1$	300	Amimoto, Force, and Wiesenfeld, 1978 [3]	(g)
Reviews and Evaluations			
$k_1 \simeq k_5 \simeq 0.5\ k = 1.2\times 10^{-10}$	200–300	NASA, 1979 [10]	(h)
$k_1 \simeq k_5 \simeq 0.5\ k = 1.2\times 10^{-10}$	200–300	NASA, 1981 [11]	(h)

Comments

(a) $\mathrm{O(^1D)}$ production by flash photolysis of $\mathrm{O_3}$ in a flow system. $\mathrm{O(^1D)}$ detection by resonance absorption at 115 nm. This value is not influenced by the error in the Lambert-Beer γ-value present in other $\mathrm{O(^1D)}$ reactions of this work, see discussion in ref. [4].

(b) $\mathrm{O(^1D)}$ production by laser flash photolysis of $\mathrm{O_3}$ at 266 nm in a flow system. $\mathrm{O(^1D)}$ followed by $\mathrm{O(^1D)} \rightarrow \mathrm{O(^3P)}$ emission at 630 nm.

(c) $\mathrm{O(^1D)}$ production by laser flash photolysis of $\mathrm{O_3}$ at 248 nm in a flow system. $\mathrm{O(^3P)}$ detection by resonance absorption at 130 nm, see also discussion of these results in ref. [4].

(d) $\mathrm{O(^1D)}$ production by laser flash photolysis of $\mathrm{O_3}$ at 266 nm. $\mathrm{O(^3P)}$ detection by resonance fluorescence at 130 nm.

(e) Flash photolysis of $\mathrm{O_3}$ with $\mathrm{O(^3P)}$ detection; analysis of the early part of the $\mathrm{O(^3P)}$ profile taking into account Slanger and Black's results on the rate of the reaction $\mathrm{O_2(^1\Sigma_g^+) + O_3}$([8]).

(f) Resonance fluorescence detection of O atoms. One $\mathrm{O(^3P)}$ formed per $\mathrm{O(^1D)}$ consumed. This can either be explained by $k_2/k \simeq 1$ or by $k_5/k_1 \simeq 1$.

(g) Observation of one $\mathrm{O(^3P)}$ formed per $\mathrm{O(^1D)}$ consumed. These authors favour $k_2/k \simeq 1$ instead of $k_5/k_1 \simeq 1$ to explain their results, on the basis of the postulated existence of a stable $\mathrm{O_3}$ species at energies above the dissociation energy of $\mathrm{O_3}$. As long as there is no unambiguous experimental confirmation, we prefer the interpretation of these data by $k_5/k_1 \simeq 1$.

(h) Branching ratio from ref. [9], absolute value from refs. [1]–[5].

Preferred Values

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

$k_1/k \simeq k_5/k \simeq 0.5$.

Reliability

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

$\Delta \log k_1/k = \Delta \log k_5/k - \pm 0.1$.

Comments on Preferred Values

The accuracy of the overall rate constant k apparently is quite good. The given value is based on the data from refs. [2], [3], [5], and [6]. The observation of the appearance of one $O(^3P)$ per $O(^1D)$ consumed also appears well established. The interpretation of this observation by assuming $k_1 \simeq k_5$ appears most probable, although the alternative $k_2/k \simeq 1$ cannot be ruled out at present.

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

$\Delta H^\circ = -94.3$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
1.4×10^{-19}	N_2	300	Collins, Husain, and Donovan, 1973 [1]	(a)
$2.22 \times 10^{-18}(T/300)^{0.78}$	O_2	285–322	Findlay and Snelling, 1971 [2]	(b)
$(5.6 \pm 0.36) \times 10^{-18}$	H_2O	298	Findlay and Snelling, 1971 [2]	(b)
$(4 \pm 1) \times 10^{-18}$	H_2O	298	Becker, Groth, and Schurath, 1971 [3]	(c)
$<1.5 \times 10^{-20}$	CO_2	298	Findlay and Snelling, 1971 [2]	(b)
$<8 \times 10^{-20}$	CO_2	298	Becker, Groth, and Schurath, 1971 [3]	(c)
Reviews and Evaluations				
$2.2 \times 10^{-18}(T/300)^{0.8}$	O_2	285–322	Hampson et al., 1973 [4]	(d)
$<2 \times 10^{-20}$	N_2	300		

Comments

(a) VUV absorption measurements of $O_2(^1\Delta_g)$ decay. As discussed by the authors this is the most direct study of $O_2(^1\Delta_g)$ quenching by N_2.

(b) $O_2(^1\Delta_g)$ formed by photolysis of O_2-C_6H_6 mixtures by energy transfer from a benzene triplet state. $O_2(^1\Delta_g)$ monitored by 1.27 μ emission.

(c) Measurements in reaction cell of 220 m^3 volume. $O_2(^1\Delta_g)$ detection by emission from the energy pooling reaction $2O_2(^1\Delta_g) \to O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$

(d) Revew of literature up to 1971. Preferred room temperature value for $M = O_2$ is a consensus value from several studies; the temperature coefficient is from Findlay and Snelling [2]. Upper limits of k for $M = N_2$ vary between 1.1×10^{-19} and 3×10^{-21}.

Preferred Values

$k = 2.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K..

$k \leqslant 1.4 \times 10^{-19}$ 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.

$k \leqslant 8 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} for $M = CO_2$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ for $M = O_2$, and for $M = H_2O$.

Comments on Preferred Values

Whereas the values for $M = O_2$ and H_2O appear to be reliable, the smaller values for $M = N_2$ and CO_2 need further confirmation. The temperature coefficient appears to be small, however, more extensive data are needed before safe conclusions on k at stratospheric temperatures can be given.

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$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$

$\Delta H^\circ = +12.2$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$6.6\times10^{-13}\exp(-1560/T)$	195–439	Clark, Jones, and Wayne, 1970 [1]	(a)
$(3.5\pm1.3)\times10^{-15}$	298		
$4.5\times10^{-11}\exp(-(2830\pm180)/T)$	283–321	Findlay and Snelling, 1971 [2]	(b)
3.4×10^{-15}	298		
$6.0\times10^{-11}\exp(-2850/T)$	296–360	Becker, Groth, and Schurath, 1972 [3]	(c)
4.2×10^{-15}	298		
$(4.4\pm1.3)\times10^{-15}$	300	Collins, Husain, and Donovan, 1973 [4]	(d)
$<5\times10^{-13}$ $(v\geq1)$	298	Klais, Laufer, and Kurylo, 1980 [5]	(e)
Reviews and Evaluations			
$4.5\times10^{-11}\exp(-2830/T)$	283–321	Schofield, 1972 [6]	(f)
$1.2\times10^{-11}\exp(-2400/T)$	200–350	Hampson, 1980 [7]	(g)

Comments

(a) Microwave discharge flow system for the generation of $O_2(^1\Delta_g)$, O_3 added downstream. Detection of $O_2(^1\Delta_g)$ via selective photoionization by argon resonance radiation at 106.7 and 104.8 nm.

(b) $O_2(^1\Delta_g)$ produced by O_3 photolysis by Hg resonance radiation; $O_2(^1\Delta_g)$ concentrations monitored via 1.27 μ emission.

(c) Static reactor of 220 m^3 volume. $O_2(^1\Delta_g)$ formation by microwave discharge in O_2. $O_2(^1\Delta_g)$ detection by 1.27 μ emission. Preexponential factor can be 50% lower if $O_2(^1\Sigma_g^+)$ yield from the $O(^3P) + O_3$ reaction is interpreted differently.

(d) $O_2(^1\Delta_g)$ produced by uv flash photolysis of O_3; $O_2(^1\Delta_g)$ detected by time resolved absorption spectroscopy near 144 nm.

(e) Flash photolysis of O_3, detection of $O_2(^1\Delta_g)_{v=0,2,3}$ near 144 nm in absorption.

(f) Preferred values from ref. [2].

(g) Room temperature average value combined with average activation energy.

Preferred Values

$k = 3.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.2\times10^{-11}\exp(-2840/T)$ over range 280–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

Whereas there is good agreement on the room temperature value, the temperature coefficient appears less certain. In view of the coincidence of the results from refs. [2] and [3], which were obtained by two completely different techniques, we favour their temperature coefficient over that from ref. [1].

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$O_2(^1\Delta_g)_{v\geq 1} + M \rightarrow O_2(^1\Delta_g)_{v=0} + M$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(8.4 \pm 3.0)\times 10^{-14}$	N_2	298	Klais, Laufer, and Kurylo, 1980 [1]	(a)
$(3.4 \pm 2.0)\times 10^{-14}$	Ar	298		
$(4.7 \pm 2.0)\times 10^{-12}$	O_3	298		

Comments

(a) $O_2(^1\Delta_g)_{v>1}$ formed by flash photolysis of O_3 at 240–257 nm. The photolysis channel $O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^3P)$ produces $O_2(^1\Delta_g)_{v=1}$ and $O_2(^1\Delta_g)_{v=0}$ with yields of 0.6 ± 0.2 and 0.4 ± 0.15, respectively.

Preferred Value

$k = 8\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = N_2$ at 298 K.

Reliability

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

Comments on Preferred Value

This is a single determination and more data are desirable. In particular the rate coefficient for $M = O_2$ should be measured.

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

$\Delta H^\circ = -156.9$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
$(4.6 \pm 1)\times 10^{-17}$	O_2	294	Thomas and Thrush, 1975 [1]	(a)
$(4.0 \pm 0.4)\times 10^{-17}$	O_2	298	Martin, Cohen, and Schatz, 1976 [2]	(b)
$(3.8 \pm 0.3)\times 10^{-17}$	O_2	300	Lawton et al., 1977 [3]	(b)
$(2.5 \pm 0.2)\times 10^{-17}$	O_2	298	Chatha et al., 1979 [4]	(c)
$(2.2 \pm 0.1)\times 10^{-15}$	N_2	298	Martin, Cohen, and Schatz, 1976 [2]	(b)
$(1.7 \pm 0.1)\times 10^{-15}$	N_2	298	Chatha et al., 1979 [4]	(c)
4.6×10^{-12}	H_2O	294	*Thomas and Thrush, 1975 [1]*	*(a)*
$(8.0 \pm 2.0)\times 10^{-14}$	O	300	Slanger and Black, 1979 [5]	(d)
Reviews and Evaluations				
1.5×10^{-16}	O_2	300	Hampson et al., 1973 [6]	
2.0×10^{-15}	N_2	300		
4.0×10^{-12}	H_2O	300		

Comments

(a) Microwave discharge system; $O_2(^1\Sigma_g^+)$ detection by 1.91 μ radiation. Data also for $M = H_2$.

(b) Optical excitation of $O_2(^1\Sigma_g^+)_{v=1}$, fast relaxation of $v = 1$ to $v = 0$ before electronic quenching.

(c) $O_2(^1\Sigma_g^+)$ formed by energy pooling $2O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-)$ in a discharge flow system. Data also for M = He.

(d) $O_2(^1\Sigma_g^+)$ produced by the $O(^1D) + O_2$ reaction, $O_2(^1\Sigma_g^+)$ monitored by 761.8 nm emission.

Preferred Values

$k = 4.0\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k = 2.0\times 10^{-15}$ *cm^3 molecule^{-1} s^{-1}* for $M = N_2$ at 298 K.

$k = 8.0\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $M = O$ at 298 K.

$k = 4.0\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for $M = H_2O$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ for $M = O_2$, O, and H_2O, ± 0.1 for $M = N_2$.

Comments on Preferred Values

More recent values of k for $M = O_2$ are systematically lower than earlier values, whereas data for $M = N_2$ appear well established. Temperature coefficients as well as information on the reaction $O_2(^1\Sigma_g^+) + O(^3P) \rightarrow O_2(^1\Delta_g) + O(^3P)$ are urgently required because of their possible importance for the overall quenching rates of $O_2(^1\Sigma_g^+)$ in the atmosphere, see discussion in ref. [5].

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$$\begin{aligned} O_2(^1\Sigma_g^+) + O_3 &\rightarrow O + 2O_2 && (1)\\ &\rightarrow O_2(^1\Delta_g) + O_3 && (2)\\ &\rightarrow O_2(^3\Sigma_g^-) + O_3 && (3)\end{aligned}$$

$\Delta H°(1) = -50.4$ kJ mol^{-1}
$\Delta H°(2) = -62.6$ kJ mol^{-1}
$\Delta H°(3) = -156.9$ 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			
$(2.5 \pm 0.5)\times10^{-11}$	295	Gilpin, Schiff, and Welge, 1971 [1]	(a)
$(2.3 \pm 0.5)\times10^{-11}$	295	Snelling, 1974 [2]	(b)
$(2.2 \pm 0.2)\times10^{-11}$	295	Slanger and Black, 1979 [3]	(c)
$(1.8 \pm 0.2)\times10^{-11}$	295	Amimoto and Wiesenfeld, 1980 [4]	(d)
Branching Ratios			
$k_1/k \simeq 0.62 \pm 0.22$	298	Slanger and Black, 1979 [3]	(c, e)
$k_1/k = 0.79 \pm 0.08$	295	Amimoto and Wiesenfeld, 1980 [4]	(d, f)

Comments

(a) Flash photolysis of O_3 in the presence of O_2. $O_2(^1\Sigma_g^+)$ formed by the reaction $O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$. $O_2(^1\Sigma_g^+)$ detected by emission at 761.8 nm.

(b) Flash photolysis of O_3, $O_2(^1\Sigma_g^+)$ formation by $O(^1D)$ quenching by O_2.

(c) Flash photolysis of O_2 in a discharge flow system, $O_2(^1\Sigma_g^+)$ formation by quenching of $O(^1D)$ by O_2. $O_2(^1\Sigma_g^+)$ detected by emission at 761.8 nm.

(d) O_2 laser flash photolysis at 248 nm. $O(^3P)$ detection by resonance absorption at 130 nm.

(e) Derived from the product $0.48 \pm 0.04 = (k_1/k)\times(k_1'/k')$ where k' corresponds to the reaction $O(^1D) + O_2 \rightarrow$ products and k_1' to the reaction $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$. $k_1'/k' = 0.77$ from Lee and Slanger [5] is used. The authors erroneously give $k_1/k = 0.67 \pm 0.22$.

(f) Based on the branching ratio $k_1'/k' = 0.77$ from Lee and Slanger [5] for the reactions $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$ and $O(^1D) + O_2 \rightarrow$ products, and on an $O(^1D)$ quantum yield of $\phi = 0.9$ for O_3 photolysis.

Preferred Values

$k = 2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.7$ at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (k_1/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values are simple averages of the given data. Information on the temperature dependences is required. The temperature dependence is likely to be small.

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$O_2(^1\Sigma_g^+)_{v=1} + O_2 \rightarrow O_2(^1\Sigma_g^+)_{v=0} + O_2$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_{v=1} = 1.5\times10^{-11}$	300	Gauthier and Snelling, 1974 [1]	(a)
$k_{v=1} = 2.2\times10^{-11}$	300	Lee and Slanger, 1978 [2]	(b)
$k_{v=2} = (9 \pm 1)\times10^{-13}$	300	Schurath, 1975 [3]	(c)

Comments

(a) $O_2(^1\Sigma_g^+)_{v=1}$ produced by the reaction $O(^1D) + O_2(^3\Sigma_g^-)$ and measured by emission at 760–785 nm; in this reaction 25% of the $O_2(^1\Sigma_g^+)$ formed is in the $v = 1$ state, the remainder in the $v = 0$ state. Measurements under steady state conditions.

(b) $O_2(^1\Sigma_g^+)_{v=1}$ produced by the reaction $O(^1D) + O_2(^3\Sigma_g^-)$, $O_2(\Sigma_g^+)_v$ detected by time resolved emission in the range 760–785 nm.

(c) $O_2(^1\Sigma_g^+)_{v=2}$ formed as predominant product of the energy pooling reaction $2O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + O_2(^1\Sigma_g^+)$.

Preferred Values

$k_{v=1} = 1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_{v=2} = 9\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_{v=1} = \pm 0.3$ at 298 K.

$\Delta \log k_{v=2} = \pm 0.5$ at 298 K.

Comments on Preferred Values

More information on temperature coefficients and "normal" relaxation in collisions with other colliders is required.

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$O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0° kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	(1)	493.56	242.4
$\rightarrow O(^3P) + O(^1D)$	(2)	683.38	175.0
$\rightarrow O(^1D) + O(^1D)$	(3)	873.20	137.0
$\rightarrow O(^3P) + O(^1S)$	(4)	897.80	132.2

Preferred Values

Absorption cross sections and quantum yields for O_2 photolysis at 298 K

λ /nm	$10^{19}\sigma/cm^2$	ϕ_2	λ /nm	$10^{19}\sigma/cm^2$	ϕ_2
140.8–142.8	140	1	158.7–161.3	49.7	1
142.8–144.9	148	1	161.3–163.9	34.5	1
144.9–147.0	141	1	163.9–166.7	20.8	1
147.0–149.2	129	1	166.7–169.5	12.3	1
149.2–151.5	115	1	169.5–172.4	7.22	1
151.5–153.8	99.1	1	172.4–173.9	4.58	1
153.8–156.2	82.4	1	173.9–175.4	2.74	1
156.2–158.7	65.8	1	176 –200	(see below)	0

λ /nm	$10^{23}\langle\sigma\rangle$ (300 K)/cm^2	$10^{23}\langle\sigma\rangle$ (200 K)/cm^2	$10^{23}\langle\sigma\rangle$ (160 K)/cm^2
175.4–177.0	12800	15000	15700
178.6	11800	11900	11800
180.2	7370	6470	6060
181.8	4770	5050	5210
183.5	3160	3020	2940
185.2	1610	1400	1330
186.9	874	757	725
188.7	419	348	340
190.5	190	144	137
192.3	94.8	60.4	48.4
194.2	62.4	57.2	57.2
196.1	21.5	18.7	18.7
198.0	7.56	5.4	5.42
200.0	3.06	1.83	1.77
202.0	1.94	1.54	1.49

λ /nm	$10^{24}\sigma/cm^2$	λ /nm	$10^{24}\sigma/cm^2$
200	12.0	225	5.3
205	10.2	230	4.0
210	9.3	235	2.8
215	7.9	240	1.0
220	6.5	245	0.5

Comments on Preferred Values

The absorption cross sections for $\lambda < 175$ nm and $200 < \lambda < 245$ nm are from Ackermann [1], average cross sections over the Schumann-Runge bands for $175 < \lambda < 200$ nm are from Kockarts [2]; there is considerable scatter of data at $\lambda \geqslant 200$ nm with an uncertainty of $\pm$ 20% for 200–230 nm. The onset of the $O(^1D)$ production near 175 nm is given by a smooth, probably temperature dependent function, see ref. [3]. For $175 < \lambda < 200$ nm we prefer $\phi_1 \cong 1$. The preferred values are unchanged from those given in the previous evaluation, CODATA, 1980 [4], where more detailed information can be found.

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$O_3 + h\nu \rightarrow$ products

Reaction		ΔH°_0 / kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	(1)	101.4	1180
$\rightarrow O(^3P) + O_2(a\ ^1\Delta_g)$	(2)	195.7	611
$\rightarrow O(^3P) + O_2(b\ ^1\Sigma_g^+)$	(3)	258.3	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	(4)	291.2	411
$\rightarrow O(^1D) + O_2(a\ ^1\Delta_g)$	(5)	385.5	310
$\rightarrow O(^1D) + O_2(b\ ^1\Sigma_g^+)$	(6)	448.1	267

Quantum yield data and evaluations

Quantum yields	Wavelength/nm	Reference	Comments
$\phi_5 = 0.99 \pm 0.01$	248	Amimoto, Force, and Wiesenfeld, 1978 [1]	(a)
$\phi_5 = 1.00 \pm 0.05$	230–280	Kajimoto and Cvetanovic, 1979 [2]	(b)
$\phi_1 = 0.1$	274	Fairchild, Stone, and Lawrence, 1978 [3]	(c)
$\phi_1(v)$, $\phi_5(v)$	270–300		
$\phi_1(v)$	600		
$\phi_1 = 0.1$	266	Sparks et al., 1980 [4]	(d)
$\phi_5(v = 0–3)$	266		
$\phi_1 = 0.15 \pm 0.02$	248	Amimoto et al., 1980 [5]	(e)
ϕ_5 fall-off	297.5–325	Brock and Watson, 1980 [6]	(f)
$\phi_1 = 0.12 \pm 0.02$	266	Brock and Watson, 1980 [7]	(g)

Comments

(a) Laser flash photolysis of O_3 at 248 nm, $O(^3P)$ resonance absorption detection at 130 nm. Work superseded by ref. [5] (better time resolution).

(b) Quantum yield determined by the use of the isotope exchange reaction $C^{16}O_2 + {}^{18}O(^1D)$.

(c) Photofragment spectroscopy of ozone at 270–310 nm and 600 nm. At 274 nm, $O(^3P)$ atoms together with $O_2(^3\Sigma^-)$ are formed with a quantum yield of about 0.1, whereas $O(^1D)$ is formed together with $O_2(^1\Delta_g)$; $O_2(^3\Sigma_g^-)$ is formed in all vibrational states $v = 0–10$, $O_2(^1\Delta_g)$ is formed 26, and 10%, respectively.

(d) High resolution photofragment spectroscopy of ozone at 266 nm giving $\phi_1 \simeq 0.1$. Relative yields for vibrational states of $O_2(^1\Delta_g)$ in $v = 0, 1, 2$, and 3 are 57, 24, 12, 7%.

(e) Laser flash photolysis of O_3 at 248 nm, $O(^3P)$ resonance absorption detection at 130 nm. Improved time resolution, supersedes ref. [1].

(f) Laser flash photolysis of O_3, $O(^1D)$ detection by $O(^1D) + N_2O \rightarrow 2NO$, $NO + O_3 \rightarrow NO_2^* + O_2$ chemiluminescence technique. This work supersedes earlier work by Philen, Watson, and Davis [8]. Results confirm ϕ_5 data preferred in ref. [9] for the range 297.5–311 nm; however, they give a considerably larger long wavelength tail of ϕ_5 in the range 311–325 nm. The normalization of relative quantum yields ϕ_5 in the range 260–300 nm is still controversial, a decrease from $\phi_5 = 0.96$ at 300 nm to $\phi_5 = 0.88$ at 266 nm being possible. However, $\phi_5 = 0.88$ for the whole range 266–304 nm cannot be ruled out.

(g) Laser flash photolysis of O_3 at 266 nm. $O(^3P)$ detection by resonance fluorescence.

Preferred Values

Absorption cross sections at 298 K

λ /nm	$10^{19}\sigma/\mathrm{cm}^2$	λ /nm	$10^{19}\sigma/\mathrm{cm}$	λ /nm	$10^{19}\sigma/\mathrm{cm}^2$
119.8–120.5	184	198.0–200.0	3.30	277.8–281.7	39.9
129.9–130.7	124	208.3–210.5	4.84	289.9–294.1	11.4
139.9–140.8	71.7	219.8–222.2	19.7	298.5–303.0	3.69
149.2–151.5	36.9	229.9–232.6	48.3	310	see below
158.7–161.3	12.0	238.1–241.0	79.7	320	see below
169.5–172.4	8.17	246.9–250.0	111	330	0.0778
178.5–180.2	7.86	259.7–263.2	103	340	0.0171
188.7–190.5	5.31	266.7–270.3	82.3	350	0.00266
				360	0.00055

λ /nm	$10^{23}\sigma/\mathrm{cm}^2$	λ /nm	$10^{23}\sigma/\mathrm{cm}^2$
410	2.91	580	455
420	3.99	600	489
440	12.5	620	390
460	35.7	640	274
480	71.1	660	207
500	122	680	137
520	178	700	91.3
540	288	720	64.0
560	388	730	51.4

λ /nm	$10^{19}\sigma/\mathrm{cm}^2$	λ /nm	$10^{19}\sigma/\mathrm{cm}^2$
304	2.32	314	0.617
306	1.77	316	0.456
308	1.28	318	0.340
310	0.990	320	0.315
312	0.757		

Temperature coefficient of absorption cross sections

λ /nm	σ(214 K)/σ(300 K)	λ /nm	σ(214 K)/σ(300 K)
250	0.98	300	0.91
260	0.98	310	0.88
270	0.97	320	0.73
280	0.96	330	0.86
290	0.94	340	0.86

Quantum yields for O_3 photolysis

Wavelength/nm	Quantum yield	Temp./K
248–266	$\phi_5 = 0.88, \phi_1 = 0.12$	200–300
250–300	$\phi_1 + \phi_5 = 1, \phi_5 > 0.88$	200–300
304	$\phi_5 = 0.99$	235
306	0.90	235
307	0.80	235
308	0.55	235
309	0.35	235
310	0.25	235
311	0.15	235
312	0.10	235
313	0.07	235
314	0.04	235
315	0.02	235
316	0	235
304	1.00	235
306	0.96	298
308	0.83	298
310	0.56	298
312	0.31	298
314	0.15	298
316	0.06	298
318	0.03	298
320	0.00	298

Comments on Preferred Values

Absorption cross sections are unchanged from CODATA, 1980 [9] except for the new details in the range 304–320 nm which are from ref. [10]. The quantum yields for 235 K in the range 304–316 nm are unchanged from CODATA, 1980 [9]. For 298 K, $\phi_5 = 0.88 \pm 0.03$ appears to be well established for wavelengths 248–266 nm. However, it remains to be confirmed that ϕ_5 increases with increasing wavelengths to values near unity at $\lambda = 300$ nm. The preferred values given refer to a normalization of $\phi_5 = 1$ at $\lambda = 300$ nm. The given values of ϕ_5 in the range 304–312 nm are averages of the results from refs. [6], [11], and [12], the values at 314–320 are averages from refs. [11] and [12]. The tail of the ϕ_5 curve observed in ref. [6] for $\lambda \geqslant 312$ nm needs further substantiation and is not included in the preferred values.

There have been several recent investigations (see, e.g., refs. [13]–[15]) of absorption spectra in the range 250–350 nm due to nascent O_3^* formed during the recombination reaction $O + O_2 \rightarrow O_3^*$. These spectra are considerably broader than the Hartley continuum; at 250 nm, σ is much below the normal O_3 value. These spectra have been shown to be due to vibrationally excited O_3^* and not to electronically excited O_3 (e.g., ref. [15]). High temperature spectra of O_3 show a similar broadening of the Hartley continuum, see ref. [16]. With the known rates of vibrational deexcitation one estimates only negligible contributions of such spectra to the O_3 photolysis under atmospheric conditions.

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5.2. Hydrogen Compounds

$H + O_3 \rightarrow HO + O_2$ (1)
$\rightarrow HO_2 + O$ (2)

$\Delta H^\circ(1) = -321.7$ kJ mol^{-1}

$\Delta H^\circ(2) = -101.0$ kJ mol^{-1}

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratio			
$k_2/k = 0.2$–0.3	299	Finlayson-Pitts and Kleindienst, 1979 [1]	(a)
$k_2/k \leqslant 0.03$	~298	Howard and Finlayson-Pitts, 1980 [2]	(b)
$k_2/k \simeq 0.4$	295	Force and Wiesenfeld, 1981 [3]	(c)
$k_2/k \leqslant 0.02$	298	Finlayson-Pitts et al., 1981 [4]	(d)
Reviews and Evaluations			
$1.4 \times 10^{-10} \exp(-470/T)$	200–300	NASA, 1979 [5]	
$1.4 \times 10^{-10} \exp(-480/T)$	220–360	CODATA, 1980 [6]	
$1.4 \times 10^{-10} \exp(-470/T)$	200–300	NASA, 1981 [7]	

Comments

(a) Discharge-flow system; [O(^{3}P)] monitored by resonance fluorescence; [HO] measured indirectly from known [H] and [O_3].

(b) Discharge-flow system; [HO] and [HO_2] monitored by laser magnetic resonance.

(c) Pulsed laser photolysis of O_3 at 248 nm; H generated by $O(^1D) + H_2 \rightarrow HO + H$; [H] and [O] monitored by time-resolved resonance absorption spectroscopy.

(d) Similar experimental technique to comment (a) but with [HO] monitored by resonance fluorescence.

Preferred Values

$k = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-10} \exp(-480/T)$ cm^3 molecule^{-1} s^{-1} over range 220–360 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values are unaltered from the CODATA, 1980, evaluation [6]. The high values of the branching ratio, $k_2/k = 0.2$–0.3, originally reported by Finlayson-Pitts and Kleindienst [1] on the basis of the yields of $O(^3P)$ atoms, were subsequently shown to be erroneously interpreted, by the experiments of Howard and Finlayson-Pitts [2], which attempted to directly monitor the yields of HO_2. This latter study produced an upper limit of $k_2/k \leqslant 0.03$. A more recent report by Force and Wiesenfeld [3] suggests that the branching ratio, k_2/k, could be as high as 0.4. This latter study, however, takes no account of the high level of vibrational excitation in the HO radicals generated in the system, which can lead to the formation of $O(^3P)$ atoms via reactions with H and O_3 [4]. We have accepted the findings of Howard and Finlayson-Pitts et al. [2,4], which essentially confirm that reaction (2) can be neglected.

References

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$H + O_3 \rightarrow HO^*(v = n) + O_2$

Rate coefficient data ($k = k_{v=3\ \mathrm{to}\ 9}$)

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Branching Ratios			
$k_{v=3}/k \simeq 0.07$	~298	Charters, Macdonald, and Polanyi, 1971 [1]	(a)
$k_{v=4}/k \simeq 0.09$	~298		
$k_{v=5}/k \simeq 0.10$	~298		
$k_{v=6}/k < 0.11$	~298		
$k_{v=7}/k \sim 0.11$	~298		
$k_{v=8}/k = 0.23$	~298		
$k_{v=9}/k = 0.28$	~298		

Comments

(a) Flow system; HO* monitored by Fourier transform infrared spectroscopy.

Preferred Values

$k_{v=3} = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=4} = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=5} = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=6} \leqslant 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=7} = 3.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=8} = 6.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=9} = 7.8 \times 10^{-12}$ 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 rate constants for the formation of HO* in vibrational levels up to $v = 9$ have been derived from the branching ratios listed above and the total rate constant of the reaction $H + O_3 \rightarrow HO^* + O_2$ at 298 K, i.e., $k = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA Evaluation). The branching ratios were calculated from the relative rate constants for the formation of HO* in the different levels v, i.e., $k(v = 3) \simeq 0.26$, $k(v = 4) \simeq 0.33$, $k(v = 5) \simeq 0.36$, $k(v = 6) < 0.4$, $k(v = 7) \simeq 0.4$, $k(v = 8) \simeq 0.8$, and $k(v = 9) = 1.00$, as measured by Charters, Macdonald, and Polanyi [1]. We have assumed negligible formation of HO* in levels $v = 0$ to 2.

References

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$O + H_2 \rightarrow HO + H$

$\Delta H^\circ = 7.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(0.88 \pm 0.50)\times10^{-11}$ exp$((-4200 \pm 240)/T)$	347–742	Dubinsky and McKenney, 1975 [1]	(a)
6.7×10^{-18}	298*		
$(0.83 \pm 0.38)\times10^{-11}((-4330 \pm 240)/T)$	495–832	Dubinsky and McKenney, 1975 [1]	(b)
4.1×10^{-18}	298*		
$(5.2 \pm 0.8)\times10^{-11}$ exp$((-4950 \pm 300)/T)$	363–490	Campbell and Handy, 1975 [2]	(c)
3.2×10^{-18}	298*		
Reviews and Evaluations			
3.0×10^{-14} T exp$(-4480/T)$	400–2000	Baulch et al., 1972 [3]	
1.6×10^{-11} exp$(-4570/T)$	350–830	Dubinsky and McKenney, 1975 [1]	(d)

Comments

(a) Discharge-flow system; O generated from $N + NO \rightarrow N_2 + O$ and [O] monitored by air afterflow technique; kinetic analysis involves additional reactions $O + HO \rightarrow O_2 + H$ and $HO + H_2 \rightarrow H_2O + H$.

(b) Same system as in comment (a) but with [O] monitored by atomic resonance fluorescence.

(c) Discharge-flow stirred-reaction system; O generated from $N + NO \rightarrow N_2 + O$ and [O] monitored by air afterglow technique.

(d) Evaluation of literature data over temperature range 347–832 K, but not including data of Campbell and Handy, 1975 [2]; data obtained from a weighted least-mean-squares analysis of literature rate coefficients.

Preferred Values

$k = 3.5\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6\times10^{-11}$ exp$(-4570/T)$ over range 298–830 K.

Reliability

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

Comments on Preferred Values

This reaction is very slow and consequently there have been few measurements of the rate coefficient at temperatures below 350 K. The analysis of the considerable literature data over the range 350–830 K by Dubinsky and McKenney [1] is selected as the basis of our preferred values. We have recommended the use of the Arrhenius expression derived by Dubinsky and McKenney down to temperatures of 250 K, with the inclusion of reasonably wide error limits.

References

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$O + HO \rightarrow O_2 + H$

$\Delta H^\circ = -70.2$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.8 \pm 0.9)\times10^{-11}$	298	Howard and Smith, 1980 [1]	(a)
$(2.01 \pm 0.18)\times10^{-11}$ exp$((112 \pm 29)/T)$	221–499	Lewis and Watson, 1980 [2]	(b)
$(3.1 \pm 0.8)\times10^{-11}$	298		
$(6.65 \pm 0.23)\times10^{-10}$ $T^{(-0.50 \pm 0.12)}$	250–500	Howard and Smith, 1981 [3]	(a), (c)
$(3.53 \pm 0.31)\times10^{-11}$	300		
Reviews and Evaluations			
4.0×10^{-11}	200–300	NASA, 1979 [4]	
3.8×10^{-11}	298	CODATA, 1980 [5]	
2.3×10^{-11} exp$(110/T)$	200–300	NASA, 1981 [6]	

Comments

(a) Discharge-flow system; generation of O from N + NO; combined with flash photolysis of H_2O and resonance fluorescence measurement of [HO].

(b) Low-pressure discharge-flow system; generation of O from O_2 discharge an HO from $H + NO_2$; resonance fluorescence measurement of [HO]; alternative rate expression given by authors: $k = (2.37^{+1.23}_{-0.81}) \times 10^{-10} \times T^{-(0.362 \pm 0.072)}$ cm^3 $molecule^{-1}$ s^{-1}.

(c) The rate coefficient at 300 K includes the previous data of ref. [1].

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 range 220–500 K.

Reliability

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

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

Comments on Preferred Values

There is good agreement between the data of Howard and Smith [1] and of Lewis and Watson [2]. The preferred values have been derived from a rounded-off least-mean-squares treatment of the rate coefficients of these two most recent studies.

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$O + HO_2 \rightarrow HO + O_2$

$\Delta H^\circ = -220.7$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.2 \pm 1.2) \times 10^{-11}$	298	Hack et al., 1979 [1]	(a)
$(7 \pm 2) \times 10^{-11}$	298	Lii, Sauer, and Gordon, 1980 [2]	(b)
Relative Rate Coefficients			
$(2.8 \pm 1.4) \times 10^{-11}$	298	Hack et al., 1979 [1]	(c)
Reviews and Evaluations			
3.5×10^{-11}	200–300	NASA, 1979 [3]	
3.1×10^{-11}	298	CODATA, 1980 [4]	
4.0×10^{-11}	200–300	NASA, 1981 [5]	

Comments

(a) Discharge-flow system; O from microwave discharge of O_2; [O] monitored by ESR; HO_2 from $H + O_2 + M$ or from $F + H_2O_2$; $[HO_2]$ and [HO] monitored by LMR; rate coefficient is the average from two systems: (a) $[O] \gg [HO_2]$, $k = (4.2 \pm 1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (corrected to allow for more recent data on the $HO + H_2O_2$ reaction) and (b) $[O] \ll [HO_2]$, $k = (4.1 \pm 1.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

(b) HO_2 generated by electron pulse radiolysis of H_2 in presence of O_2; $[HO_2]$ monitored by absorption at 265 nm; rate coefficient derived from kinetic model involving ten reactions.

(c) Same experimental system as described in comment (a); ratio $k/k(O + HO) = 0.86 \pm 0.4$ determined by measuring the stationary [HO], and rate coefficient calculated taking $k(O + HO) = 3.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. (CODATA Evaluation).

Preferred Value

$k = 3.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The preferred rate coefficient at 298 K is the average from the three determinations of Hack et al., [1]. The previous data of Burrow et al., [6] are no longer internally consistent, owing to the change in the preferred value for the rate coefficient of the reference reaction: $HO + H_2O_2$. The recent data of Lii et al., [2] are limited and very indirect.

References

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$O + H_2O_2 \rightarrow HO + HO_2$

$\Delta H^\circ = -63.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.75 \pm 0.41) \times 10^{-12} \exp(-(2125 \pm 261)/T)$	283–368	Davis, Wong, and Schiff, 1974 [1]	(a)
2.2×10^{-15}	298		
Reviews and Evaluations			
$2.8 \times 10^{-12} \exp(-2125/T)$	200–300	NASA, 1979 [2]	
$2.7 \times 10^{-12} \exp(-2100/T)$	283–368	CODATA, 1980 [3]	
$2.8 \times 10^{-12} \exp(-2125/T)$	200–300	NASA, 1981 [4]	

Comments

(a) O from laser flash photolysis of O_3 at 600 nm; [O] monitored by resonance fluorescence spectroscopy.

Preferred Values

$k = 2.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.0 \times 10^{-11} \exp(-2500/T)$ cm^3 molecule^{-1} s^{-1} over range 250–370 K.

Reliability

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

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

Comments on Preferred Values

There have been no new data reported on this reaction and the preferred values are still based on the work of Davis, Wong, and Schiff [1]. Since, however, the experimentally determined A-factor [1] is low in relation to those of other atom-molecule reactions we have obtained the preferred temperature coefficient from an estimated A-factor and the experimental rate coefficient at 298 K. In the absence of evidence to the contrary, we have disregarded any contribution from the possible second channel $O + H_2O_2 \rightarrow O_2 + H_2O$.

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

$\Delta H^\circ(1) = -181.4$ kJ mol^{-1}

$\Delta H^\circ(2) = -189.2$ 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			
$(11.8 \pm 1.2) \times 10^{-11}$	297	Wine and Ravishankara, 1981 [1]	(a)
Reviews and Evaluations			
9.9×10^{-11}	200–300	NASA, 1979 [2]	
2.0×10^{-10}	200–350	CODATA, 1980 [3]	
9.9×10^{-11}	200–300	NASA, 1981 [4]	

Comments

(a) Laser flash photolysis of O_3 at 266 nm; rate of formation of $O(^3P)$ monitored by laser resonance fluorescence.

Preferred Value

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

Reliability

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

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

Comments on Preferred Value

Whereas the previous CODATA evaluation [3] was based on an average of the data of the Cambridge Laboratory [5,6] and the NOAA Laboratories [7], the recent studies on the reactions of $O(^1D)$ with atmospheric gases [1,8,9] have supported the findings of the NOAA Laboratories [7]. The preferred value is a rounded-off average of the results of Davidson et al. [7] and of Wine and Ravishankara [1].

References

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$$\begin{aligned} O(^1D) + H_2O &\rightarrow 2HO \quad &(1)\\ &\rightarrow H_2 + O_2 \quad &(2)\\ &\rightarrow O(^3P) + H_2O \quad &(3) \end{aligned}$$

$\Delta H°(1) = -118.7$ kJ mol^{-1}

$\Delta H°(2) = -196.59$ kJ mol^{-1}

$\Delta H°(3) = -189.2$ 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			
$(1.95 \pm 0.3)\times 10^{-10}$	295	Amimoto et al., 1979 [1]	(a)
$(2.6 \pm 0.5)\times 10^{-10}$	300	Lee and Slanger, 1979 [2]	(b)
$(1.95 \pm 0.2)\times 10^{-10}$	298	Wine and Ravishankara, 1981 [3]	(c)
Branching Ratios			
$k_3/k = 0.14 \pm 0.04$	295	Amimoto et al., 1979 [1]	(a)
$k_3/k = 0$	295	Amimoto et al., 1980 [4]	(a), (d)
$k_2/k_1 = 0.01^{+0.005}_{-0.01}$	298	Zellner, Wagner, and Himme, 1980 [5]	(e)
Reviews and Evaluations			
2.3×10^{-10}	200–300	NASA, 1979 [6]	
2.8×10^{-10}	200–350	CODATA, 1980 [7]	
2.2×10^{-10}	200–300	NASA, 1981 [8]	

Comments

(a) Pulsed laser photolysis of O_3 at 248 nm; $O(^3P)$ monitored by time-resolved atomic resonance absorption spectroscopy.

(b) Pulsed laser photolysis of O_2 at 160 nm; $O(^1D)$ monitored directly by absorption at 630 nm and indirectly by $O_2(^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-)$ emission at 720 nm.

(c) Laser flash photolysis of O_3 at 266 nm; rate of formation of $O(^3P)$ monitored by resonance fluorescence.

(d) Repeat of experiments of ref. [1] with improved high-speed detection electronics; previous data were derived on the assumption that $\phi_1 = 1.0$ for $O_3 + 248\ \text{nm} \rightarrow O(^1D) + O_2$, whereas ϕ_1 is $<$ unity ($\phi_1 \simeq 0.85$ at 248 nm).

(e) Flash photolysis of $O_3/H_2O/He$ mixtures; rate coefficient ratio determined by direct measurement of yields of H_2 and HO (resonance absorption).

Preferred Value

$k = 2.3\times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–350 K.

Reliability

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

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

Comments on Preferred Value

The preferred rate coefficient at 298 K is an average of the data of Amimoto et al. [1], Lee and Slanger [2], Wine and Ravishankara [3] and of Streit et al. [9], which are all in reasonable agreement. The earlier data of Heidner et al. [10] are now rejected. The temperature dependence observed by Streit et al. [9] is accepted here.

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$HO + H_2 \rightarrow H_2O + H$

$\Delta H^\circ = -62.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.12\times10^{-19}\,T^{2.44}\exp(-1281/T)$	298–992	Tully and Ravishankara, 1980 [1]	(a)
$(6.08\pm0.37)\times10^{-15}$	298		
$(4.9\pm0.5)\times10^{-12}\exp((-1990\pm340)/T)$	250–400	Ravishankara et al., 1981 [2]	(a)
$(5.64\pm0.60)\times10^{-15}$	295		
Reviews and Evaluations			
$1.83\times10^{-15}\,T^{1.3}\exp(-1835/T)$	250–3000	Cohen and Westberg, 1979 [3]	
$1.2\times10^{-11}\exp(-2200/T)$	200–300	NASA, 1979 [4]	
$1.8\times10^{-11}\exp(-2330/T)$	210–300	CODATA, 1980 [5]	
$1.2\times10^{-11}\exp(-2200/T)$	200–300	NASA, 1981 [6]	

Comments

(a) Flash photolysis of H_2O with resonance fluorescence monitoring of [HO].

Preferred Values

$k = 6.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.7\times10^{-12}\exp(-2100/T)$ cm^3 molecule^{-1} s^{-1} over range 200–450 K.

Reliability

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

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

Comments on Preferred Values

The recent measurements of Ravishankara and co-workers [1,2] are in good agreement with previous data for this reaction. The preferred rate coefficient at 298 K is the mean of these new data [1,2] and of the data of Stuhl and Niki [7], Westenberg and de Haas [8], Smith and Zellner [9], and Overend et al. [10], and Atkinson et al. [11]. Since the measured rate coefficients are not published in reference [9] it is not possible to carry out a least-mean-squares treatment of all the data to obtain the temperature coefficient. The preferred value of E/R is the mean of the data of Smith and Zellner [9], Atkinson et al. [11] and Ravishankara et al. [2]. The preferred A-factor is calculated from the preferred rate coefficient at 298 K and the preferred value of E/R.

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$HO + HO \rightarrow H_2O + O$

$\Delta H^\circ = -70.6$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\pm0.2)\times10^{-12}$	298	Farquharson and Smith, 1980 [1]	(a)
Reviews and Evaluations			
$1\times10^{-11}\exp(-500/T)$	200–300	NASA, 1979 [2]	(b)
1.8×10^{-12}	298	CODATA, 1980 [3]	(c)
$4.5\times10^{-12}\exp(-275/T)$	200–300	NASA, 1981 [4]	(d)

Comments

(a) Discharge-flow system; HO generated by H + NO_2 and monitored by resonance fluorescence.

(b) Based on a re-evaluation of data of refs. [5–8].

(c) Mean of results from refs. [5–13].

(d) Based on average of data from refs. [5–7] and [13] with T dependence from ref. [13].

Preferred Value

$k = 1.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The recent measurements of Farquharson and Smith [1] are in excellent agreement with the previous CODATA evaluation [3] of the preferred rate coefficient at 298 K, which is accepted here. The temperature coefficient of this reaction still needs to be measured.

References

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$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H^\circ = -291.3$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.9 \pm 0.12) \times 10^{-11}$	308	Lii et al., 1980 [1]	(a)
$(11.6 \pm 2.5) \times 10^{-11}$	298	Hochanadel, Sworski, and Ogren, 1980 [2]	(b)
$(6.2 ^{+4.0}_{-2.0}) \times 10^{-11}$	288–348	Burrows, Cox, and Derwent, 1981 [3]	(c)
$(6.4 \pm 1.5) \times 10^{-11}$	299	Keyser, 1981 [4]	(d)
Reviews and Evaluations			
4.0×10^{-11}	200–300	NASA, 1979 [5]	
3.5×10^{-11}	298	CODATA, 1980 [6]	
4.0×10^{-11}	200–300	NASA, 1981 [7]	

Comments

(a) HO_2 generated by electron pulse radiolysis of H_2 in presence of O_2; [HO_2] and [HO] monitored by absorption at 230 and 308.7 nm, respectively; rate coefficient derived from computer modeling of mechanism consisting of 14 elementary reactions.

(b) HO_2 generated by flash photolysis of H_2O in an atm of CO containing 2% O_2; [HO_2] monitored by absorption at 220 nm; rate coefficient obtained from computer fit of proposed mechanism.

(c) Pulsed photolysis of O_3, H_2O, O_2, N_2 (He) mixtures at 1 atm; [HO] and [HO_2] monitored by molecular modulation ultraviolet absorption spectrometry at 308.2 and 210 nm, respectively; rate coefficient obtained by computer simulation of data.

(d) Discharge-flow system at 1 Torr total pressure; resonance fluorescence monitoring of [HO] under pseudo first-order conditions; $[HO_2] \gg [HO]$; HO generated from $F + H_2O$ (and other sources); HO_2 generated from $F + H_2O_2$ and measured by conversion to HO; secondary reactions of O and H atoms were shown to be unimportant.

Preferred Value

$k = 8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

Despite several recent attempts to study this reaction there have been no really definitive measurements of the rate coefficient owing to the considerable difficulties in devising experiments to produce and monitor HO and HO_2 radicals in a "clean" system.

The previous relative rate coefficient measurements of Burrows et al. [8], which yielded $k/k(HO + H_2O_2) = 63.6$, now give $k = 1.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K, in the light of the new recommendation $k(HO + H_2O_2) = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. This revised rate coefficient of the reaction, $HO + H_2O_2 \rightarrow H_2O + HO_2$, also affects the absolute rate data of Hack et al. [9] although to an extent which is difficult to assess from the data given by these authors.

Looking back at the data which are listed in the previous CODATA evaluation [6], the measurements of DeMore and Tschuikow-Roux, [10], Glanzer and Troe, [11] and DeMore, [12], all yielded approximate rate coefficients. The system of Hochanadel et al. [13] is very indirect. The system of Chang and Kaufman [14], recently re-investigated by Keyser [4], is also complex. This latter study, however, brings the rate coefficient measured in the "low-pressure" region more in line with the "high-pressure" studies [1,2,3,10,13]. The recent measurements of Lii et al. [1], Hochanadel et al. [2] and Burrows et al. [3] are all derived indirectly from fairly complex systems.

All the reported values of the rate coefficient which appear to be reasonable, within the experimental limitations of the various systems, lie within the range 6 to 12×10^{-11} cm^3 molecule^{-1} s^{-1}. A median value of 8×10^{-11} cm^3 molecule^{-1} s^{-1} with an uncertainty of a factor of 2 is therefore recommended.

References

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H^\circ = -134.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.51 \pm 0.6)\times10^{-12}\exp((-126 \pm 76)/T)$	245–423	Keyser, 1980 [1]	(a)
$(1.64 \pm 0.32)\times10^{-12}$	298		
$(2.96 \pm 0.50)\times10^{-12}\exp((-164 \pm 52)/T)$	250–459	Sridharan, Reimann, and Kaufman, 1980 [2]	(b)
$(1.69 \pm 0.26)\times10^{-12}$	298		
Relative Rate Coefficients			
1.65×10^{-12}	293	Hack et al., 1981 [3]	(c)
Reviews and Evaluations			
$1.0\times10^{-11}\exp(-750/T)$	200–300	NASA, 1979 [4]	
$7.6\times10^{-12}\exp(-670/T)$	200–700	CODATA, 1980 [5]	
$2.7\times10^{-12}\exp(-145/T)$	200–300	NASA, 1981 [6]	

Comments

(a) Discharge-flow system; [HO] monitored by resonance fluorescence; $[H_2O_2]$ determined photometrically at 199.5 nm.

(b) Discharge-flow system; [HO] monitored by laser-induced fluorescence; $[H_2O_2]$ determined photometrically at 213.9 nm.

(c) Discharge-flow system with LMR detection of HO_2 in study of reaction $HO_2 + NO \rightarrow HO + NO_2$; HO_2 generated from $F + H_2O_2$; ratio $k/k(HO_2 + NO) = 0.2$ at 293 K derived from computer simulation of proposed mechanism; k calculated from $k(HO_2 + NO) = 8.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 293 K (CODATA Evaluation).

Preferred Values

$k = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9\times10^{-12}\exp(-160/T)$ cm^3 molecule^{-1} s^{-1} over 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 preferred data were obtained from a rounded-off least-mean-squares calculation on the rate coefficients of Keyser [1] and of Sridharan et al. [2], which are in good agreement. The much lower rate coefficients previously obtained by Greiner [7], Hack et al. [8] and Harris and Pitts [9] are now believed to be in error, owing to the regeneration in their system of HO radicals from the HO_2 product.

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$HO + O_3 \rightarrow HO_2 + O_2$

$\Delta H^\circ = -171.2$ 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)
Relative Rate Coefficients			
$(7.0 \pm 0.8) \times 10^{-14}$	300	Zahniser and Howard, 1980 [1]	(b)
Reviews and Evaluations			
$1.6 \times 10^{-12} \exp(-940/T)$	200–300	NASA, 1979 [2]	(c)
$1.9 \times 10^{-12} \exp(-1000/T)$	220–450	CODATA, 1980 [3]	(d)
$1.6 \times 10^{-12} \exp(-940/T)$	200–300	NASA, 1981 [4]	(e)

Comments

(a) Discharge-flow system; HO generated from $H + NO_2$ and monitored by laser magnetic resonance.

(b) Discharge-flow system; HO generated from $H + NO_2$ and $H + O_3$; HO_2 generated from $H + O_2 + M$; $[HO_2]$ and $[HO]$ monitored by laser magnetic resonance; k obtained from measured ratio, $k/k(HO_2 + O_3) = 35 \pm 4$ (average of three systems studied) and taking $k(HO_2 + O_3) = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K (CODATA Evaluation).

(c) Average of the data of refs. [5–9].

(d) Average of the data of refs. [5,6] and refs. [8–10].

(e) Unchanged from ref. [2].

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 range 220–450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The recent single temperature measurements of this rate coefficient by Zahniser and Howard [1] are in excellent agreement with the preferred values of the previous CODATA evaluation in [3] which is accepted here.

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$HO^*(v=n) + M \rightarrow HO(v<n) + M$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$M = N_2$			
$k_{v=4} = 0.78 \times 10^{-13}$	~298	Streit and Johnston, 1976 [1]	(a)
$k_{v=5} = 2.1 \times 10^{-13}$	~298		
$k_{v=6} = 5.0 \times 10^{-13}$	~298		
$k_{v=7} = 5.5 \times 10^{-13}$	~298		
$k_{v=8} = 3.7 \times 10^{-13}$	~298		
$k_{v=9} = (3.6 \pm 0.5) \times 10^{-15}$	~298	Worley, Coltharp, and Potter, 1972 [2]	(b)
$= 4.4 \times 10^{-13}$	~298	Streit and Johnston, 1976 [1]	(a)
$M = O_2$			
$k_{v=4} = 1.4 \times 10^{-13}$	~298	Streit and Johnston, 1976 [1]	(a)
$k_{v=5} = 3.2 \times 10^{-13}$	~298		
$k_{v=6} = 7.3 \times 10^{-13}$	~298		
$k_{v=7} = 7.8 \times 10^{-13}$	~298		
$k_{v=8} = 5.4 \times 10^{-13}$	~298		
$k_{v=9} = (1.0 \pm 0.1) \times 10^{-14}$	~298	Worley, Coltharp, and Potter, 1972 [2]	(b)
$= 3.5 \times 10^{-13}$	~298	Streit and Johnston, 1976 [1]	(a)
$M = H_2O$			
$k_{v=1} = (1.35 \pm 0.50) \times 10^{-11}$	295	Spencer and Glass, 1977 [3]	(c)
$k_{v=9} = (2.0 \pm 1.6) \times 10^{-13}$	~298	Worley, Coltharp, and Potter, 1972 [2]	(b)
$M = CO_2$			
$k_{v=9} = (2.4 \pm 1.0) \times 10^{-14}$	~298	Worley, Coltharp, and Potter, 1972 [2]	(b)

Comments

(a) Low-pressure static system; chemiluminescence emission of HO* in the overtone bands in the region 550–850 nm.

(b) Fast-flow system; measurements made of the rate of decay in the intensity of the 9–7 emission of HO*.

(c) Fast-flow system; rate of decay of HO* measured by EPR spectroscopy.

Preferred Values

No recommendations.

Comments on Preferred Values

All of the systems described above are complex. Additional work is clearly desired to resolve the considerable discrepancies in the published data, none of which can be recommended at present.

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$HO^*(v = n) + O_3 \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_{v=2} = (1.9 \pm 1.1) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$k_{v=3} = (2.4 \pm 0.9) \times 10^{-12}$	~298		
$k_{v=4} = (2.8 \pm 0.8) \times 10^{-12}$	~298		
$= (3.7 \pm 0.10) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)
$k_{v=5} = (3.4 \pm 0.7) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$= (4.5 \pm 0.13) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)
$k_{v=6} = (5.3 \pm 0.6) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$= (7.1 \pm 0.18) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)
$k_{v=7} = (6.5 \pm 0.5) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$= (8.5 \pm 0.23) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)
$k_{v=8} = (6.7 \pm 0.5) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$= (8.9 \pm 0.24) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)
$k_{v=9} = (7.7 \pm 0.3) \times 10^{-12}$	~298	Coltharp, Worley, and Potter, 1971 [1]	(a)
$= (11 \pm 0.40) \times 10^{-12}$	~298	Streit and Johnston, 1976 [2]	(b)

Comments

(a) Fast-flow system; measurements made of the rate of decay in the intensity of the $v = 9 - 7$ emission of HO^*.

(b) Low-pressure static system; chemiluminescence emission of HO^* observed in the overtone bands in the regions 550–850 nm.

Preferred Values

$k_{v=2} = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=3} = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=4} = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=5} = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=6} = 6.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=7} = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=8} = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_{v=9} = 9.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

While there is much better agreement between the two sets of measurements for these reactions than for the other quenching reaction, $HO^* + M$, this may well be fortuitous in view of the large discrepancies associated with the latter reactions. Accordingly, although we have simply taken the average of the two results from Coltharp et al. [1] and Streit and Johnston [2], for the recommended data, we have assigned large error limits to reflect the considerable doubt involved with these studies.

References

[1] Coltharp, R. N., Worley, S. D., and Potter, A. E., Appl. Opt. **10**, 1786 (1971).
[2] Streit, G. E., and Johnston, H. S., J. Chem. Phys. **64**, 95 (1976).

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

$\Delta H° = -157.2$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.8 \pm 1.4) \times 10^{-14} \exp((1250 \pm 200)/T)$	273–339	Cox and Burrows, 1979 [1]	(a)
$(2.35 \pm 0.2) \times 10^{-12}$	298		
$(4.6 \pm 0.5) \times 10^{-12}$	298	Tsuchiya and Nakamura, 1979 [2]	(b)
$(2.9 \pm 1.2) \times 10^{-13}$	(2 Torr He)298	Thrush and Wilkinson, 1979 [3]	(c)
$(4.3 \pm 1.8) \times 10^{-13}$	(3 Torr He)298		
$(5.5 \pm 1.4) \times 10^{-13}$	(4 Torr He)298		
$(7.4 \pm 3.3) \times 10^{-13}$	(2 Torr Ar)298		
$(1.14 \pm 0.16) \times 10^{-13} \exp((1100 \pm 180)/T)$	276–400	Lii et al., 1979 [4]	(d)
$(4.6 \pm 0.2) \times 10^{-12}$	298		
See comment (e)	290–400	Lii et al., 1980 [5]	(e)
$(6.6 \pm 1.2) \times 10^{-12}$	298	Hochanadel, Sworski, and Ogren, 1980 [6]	(f)
Relative Rate Coefficients			
3.8×10^{-12}	300	Graham et al., 1979 [7]	(g)
Reviews and Evaluations			
2.5×10^{-12}	200–300	NASA, 1979 [8]	
2.3×10^{-12}	298	CODATA, 1980 [9]	(h)
See comment (i)	200–300	NASA, 1981 [10]	(i)

Comments

(a) HO_2 generated by pulsed photolysis (310–410 nm) of Cl_2 in presence of O_2 and H_2 or HCHO; $[HO_2]$ monitored by molecular modulation ultraviolet absorption spectrometry; data refer to pressure of 760 Torr with no H_2O present; data yield $k/\sigma_{220} = (1.1 \pm 0.8) \times 10^4 \exp((1245 \pm 184)/T)$ cm^3 s^{-1} $\sigma_{220} = 3.45 \times 10^{-18}$ cm^2 $molecule^{-1}$; the rate coefficient was increased by the presence of H_2O vapour.

(b) HO_2 generated by pulsed Hg-photosensitization (253.7 nm) of H_2/O_2 (1%) mixture in flow system; $[HO_2]$ monitored by absorption spectroscopy at 205 nm; $\sigma_{205} = (2.99 \pm 0.23) \times 10^{-18}$ cm^2 $molecule^{-1}$; no H_2O present; there appears to be an arithmetical error in the calculation of the rate coefficient in this paper.

(c) Fast-flow system; $F + H_2O \rightarrow HF + HO_2$; $[HO_2]$ monitored by laser magnetic resonance; rate coefficient determined from measurement of the second-order decay of HO_2; rate coefficient found to be pressure dependent; 10^{13} k/cm^3 $molecule^{-1}$ s^{-1} = 2.9 (2 Torr He), 4.3 (3 Torr He), 5.5 (4 Torr He), 7.4 (2.2 Torr Ar).

(d) HO_2 generated by electron-pulse radiolysis of H_2 in presence of O_2; $[HO_2]$ monitored by absorption at 230.5 nm; rate coefficients based on $\sigma_{230} = 2.17 \times 10^{-18}$ cm^2 $molecule^{-1}$; data refer to 1200 Torr H_2, 5 Torr O_2, with no H_2O present.

(e) Same system as for ref. [4], comment (d), but with up to 100 Torr added NH_3 present; apparent rate coefficient for rate of disappearance of HO_2 varied with $[NH_3]$ added; with $[NH_3] = 2.4 \times 10^{17}$ molecule cm^{-3} apparent rate coefficient for disappearance of HO_2 had a negative temperature coefficient corresponding to $E/R = -2200$ K; it is not certain in this system that the spectrum assigned to HO_2 arises exclusively from that radical.

(f) HO_2 generated by flash-photolysis of H_2O in an atm of He containing 2% O_2; $[HO_2]$ monitored by absorption at 220 nm; σ_{220} determined to be $(4.00 \pm 0.23) \times 10^{-18}$ cm^2 $molecule^{-1}$; 21 Torr H_2O present; rate coefficient derived from computer fit of proposed mechanism.

(g) HO_2 generated from $HO_2NO_2 \rightarrow HO_2 + NO_2$; rate coefficient derived from measurements of $-d[HO_2NO_2]/dt$ and $+d[NO_2]/dt$; measured relative to $K = k_2/k_1 = 8.1 \times 10^{10}$ molecule cm^{-3} for reactions $HO_2 + NO_2 \rightleftharpoons HO_2NO_2$ (1,2); the total uncertainty in the derived value of k ($HO_2 + HO_2$) was estimated by the authors to be a factor of 2.

(h) 1 atm pressure.

(i) Since the rate coefficient is a function of pressure, temperature and $[H_2O]$, a set of atmospheric empirical rate coefficients was recommended for use by modellers.

Preferred Values

$k = 2.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K; 1 atmosphere pressure, no H_2O present.

$k = 4.5 \times 10^{-14} \exp(+1200/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 275–400 K; 1 atmosphere pressure, no H_2O present.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K and 1 atmosphere pressure.

$\Delta (E/R) = \pm 300$ K over range 275–400 K and 1 atmosphere pressure.

Comments on Preferred Values

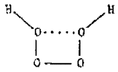
It should be stressed that the preferred data refer only to 1 atm pressure and in the absence of H_2O vapour. The error limits encompass any differences that might arise due to the identity of the diluent gas.

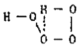
It is worth noting that previous discrepancies in the determination of this rate coefficient which have arisen from differences in the measured absorption cross-section of HO_2 have now been resolved [1,6].

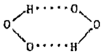
The negative temperature coefficient first reported by Cox [11] has subsequently been confirmed by the studies of Lii et al. [4] at 1 atmosphere pressure. Our recommended temperature coefficient is derived from a rounded-off mean from these two studies.

The studies of Cox [11] and Cox and Burrows [1] first showed that the rate coefficient decreases with decreasing pressure below 25 Torr. Additional evidence for a pressure dependence of the rate coefficient at low pressures comes from the work of Thrush and Wilkinson [3], who found that, over the range 2–4 Torr He, the second-order rate coefficient was directly proportional to pressure [12]. Additional work is still required on the pressure and temperature dependence of this reaction.

The pressure-dependence and negative temperature coefficient of the rate coefficient have led to speculation that the reaction proceeds through the formation of an $H_2O_4^*$ complex, [1,3,13]. Niki and co-workers [14] have made product studies of the interactions of HO_2 radicals using an FTIR system, and with and the aid of ^{18}O labelling have ruled out the participation of the proposed transition state (I). At the same time, however, their results could not distinguish between transition state (II) and a doubly hydrogen-bonded complex (III). These experiments also indicate that the lifetime of the $H_2O_4^*$ complex is less than 10 ms and thus rule out the participation of a long-lived (1 s) stable intermediate.


(I)


(II)


(III)

It is well established [15,11,1] that the rate coefficient increases with increasing water vapour concentration, an aspect which has been fully discussed by Howard [12].

References

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[2] Tsuchiya, S., and Nakamura, T., Bull. Chem. Soc. Japan **52**, 1527 (1979).
[3] Thrush, B. A., and Wilkinson, J. P. T., Chem. Phys. Lett. **66**, 441 (1979)
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[11] Cox, R. A., presented at WMO Symposium, Toronto, 26–30 June 1978.
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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H^\circ = -114.2$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.4) \times 10^{-14} \exp((-580 \pm 100)/T)$ 2.0×10^{-15}	245–365 298	Zahniser and Howard, 1980 [1]	(a)
Reviews and Evaluations			
$1.1 \times 10^{-14} \exp(-580/T)$	200–300	NASA, 1979 [2]	(b)
$1.4 \times 10^{-13} \exp(-600/T)$	250–400	CODATA, 1980 [3]	(c)
$1.1 \times 10^{-14} \exp(-580/T)$	200–300	NASA, 1981 [4]	(d)

Comments

(a) Discharge-flow system; HO_2 generated from $H + O_2 + M$ and monitored by laser magnetic resonance; C_2F_3Cl added to scavenge HO product.

(b) Average of data from refs. [5–8].

(c) Based on data from refs. [1] and [5].

(d) Average of data from refs. [1] and [5–8].

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 range 250–400 K.

Reliability

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

$\Delta (E/R) = {}^{+500\text{ K}}_{-100\text{ K}}$.

Comments on Preferred Values

The paper of Zahniser and Howard [1] reports in full data considered in preliminary form in the previous CODATA evaluation [3]. Direct confirmation of the rate data is still needed.

References

[1] Zahniser, M. S., and Howard, C. J., J. Chem. Phys. **73**, 1620 (1980).

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$H_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0°/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$H_2O + h\nu \rightarrow H_2 + O(^3P)$	(1)	485.70	246
$\rightarrow H + HO$	(2)	493.65	242
$\rightarrow H_2 + O(^1D)$	(3)	675.52	177

Preferred Values

Absorption cross-sections and quantum yields

λ/nm	$10^{20}\sigma$/cm^2	ϕ_2
175.5	262.8	1.0
177.5	185.4	1.0
180.0	78.08	1.0
182.5	23.03	1.0
185.0	5.546	1.0
186.0	3.110	1.0
187.5	1.571	1.0
189.3	0.6978	1.0

Comments on Preferred Values

The recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [1].

References

[1] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$H_2O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0°/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$H_2O_2 + h\nu \rightarrow 2HO$	(1)	207	578
$\rightarrow H_2O + O(^1D)$	(2)	328	365
$\rightarrow H + HO_2$	(3)	360	332
$\rightarrow 2H + O_2$	(4)	562	213
$\rightarrow HO + HO(^2\Sigma)$	(5)	598	200
$\rightarrow H_2 + 2O$	(6)	624	192
$\rightarrow 2H + O_2(^1\Delta_g)$	(7)	656	182
$\rightarrow 2H + O_2(^1\Sigma_g)$	(8)	719	166

Preferred Values

Absorption cross-sections and quantum yields for H_2O_2 photolysis at 298 K

λ /nm	$10^{20}\sigma$/cm^2	ϕ_1	λ /nm	$10^{20}\sigma$/cm^2	ϕ_1	λ /nm	$10^{20}\sigma$/cm^2	ϕ_1
190	69.2		245	11.0	1.0	300	0.708	1.0
195	60.3		250	8.91	1.0	305	0.538	1.0
200	52.5	1.0	255	7.24	1.0	310	0.417	1.0
205	44.7	1.0	260	5.62	1.0	315	0.316	1.0
210	38.0	1.0	265	4.47	1.0	320	0.245	1.0
215	32.4	1.0	270	3.55	1.0	325	0.186	1.0
220	26.9	1.0	275	2.75	1.0	330	0.141	1.0
225	23.4	1.0	280	2.09	1.0	335	0.110	1.0
230	19.5	1.0	285	1.62	1.0	340	0.0832	1.0
235	16.2	1.0	290	1.23	1.0	345	0.0631	1.0
240	13.5	1.0	295	0.933	1.0	350	0.0479	1.0

Absorption cross-sections and quantum yields for H_2O_2 photolysis at 600 and 1100 K.

λ /nm	$10^{20}\sigma$/cm^2	ϕ_1	Temp./K	λ /nm	$10^{20}\sigma$/cm^2	ϕ_1	Temp./K
220	28	1.0	600	220	26	1.0	1100
230	25	1.0	600	230	25	1.0	1100
240	20	1.0	600	240	22	1.0	1100
250	15	1.0	600	250	19	1.0	1100
260	10	1.0	600	260	15	1.0	1100
270	6.5	1.0	600	270	9.9	1.0	1100
280	4.2	1.0	600	280	7.3	1.0	1100
290	2.3	1.0	600	290	5.0	1.0	1100

Comments on Preferred Values

The recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [1].

References

[1] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data 9, 295 (1980).

5.3. Nitrogen Compounds

$N + HO \rightarrow NO + H$

$\Delta H° = -203.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.2)\times10^{-11}$	298	Howard and Smith, 1980 [1]	(a)
$(2.21 \pm 0.18)\times10^{-10}(T)^{-0.25\pm0.17}$	250–515	Howard and Smith, 1981 [2]	(a), (b)
$(4.74 \pm 0.64)\times10^{-11}$	300		
Relative Rate Coefficients			
4.6×10^{-11}	320	Campbell and Thrush, 1968 [3]	(c)
Reviews and Evaluations			
5.3×10^{-11}	300	Baulch, Drysdale, and Horne, 1973 [4]	(d)

Comments

(a) Discharge-flow system to produce N atoms. Flash photolysis of H_2O to give HO. First order decay of [HO] monitored by resonance fluorescence.

(b) From the values of k tabulated the following Arrhenius expression has been derived: $k = 3.8\times10^{-11}\exp(85/T)$ cm^3 molecule^{-1} s^{-1}.

(c) Discharge-flow system; atom decay rates measured in $N/O/H_2$ system. This value of k derived from measured ratio $k/k(O + HO) = 1.4 \pm 0.1$ and $k(O + HO) = 3.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(d) Based on ratio reported in reference [3].

Preferred Values

$k = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.8 \times 10^{-11} \exp(+85/T)$ cm^3 molecule^{-1} s^{-1} over range 250–500 K.

Reliability

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

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

Comments on Preferred Values

The preferred values are based on the recent results reported by Howard and Smith [1,2]. Although a negative temperature dependence has been derived from the tabulated data, the uncertainty given for (E/R) allows for the possibility of a temperature-independent value. In these studies the absolute value of k(O + HO) was also measured. The ratio k/k(O + HO) derived from these absolute values agrees with the value of the ratio measured directly by Campbell and Thrush [3].

Refereces

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$N + NO \rightarrow N_2 + O$

$\Delta H^\circ = -313.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.5 \pm 0.2) \times 10^{-11}$	300	Husain and Slater, 1980 [1]	(a)
$(1.9 \pm 0.2) \times 10^{-11}$	298	Sugawara, Ishikawa, and Sato, 1980 [2]	(b)
$(3.4 \pm 0.3) \times 10^{-11}$	298	Cheah and Clyne, 1980 [3]	(c)
Reviews and Evaluations			
3.4×10^{-11}	200–300	NASA, 1979 [4]	(d)
3.4×10^{-11}	200–400	CODATA, 1980 [5]	(d)
3.4×10^{-11}	200–300	NASA, 1981 [6]	(d)

Comments

(a) Pulse photolysis of N_2O. First order decay of [N] in added NO monitored by resonance fluorescence at 120 nm.

(b) Pulse radiolysis of N_2/NO mixtures. First order decay of [N] in excess NO monitored by resonance absorption.

(c) Discharge flow system. First order decay of [N] in excess NO monitored by resonance fluorescence at 120 nm.

(d) Based on results of Lee et al. [7].

Preferred Value

$k = 3.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

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

Comments on Preferred Value

The preferred value at 298 K is the average of the six results by independent techniques reported by Lee et al. [7], Clyne and McDermid [8], Husain and Slater [1], Sugawara et al. [2], and Cheah and Clyne [3]. The temperature independence of the rate coefficient reported by Lee et al. [7] is accepted.

References

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[3] Cheah, C. T., and Clyne, M. A. A., J. Chem. Soc. Faraday Trans. II **76**, 1543 (1980).

[4] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, editors (1979).

[5] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

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$N + NO_2 \rightarrow N_2O + O$ (1)
$\rightarrow NO + NO$ (2)
$\rightarrow N_2 + O_2$ (3)
$\rightarrow N_2 + 2O$ (4)

$\Delta H°(1) = -175$ kJ mol^{-1}
$\Delta H°(2) = -325$ kJ mol^{-1}
$\Delta H°(3) = -506$ kJ mol^{-1}
$\Delta H°(4) = -8$ 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			
$(3.8 \pm 0.1) \times 10^{-11}$	300	Husain and Slater, 1980 [1]	(a)
Reviews and Evaluations			
$2.1 \times 10^{-11} \exp(-800/T)$	200–300	NASA, 1979 [2]	(b)
1.4×10^{-12}	298	CODATA, 1980 [3]	(b)
$2.1 \times 10^{-11} \exp(-800/T)$	200–300	NASA, 1981 [4]	(b)

Comments

(a) Pulsed photolysis of N_2O. First order decay of [N] in added NO_2 monitored by resonance fluorescence at 120 nm. Reported value is for the total removal of N by NO_2 through all occurring reaction channels.

(b) Based on room temperature result of Clyne and McDermid, 1975 [5].

Preferred Values

$k = 1.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 1$.

Reliability

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

Comments on Preferred Values

Unchanged from previous evaluation, CODATA, 1980 [3]. Based on results reported by Clyne and McDermid, [5]. The new, much higher value of Husain and Slater, [1] may indicate the presence of catalytic cycles as discussed by Clyne and McDermid, [5] in comparing their results with the earlier results of Phillips and Schiff, 1965 [6]. Until this question is resolved, we have chosen to retain our previous preferred value. Confirmation of the indicated reaction mechanism is needed, and temperature dependent studies are needed.

References

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$N + O_2(^1\Delta) \rightarrow NO + O$ (1)
$\rightarrow N + O_2(^3\Sigma)$ (2)

$\Delta H°(1) = -227.6$ kJ mol^{-1}

$\Delta H°(2) = -94.3$ 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			
$(1.8 \pm 1.2)\times 10^{-15}$	195	Clark and Wayne, 1970 [1]	(a)
$(2.7 \pm 1.0)\times 10^{-15}$	300		
$(2.3 \pm 2.0)\times 10^{-15}$	409		
$(3.0 \pm 1.5)\times 10^{-15}$	431		
Relative Rate Coefficients			
$k_1 \leqslant 9\times 10^{-17}$	195–300	Westenberg, Roscoe, and deHaas, 1970 [2]	(b)
$k_1 < 9\times 10^{-17}$	300	Schmidt and Schiff, 1973 [3]	(c)

Comments

(a) Discharge-flow system. Decay of $O_2(^1\Delta)$ monitored by photoionization technique. Total rate of decay was measured and thus the observed rate which includes physical deactivation gives an upper limit to the value of k_1. Authors also derived the following upper limits: $E_{act} \leqslant 5$ kJ mol^{-1} and $A \leqslant 2\times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

(b) Discharge-flow system with ESR detection of N atom decay and O atom formation. No evidence for chemical reaction found. Value of k_1 given here is based on ratio $k_1/k(N + O_2) \leqslant 1$ and $k(N + O_2) = 8.9\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(c) Discharge-flow system with mass spectrometric detection of $O_2(^1\Delta)$ disappearance which authors attributed to interaction with some constituent of discharged nitrogen. Value of k_1 given here is based on ratio $k_1/k(N + O_2) < 1$ and $k(N + O_2) = 8.9\times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

Preferred Value

$k_1 \leqslant 1\times 10^{-16}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Comments on Preferred Value

The preferred value for k_1 accepts the results reported in references [2 and 3] which indicate that any chemical reaction of N atoms with $O_2(^1\Delta)$ is slower than with ground state O_2. This interpretation attributes the overall disappearance of $O_2(^1\Delta)$ observed in references [1 and 3] to physical deactivation by some constituent of discharge nitrogen. The upper limit recommended for k_1 is based on the room temperature value for the rate of reaction of N atoms with ground state O_2 molecules.

References

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

$\Delta H° = -306.2$ 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			
$(1.27 \pm 0.2)\times 10^{-32} \exp((508 \pm 50)/T)$ [Ar] $(7.20 \pm 1.2)\times 10^{-32} (T/300)^{-1.7}$ [Ar]	240–360	Anderson and Stephens, 1979 [1]	(a)
$(7.7 \pm 0.5)\times 10^{-32}$ [N_2]	298	Sugawara, Inshikawa, and Sato, 1980 [2]	(b)
Reviews and Evaluations			
$1.2\times 10^{-31} (T/300)^{-1.8}$ [N_2]	200–300	NASA, 1979, [3], 1981 [4]	(c)
$1.2\times 10^{-31} (T/300)^{-1.82}$ [N_2]	200–300	CODATA, 1980 [5]	(d)
$6.4\times 10^{-32} (T/300)^{-1.8}$ [Ar]	200–300	CODATA, 1980 [5]	(d)

Comments

(a) O production by vacuum UV flash photolysis of NO, detection of O by means of NO_2 chemiluminescence.

(b) Pulse radiolysis of N_2 and NO mixtures.

(c) Values from CODATA 1980 [4].

(d) Values at 200–300 K taken from refs. [5] and [6].

Preferred Values

$k_0 = 6.4\times10^{-32}\,(T/300)^{-1.8}\,[\mathrm{Ar}]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k_0 = 1.2\times10^{-31}\,(T/300)^{-1.82}\,[\mathrm{N_2}]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$.

Comments on Preferred Values

The new determination for M = Ar agrees well within the error limits with the earlier preferred value. Averaging the new value with all earlier absolute measurements from CODATA, 1980 [4] gives a value very close to the old preferred value which is retained here. The value for M = N_2 from ref. [2] is substantially lower than earlier results and is not included. No new measurements in the high pressure range are reported.

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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			
$(2.4 \pm 0.1)\times10^{-11}$	295	Amimoto et al., 1979 [1]	(a)
$(2.77 \pm 0.40)\times10^{-11}$	298	Brock and Watson, 1980 [2]	(b)
$(2.52 \pm 0.25)\times10^{-11}$	297	Wine and Ravishankara, 1981 [3]	(b)
Reviews and Evaluations			
$2.0\times10^{-11}\exp(107/T)$	200–300	NASA, 1979 [4]	(c)
$3.2\times10^{-11}\exp(107/T)$	200–350	CODATA, 1980 [5]	(d)
$1.8\times10^{-11}\exp(107/T)$	200–300	NASA, 1981 [6]	(e)

Comments

(a) Pulsed photolysis of O_3 at 248 nm with a KrF excimer laser. Rate of appearance of product $O(^3P)$ monitored by resonance absorption at 130 nm.

(b) Laser flash photolysis of O_3 at 266 nm with a frequency quadrupled Nd:Yag laser. Rate of appearance of product $O(^3P)$ monitored by resonance fluorescence at 130 nm.

(c) Based on results of Streit et al. [7].

(d) Based on averaging the room temperature results in Streit et al. [7], in Heidner et al. [8] and in Cvetanovic's review of relative rate data [9]. Temperature dependence is from Streit et al. [7].

(e) Based on room temperature results in references [1, 2, 3, and 7]. Temperature dependence is from Streit et al. [7].

Preferred Values

$k = 2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8\times10^{-11}\exp(+107/T)$ cm^3 molecule^{-1} s^{-1} over range 200–350 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at room temperature is the average of the results reported in references [1, 2, 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 in reference [7] is accepted, and the pre-exponential factor has been adjusted to fit the preferred room temperature value.

References

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$$
\begin{aligned}
O(^1D) + N_2O &\rightarrow N_2 + O_2 && (1)\\
&\rightarrow 2NO && (2)\\
&\rightarrow O(^3P) + N_2O && (3)
\end{aligned}
$$

$\Delta H^\circ(1) = -521.0\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^\circ(2) = -340.4\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^\circ(3) = -189.7\ \mathrm{kJ\ mol^{-1}}$

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			
$k_1 = 4.8\times 10^{-11}$ $k_2 = 6.2\times 10^{-11}$	200–300	NASA, 1979 [6]	(f)
$k_1 = 7.4\times 10^{-11}$ $k_2 = 8.6\times 10^{-11}$	200–350	CODATA, 1980 [7]	(g)
$k_1 = 5.1\times 10^{-11}$ $k_2 = 6.6\times 10^{-11}$	200–300	NASA, 1981 [8]	(h)

Comments

(a) Pulsed photolysis of O_3 at 248 nm with a KrF excimer laser. Rate of appearance of product $O(^3P)$ monitored by resonance absorption at 130 nm.

(b) Laser flash photolysis of O_3 at 266 nm with a frequency quadrupled Nd:Yag laser. Rate of appearance of product $O(^3P)$ monitored by resonance fluorescence at 130 nm.

(c) Steady 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 (200–335 nm with maximum output at 235 nm). Amount of NO produced measured with a chemiluminescent NO analyser. The 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 value of 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} (CODATA 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 photolysis of N_2O/He mixtures at 185 nm and at 206 nm. Most determinations of the branching ratio were based on measurement of the ratio $[N_2]/[O_2]$ every three minutes by gas chromatography. Independent confirmation of the results was obtained by determining the ratio $[N_2]/[NO]$ using gas chromatography and an NO chemiluminescent 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 gives a value of 0.85 ± 0.02 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 the absolute value reported by Davidson et al. [9] and branching ratio results reported in references [4, 10, and 11].

(g) Based on averaging the room temperature results in Davidson et al. [9], in Heidner and Husain, [12] and in Cvetanovic's review of relative rate data [13]. Temperature independent is from Davidson et al. [9]. Branching ratio is based on results in Davidson et al. [10] and in Volltrauer et al. [11].

(h) Based on absolute values reported in references [1, 2, and 9] and branching ratio results reported in references [4, 10, and 11].

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}.
$k_3 < 0.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
Independent of temperature over range 200–350 K.

Reliability

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

Comments on Preferred Values

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, [12]. 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 recent study by Marx et al. 1979 [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 references [10 and 11], (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 references [3, 4, 10, and 11] 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 references [5 and 10].

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$NH_2 + HO \rightarrow NH + H_2O$ (1)
$\rightarrow NH_3 + O$ (2)

$\Delta H°(1) = -123$ kJ mol^{-1}
$\Delta H°(2) = -21$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$k_2 = 1 \times 10^{-13} \exp(-2500/T)$	300–1000	Baulch, Drysdale, and Horne, 1973 [1]	(a)
$k_2 = 1 \times 10^{-13}$	300–1000	Hampson, 1980 [2]	(b)

Comments

(a) Calculated from rate of reverse reaction and equilibrium constant.

(b) Adjusted from expression in Baulch et al. [1] on the basis of a revised value of $\Delta H^\circ(NH_2) = 185$ kJ mol^{-1} (see Appendix 1).

Preferred Value

No recommendations for k_1 or k_2.

Comments on Preferred Value

Based on mechanistic and thermodynamic considerations, reaction channel (1) is expected to be a rapid reaction pathway. However no data direct or indirect exist for this channel. Until the value for $\Delta H^\circ(NH_2)$ is resolved we cannot make a recommendation for k_2 based on the reverse rate and equilibrium date.

References

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$NH_2 + HO_2 \rightarrow$ products

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.1 \pm 1.0)\times10^{-11}$	298	Kurasawa and Lesclaux, 1980 [1]	(a)
Relative Rate Coefficients			
$(2.5 \pm 0.5)\times10^{-11}$	298	Cheskis and Sarkisov, 1979 [2]	(b)
2.7×10^{-11}	349	Pagsberg, Eriksen, and Christensen, 1979 [3]	(c)

Comments

(a) Flash photolysis of NH_3/O_2 mixtures at low pressure (3 Torr O_2) and at high pressure (100 Torr O_2 or 3 Torr O_2 + 97 Torr N_2). $[NH_2]$ decay monitored by laser resonance absorption at 598 nm and simulated with a mechanism consisting of five reactions.

(b) Flash photolysis of NH_3/O_2 mixtures. $[NH_2]$ decay monitored by intracavity laser absorption spectroscopy at 598 nm. Reported value is based on ratio $k/k(NH_2 + NH_2) = 1.1$ at 570 Torr N_2 and $k(NH_2 + NH_2) = 2.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} [4]. Same value of k derived from measurements at 100 Torr N_2.

(c) Pulse radiolysis of NH_3/O_2 mixtures. $[NH_2]$ decay monitored by absorption spectrometry at 598 nm. Absence of any effect of O_2 on the $[NH_2]$ decay was interpreted by authors to imply that $k = k(H + NH_2)$. Value given here is the value of $k(H + NH_2)$ determined in the same study.

Preferred Value

$k = 3.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

Comments on Preferred Value

The preferred value at 298 K is the average of the values reported in references [1–3]. The identity of the products is not known. However, Kurasawa and Lesclaux [1] suggest that the most probable reaction channels give either $NH_3 + O_2$ or $HNO + H_2O$ as products. There is a need for determination of the reaction mechanism.

References

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$NH_2 + NO \rightarrow N_2 + H_2O$ (1)
$\rightarrow N_2 + H + HO$ (2)
$\rightarrow NH + HNO$ (3)
$\rightarrow NH_2NO$ (4)

$\Delta H°(1) = -517$ kJ mol^{-1}
$\Delta H°(2) = -18$ kJ mol^{-1}
$\Delta H°(3) = +167$ 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			
2.7×10^{-11}	300	Gordon, Mulac, and Nangia, 1971 [1]	(a)
$(8.3\pm1.7)\times10^{-12}$	298	Gehring et al., 1973 [2]	(b)
$2.1\times10^{-8}(T)^{-1.25}$	300–500	Lesclaux et al., 1975 [3]	(c)
$(1.8\pm0.3)\times10^{-11}$	300		
$(2.1\pm0.2)\times10^{-11}$	298	Hancock et al., 1975 [4]	(d)
$(1.7\pm0.4)\times10^{-11}$	298	Sarkisov, Cheskis, and Sviridenkov, 1978 [5]	(e)
$4.5\times10^{-7}(T)^{-1.85}$	210–500	Hack et al., 1979 [6]	(f)
9.7×10^{-12}	298		
Reviews and Evaluations			
2.1×10^{-11}	298	Hampson, 1980 [7]	(g)

Comments

(a) Pulsed radiolysis of NH_3/NO mixtures at 500 Torr. First order decay of $[NH_2]$ monitored by absorption spectrometry at 598 nm.

(b) Discharge-flow system with NO_2 added to excess H atoms followed by addition of excess NH_3. Analysis by time-of-flight mass spectrometry. Total pressure of 2.4 Torr. Strong vibrational excitation in product H_2O was observed. Also the addition product NH_2NO was observed to the extent of 5% of the N_2 formed.

(c) Flash photolysis of NH_3/NO mixtures. First order decay of $[NH_2]$ monitored by absorption spectrometry at 598 nm. No change in the value of the rate coefficient was observed over the pressure range 2 to 700 Torr N_2.

(d) Flash photolysis of NH_3/NO mixtures at wavelengths greater than 170 nm and total pressure of 1 Torr. First order decay of $[NH_2]$ monitored by laser induced fluorescence at 570 nm.

(e) Flash photolysis of NH_3/NO mixtures. First order decay of $[NH_2]$ monitored by intracavity laser absorption at 598 nm. No effect of pressure on the value of the rate coefficient was observed over the range 0.1 to 1 Torr.

(f) Discharge-flow system. NH_2 radicals produced by reaction of F atoms with NH_3. First order decay of $[NH_2]$ in excess NO monitored by laser induced fluorescence at 598 nm. Total pressure was 0.6 to 4 Torr.

(g) Based on results of Hancock et al., 1975 [4].

Preferred Values

$k = 1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7\times10^{-11}\,(T/298)^{-1.6}$ cm^{3}molecule^{-1} s^{-1} over range 210–500 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$ over range 210–500 K.

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported in references [1–6], and the preferred temperature dependence is the mean of the temperature dependences reported in Lesclaux et al. [3] and Hack et al. [6]. While there are many conceivable reaction channels, reaction (1) appears to be the dominant channel with strong vibrational excitation of the product H_2O observed by Gehring et al. [2]. These authors also report observation of the addition product NH_2NO in an amount corresponding to 5% of the N_2 formed.

References

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

$\Delta H°(1) = -378$ kJ mol^{-1}

$\Delta H°(2) = -355$ 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			
$3.2\times10^{-4}(T)^{-3.0}$	250–500	Hack et al., 1979 [1]	(a)
1.0×10^{-11}	295		
$3.8\times10^{-8}(T)^{-1.30}$	298–508	Kurasawa and Lesclaux, 1979 [2]	(b)
$(2.3\pm0.2)\times10^{-11}$	298		

Comments

(a) Discharge-flow system. NH_2 radicals produced by reaction of F atoms with NH_3. First order decay of $[NH_2]$ in excess NO_2 monitored by laser induced fluorescence at 598 nm. Total pressure of 1 Torr. Products were analyzed by mass spectrometry in another flow system at a pressure of 2.3 Torr with NO_2 in large excess over NH_2. Results were interpreted to indicate that at least 95% of the reaction proceeds through reaction channel (1).

(b) Flash photolysis of NH_3/NO_2 mixtures. First order decay of $[NH_2]$ monitored by laser induced resonance fluorescence at 598 nm. Total pressure of 3 to 10 Torr.

Preferred Values

$k = 1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7\times10^{-11}$ $(T/298)^{-2.2}$ cm^3 molecule^{-1} s^{-1} over range 250–500 K.

Reliability

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

$\Delta n = \pm 1.5$ over range 250–500 K.

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported by Hack et al. [1] and Kurasawa and Lesclaux [2]. Also, the temperature dependence of the preferred value averages the temperature dependences reported in these two studies. There is very poor agreement between these studies both for k_{298} and for the temperature dependence. Hack et al. [1] have shown 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

[1] Hack, W., Sachacke, H., Schroter, M., and Wagner, H. Gg., 17th Int. Symp. on Combustion, p. 505 (1979).
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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			
$<(2\pm1)\times10^{-18}$	289, 500	Lesclaux and Demissy, 1977 [1]	(a)
$<8\times10^{-15}$	349	Pagsberg, Eriksen, and Christensen, 1979 [2]	(b)
$<1.5\times10^{-17}$	298	Cheskis and Sarkisov, 1979 [3]	(c)
Relative Rate Coefficients			
$>4\times10^{-15}$	298	Jayanty, Simonaitis, and Heicklen, 1976 [4]	(d)

Comments

(a) Flash photolysis of NH_3/O_2 mixtures. $[NH_2]$ decay monitored by absorption spectrometry at 598 nm. Complex decay kinetics observed indicates that more than one reaction is occurring. The authors inferred that only radical-radical processes are important. Upper limit only.

(b) Pulse radiolysis of NH_3/O_2 mixtures. $[NH_2]$ decay monitored by absorption spectrometry at 598 nm. Upper limit only.

(c) Flash photolysis of NH_3/O_2 mixtures. $[NH_2]$ decay monitored by intracavity laser absorption spectroscopy at 598 nm. Upper limit based on independence of NH_2 decay rate with

O_2 pressure between 1 and 570 Torr.

(d) Photolysis of NH_3/O_2 mixtures at 214 nm. Quantum yields for production of N_2 and N_2O were measured. Lower limit given here is based on observation that the reaction of two NH_2 radicals is negligible compared to the disappearance of NH_2 by reaction with O_2. Authors concluded that reaction proceeds predominantly (> 98%) by addition to form NH_2O_2.

Preferred Value

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

Comments on Preferred Value

The preferred value is the upper limiting value based on the results reported by Lesclaux and Demissy, [1]. Their results indicate that NH_2 radicals are removed by radical-radical combination and not by reaction with O_2. These relatively direct results are preferred to those derived from the analysis of the steady-state photolysis experiments of Jayanty et al. [4]. The less sensitive upper limits reported by Cheskis and Sarkisov [3] and by Pagsberg et al. [2] also indicate that this reaction is unimportant. It should be noted that the reaction mechanism is uncertain. In a study of the explosive oxidation of NH_3, Husain and Norrish [5] concluded that the major reaction channel gives HNO + HO as products, but Jayanty et al. [4] concluded that even at a pressure of several Torr the predominant pathway is the addition reaction to give NH_2O_2.

References

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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			
$4.2 \times 10^{-12} \exp(-(1250 \pm 250)/T)$	298–380	Kurasawa and Lesclaux, 1980 [1]	(a)
$(6.3 \pm 1.0) \times 10^{-14}$	298		
$(1.2 \pm 0.3) \times 10^{-13}$	298	Bulatov et al., 1980 [2]	(b)
$(2.01 \pm 0.12) \times 10^{-12} \exp(-(710 \pm 50)/T)$	250–358	Hack, Horie, and Wagner, 1981 [3]	(c)
$(1.84 \pm 0.16) \times 10^{-13}$	295		

Comments

(a) Flash photolysis of NH_3/O_3 mixtures at wavelengths greater than 180 nm. First order decay of $[NH_2]$ monitored by laser induced fluorescence at 598 nm. Total pressure of 5 to 12 Torr.

(b) Flash photolysis of NH_3/O_3 mixtures at wavelengths greater than 250 nm. First order decay of $[NH_2]$ monitored by intracavity laser absorption spectroscopy at 598 nm for pressure of O_3 less than 0.5 Torr and an NH_3 pressure of 5 Torr. A deviation from first order decay kinetics at higher O_3 pressures was observed and was interpreted by the authors to indicate that the main reaction channel leads to the products $NH_2O + O_2$.

(c) Discharge-flow reactor. NH_2 radicals produced by reaction of F atoms with NH_3. First order decay of $[NH_2]$ in excess O_3 monitored by laser induced fluorescence at 598 nm. Total pressure of 3 to 15 Torr. A deviation from first order decay kinetics at higher O_3 pressures was observed and was interpreted by the authors to indicate that the main reaction channel leads to the products $NH_2O + O_2$.

Preferred Values

$k = 1.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.4 \times 10^{-12} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over range 250–380 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported in references [1–3]. The temperature dependence averages the temperature dependences in Kurasawa and Lesclaux [1] and in Hack et al. [3], and the preexponential factor has been selected to fit the recommended room temperature value. The deviation from first order decay kinetics at higher pressures of O_3 was reported in references [2 and 3] and in both instances was interpreted to indicate that the principal reaction channel leads to formation $NH_2O + O_2$ which is followed by the reaction of NH_2O with O_3 to regenerate NH_2.

References

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$NO + O_3 \rightarrow NO_2 + O_2$

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

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.3 \pm 0.6)\times 10^{-12} \exp(-(1598 \pm 50)/T)$	283–443	Lippmann, Jesser, and Schurath, 1980 [1]	(a)
$(2.14 \pm 0.11)\times 10^{-14}$	304		
$(3.16 \pm 0.45)\times 10^{-12} \exp(-(1556 \pm 40)/T)$	212–422	Ray and Watson, 1981 [2]	(b)
$(1.80 \pm 0.04)\times 10^{-14}$	299		
Reviews and Evaluations			
$2.3\times 10^{-12} \exp(-1450/T)$	200–300	NASA, 1979 [3]	(c)
$2.3\times 10^{-12} \exp(-1450/T)$	200–360	CODATA, 1980 [4]	(c)
$2.3\times 10^{-12} \exp(-1450/T)$	200–300	NASA, 1981 [5]	(c)

Comments

(a) First order decay of $[O_3]$ in presence of excess NO monitored by chemiluminescent detection under stopped-flow conditions in a 220 m^3 stainless steel sphere at total pressures below 0.1 mTorr.

(b) Discharge flow, mass spectrometric study. First order decay of $[O_3]$ in presence of excess NO. Total pressure was in the range of 1.0 to 2.2 Torr.

(c) Based on results of Birks et al. [6] and room temperature results in references [7 and 8].

Preferred Values

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

$k = 3.6\times 10^{-12} \exp(-1560/T)$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

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

Comments onPreferred Values

The preferred value at room temperature is the mean of the values reported in references [1, 2, 6–8]. The preferred temperature dependent expression has been derived by a least squares analysis of the data reported in the recent studies by Lippman et al. [1], Ray and Watson [2] and Birks et al. [6], with the data at closely spaced temperatures in reference [1] being grouped together so that these three studies are weighted equally. This expression fits all but one data point reported in these three studies to within 15 precent. An analysis of the data below 300 K only yields the alternative expression: $k = 2.8\times 10^{12} \exp(-1500/T)$ cm^3 molecule^{-1} s^{-1}. This lower value of E/R suggests the possibility of curvature in the Arrhenius plot; however, since the data for $T > 300$ are predominantly from one study (reference [1]), this may simply reflect a systematic difference between studies. These two alternative Arrhenius expressions agree to within 5 percent over the range 200 to 300 K.

References

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

$\Delta H° = -92.9$ 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			
$9.6 \times 10^{-33} \exp(+1550/T)$ [N_2]	262-295	Connell and Johnston, 1979 [1]	(a), (b)
1.7×10^{-30} [N_2]	298		
$1.35 \times 10^{-32} \exp(+1270/T)$ [N_2]	285-384	Viggiano et al., 1981 [2]	(c), (b)
9.6×10^{-31} [N_2]	298		
Reviews and Evaluations			
$1.5 \times 10^{-30} (T/300)^{-4.6}$ [N_2]	300-340	CODATA, 1980 [3]	(d), (b)
$1.4 \times 10^{-30} (T/300)^{-2.8}$ [N_2]	200-300	NASA, 1981 [4]	(e), (b)
$3.7 \times 10^{-30} (T/300)^{-4.1}$ [N_2]	220-300	Malko and Troe, 1982 [5]	(f), (b)

Comments

(a) From study of N_2O_5 decomposition, see comment (b) for $N_2O_5 \rightarrow NO_2 + NO_3$ (k_0).

(b) Converted with the equilibrium constant $K_{eq} = 8.4 \times 10^{26} \exp(-11180/T)$ molecule cm^{-3} from ref. [6].

(c) From study of N_2O_5 decomposition, see comment (c) for $N_2O_5 \rightarrow NO_2 + NO_3$ (k_0).

(d) Based on evaluation of earlier data, which are superseded by the present references.

(e) From data of refs. [1] and [2].

(f) Theoretical analysis of N_2O_5 decomposition fall-off curves, see comment (e) for $N_2O_5 \rightarrow NO_2 + NO_3$ (k_0).

Preferred Value

$k_0 = 3.7 \times 10^{-30}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 3.7 \times 10^{-30} (T/300)^{-4.1}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 220-300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ over range 220-300 K.

$\Delta n = \pm 0.5$

Comments on Preferred Values

From the theoretical analysis of the data in ref. [5] which gives a consistent representation of all experiments of refs. [1] and [2].

High pressure rate coefficient

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-10} \exp(-1360/T)$	262-295	Connell and Johnston, 1979 [1]	(a), (b)
2.2×10^{-12}	298		
$1.5 \times 10^{-10} \exp(-1610/T)$	285-384	Viggiano et al., 1981 [2]	(c), (b)
6.8×10^{-13}	298		
Reviews and Evaluations			
5×10^{-12}	200-400	CODATA, 1980 [3]	(d), (b)
8.0×10^{-13}	200-300	NASA, 1981 [4]	
$1.6 \times 10^{-12} (T/300)^{0.2}$	220-520	Malko and Troe, 1982 [5]	(e), (b)

Comments

(a)-(e). See comments for k_0.

Preferred Values

$k_\infty = 1.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_\infty = 1.6 \times 10^{-12} (T/300)^{+0.2}$ cm^3 molecule^{-1} s^{-1} over range 220-520 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$ over range 220-520 K.

Comments on Preferred Values

From the theoretical analysis of the data in ref. [5] which gives a consistent representation of all experiments of refs. [1] and [2].

Intermediate Fall-off Range

From the preferred values of k_0 and k_∞ one derives $[N_2]_c = 1.1\times10^{17}$ at 220 K, 2.7×10^{17} at 269 K, 4.1×10^{17} at 295 K, and 8.0×10^{19} molecule cm^{-3} at 520 K. The broadening factors, according to ref. [5] can be represented by $F_c \cong \exp(-T/250)+\exp(-1050/T)$, giving $F_c = 0.42$ at 220 K, 0.36 at 268 K, 0.34 at 295 K, and 0.26 at 520 K.

References

[1] Connell, P., and Johnston, H. S., Geophys. Res. Letters **6**, 553 (1979).

[2] Viggiano, A. A., Davidson, J. A., Fehsenfeld, F. C., and Ferguson, E. E., J. Chem. Phys. **74**, 6113 (1981).

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

$\Delta H^\circ = +92.9$ kJ mol^{-1}

Low pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$8.3\times10^{-8}\exp(-8300/T)$ [Ar]	450–550	Schott and Davidson, 1958 [1]	(a)
$8.05\times10^{-6}\exp(-9630/T)$ [N_2]	262–295	Connell and Johnston, 1979 [2]	(b)
7.4×10^{-20} [N_2]	298		
$1.15\times10^{-5}\exp(-9914/T)$ [N_2]	285–384	Viggiano et al, 1981 [3]	(c)
4.1×10^{-20} [N_2]	298		
Reviews and Evaluations			
$8.8\times10^{-6}\exp(-9700/T)$ [N_2]	300–340	CODATA, 1980 [4]	(d)
$2.2\times10^{-3}(T/300)^{-4.4}\exp(-11080/T)$ [N_2]	220–300	Malko and Troe, 1982 [5]	(e)
$2.2\times10^{-3}(T/300)^{-6.1}\exp(-11080/T)$ [N_2]	300–500		

Comments

(a) Shock wave study of N_2O_5 decomposition in argon at concentrations [Ar] $= 1.8\times10^{18} - 5.4\times10^{18}$ molecule cm^{-3}. Reaction believed to be near the low pressure limit, however, some deviations from this behavior were seen experimentally. The analysis of ref. [5] indicates that these experiments correspond to conditions near the center of the intermediate fall-off curve, the true k_0 being about 4 times larger than the given value.

(b) Static reaction (63 1) study with multi-reflection White-cell arrangement for the time resolved detection of N_2O_5 IR absorption at 8.028 μ. Fall-off curves were measured with $[N_2] = 10^{15} - 3\times10^{19}$ molecule cm^{-3}. Low pressure data in good agreement with earlier data of Johnston and Perine [6]. Combination with these data gives $k_0 = [N_2]\ 6.1\times10^{-6}\exp(-(9570\pm200)/T)$ s^{-1} over the range 262–345 K. According to the analysis of fall-off curves in ref. [5], these expressions should be corrected slightly upward to arrive at the low pressure limiting value.

(c) Flow system with reactors of various size. N_2O_5 detected by ion-molecule reactions in a flowing afterglow set up. Measurements at $[N_2] = 2.5\times10^{17} - 2.7\times10^{19}$ molecule cm^{-3}. These experiments were made near the center of the fall-off curve. Extrapolation to the limits had to cover relatively large pressure ranges.

(d) Based on critical evaluation of earlier data including ref. [6].

(e) Theoretical analysis of the experimental data from refs. [1]–[3]. Construction of a consistent set of fall-off curves and fit to all data from these references, discarding some low pressure points from ref. [2] at 268 K because of inconsistencies with theory. This analysis leads to a modification of the fall-off curves and expressions for k_0 and k_∞ given by the authors of refs. [1]–[3]. The analysis is based on value of $\Delta H^\circ_0/R = 11080$ K which is consistent with the experiments and also the equilibrium constants given by Graham and Johnston [7], $K_{eq} = (8.4\pm1.8)\times10^{26}\exp(-(11180\pm100)/T)$ molecule cm^{-3} (298–329 K).

Preferred Values

$k_0 = 1.6\times10^{-19}$ [N_2] s^{-1} at 298 K.

$k_0 = 2.2\times10^{-3}(T/300)^{-4.4}\exp(-11080/T)$ [N_2] s^{-1} over range 220–300 K.

$k_0 = 2.2\times10^{-3}(T/300)^{-6.1}\exp(-11080/T)$ [N_2] s^{-1} over range 300–500 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ over range 220–500 K.

$\Delta n = \pm 0.5$ over range 220–500 K.

Comments on Preferred Values

These are the evaluated data from ref. [5] based on the experiments from refs. [1]–[3]. For conditions of atmospheric interest the intermediate fall-off curve must always be used in connection with these data.

High pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.78\times10^{17}\exp(-(12540\pm130)/T)$	262-295	Connell and Johnston, 1979 [2]	(a)
9.4×10^{-2}	298		
$1.21\times10^{17}\exp(-12787/T)$	285-384	Viggiano et al., 1981 [3]	(b)
2.8×10^{-2}	298		
Reviews and Evaluations			
$5.7\times10^{14}\exp(-10600/T)$	273-300	CODATA, 1980 [4]	(c)
$9.7\times10^{14}(T/300)^{+0.1}\exp(-11080/T)$	220-300	Malko and Troe, 1982 [5]	(d)

Comments

(a) See comment (b) of k_0. Fall-off curves of this work at 262–295 K were extrapolated to high pressure together with earlier data by Mills and Johnston [6] from their medium pressure apparatus; earlier data by Mills and Johnston at high pressures were inconsistent with the present data and rejected.

(b) See comment (c) of k_0. Data obtained from extrapolation of data in a relatively narrow pressure range near the center of the fall-off curves.

(c) Based on high pressure data by Mills and Johnston [6] and a temperature coefficient derived from ΔH°_0 as given by the measurements of the equilibrium constant from ref. [7].

(d) Combination of extrapolated fall-off curves from refs. [2] and [3] with theory [8].

Preferred Values

$k_\infty = 6.9\times10^{-2}\ \mathrm{s}^{-1}$ at 298 K.

$k_\infty = 9.7\times10^{14}(T/300)^{+0.1}\exp(-11080/T)\mathrm{s}^{-1}$ over range 220-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 220–300 K.

$\Delta n = \pm 0.2$

Comments on Preferred Values

The earlier high pressure data of k_∞ by Mills and Johnston [6] have not been confirmed by the recent measurements of refs. [2] and [3]. The analysis of the data given by refs. [2] and [3] has been shown in ref. [5] to be inconsistent with theory. We therefore accept the analysis from ref. [5] which is based on theory and the experimental data from refs. [1]–[3].

Intermediate Fall-off Range

From the preferred values of k_0 and k_∞ one derives $[N_2]_c = 1.1\times10^{17}$ at 220 K, 2.7×10^{17} at 268 K, 4.1×10^{17} at 295 K, and 8.0×10^{18} molecule cm^{-3} at 520 K. The broadening factors, according to ref. [5] can be represented by $F_c \simeq \exp(-T/250)+\exp(-1050/T)$, giving $F_c = 0.42$ at 220 K, 0.36 at 268 K, 0.34 at 295 K, and 0.26 at 520 K.

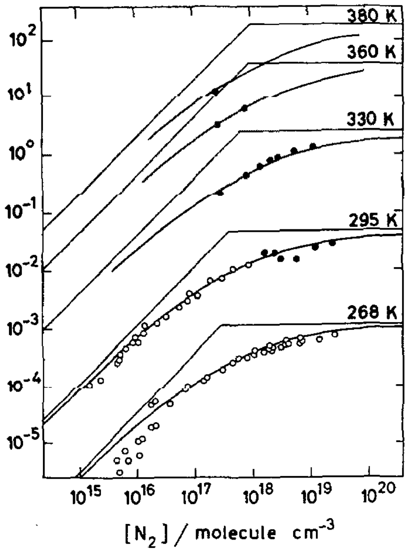

FIGURE 5. Fall-off curves of the thermal decomposition of N_2O_5 in N_5 (Experiments: ○, ref. [2]; ●, ref. [3]; theoretical analysis: full lines, ref. [5]).

References

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$HO + NH_3 \rightarrow H_2O + NH_2$

$\Delta H^\circ = -50$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.4) \times 10^{-13}$	298	Stuhl, 1973 [1]	(a)
$(4.1 \pm 0.5) \times 10^{-14}$	298	Kurylo, 1973 [2]	(b)
$(5.3 \pm 0.8) \times 10^{-12} \exp(-920/T)$	298–669	Hack, Hogermann and Wagner, 1974 [3]	(c)
$(2.5 \pm 0.8) \times 10^{-13}$	298		
$(4.3 \pm 0.5) \times 10^{-13}$	418	Gordon and Mulac, 1975 [4]	(d)
$2.3 \times 10^{-12} \exp(-800/T)$	228–472	Smith and Zellner, 1975 [5]	(e)
1.57×10^{-13}	298		
$2.93 \times 10^{-12} \exp(-(860 \pm 150)/T)$	298–427	Perry, Atkinson, and Pitts, 1979 [6]	(f)
$(1.64 \pm 0.16) \times 10^{-13}$			
$1.2 \times 10^{-12} \exp(-440/T)$	298–365	Pagsberg, Eriksen, and Christensen, 1979 [7]	(d)
$(2.7 \pm 0.3) \times 10^{-13}$	298		
$(5.41 \pm 0.86) \times 10^{-12} \exp(-(1070 \pm 70)/T)$	294–1075	Silver and Kolb, 1980 [8]	(g)
$(1.44 \pm 0.29) \times 10^{-13}$	294		
Relative Rate Coefficients			
2.1×10^{-13}	296	Cox, Derwent, and Holt, 1975 [9]	(h)
Reviews and Evaluations			
$2.3 \times 10^{-12} \exp(-800/T)$	228–472	Hampson, 1980 [11]	(i)

Comments

(a) Pulsed photolysis of H_2O; resonance fluorescence detection of first-order [HO] decay.

(b) Flash photolysis of O_2/NH_3 system; resonance fluorescence detection of first-order [HO] decay.

(c) Discharge-flow system; ESR detection of first-order [HO] decay.

(d) Pulsed radiolysis of H_2O; resonance absorption detection of first-order [HO] decay.

(e) Flash photolysis of H_2O; resonance absorption detection of first-order [HO] decay.

(f) Flash photolysis of H_2O; resonance fluorescence detection of first-order [HO] decay.

(g) Discharge-flow system; resonance fluorescence detection of first-order [HO] decay.

(h) Flow system photolysis of NH_3/HONO mixtures. Value given here is based on measured ratio $k/k(OH + HONO) = 0.032$ and $k(OH + HONO) = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, Cox et al., 1976 [10].

(i) Based on data published prior to 1979; accepted low temperature results of Smith and Zellner, 1975 [5].

Preferred Values

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

$k = 3.3 \times 10^{-12} \exp(-900/T)$ cm^3 molecule^{-1} s^{-1} over range 230–450 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported in references [1, 5, 6, and 8]. The lower value is reference [2] and the higher values in references [3 and 7] are not included. The temperature dependence is based on the results reported in references [3, 5, 6, and 8], and the preexponential factor has been selected to fit the recommended room temperature value.

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

$\Delta H^\circ = -207$ 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			
$(2.6 \pm 0.4) \times 10^{-30} (T/300)^{-2.8}$ [N$_2$]	247–352	Wine, Kreutter, and Ravishankara, 1979 [1]	(a)
$(2.3 \pm 0.6) \times 10^{-30} (T/300)^{-2.9}$ [N$_2$]	225–389	Anderson, 1980 [3]	(b)
Reviews and Evaluations			
$2.6 \times 10^{-30} (T/300)^{-2.9}$ [N$_2$]	200–300	NASA, 1979 [4]	
$2.6 \times 10^{-30} (T/300)^{-2.7}$ [N$_2$]	220–550	CODATA, 1980 [5]	
$2.6 \times 10^{-30} (T/300)^{-2.9}$ [N$_2$]	200–300	NASA, 1981 [6]	

Comments

(a) Flash photolysis-resonance fluorescence technique; bath gas concentrations $(5.4 - 230) \times 10^{17}$ molecule cm^{-3}. The experiments covered an essential part of the fall-off curve, approaching the low pressure limit. Data are in good agreement with earlier work, suggesting however a higher high pressure limit than derived earlier by Anastasi and Smith [2]. Measurements performed with M = He, Ar, N_2, SF_6.

(b) Discharge flow system with resonance fluorescence detection. Pressure range 0.8–2.7 Torr. Fall-off corrections with $F_c = 0.8$ applied.

Preferred Values

$k_0 = 2.6 \times 10^{-30}$ [N$_2$] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 2.6 \times 10^{-30} (T/300)^{-2.9}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 200–300 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The new measurements are in excellent agreement with older data and do not change the older preferred values. A final derivation of k_0 must wait for a full analysis of the fall-off curve including measurements at pressures higher than studied at present.

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3.5×10^{-11}	297	Wine, Kreutter, and Ravishankara, 1979 [1]	(a)
See comment (b)	301	O'Brien, Green, and Doty, 1979 [7]	(b)
Reviews and Evaluations			
$2.4 \times 10^{-11} (T/300)^{-1.3}$	200–300	NASA, 1979 [4]	(c)
1.6×10^{-11}	200–360	CODATA, 1980 [5]	(d)
$2.4 \times 10^{-11} (T/300)^{-1.3}$	200–300	NASA, 1981 [6]	(c)

Comments

(a) See comment (a) of k_0. Extrapolation of the fall-off curve with $F_c \simeq 0.70$ leads to $k_\infty \gtrsim 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(b) Smog chamber experiment at 1 atm air and 11 Torr of H_2O. Measured ratio k/k(HO + toluene) $= 2.2 \pm 0.2$ with k(HO + toluene) $= 6.08 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (average of literature values) leads to $k = (1.3 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1 atm. This value is in good agreement with the preferred fall-off expression and the measurements of ref. [1].

(c) Based on RRKM analysis by Baldwin and Golden [8].

(d) Based on the fall-off expression from ref. [32] for 300 K and a reevaluation of earlier data. A temperature independence of k_∞ was postulated on the basis of a theoretical analysis of many other high pressure studies of recombination reactions.

Preferred Value

$k_\infty = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over range 200–300 K.

Comments on Preferred Value.

The measurements of ref. [1], as well as recent unpublished measurements by Smith and coworkers [9] at CF_4-bath gas pressures of 10 atm giving $k_\infty \geqslant 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} indicate that the previously preferred value of ref. [5] was too low. The k_∞ value should still be used with caution until measurements at pressures near 100 atm have been made. Together with the F_c values given below, it is in agreement with the available data at pressures up to 1 atm.

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c = 1.3 \times 10^{19}$ at 300 K and $[N_2]_c = 5.5 \times 10^{18}$ molecule cm^{-3} at 220 K. A preliminary theoretical prediction of F_c with the techniques of ref. [10] leads to $F_c \simeq 0.70$ at 300 K and $F_c \simeq 0.8$ at 200 K which are in agreement with the experimentally observed fall-off curve. A more detailed analysis similar to that of the $N_2O_5 \rightleftharpoons NO_2 + NO_3$ system is required as soon as extended high pressure measurements are available.

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$HO + HNO_3 \rightarrow H_2O + NO_3$ (1)
$\rightarrow H_2O_2 + NO_2$ (2)

$\Delta H^\circ(1) = -75$ kJ mol^{-1}

$\Delta H^\circ(2) = -7$ 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			
$(1.52 \pm 0.38) \times 10^{-14} \exp((649 \pm 69)/T)$	224–366	Wine et al., 1981 [1]	(a)
$(1.25 \pm 0.05) \times 10^{-13}$	298		
$(8.2 \pm 1.8) \times 10^{-14}$	298	Nelson, Marinelli, and Johnston, 1981 [2]	(b)
Reviews and Evaluations			
8.5×10^{-14}	200–300	NASA, 1979 [3]	(c)
8.5×10^{-14}	240–470	CODATA, 1980 [4]	(c)
$1.5 \times 10^{-14} \exp(650/T)$	200–300	NASA, 1981 [5]	(d)

Comments

(a) Flash photolysis of HNO_3 at wavelengths greater than 165 nm. In other experiments HNO_3 was photolyzed at 249 nm with a KrF excimer laser. First order decay of [HO] was monitored by resonance fluorescence at 310 nm. $[HNO_3]$ measured by absorption at 184.9 nm.

(b) Laser flash photolysis of HNO_3 at 249 nm. First order decay of HO monitored by resonance fluorescence at 310 nm. Pressure range of 10–50 Torr. In separate experiments the rate of production of NO_3 was monitored in absorption at 623.5 nm to give $k_1 = (10.6 \pm 3.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Quantum yield for production of NO_3 was determined to be approximately unity with the precise value dependent on value selected for absorption cross section of NO_3 at 623.5 nm.

(c) Based on temperature-independent results reported by Smith and Zellner, [6] and Margitan et al. [7].

(d) Based on results reported by Wine et al. [1].

Preferred Values

$k = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5 \times 10^{-14} \exp(650/T)$ cm^3 molecule^{-1} s^{-1} over range 220–360 K.

Reliability

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

$\Delta (E/R) = \pm 300$ K over range 220–360 K.

Comments on Preferred Values

The preferred value is based on the results reported by Wine et al. [1]. There is a significant discrepancy between these results and those reported in references [6 and 7], particularly at low temperatures. It is felt that the results obtained in this recent study over a wide range of experimental conditions are more reliable. Confirmation of these results is needed, particularly for the reported negative temperature dependence. Reaction channel (1) yielding NO_3 appears to be the dominant channel based on the NO_3 quantum yield of approximately unity reported by Nelson et al. [2]. NO_3 was also observed directly in absorption at 650 nm by Glanzer and Troe [8] in studies of the thermal decomposition of HNO_3 at 1000 K.

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

$\Delta H°(1) = -194$ kJ mol^{-1}

$\Delta H°(2) = -50$ 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			
$<3\times10^{-12}$	261–295	Graham, Winer, and Pitts, 1978 [1]	(a)
$(4.0\pm1.6)\times10^{-12}$	246–324	Trevor, Black, and Barker, 1982 [2]	(b)
Reviews and Evaluations			
5×10^{-13}	200–300	NASA, 1979 [3]	(c)
No recommendation		CODATA, 1980 [4]	(d)
8×10^{-13}	200–300	NASA, 1981 [5]	(e)

Comments

(a) Upper limit only. This limit is based on results obtained in a study of the decomposition of HO_2NO_2 at low pressure in the presence of added NO. The addition of n-butane to scavenge the HO radicals produced by the reaction of HO_2 with NO had no effect on the rate of decomposition of HO_2NO_2, implying that the reaction of HO with HO_2NO_2 is not important in this system and permitting the authors to derive this upper limit for the value of k.

(b) Laser flash photolysis resonance fluorescence technique. First order decay of [HO] monitored by resonance fluorescence at 310 nm in presence of excess HO_2NO_2 measured by mass spectrometry. HO radicals were produced by laser flash photolysis of O_3 at 249 nm or 266 nm in presence of H_2 and/or H_2O. Rate coefficient was independent of total pressure over the range 3 to 15 Torr Helium. HO_2NO_2 was produced batch-wise by adding NO_2BF_4 to 90% solution of H_2O_2. Correction was made for the contribution by the H_2O_2 impurity which was explicitly measured in all experiments. Reaction products were not identified. Authors recommend temperature-independent value given above but also give expression $k = (8.05\pm5.69)\times10^{-12}\exp(-(193\pm194)/T)$ cm^3 molecule^{-1} s^{-1}.

(c) Order-of-magnitude estimate by analogy with $k(HO + H_2O_2) = 8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} in the same evaluation.

(d) No recommendation was given, since no direct study had been reported.

(e) Order-of-magnitude estimate by analogy with $k(HO + H_2O_2) = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} in the same evaluation.

Preferred Value

$k = 4.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 246–324 K.

Reliability

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

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

Comments on Preferred Value

The preferred value is that reported by Trevor et al. [2], which is the only reported direct study of this reaction. The error limits given here have been substantially increased over those suggested by the authors because this is the only direct study and because of the inherent difficulties of preparing and handling HO_2NO_2.

The reaction products have not been identified. Those suggested here are the most likely products, although other reaction channels are thermodynamically possible. Confirmation of these kinetic results and mechanistic studies to identify products are needed.

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$HO_2 + NO \rightarrow HO + NO_2$

$\Delta H^\circ = -28$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.3)\times 10^{-11}$	297	Glaschick-Schimpf et al., 1979 [1]	(a)
$(7.6 \pm 1.7)\times 10^{-12}$	293	Hack et al., 1980 [2]	(b)
$(3.57 \pm 0.23)\times 10^{-12} \exp((226 \pm 41)/T)$	423–1271	Howard, 1980 [3]	(c)
7.6×10^{-12}	298*		
Reviews and Evaluations			
$4.3\times 10^{-12} \exp(200/T)$		NASA, 1979 [4]	(d)
$4.3\times 10^{-12} \exp(200/T)$		CODATA, 1980 [5]	(d)
$3.5\times 10^{-12} \exp(250/T)$		NASA, 1981 [6]	(e)

Comments

(a) Discharge-flow system. HO_2 was produced by reaction $H + O_2 + M \rightarrow HO_2 + M$. Total pressure of 7.5 Torr. First order decay of $[HO_2]$ in presence of excess NO monitored by emission at 1.43 nm after energy transfer from $O_2(^1\Delta)$ produced by a microwave discharge in O_2. No isotope effect was observed when DO_2 was substituted for HO_2.

(b) Discharge-flow reactor connected to a combined LMR-ESR spectrometer. HO_2 was produced by the reaction $H + O_2 + M \rightarrow HO_2 + M$ or $F + H_2O_2 \rightarrow HO_2 + HF$. First order decay of $[HO_2]$ in presence of excess NO monitored by laser magnetic resonance and electron spin resonance. The rate coefficient was found to be independent of total pressure over the range of 1.6 to 12.5 Torr.

(c) Discharge-flow reactor. HO_2 was produced by the reaction $H + O_2 + M \rightarrow HO_2 + M$. Total pressure of 1 to 3 Torr. First order decay of $[HO_2]$ in presence of excess NO monitored by laser magnetic resonance. The author combined these data with his previously reported data for the low temperature range 232–432 K (Howard, 1979 [1]) to derive the following expression over the combined temperature range 232–1271 K: $k = (3.51 \pm 0.35)\times 10^{-12} \exp((240 \pm 30)/T)$ cm^3 molecule^{-1} s^{-1}. The author also measured the rate of the reverse reaction over the temperature range 452–1115 K and thereby derived a value for the heat of formation of the HO_2 radical: $\Delta H_f^\circ(HO_2) = 10.5 \pm 2.5$ kJ at 298 K.

(d) Based on results of temperature dependent studies by Howard, [7] and Leu, [8] and room temperature results reported in references [9–11].

(e) Based on temperature dependent studies by Howard in references [3 and 7] and room temperature results in references [1 and 8–10].

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 range 230–500 K.

Reliability

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

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

Comments on Preferred Values

Preferred value at 298 K is the average of the values reported [7–10 and 2]. The value reported in reference [1] is higher but in agreement within the stated uncertainty. It should be noted that the value derived from the ratio measurement of Burrows et al. [11] is no longer in good agreement with other recent results due to an increase by a factor of two in the recommended value of the rate constant for the reference reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$.

The temperature dependence is that reported by Howard [3] for the combined temperature range 232–1271 K based on high temperature data in this reference and low temperature data in Howard [7]. This temperature dependence measured over a very large temperature range is preferred to that reported by Leu [8] over a much smaller temperature range. The pre-exponential factor reported in reference [3] has been adjusted here to give the preferred value of the rate coefficient at 298 K.

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$HO_2 + NO_2 + M \rightarrow HOONO_2 + M$

$\Delta H^\circ = -97.7$ 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			
$2.1\times10^{-31}(T/300)^{-5}[N_2]$	200–300	NASA, 1979 [1], 1981 [3]	(a)
$2.1\times10^{-31}[N_2]$	300	CODATA, 1980 [2]	

Comments

(a) T-dependence from a theoretical analysis.

Preferred Value

$k_0 = 2.1\times10^{-31}\ (T/300)^{-5}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

Comments on Preferred Value

The NASA evaluation ([1] and [3]) is accepted here.

High pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$6.5\times10^{-12}(T/300)^{-2}$	200–300	NASA, 1979 [1], 1981 [3]	(a)
5×10^{-12}	298	CODATA, 1980 [2]	

Preferred Value

$k_\infty = 5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ at 298 K.

Comments on Preferred Value

In contrast to refs. [1] and [3], no major temperature dependence of k_∞ is assumed here. One should note that the preferred value of this evaluation for the dissociation reaction together with an equilibrium constant of $1.68\times10^{28}\exp(-11977/T)$ molecule cm^{-3} from ref. [4] leads to $k_\infty = 3.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Intermediate Fall-off Range

$F_c \simeq 0.4$ at 298 K is chosen analogous to the $N_2O_5 \rightarrow NO_2 + NO_3$ reaction.

References

[1] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Reed, E. I. editors (1979).

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data 9, 295 (1980).

[3] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratosphere Modelling," DeMore, W. B., Stief, L. J., Golden, D. M., Hampson, R. F., Jr., Kurylo, M. J., Margitan, J. J., Molina, M. J., Watson, R. T., JPL Publ. 81-3 (1981).

[4] Uselman, W. M., Levine, S. Z., Chan, W. H., Calvert, J. G., and Shaw, J. H., Chem. Phys. Lett. 58, 437 (1978).

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

$\Delta H^\circ = +97.7$ kJ mol^{-1}

Low pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.2\times10^{-6}\exp(-(10014\pm250)/T)\,[N_2]$	261–295	Graham, Winer, and Pitts, 1978 [1]	(a)
$1.3\times10^{-20}\,[N_2]$	298		
Reviews and Evaluations			
$1.2\times10^{-20}\,[N_2]$	298	CODATA, 1980 [2]	(b)

Comments

(a) Fourier transform-IR spectroscopic study in a 5800 1 chamber. Measurements at 1–7 Torr of N_2, at higher pressures (≫7 Torr) intermediate fall-off effects are visible.

(b) Evaluation based only on measurements of the reverse reaction.

Preferred Values

$k_0 = 5\times10^{-6}\exp(-10000/T)$ $[N_2]$ s^{-1} over range 260–300 K.

$k_0 = 1.3\times10^{-20}\,[N_2]$ s^{-1} at 298 K.

Reliability

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

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

Comments on Preferred Values

Values for the forward and reverse reaction agree very well. We prefer this direct study over the measurements of the reverse process, since no conversion by the equilibrium constant is required.

High pressure rate coefficient

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
>0.018	278	Graham, Winer, and Pitts, 1978 [1]	(a)
Reviews and Evaluation			
$>1.4\times10^{14}\exp(-10420/T)$	250–300	CODATA, 1980 [2]	(b)
>0.09	298		

Comments

(a) See comments (a) for k_0. This is a lower limit since a linear Lindeman-Hinshelwod evaluation of the fall-off curve was made for the pressure range 10–760 Torr of N_2.

(b) Based on earlier data from the authors of ref. [1].

Preferred Values

$k_\infty = 3.5\times10^{14}\exp(-10420/T)$ s^{-1} over range 250–300 K.

$k_\infty = 0.23$ s^{-1} at 298 K.

Reliability

$$\Delta \log k_\infty = \pm 0.6 \text{ at } 298 \text{ K}.$$
$$\Delta (E/R) = \pm 500 \text{ K}.$$

Comments on Preferred Values

Theoretical analysis of the fall-off curve is required in order to obtain a better extrapolation. k_∞ chosen to be in accord with $F_c \simeq 0.4$ at 278 K and the measured k (1 atm) (see below). The recombination data of this evaluation would suggest an up to 1.3 time higher preexponential factor of k_∞ (see data sheet for $HO_2 + NO_2$).

Intermediate Fall-off Range

$F_c \simeq 0.4$ chosen analogous to the $N_2O_5 \rightarrow NO_2 + NO_3$ reaction. k_∞ constructed to obtain agreement with the measured rate constant at 760 Torr of N_2 and 277.7 K, $k = (714 \pm 43) \times 10^{-5}$ s^{-1}, from ref. [1]. A recent much less direct determination of k at 1 atm by Simonaitis and Heicklen, 1978 [3] gave $k = 6 \times 10^{17} \exp(-13080/T)$ s^{-1}. For 298 K, this value (k = 0.051 s^{-1}) agrees very well with the corresponding value from this evaluation ($k = 0.054$ s^{-1}) which is based on the fall-off curve from ref. [1]; however, the temperature coefficient from ref. [3] appears to be incorrect.

References

[1] Graham, R. A., Winer, A. M., and Pitts, J. N., J. Chem. Phys. **68**, 4505 (1978).

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

[3] Simonaitis, R. and Heicklen, J., Int. J. Chem. Kin. **10**, 67 (1978).

$NO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$NO + h\nu + N(^4S) + O(^3P)$	627.9	190.5
$\rightarrow N(^4S) + O(^1D)$	817.7	146.3
$\rightarrow N(^2D) + O(^3P)$	857.8	139.5
$\rightarrow N(^4S) + O(^1S)$	1032.1	115.9
$\rightarrow N(^2D) + O(^1D)$	1047.6	114.2
$\rightarrow N(^2D) + O(^1S)$	1262.1	94.8

Electronic energy levels of NO and transitions

State	T_0/cm^{-1}	λ (vac)/nm	Transition
$X(^2\pi_{1/2})$	0		
$A(^2\Sigma)$	44199	226.2	A–X (γ)
$B(^2\pi)$	45505	219.8	B–X (β)
$C(^2\pi)$	52372	190.9	C–X (δ)
$D(^2\pi)$	53291	187.6	D–X (ϵ)

Energy levels are from [1].

Calculation of the rate of dissociation of nitric oxide in the stratosphere and mesosphere. It is recommended that the reader use the values of the dissociation rate given as a function of altitude and solar zenith angle in table 4 of Frederick and Hudson [2]. This recommendation is unchanged from that given in the previous evaluation, CODATA [3] where detailed discussion can be found.

References

[1] Miescher, E., and Akermann, F., in "Stratroscopic Data Relative to Diatomic Molecules" B. Rosen, editor, International Tables of Selected Constants (Pergamon Press, 1970, vol. 17, p. 277.

[2] Frederick, J. E., and Hudson, R. D., J. Atoms. Sci. **36**, 737 (1979).

[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	298
$\rightarrow NO + O(^1D)$ (2)	490	244

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$	λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
185	26.0	245	4.3	305	16.6	365	57.8
190	29.3	250	2.8	310	17.6	370	54.2
195	24.2	255	1.4	315	22.5	375	53.5
200	25.0	260	1.9	320	25.4	380	59.9
205	37.5	265	2.0	325	27.9	385	59.4
210	38.5	270	3.1	330	29.9	390	60.0
215	40.2	275	4.0	335	34.5	395	58.9
220	39.6	280	5.5	340	38.8	400	67.6
225	32.4	285	7.0	345	40.7	405	63.2
230	24.3	290	8.2	350	41.0	410	57.7
235	14.8	295	9.7	355	51.3		
240	6.7	300	11.7	360	45.1		

Quantum yields

λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1
376	0.75	386	0.74	396	0.78	406	0.30
378	0.74	388	0.76	398	0.72	408	0.18
380	0.81	390	0.74	400	0.65	410	0.14
382	0.65	392	0.73	402	0.57	415	0.067
384	0.66	394	0.83	404	0.40	420	0.023

The above table gives values of ϕ_1 at closely spaced wavelength values in the neighbourhood of the thermodynamic threshold for photodissociation. For shorter wavelengths (295–365 nm) use the formula: $\phi_1(\lambda) = 1.0-0.0008\,(\lambda-275)$.

Comments on Preferred Values

The preferred absorption cross section values are those of Bass, Ledford, and Laufer [1]. The preferred quantum yield values for 375–420 nm are those reported by Harker et al. [2]. These recommendations are unchanged from those given in the previous evaulation, CODATA, [3] where detailed discussion can be found. It should be noted that the expression given in CODATA [3] for quantum yield values at shorter wavelengths does not merge smoothly with the values tabulated above, indicating a problem over the range 350 to 400 nm. If ϕ_1 is indeed less than unity at wavelengths shorter than 398 nm, there must exist a highly excited NO_2 species presently undetected.

References

[1] Bass, A. M., Ledford, A. E., and Laufer, A. H., J. Research Nat. Bur. Stand. Sect A: **80A**, 143 (1976).
[2] Harker, A. B., Ho, W., and Ratto, J. J. Chem. Phys. Lett. **50**, 394 (1977).
[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0°/kJ mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$NO_3 + h\nu \rightarrow NO + O_2(^3\Sigma_g^-)$ (1a)	13	9000
$\rightarrow NO + O_2(^1\Delta_g)$ (1b)	107	1100
$\rightarrow NO + O_2(^1\Sigma_g^+)$ (1c)	170	700
$\rightarrow NO_2 + O$ (2)	206	580

Absorption cross section data

Wavelength range/nm	Reference	Comments
498–671	Mitchell et al. 1980 [1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1\sigma$, $\phi_2\sigma$	470–685	Magnotta and Johnston, 1980 [2]	(b)

Comments

(a) NO_3 generated by reaction of NO_2 with O_3 in a recirculating flow system with excess O_3. Relative absorption spectrum shown in a figure. Also the absolute value of cross section at $\lambda = 663$ nm was determined to be $(121 \pm 20) \times 10^{-19}$ cm^2.

(b) NO_3 prepared from N_2O_5 by allowing equilibrium to be established: $N_2O_5 = NO_2 + NO_3$. NO_3 was photolyzed by a pulsed tunable dye laser. Product NO and O were measured by resonance fluorescence. These experiments are most sensitive to the value of the product $\phi\sigma$ rather than to the values of ϕ and σ individually. The authors also give values of the photodissociation rate j_i which is the integrated value of $\phi_i \sigma I$ over the absorption wavelength range. For an overhead sum and the range 470 to 700 nm, they give the following photodissociation rates: $j_i = 0.022 \pm 0.007$ s^{-1} and $j_i = 0.18 \pm 0.06$ s^{-1}.

Preferred Values

No preferred values are given for the absorption cross section (σ) or for the primary quantum yeilds (ϕ_1, ϕ_2) individually. The following table gives preferred values for the products $\phi_1\sigma$ and $\phi_2\sigma$ from 470 to 634 nm. The tabulated values are averaged over 5 nm intervals centered on the stated value of λ.

Preferred Values of $\phi_1\sigma$ and $\phi_2\sigma$

λ /nm	$10^{19}\phi_2\sigma$	λ /nm	$10^{19}\phi_2\sigma$	$10^{19}\phi_1\sigma$
472	5.9	557	37.1	
477	7.2	562	34.3	
482	7.0	567	32.7	
487	8.6	572	33.3	
492	10.0	577	40.5	
497	11.5	582	41.3	0.0
502	10.6	587	48.3	9.7
507	12.4	592	49.8	22.0
512	16.1	597	33.3	16.2
517	14.5	602	23.0	11.6
522	17.4	607	17.4	9.0
527	18.1	612	9.9	4.6
532	20.7	617	7.9	2.4
537	24.2	622	19.5	3.8
542	18.3	627	9.1	1.0
547	25.6	632	2.0	0.0
552	26.5			

Comments on Preferred Values

The preferred values for the products $\phi_1\sigma$ and $\phi_2\sigma$ are taken from the recent study of the Magnotta and Johnston, [2]. It is the product $\phi\sigma$ to which their experiments are most sensitive. The spectral resolution used in this study is much higher than that in the earlier study from the same laboratory which used broad-band light sources, Graham and Johnston, [4].

The absolute values of the absorption cross sections are uncertain, although the relative shape of the absorption spectrum seems to be well established. The one absolute value of σ given in reference [1] is 30% lower than the corresponding value is reference [4]. On the other hand, Magnotta and Johnston [2] suggest that their data may fit better if the values of σ given in reference [4] are increased by 50%. Since only the product $\phi\sigma$ is established, there is a corresponding uncertainty in the absolute values of the quantum yields.

References

[1] Mitchell, D. N., Wayne, R. P., Allen, P. J., Harrison, R. P., and Twin, R. J., J. Chem. Soc. Faraday Trans. 2 **76**, 785 (1980).

[2] Magnotta, F., and Johnston, H. S., Geophys. Res. Lett. 7, 769 (1980).

[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

[4] Graham, R. A., and Johnston, H. S., J. Phys. Chem. **82**, 254 (1978).

$N_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0 /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 at 208 K. In very good agreement with results of Selwyn et al. [2].

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma$/cm^2	λ /nm	$10^{20}\sigma$/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

$A_1 = 68.21023$ $B_1 = 123.4014$

$A_2 = -4.071805$ $B_2 = -2.116255$

$A_3 = 4.301146\times10^{-2}$ $B_3 = 1.111572\times10^{-2}$

$A_4 = -1.777846\times10^{-4}$ $B_4 = -1.881058\times10^{-5}$

$A_5 = 2.520672\times10^{-7}$

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, Podolske, and Johnston [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, [6] where detailed discussion can be found.

References

[1] Hubrich, C., and Stuhl, F., J. Photochem. **12**, 93 (1980).
[2] Selwyn, G., Podolske, J., and Johnston, H. S., Geophys. Res. Lett. **4**, 427 (1977).
[3] Paraskevopoulos, G., and Cvetanovic, R. J., J. Am. Chem. Soc. **91**, 7572 (1969).
[4] Preston, K. F., and Barr, R. F., J. Chem. Phys. **54**, 3347 (1971).
[5] Griener, N. R., J. Chem. Phys. **47**, 4373 (1967).
[6] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0 /kJ mol^{-1}	$\lambda_{threshold}$ /nm
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	(1)	89	1340
$\rightarrow N_2O_4 + O(^3P)$	(2)	242	495
$\rightarrow N_2O_4 + O(^1D)$	(3)	432	275

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma$/cm^2	λ /nm	$10^{20}\sigma$/cm^2
205	690	280	10.7
210	520	285	8.3
215	330	290	6.3
220	206	295	4.6
225	131	300	3.2
230	93	305	2.2
235	72	310	1.5
240	57	320	0.75
245	45	330	0.40
250	35	340	0.27
255	26.3	350	0.18
260	21.2	360	0.10
265	17.7	370	0.05
270	15.2	380	0.01
275	12.5		

Quantum yields
No recommendation.

Comments on Preferred Values

The preferred absorption cross section values are those reported in Graham and Johnston [1] for 205–310 nm and in Jones and Wulf [2] for 320–380 nm. These recommendations are unchanged from those given in the previous evaluation, CODATA [3] where detailed discussion can be found.

References

[1] Graham, R. A., and Johnston, H. S., J. Phys. Chem. **82**, 254 (1978).
[2] Jones, E. J., and Wulf, O. R., J. Chem. Phys. **5**, 873 (1937).
[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

HONO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$ /nm
$HONO + h\nu \rightarrow HO + NO$	(1)	202	591
$\rightarrow H + NO_2$	(2)	326	367
$\rightarrow HNO + O$	(3)	423	283

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\mathrm{cm}^2$
310	0
315	0.4
320	4.0
325	3.8
330	8.8
335	5.7
340	17.6
345	11.1
350	10.0
355	26.5
360	7.2
365	18.2
370	20.9
375	3.7
380	8.2
385	14.7
390	1.4
395	0

Quantum yields

$\phi_1 = 1.0$ throughout this wavelength region.

Comments on Preferred Values

The preferred absorption cross section values have been derived from the tabulated results in Stockwell and Calvert [1] by averaging the values over 5 nm intervals. For values at shorter wavelengths (200–310 nm) use values tabulated in Cox and Derwent [2].

Based on the results of Cox and Derwent [2], the preferred value of ϕ_1 is set equal to unity throughout this wavelength range. These recommendations are unchanged from those given in the previous evaluation CODATA [3] where detailed discussion can be found.

References

[1] Stockwell, W. R., and Calvert, J. G., J. Photochem. **8**, 193 (1978).

[2] Cox, R. A. and Derwent, R. G., J. Photochem. **6**, 23 (1976).

[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	418	286
$\rightarrow HONO + O(^1D)$	(4)	488	245

Absorption cross section data

Wavelength range/nm	Reference	Comments
190–330	Molina and Molina, 1981 [1]	(a)

Comments

(a) Measured at 298 K. In very good agreement with results of Johnston and Graham [2] except at both ends of wavelength range.

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma/\text{cm}^2$	λ /nm	$10^{20}\sigma/\text{cm}^2$
190	1320	260	1.90
195	910	265	1.80
200	550	270	1.63
205	255	275	1.40
210	97	280	1.14
215	32.8	285	0.88
220	14.4	290	0.63
225	8.51	295	0.43
230	5.63	300	0.28
235	3.74	305	0.17
240	2.60	310	0.09
245	2.10	315	0.05
250	1.95	320	0.02
255	1.94	325	0.00

Quantum yields
$\phi_1 = 1.0$ throughout this wavelength region.

Comments on Preferred Values

The preferred absorption cross section values are those of Johnston and Graham [2]. They are confirmed by the recent results of Molina and Molina [1]. The preferred value of the quantum yield (ϕ_1 equal to unity) is based on the results of Johnston et al. [3]. These recommendations are unchanged from those given in the previous evaluation, CODATA [4] where detailed discussion can be found.

References

[1] Molina, L. T., and Molina, M. J., J. Photochem. **15**, 97 (1981).
[2] Johnston, H., and Graham, R., J. Phys. Chem. **77**, 62 (1973).
[3] Johnston, H. S., and Chang, S.-G., and Whitten, G., J. Phys. Chem. **78**, 1 (1974).
[4] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0° /kJ mol^{-1}	$\lambda_{\text{threshold}}$ /nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	89	1340
$\rightarrow HO + NO_3$ (2)	164	730

Absorption cross section data

Wavelength range/nm	Reference	Comments
200–290	Morel, Simonaitis, and Heicklen, 1980 [1]	(a)
190–330	Molina and Molina, 1981 [2]	(b)

Comments

(a) Measured at 296 K. HO_2NO_2 was prepared by photolysis of Cl_2 at 366 nm in presence of 40–600 mTorr, NO_2, 20–30 Torr O_2 and H_2 at a total pressure of 750 Torr.

(b) Measured at 298 K and 1 atmosphere total pressure. HO_2NO_2 was prepared in flowing N_2 stream in the presence of H_2O, H_2O_2, HNO_3 and HO_2. The composition of the mixture was established by Fourier-transform infrared spectroscopy, by the absorption spectrum in the visible and by chemical titration after absorption in aqueous solutions. Two methods were used to prepare HO_2NO_2. The first mixed 70% nitric acid with 90% H_2O_2, while in the second method solid nitroniumtetrafluoroborate (NO_2BF_4) was added to a solution of 90% H_2O_2.

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma$/cm^2	λ /nm	$10^{20}\sigma$/cm^2
190	1010	260	27.8
195	816	265	22.4
200	563	270	17.8
205	367	275	13.4
210	241	280	9.3
215	164	285	6.3
220	120	290	4.0
225	95.2	295	2.6
230	80.8	300	1.6
235	69.8	305	1.1
240	59.1	310	0.7
245	49.7	315	0.4
250	41.8	320	0.3
255	35.1	325	0.2
		330	0.1

Quantum yields

No recommendation can be made for values of ϕ_1 and ϕ_2 since there are no data.

Comments on Preferred Values

The preferred values are those reported in the recent study by Molina and Molina [2]. In the previous evaluation, CODATA [3] no recommendation was given, but the results of Graham et al. [4] for 190–330 nm and those of Cox and Patrick [5] for 195–265 nm were tabulated. The new results in references [1 and 2] are in reasonably good agreement with each other. The critical wavelength range for atmospheric photodissociation is 290–330 nm, and data for this region are reported only in references [2 and 4]. For this wavelength region the preferred results of Molina and Molina [2] are about an order of magnitude smaller than the corresponding values reported by Graham et al. [4], although these studies are in reasonably good agreement at shorter wavelengths. Owing to the difficulties of preparing and handling HO_2NO_2, the results of Molina and Molina [2] at 298 K need to be confirmed. Also, temperature dependent studies of cross sections and quantum yield studies are needed.

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5.4. Organic Compounds

$O + CH_3 \rightarrow HCHO + H$

$\Delta H^\circ = -285.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.85 \pm 0.28)\times10^{-10}$	300	Slagle, Pruss, and Gutman, 1974 [1]	(a)
$(1.0 \pm 0.2)\times10^{-10}$	259–341	Washida and Bayes, 1976 [2]	(b)
$(1.38 \pm 0.46)\times10^{-10}$	298	Washida [3]	(c)
Relative Rate Coefficients			
1.05×10^{-10}	300	Morris and Niki, 1972 [4]	(d)
Reviews and Evaluations			
1.0×10^{-10}	200–300	NASA, 1979 [5]	(e)
1.0×10^{-10}	200–300	NASA, 1981 [6]	(e)

Comments

(a) Discharge flow-photoionisation mass spectrometric measurement of CH_3 and other species. O atom concentration determined by titration with NO_2. k determined by observation of CH_3 kinetics into steady state, in the reaction of $O + C_2H_4$. Pressure = 0.71 to 2.21 Torr.

(b) Discharge flow-photoionisation mass spectrometry. O determined by titratation with NO_2 and k determined from CH_3 approach to steady state.

(c) Similar experiment to [1] and [2]. Appears to be a less precise measurement.

(d) CH_3 produced by H + diazomethane reacted with O in a concentric double flow reactor coupled to a time-of-flight mass spectrometer. Relative rate coefficients $k / k(O + C_6H_{12}) = 1.5$($C_6H_{12}$ = tetramethylethylene) determined from relative slopes of plots of $\ln([R]/[R_0]_0)$ vs $[O]$. $k(O + C_6H_{12}) = 7.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K [7].

(e) Based on [2].

Preferred Value

$k = 1.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k = \pm 0.2$
$\Delta (E/R) = \pm 200$ K

Comments on Preferred Value

The various absolute measurements of this rate coefficient are only in moderately good agreement considering that all were made using the same experimental arrangement. The relative rate study of Morris and Niki is in agreement with the direct studies, although the authors draw attention to possible errors arising from incomplete mixing in their flow tube. The recommended value of k is a simple mean of the results from [1]–[4]. The results in ref. [1] suggest strongly that the designated reaction channel is dominant at 300 K.

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$$
\begin{aligned}
O(^1D) + CH_4 &\rightarrow HO + CH_3 && (1)\\
&\rightarrow O(^3P) + CH_4 && (2)\\
&\rightarrow H_2O + CH_2 && (3)\\
&\rightarrow CH_2O + H_2 && (4)\\
&\rightarrow CH_3OH && (5)
\end{aligned}
$$

$\Delta H°(1) = -179$ kJ mol^{-1}
$\Delta H°(2) = 189$ kJ mol^{-1}
$\Delta H°(3) = -220$ kJ mol^{-1}
$\Delta H°(4) = -472$ kJ mol^{-1}
$\Delta H°(5) = -564$ 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			
$(1.57 \pm 0.13)\times 10^{-10}$	295	Amimoto et al., 1979 [1]	(a)
Branching Ratios			
$k_2/k = 0.12 \pm 0.04$	295	Amimoto et al., 1979 [1]	(a) (b)
$k_2/k = 0$	295	Amimoto et al., 1980 [2]	(a) (c)
Reviews and Evaluations			
1.4×10^{-10}	200–300	NASA, 1979 [3]	(d)
2.4×10^{-10}	200–300	CODATA, 1980 [4]	(e)
1.5×10^{-10}	200–300	NASA, 1981 [5]	(d)

Comments

(a) 248 nm laser flash photolysis of O_3-CH_4-He mixtures. Time resolved measurement of $O(^3P)$ by atomic resonance absorption.

(b) Branching ratio based on yield of $O(^3P)$ after all $O(^1D)$ removed in above experiments.

(c) Supersedes branching ratio given in ref. [1]. $O(^3P)$ originally attributed to channel (2) shown to result from primary photolysis of O_3.

(d) Based on average of values measured by $O(^1D)$ absorption [6] and emission [7] techniques.

(e) Based on measurements using emission techniques.

Preferred Values

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

$k_1/k = 0.9$; $k_4/k = 0.1$; $k_2/k = 0$ over range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K; $\Delta k_1/k = \Delta k_4/k = \pm 0.1$.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The new direct measurements of k obtained by monitoring $O(^3P)$ formation [1] show excellent agreement with the earlier data based on time resolved emission from $O(^1D)$, and are in disagreement with the $O(^1D)$ absorption work. The latter is therefore rejected. The preferred value is now a mean of the values given in ref. [1] and Davidson et al. [7], and has a corresponding reduced uncertainty. The preferred values for the branching ratios and the temperature dependence are unchanged from the previous CODATA evaluation [4].

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$HO + CH_4 \rightarrow H_2O + CH_3$

$\Delta H^\circ = -60.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.32\times10^{-17}\,T^{1.92}\exp(-1355/T)$	298–1020	Tully and Ravishankara, 1980 [1]	(a)
$(7.50\pm0.60)\times10^{-15}$	298		
Reviews and Evaluation			
$2.4\times10^{-12}\exp(-1710/T)$	200–300	NASA, 1979 [2]	(b)
$2.4\times10^{-12}\exp(-1710/T)$	200–300	CODATA, 1980 [3]	(b)
$2.4\times10^{-12}\exp(-1710/T)$	200–300	NASA, 1981 [4]	(b)

Comments

(a) Flash photolysis of $Ar\text{-}H_2O\text{-}CH_4$ mixtures. First order decay of [HO] monitored by resonance fluorescence.

(b) Based on work of Davis et al. [5] who have reported the only data for $T < 296$ K.

Preferred Values

$k = 8.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.4\times10^{-12}\exp(-1710/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

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

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

Comments on Preferrd Values

The new data [1] confirm the previous conclusion of non-Arrhenius behavior for this reaction. The expression for the temperature dependence given in [1], fits well the data over the whole range and also a recent value at 1300 K [6], and should be used in preference to the previously recommended expression for temperatures > 300 K [3], which was based on earlier work of Zellner and Steinert [7]. The preferred value for the range 200–300 K is unchanged from the previous CODATA evaluation since no new data for $T < 298$ K have been reported. Of interest for atmospheric chemistry is the recent determination of the carbon kinetic isotope effect $^{12}k/^{13}k = 1.0028 \pm 0.0021$ where ^{12}k and ^{13}k refer to the rate coefficients for reaction of HO with $^{12}CH_4$ and $^{13}CH_4$ at room temperature [8].

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$$\begin{aligned} HO + C_2H_2 + (M) \rightarrow C_2H_2OH + (M) &\rightarrow C_2H + H_2O + (M) \quad (1)\\ &\rightarrow CH_3 + CO + (M) \quad (2)\\ &\rightarrow CH_2CO + H + (M) \quad (3)\\ &\rightarrow CH_2CHO + (M) \quad (4)\\ &\rightarrow CHCO + H_2 + (M) \quad (5) \end{aligned}$$

$\Delta H^\circ(1) = -17$ kJ mol^{-1}

$\Delta H^\circ(2) = -239$ kJ mol^{-1}

$\Delta H^\circ(3) = -109$ kJ mol^{-1}

$\Delta H^\circ(4) = -126$ kJ mol^{-1}

$\Delta H^\circ(5) = -105$ 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			
1×10^{-12}	300	Wilson and Westenberg, 1967 [1]	(a)
2.5×10^{-14}	298	Bradley and Tee, 1969 [2]	(b)
$(1.9\pm0.6)\times10^{-13}$	298	Breen and Glass, 1970 [3]	(c)
$2.0\times10^{-12}\exp(-253/T)$	210–460	Smith and Zellner, 1973 [4]	(d)
8.5×10^{-13}	298		
$(2.0\pm0.6)\times10^{-13}$	298	Pastrana and Carr, 1974 [5]	(e)
$(1.65\pm0.15)\times10^{-13}$	298	Davis et al., 1975 [6]	(f)
$1.91\times10^{-12}\exp(-(312\pm201)/T)$	298–422	Perry, Atkinson, and Pitts, 1977 [7]	(g)
$(6.79\pm0.70)\times10^{-13}$	298		
$5.31\times10^{-13}\exp(-100/T)$	570–850	Vandooren and van Tiggelen, 1977 [8]	(h)
3.8×10^{-13}	298*		
$(6.83\pm1.19)\times10^{-12}\exp(-(646\pm47)/T)$	228–413	Michael et al., 1980 [9]	(i)
$(7.76\pm0.73)\times10^{-13}$	298		
Reviews and Evaluations			
$1.26\times10^{-12}\exp(-553/T)$	300–2000	Kondratiev, 1970 [10]	(j)
2×10^{-13}	300–1000	Wilson, 1972 [14]	(k)
$2.0\times10^{-12}\exp(-251/T)$	210–460	Anderson, 1976 [15]	(l)

Comments

(a) Fast-flow-discharge study. Pressure ~1 Torr He or Ar. HO generated by H + NO_2 reaction. [HO] monitored by e.s.r. C_2H_2 in excess. Value of k quoted is actually nk where n is an undetermined stoichiometry coefficient.

(b) Fast-flow-discharge study of the O + C_2H_2 reaction. Pressure 2.4 Torr Ar. E.s.r. detection of O, H, and HO. HO removal in latter part of the reaction attributed to reaction with C_2H_2 but k could only be estimated.

(c) Fast-flow-discharge study. Pressure of Ar unspecified but presumably a few Torr. HO generated by H + NO_2 reaction. [HO] monitored by e.s.r. Stable products analyzed by mass spectrometry and hence stoichiometric coefficient for HO consumption determined. Product analysis suggests that channels (1) and (5) predominate.

(d) Flash photolysis of $H_2/N_2O/C_2H_2$ or H_2O/C_2H_2 mixtures diluted with He. Pressure range 10–20 Torr He. [HO] monitored by resonance fluorescence.

(e) Fast-flow-discharge study. Pressure 1 Torr He. HO generated by H + NO_2 reaction. [HO] monitored by absorption at 309 nm. Values of k obtained from nk using value of n measured in [3]. Value of k obtained also under conditions of large C_2H_2 excess. Values from the two sets of conditions agree.

(f) Flash photolysis of H_2O/C_2H_2 mixtures with He diluent (20–500 Torr). No pressure dependence found. Dependence of k on flash energies observed and conditions chosen to avoid such complications due to secondary reactions.

(g) Flash photolysis of H_2O/C_2H_2 mixtures with Ar diluent (25–400 Torr). Flow system used to avoid accumulation of products. Pressure dependence of k observed. Arrhenius expression is for k at 200 Torr Ar. Later study [9] suggests that at this pressure k would still be in its pressure dependent region at higher temperatures in the range studied.

(h) Low pressure C_2H_2/O_2 flame. Molecule beam sampling into mass spectrometer used to analyze for flame species. Large concentrations of ketene found and attributed to reaction (3).

(i) Flash photolysis of H_2O/C_2H_2 mixtures with Ar diluent (10–1100 Torr). Resonance fluorescence detection of HO. Pressure dependence at 5 temperatures in range studied. Arrhenius expression quoted is for high pressure limiting values of k.

(j) Based on high temperature results of [11], [12] and erroneous low temperature results of [13].

(k) Accepts room temperature value of [3] and assumes zero activation energy.

(l) Accepts results of [4].

Preferred Values

$k = 7.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr pressure.

$k = 6.5\times10^{-12}\exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the range 220–410 K, at 760 Torr pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K and 760 Torr pressure.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

Despite several studies by different techniques there is little agreement on the favored reaction channels, the characterization of the pressure dependence, and on values for the rate parameters.

Evidence from crossed molecular beam studies [16], [17] is conflicting, one favoring channel (2) and the other finding evidence only for (3). Product analysis from a fast-flow discharge system suggests the occurrence of (5) but in a flame study large concentrations of ketene were found, also supporting (3). Moreover if the reaction proceeds by addition to give an intermediate which can be stabilized by collision, the findings of these low pressure studies may not apply at higher pressures. Although the existence of any effect of pressure on the rate coefficient has been disputed two recent studies [7], [9] provide convincing evidence for it, and it seems likely that reaction occurs, at least in part, by adduct formation, the final product distribution being both pressure and temperature dependent.

There is considerable scatter in the values reported for k which, only to a degree, can be reconciled by the effects of pressure on the rate. The recent extensive study by Michael et al. [9] is considered to be the most reliable and is in agreement in the high pressure region with earlier flash photolysis work [7]. The preferred value at 298 K is based on [7] and [9]. At 1 atmosphere Ar the reaction appears to be in its limiting first order region at least to temperatures up to ~400 K [9]. The preferred temperature dependence is taken from [9] since earlier studies were carried out wholly, or in part, in the pressure dependent regime.

At low pressures there are clear discrepancies between the flash photolysis studies and between them and the flow-discharge results. Further work is required to clarify the pressure dependence of k and the product distribution.

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$HO + C_2H_4 + (M) \rightarrow CH_2CH_2OH + (M)$

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.26 \pm 0.25)\times10^{-12}\exp((455 \pm 70)/T)$	299–497	Greiner, 1970 [1]	(a)
$(5.51 \pm 0.15)\times10^{-12}$ (100 Torr He)	298		
1.8×10^{-12} (1 Torr Ar)	300	Morris, Stedman, and Niki, 1971 [2]	(b)
$7.5\times10^{-12}\exp(-110/T)$	210–460	Smith and Zellner, 1973 [3]	(c)
5.1×10^{-12} (10–20 Torr He)	300		
$(5 \pm 1.7)\times10^{-12}$ (20 Torr He)	300	Stuhl, 1973 [4]	(d)
$(5.33 \pm 0.65)\times10^{-12}$ (300 Torr He)	300	Davis et al., 1975 [5]	(e)
$(6.23 \pm 0.33)\times10^{-12}$ (760 Torr H_2O)	381	Gordon and Mulac, 1975 [6]	(f)
$(7.31 \pm 0.33)\times10^{-12}$	416		
2.5×10^{-12} (7 Torr He)	296	Howard, 1976 [7]	(g)
$2.18\times10^{-12}\exp((390 \pm 150)/T)$	298–425	Atkinson, Perry, and Pitts, 1977 [8]	(h)
$(7.85 \pm 0.79)\times10^{-12}$ (225–650 Torr Ar)	298		
$(10.0 \pm 1.7)\times10^{-12}$ (400 Torr SF_6, CF_4, He)	296	Overend and Paraskevopoulos, 1977 [9]	(i)
Relative Rate Coefficients			
$(8.1 \pm 1.6)\times10^{-12}$ (760 Torr air)	305	Lloyd et al., 1976 [10]	(j)
Reviews And Evaluations			
$2.7\times10^{-10}\exp(-2830/T)$	350–1400	Kondratiev, 1970 [11]	(k)
1.8×10^{-12}	300	Kerr and Parsonage, 1972 [12]	(l)
5×10^{-12}		Wilson, 1972 [13]	(m)

Comments

(a) Flash photolysis of $H_2O/He/C_2H_4$ mixtures. Pressures stated to be as in other experiments in the series, i.e., 100 Torr He. [HO] monitored by UV absorption using photographic detection.

(b) Fast flow discharge study. Total pressure, 1 Torr Ar. HO generated by reaction of H atoms with NO_2. Mass spectrometry used to monitor [HO] and $[C_2H_4]$. Mass peaks corresponding to adduct (C_2H_4OH) observed.

(c) Flash photolysis of $H_2O/He/C_2H_4$ mixtures. Resonance absorption used to monitor [HO]. Total pressure, 10–200 Torr He.

(d) Flash photolysis of $H_2O/He/C_2H_4$ mixtures. Resonance fluorescence and multichannel scaling used to monitor [HO]. Total pressure, 20 Torr He.

(e) Flash photolysis of $H_2O/C_2H_4/He$ or N_2 mixtures. Resonance fluorescence detection of HO. Pressure range 3–30 Torr He. Rate constant shown to be pressure dependent.

(f) Pulse radiolysis of H_2O (760 Torr) in presence of small quantities of C_2H_4. [HO] monitored by uv absorption spectroscopy.

(g) Fast-flow discharge study. HO generated by reaction of H with NO_2. [HO] monitored by laser magnetic resonance. Pressure, 0.7–7 Torr He. Second order rate constant shown to be pressure dependent. Value of k tabulated obtained from linear plot of $1/k$ versus $1/[He]$ by extrapolation to $1/[He] = 0$.

(h) Flash photolysis of flowing $H_2O/C_2H_4/Ar$ mixtures over pressures range 10–650 Torr Ar. [HO] monitored by resonance fluorescence. Second order rate constant found to be pressure dependent.

(i) Flash photolysis of H_2O/C_2H_4 and $N_2O/H_2/C_2H_4$ with a variety of diluent gases (H_2O, SF_6, CF_4, He) at pressures in range 50–400 Torr.

(j) Environmental chamber using photolysis of NO_x/air mixture at 760 Torr in the presence of small amounts of C_2H_4. [CO], $[C_2H_4]$, $[HO_x]$, $[O_3]$ measured. Results compared with similar experiments using $n\text{-}C_4H_{10}$ in the place of C_2H_4. Hence $k / k(HO + n\text{-}C_4H_{10}) = 2.88$ obtained. $k(HO + n\text{-}C_4H_{10}) = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (a mean value of several determinations [14–17]) used to calculate k.

(k) Based on high temperature data [18], [19], and erroneous low temperature results [20].

(l) Selects low pressure result of [2].

(m) Based on [1] and low pressure flow discharge study [21].

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr pressure.

$k = 2.2 \times 10^{-12} \exp(400/T)$ cm^3 molecule^{-1} s^{-1} over the range 250–500 K, at 760 Torr pressure.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K and 760 Torr pressure.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

Reaction may occur by addition or by H abstraction. Despite suggestions to the contrary [22] there is compelling evidence from the kinetics and from product analysis to suggest that at temperatures in the neighborhood of 300 K the abstrac-

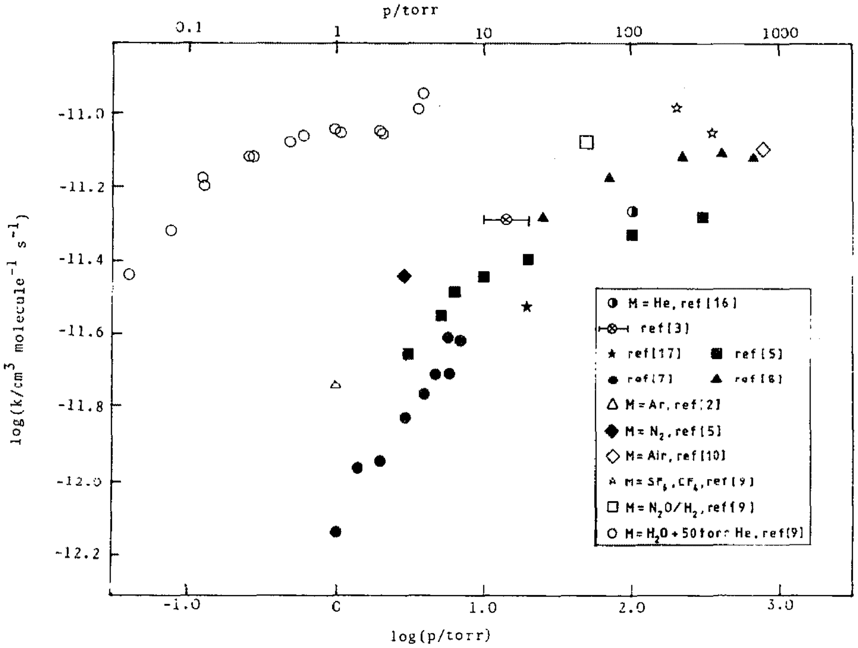

FIGURE 6. Pressure dependence of $k(HO + C_2H_4)$. For the mixtures H_2O + 50 Torr He the He pressure was held constant, and the H_2O pressure varied in the range 0.04–4 Torr. Values of k have been plotted as a function of the H_2O pressure only.

tion pathway is negligible.

Several studies have shown the second order rate constant to be pressure dependent. Fall-off is appreciable at pressures below ~200 Torr for He. The pressure dependence of k is shown in figure 6 where all the available results at 298 K are plotted. A notable feature is the apparently high efficiency of water in stabilizing the adduct, but this finding remains to be confirmed. The pressure dependence of k is largely responsible for the apparent lack of concordancy of early measurements of k which were performed at differing pressures with various diluent gases. We make no attempt to evaluate k in the fall-off region but it can probably be derived to within a factor of about 2 from the figure.

Since at 760 Torr the pressure dependence of k is small it is possible to compare results obtained at this pressure with different third bodies. At 298 K these results scatter over a range of approximately two with no obvious correlation with techniques or conditions. The preferred value is placed towards the upper end of the range to agree with most of the more recent results [8–10] with error limits which accommodate all of the results at this pressure and temperature.

The preferred temperature dependence is that of [8]. The two other studies yielding values of E/R were performed at lower pressures and are more likely to have been influenced by fall-off effects, although the results of [1] is in fair agreement with the recommended expression.

Little is known of the subsequent reactions of the thermalized adduct radical.

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$HO + C_2H_6 \rightarrow C_2H_5 + H_2O$

$\Delta H° = -89.5$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.86 \pm 0.30)\times10^{-11}\exp(-(1232 \pm 53)/T)$	300–500	Greiner, 1967, 1970 [1]	(a)
$(3.10 \pm 0.7)\times10^{-13}$	297		
$(2.64 \pm 0.17)\times10^{-13}$	295	Overend, Paraskevopoulos, and Cvetanovic, 1975 [2]	(b)
$(6.6 \pm 0.3)\times10^{-13}$	381	Gordon and Mulac, 1975 [3]	(c)
$(8.0 \pm 0.5)\times10^{-13}$	416		
$(2.9 \pm 0.6)\times10^{-13}$	296	Howard and Evenson, 1976 [4]	(d)
Reviews and Evaluations			
$1.28\times10^{-10}\exp(-1800/T)$	300–1500	Drysdale and Lloyd, 1970 [5]	(e)
$2.14\times10^{-10}\exp(-2000/T)$	302–793	Kondratiev, 1970 [8]	(f)
$(1.08 + 0.08)\times10^{-10}\exp(-1800/T)$	300–2000	Wilson, 1972 [10]	(g)

Comments

(a) Flash photolysis of $H_2O/Ar/C_2H_6$ mixtures at a pressure of 100 Torr. [HO] monitored by uv absorption spectroscopy using photographic detection.

(b) Flash photolysis of $H_2O/H_2/C_2H_6$ mixtures at 50 Torr pressure. [HO] monitored by uv absorption spectroscopy.

(c) Pulse radiolysis of H_2O (1 atmosphere) in the presence of small quantities of C_2H_6. [HO] monitored by uv absorption spectroscopy.

(d) Fast-flow discharge study. HO generated by reaction of H atoms with NO_2; C_2H_6 added downstream in large excess. [HO] monitored by laser magnetic resonance.

(e) Accepts temperature dependence of [6] but rejects absolute values of [6] in favor of the one value of [1] at 302 K. Also uses [7].

(f) Based on values of [1] at 302 K and of [9] at 793 K.

(g) Based on [1, 11–13].

Preferred Values

$k = 2.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-11} \exp(-1230/T)$ cm^3 molecule^{-1} s^{-1} over range 290–500 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

Recent measurements at ~300 K by flash photolysis and discharge flow methods are in excellent agreement [1,2,4]. The only detailed measurement of the temperature coefficient of the rate constant in the range 300–500 K is that of [1], which we adopt as our preferred value. This expression is in good agreement with other results at ~300 [2,4], the higher temperature values of [3] and, on extrapolation, is compatible with flame and shock tube measurements up to 1000 K.

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$HO + HCHO \rightarrow H_2O + HCO$ (1)
$\rightarrow H + HCOOH$ (2)
$\rightarrow H + CO + H_2O$ (3)

$\Delta H^\circ(1) = -135$ kJ mol^{-1}
$\Delta H^\circ(2) = -91$ kJ mol^{-1}
$\Delta H^\circ(3) = -64.7$ 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			
$(1.05 \pm 0.11) \times 10^{-11}$	228–363	Stief et al., 1980 [1]	(a)
Branching Ratios			
$k_2 = 0$ $k_3 > 0$	296	Morrison and Heicklen, 1980 [2]	(b)
$k_2/k \leqslant 0.18$	300	Cox et al., 1980 [3]	(c)
Reviews and Evaluations			
1.0×10^{-11}	200–300	NASA, 1979 [4]	(d)
1.3×10^{-11}	200–400	CODATA, 1980 [5]	(e)
1.0×10^{-11}	200–300	NASA, 1981 [6]	(d)

Comments

(a) Flash photolysis-resonance fluorescence study; k independent of [HCHO] (0.6–2.5 mTorr), [Ar] (20–80 Torr) and flash intensity (i.e., initial [HO]).

(b) Results based on absence of HCOOH formation and observed ϕ (CO) + ϕ (CO$_2$) in the photolysis of HCHO-NO$_2$ mixtures at 366 nm.

(c) Results based on computer modelling of earlier data [7] for HCOOH formation in photo-oxidation of CH_3ONO, and assuming channel (2) is only source of HCOOH in the system. Recent work suggests that the latter assumption is probably incorrect [8].

(d) Based on direct measurements including [1].

(e) Average of k values from direct studies [9,10].

Preferred Value

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–425 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Value.

The new data ref. [1] are in excellent agreement with the previous flash photolysis study of Atkinson and Pitts [9], but slightly lower than the discharge flow result of Morris and Niki [10] and the relative rate study at 1 atm pressure of Niki et al. [11] i.e. 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}. The preferred value of k is a mean of values from refs. [1], [9] and [10] and is independent of temperature. It seems clear that (1) is the major reaction channel. It would appear from the results in ref. [2] that channel (2) does not occur, but it is probable that a fraction of the product HCO species are sufficiently energetic to decompose to H + CO within a short time, making the overall channel (3) a significant pathway.

The branching ratio k_3/k may be pressure dependent, but the data relating to the branching ratio are not sufficiently reliable to provide a basis for recommendation.

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$HO + CH_3OH \rightarrow H_2O + CH_2OH$ (1)
$\rightarrow H_2O + CH_3O$ (2)

$\Delta H°(1) = -106.0$ kJ mol^{-1}
$\Delta H°(2) = -65.5$ 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			
$(1.06 \pm 0.10)\times10^{-12}$	296	Overend and Pareskevopoulos, 1978 [1]	(a)
$(1.0 \pm 0.1)\times10^{-12}$	298	Ravishankara et al., 1978 [2]	(b)
Relative Rate Coefficients			
$(9.4 \pm 1.5)\times10^{-14}$	298	Osif, Simonaitis, and Heicklen, 1975 [3]	(c)
$(1.47 \pm 0.30)\times10^{-14}$	350		
$(1.06 \pm 0.11)\times10^{-12}$	292	Campbell, McLaughlin, and Handy, 1976 [4]	(d)

Comments

(a) Flash photolysis; resonance absorption measurement of HO decay under pseudo first order conditions.

(b) Flash photolysis; HO followed by time resolved resonance fluorescence.

(c) Steady state photolysis of N_2O at 213.9 nm in presence of CH_3OH and CO. Relative rate ratios given: $k/k(HO + CO) = 0.63 \pm 0.10$ at 298 K and 0.98 ± 0.20 at 350 K. Total pressure 28–203 Torr. The values given are obtained using $k(HO + CO) = 1.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} the CODATA recommended value for <100 Torr and O_2 absent, at both temperatures.

(d) Thermal decomposition of H_2O_2-NO_2-CH_3OH-CO mixtures. k measured relative to reaction of HO with CO $k/k(HO + CO) = 6.7 \pm 0.7$ at 292 K. k calculated using low pressure, O_2 free value of $k(HO + CO) = 1.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k = 1.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The recommended value 298 K is based on the two direct studies [1, 2] which are in excellent agreement with each other and with the relative rate study of Campbell et al. [3]. The results of Osif et al. [4] seem to be seriously in error, probably as a result of misinterpretation of the complex chemical system used. Furthermore, it is unclear which value for $k(HO + CO)$ (see data sheet for HO + CO) is appropriate for the system. The results are therefore rejected.

There is no reliable temperature dependence study of this reaction and therefore an Arrhenius expression cannot be given. There are also no experimental data for the branching ratio k_1/k_2. However it is probable that the more exoergic channel (1) is dominant on energetic grounds.

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$HO + CH_3CHO \rightarrow CH_3CO + H_2O$

$\Delta H^\circ = -138$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.38) \times 10^{-11}$	300	Morris, Stedman, and Niki, 1971 [1]	(a)
$6.87 \times 10^{-12} \exp((260 \pm 150)/T)$	299–426	Atkinson and Pitts, 1978 [2]	(b)
$(1.60 \pm 0.16) \times 10^{-1}$	299		
Relative Rate Coefficients			
$\leqslant 2 \times 10^{-11}$	295	Cox et al., 1976 [3]	(c)
$(1.5 \pm 0.16) \times 10^{-11}$	298	Niki et al., 1978 [4]	(d)
$(1.20 \pm 0.4) \times 10^{-11}$	298	Kerr and Sheppard, 1981 [5]	(e)

Comments

(a) Fast-flow discharge study. HO produced by $H + NO_2$ reaction. [HO] and [CH_3CHO] monitored by mass spectrometry.

(b) Flash photolysis of $H_2O/Ar/CH_3CHO$ mixtures. [HO] monitored by resonance fluorescence. Gases flowed through reaction cell to avoid accumulation of products.

(c) Photolysis of dilute mixtures of HONO, NO, NO_2, and CH_3CHO in synthetic air at atmospheric pressure [NO] and [NO_2] monitored by ozone-chemiluminescence technique. CH_3CHO determined by gas chromatography. $k/k(HO + HONO) \leqslant 3.1 \pm 0.4$ measured. $k(HO + HONO) = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (authors' value) used.

(d) Photolysis of HONO in C_2H_4/CH_3CHO/air mixture. [C_2H_4] and [CH_3CHO] monitored by long path Fourier transform infra-red spectroscopy. $k/k(HO + C_2H_4) = 1.9 \pm 0.2$ obtained. Value of k found using $k(HO + C_2H_4) = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(e) Photolysis of HONO/synthetic air mixtures containing traces of C_2H_4 and CH_3CHO. [C_2H_4] and [CH_3CHO] monitored by gas chromatography. $k/k(HO + C_2H_4) = 1.50 \pm 0.50$ measured. $k(HO + C_2H_4) = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation) used.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.9 \times 10^{-12} \exp(260/T)$ cm^3 molecule^{-1} s^{-1} over range 298–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 300$.

Comments on Preferred Values

All the available data at ambient temperatures are in excellent agreement. In the only study of the temperature variation of the rate coefficient a small negative value was obtained [2]. Although there appear to be a few other examples of such negative dependences for hydrogen abstraction reactions, it is unusual, and until confirmed wider error limits are suggested for this value of E/R.

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$HO + CH_3CO_3NO_2 \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1.7\times10^{-13}$	299	Winer et al., 1977 [1]	(a)

Comments

(a) Flash photolysis of $H_2O/CH_3CO_3NO_2/N_2/Ar$ mixtures. [HO] monitored by resonance fluorescence.

Preferred Value

$k \leqslant 2\times10^{-13}$ at 298 K.

Comments on Preferred Value

Only an upper limit is available.

References

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$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$ (1)
$\rightarrow HO + O_2 + CH_3O$ (2)

$\Delta H°(1) = -157.2$ kJ mol^{-1}

$\Delta H°(2) = +27.4$ 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			
1.3×10^{-12}	298	Kan, Calvert, and Shaw, 1980 [1]	(a)
Reviews and Evaluations			
6.0×10^{-12}	298	NASA, 1979 [2]	(b)
6.5×10^{-12}	298	CODATA, 1980 [3]	(b)
$7.7\times10^{-14}\exp(+1300/T)$	298	NASA, 1981 [4]	(b)

Comments

(a) Steady state photolysis of $(CH_3)_2N_2$-O_2 mixtures with product analysis by FTIR Spectroscopy. Rate coefficient obtained from computer simulation of product CH_3OOH, assuming formation only by reaction of CH_3O_2 and HO_2, the latter being produced in secondary reactions in the system. The value of k was dependent on the rate coefficients for reactions forming and removing HO_2, as well as the branching ratio for CH_3O_2 disproportionation.

(b) Based on a direct measurement, ref. [5].

Preferred Values

$k_1 = 6.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr pressure.

$k_1 = 7.7\times10^{-14}\exp(+1300/T)$ cm^3 molecule^{-1} s^{-1} over range 275–338 K and 760 Torr pressure.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K and 760 Torr pressure.

$\Delta (E/R) = \pm 700$ K at 760 Torr pressure.

Comments on Preferred Values

The preferred value for k_1 is based on the Arrhenius expression given by Cox and Tyndall [5] using molecular modulation. In view of possible pressure dependence from a complex reaction mechanism (c.f. the reaction $HO_2 + HO_2 \rightarrow$ products) the preferred value is only recommended for 760 Torr pressure. Channel (2) is considered negligible at low temperatures in view of the reaction endothermicity.

The new relative rate data gives k_1 at 298 approximately a factor of 4 lower than recommended. In view of the uncertainties in the complex chemical system employed, no weight is given to this result at this time. However, there is need for further studies of the kinetics of this reaction and until more information is available we have widened the uncertainty limits to encompass the new data.

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$CH_3 + O_2 \rightarrow HCHO + HO$

$\Delta H° = -215$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 5\times10^{-17}$	1000–1220	Baldwin and Golden, 1978 [1]	(a)
$\leq 3\times10^{-16}$	368	Klais, et al., 1979 [2]	(b)
Relative Rate Coefficients			
$(1.7 \pm 1.6)\times10^{-14}$	298	Washida, 1980 [3]	(c)
Reviews and Evaluations			
$<10^{-16}$	298	NASA, 1981 [4]	(d)

Comments

(a) Very low Pressure Pyrolysis (VLPP) system. Products of pyrolysis of $(CH_3)_2N_2$ in presence of O_2 determined by mass spectrometry.

(b) Flash photolysis of $(CH_3)_2N_2/O_2$ mixtures. Resonance fluorescence detection of HO. Upper limit based on absence of observable HO signal attributable to reaction $CH_3 + O_2$.

(c) Discharge flow-photoionization mass spectrometry for detection of CH_3. $[CH_3]$ steady state monitored in reaction system: $O + C_2H_4 + O_2$. Reference reaction: $k(O + CH_3 \rightarrow H + HCHO) = (1.38 \pm 0.46)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}. $k/k(O + CH_3) = (1.23 \pm 1.16)\times10^{-4}$ [CODATA evaluation].

Preferred Value

$k < 5\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The new relative rate coefficient measurement [3] was made in an identical system to that used previously by Washida & Bayes [5] and gave similar results, but with larger error limits. The study therefore provides no additional information of value. There seems now a consensus opinion, refs. [2, 3] that the presence of HO_2 radicals, formed in the $O + C_2H_4$ system via the secondary reaction $HCO + O_2 \rightarrow HO_2 + CO$, is a source of complication in these experiments. The reliability of the value for k, which is based on extrapolation of the total rate coefficient for $CH_3 + O_2$ reaction to zero pressure, when the rate of the 3 body reaction $CH_3 + O_2 + M \rightarrow CH_3O + M$ is zero, is therefore suspect and the values rejected from the evaluation.

The results of the recent absolute rate determinations refs. [1, 2] show clearly that the bimolecular reaction between CH_3 and O_2 is negligible at least at temperatures up to 1000 K. The preferred upper limit is based on these studies.

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$HCO + O_2 \rightarrow CO + HO_2$ (1)
$HCO + O_2(+M) \rightarrow HCO_3(+M)$ (2)

$\Delta H^\circ(1) = -137.5$ kJ mol^{-1}

$\Delta H^\circ(2) = -120$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
5.0×10^{-12}	230–300	NASA, 1979 [1]	(a)
5.1×10^{-12}	298	CODATA, 1980 [2]	(a)
5.0×10^{-12}	200–300	NASA, 1981 [3]	(a)

Comments

(a) Recommended value for k_1 only

Preferred Values

$k_1 = 5.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 \ll k_1$ at 1 atm.

Reliability

$\Delta \log k = \pm 0.1$

Comments on Preferred Values

New information has been reported concerning the mechanism of formic acid formation in formaldehyde photooxidation at low temperatures, refs. [4,5]. HCOOH formation in HCHO oxidation was originally attributed [6] to reactions of HCO_3 formed in the addition channel (2) but this mechanism can now be discounted. It now appears that reaction (2) is negligible compared with the bimolecular step (1), even at pressures near 1 atm. A new ultraviolet absorption attributed to HCO has recently been reported, ref. [7]; this has been used for kinetic spectroscopy of HCO, but not in its reaction with O_2. A temperature dependence study of k_1 is clearly required.

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$CH_3O + NO + M \rightarrow CH_3ONO + M$

$\Delta H^\circ = -170$ kJ mol^{-1}

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.1×10^{-11}	440–473	Batt, Milne, and McCulloch, 1977 [1]	(a)
$(2.08 \pm 0.12) \times 10^{-11}$	298	Sanders et al., 1980 [2]	(b)

Comments

(a) Thermal decomposition of methylnitrite in presence of NO and t-BuH. Combination of these data with the equilibrium constants gives the values indicated. For the second channel, $k(CH_3O + NO \rightarrow CH_2O + HNO)/k_\infty(CH_3O + NO \rightarrow CH_3ONO) \simeq 0.17$ was estimated.

(b) Photolysis of methylnitrite at 266 nm with CH_3O detection by laser induced fluorescence at He pressures of 10–50 Torr. HNO as a reaction product was also detected by laser induced fluorescence, however, no absolute estimate of its yield could be made.

Preferred Value

$k_\infty = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over range 200–400 K.

Comments on Preferred Value

Although the data agree, the preferred value remains uncertain as long as no experimental study of the pressure dependence has been made or a theoretical analysis of the pressure dependence which is based on high temperature fall-off curves of methylnitrite decomposition. The probably pressure dependent branching of the reaction into CH_3ONO and $HNO + CH_2 + O$ also has to be reinvestigated.

References

[1] Batt, L., Milne, R. T., and McCulloch, R. D., Int. J. Chem. Kinet. **9**, 567 (1977).

[2] Sanders, N., Butler, J. E., Pasternack, L. R., and McDonald, J. R., Chem. Phys. Lett. **48**, 203 (1980).

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$\Delta H^\circ = -112.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.66^{+6.0}_{-1.2})\times10^{-12}\exp(-(2416\pm554)/T)$	389–433	Batt and Robinson, 1979 [1]	(a)
5.0×10^{-16}	297		
$(1.21\pm0.36)\times10^{-15}$	298	Cox et al., 1980 [2]	(b)
Reviews and Evaluations			
$5\times10^{-13}\exp(-2000/T)$	200–300	NASA, 1979 [3]	(c)
$5\times10^{-13}\exp(-2000/T)$	300–450	CODATA, 1980 [4]	(c)
$1.26\times10^{-13}\exp(-1352/T)$	296–450	Cox et al., 1980 [2]	(d)
$9.2\times10^{-13}\exp(-2200/T)$	200–300	NASA, 1981 [5]	(e)

Comments

(a) Pyrolysis of dimethyl peroxide in the presence of NO_2 and O_2. Product analysis by gas chromatography. Reference reaction: $CH_3O + NO_2(+M) = CH_3ONO_2(+M)$; $k(CH_3O + NO_2) = 1.32\times10^{-11}$ cm^3 molecule^{-1} s^{-1} ref. [6] $k/k(CH_3O + NO_2) = (0.126^{+0.375}_{-0.094})\exp(-(2416\pm554)/T)$.

(b) Photolysis of methyl nitrite in the presence of O_2. Product analysis by gas chromatography. Reference reaction: $CH_3O + NO_2(+M) = CH_3ONO_2(+M)$; $k(CH_3O + NO_2) = 1.03\times10^{-11}$ cm^3 molecule^{-1} s^{-1} $k/k(CH_3O + NO_2) = (11.65\pm0.35)\times10^{-5}$ at 298 K. $k(CH_3O + NO_2)$ was based on $k(CH_3O + NO \rightarrow CH_3ONO)$ ref. [7] together with data from [6].

(c) Based on work of Barker et al. [8].

(d) Arrhenius expression obtained from least squares analysis of all available literature data over the range 296–450 K, including that from ref. [1].

(e) Based on refs. [1] and [8].

Preferred Values

$k = 1.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3\times10^{-13}\exp(-1350/T)$ over range 298–450 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

$\Delta (E/R) = ^{+1100}_{-500}$ K.

Comments on Preferred Values

The two new relative rate studies of this reaction, refs. [1,2] both employ the same reference reaction, and give results of similar magnitude where the temperature ranges overlap. There is nevertheless disturbing variability in the experimental results and the Arrhenius parameters given in ref. [1] are probably less reliable than ref. [2], which covered a larger temperature range. Furthermore, data from the lower end of the temperature range were rather arbitrarily omitted in [1]. Since the Arrhenius expression in ref. [2] takes into account all available data for $k(CH_3O + O_2)$ without bias, we have used this as a basis for the new preferred value. It should be noted that the preferred A factor is somewhat lower than expected for a reaction of this type. Uncertainty limits have been widened since our previous evaluation [4] to take into account (a) the divergently reported T dependences and (b) possible errors in the rate coefficient for the reference reactions of CH_3O and NO and NO_2, which are indicated by preliminary direct studies of CH_3O reactions using the laser induced fluorescence technique [9].

References

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$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$\Delta H° = -72.3$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.95\times10^{-13}\,T^{1/2}\exp(-(1250\pm250)/T)$	363–428	Avramenko and Kolesnikova, 1961 [1]	(a)
(5.0×10^{-14})	300*		
$2^{+2}_{-1}\times10^{-12}$	300	Radford, 1980 [2]	(b)

Comments

(a) Discharge flow-product HO_2 inferred from formation of H_2O_2. CH_2OH produced from $H + CH_3OH$.

(b) Discharge flow-laser magnetic resonance detection of HO_2 product from reaction of O_2 with CH_2OH generated from $Cl + CH_3OH$ reaction. It was also shown that under conditions of earlier work [1], the apparent value of k was a factor of 20 slower, due to slow rate of CHOH production from $H + CH_3OH$ source.

Preferred Value

$k = 2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Value

The preferred value is the direct measurement of Radford [1], who demonstrated that the earlier work was in error. Support for a rapid rate of this type of reaction comes from steady state photooxidation studies which showed that C_2 and C_4 α-hydroxyalkyl radicals derived from C_2H_5OH and C_4H_9OH, react rapidly with O_2 to form HO_2 and the corresponding aldehyde or ketone [3]. Addition of O_2 to these radicals does not appear to occur. In the absence of reliable data on the temperature dependence a value for E/R is not recommended. However any T dependence is likely to be small in view of the rapid rate at 298 K for a radical + molecule reaction of this type, e.g., $HCO + O_2 \rightarrow HO_2 + CO$.

References

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$CH_3O_2 + NO \rightarrow CH_3O + NO_2$ (1)
$CH_3O_2 + NO(+M) \rightarrow CH_3O_2NO(+M)$ (2)

$\Delta H°(1) = -58.3$ kJ mol^{-1}

$\Delta H°(2) \simeq -80$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0\pm0.2)\times10^{-12}$	300	Adachi and Basco, 1979 [1]	(a)
$(7.1\pm1.4)\times10^{-12}$	298	Sander and Watson, 1980 [2]	(b)
$(8.1\pm1.6)\times10^{-12}$	240–339	Ravishankara et al., 1981 [3]	(c)
Reviews and Evaluations			
7.0×10^{-12}	200–300	NASA, 1979 [4]	
7.5×10^{-12}	200–300	CODATA, 1980 [5]	
7.4×10^{-12}	200–300	NASA, 1981 [6]	

Comments

(a) Flash photolysis $(CH_3)_2N_2$-O_2-Ar-NO mixtures; CH_3O_2 decay determined by time resolved absorption spectroscopy at 245 nm; pseudo first order conditions.

(b) Flash photolysis Cl_2-CH_4-O_2-NO mixtures; CH_3O_2 by time resolved absorption in a long path system. Some indication of a slight pressure effect: $10^{12}k$ (cm^3 molecule^{-1} s^{-1}) was (6.1 ± 0.7) with 75 Torr He, (6.3 ± 0.9) with 350 Torr He, (8.2 ± 1.1) with 700 Torr He and (8.9 ± 0.7) at 700 Torr N_2 added; pseudo first order conditions.

(c) Laser flash photolysis of azomethane + O_2 and $Cl_2 + CH_4 + O_2$ with NO; NO_2 product followed by time resolved laser induced fluorescence under pseudo first order conditions. No effect of pressure or bath gas using 40–100 Torr Ar and 50 Torr CH_4. The yield of NO_2 formed for each CH_3O_2 produced was 1.06 ± 0.24 showing that reaction occurs exclusively via channel (1). Slight negative T dependence $(E/R = -(86 \pm 112))$ not considered significant.

Preferred Value

$k_1 = 7.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Value

The results from the direct studies reported in [2] and [3] are in excellent agreement with earlier direct measurements on which the previous evaluations [4–6] were based. Furthermore the observation of the time profile and yield for NO_2 formation [3] confirms that channel (1) is dominant in the reaction of CH_3O_2 with NO at temperatures and pressures relevant to this evaluation.

The low value in [1] is almost certainly due to failure to take into account the formation of CH_3ONO product from the fast secondary reaction of $CH_3O + NO$, which absorbs strongly at the monitoring wavelength of CH_3O_2. A value identical with [1] has been reported recently by Simonaitis and Heicklen [7] in which k was measured relative to the reaction of CH_3O_2 with SO_2; $k/k(CH_3O_2 + SO_2) = (4.0 \pm 0.8) \times 10^3$. However since it is now known that the reference reaction is very slow, $k(CH_3O_2 + SO_2) < 10^{-18}$ cm^3 molecule^{-1} s^{-1} [CODATA evaluation], the interpretation of these data is almost certainty erroneous. The preferred value is a simple mean of the direct measurements reported in [2], [3] and by Plumb et al. [5] and Cox and Tyndall [9]. If the apparent small pressure effect on k, noted in [2] were real, the earlier low pressure discharge flow study [8] would have been expected to yield a lower value for k. Since the reported values in both pressures regions are equal within experimental error, there is no firm basis for recommendation of a pressure dependent rate coefficient.

References

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$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$

$\Delta H^\circ \simeq -80$ 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			
$1.5 \times 10^{-30}(T/300)^{-4.0}[N_2]$		NASA, 1981 [3]	(c)

Comments

(a) Flash photolysis/uv absorption technique. Studied pressure range 50–700 Torr, M = He, N_2, and SF_6. Complete analysis of the fall-off curve with a theoretical F_c value of 0.39 in good agreement with the fitted value of 0.4 ± 0.10.

(b) Laser flash photolysis with long absorption path detection system. Pressure range 76–722 Torr, bath gas N_2. Complete analysis of the fall-off curve for 253, 298, and 353 K with $F_c = 0.4$ independent of temperature.

(c) Based on preliminary data from refs. [1] and [2].

Preferred Values

$k_0 = 2.3\times10^{-30}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.
$k_0 = 2.3\times10^{-30}$ $(T/300)^{-4.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 2$ over range 200–300 K.

Comments on Preferred Values

The data from refs. [1] and [2] agree very well confirming the fall-off character of this reaction. We prefer a larger negative temperature coefficient than described in ref. [2] analogous to those generally observed for large molecules under these conditions; see, e.g., this evaluation for the reaction $NO_2 + NO_3 + N_2 \rightarrow N_2O_5 + N_2$ for which $n = -4.1$ was derived over the range 200–300 K.

High pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.0 \pm 1.0)\times10^{-12}$	298	Sander and Watson, 1980 [1]	(a)
$7\times10^{-12}(T/298)^{-3.5}$	253–353	Ravishankara, Eisele, and Wine, 1980 [2]	(b)
Review and Evaluations			
$6.5\times10^{-12}(T/300)^{-2.0}$		NASA, 1981 [3]	(c)

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0. We consider the large negative temperature coefficient an artifact of the interpretation. If a larger negative T-exponent for k_0 and a smaller F_c value at higher temperatures are used, the large negative T-exponent of k_∞ will decrease considerably.

(c) Based on a theoretical analysis of k_∞ with postulated activated complex properties.

Preferred Value

$k_\infty = 8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over range 200–400 K.

Comments on Preferred Value

There is good agreement about k_∞ at 298 K. We prefer a temperature independent value of k_∞ by analogy with the $NO_2 + NO_3 \rightarrow N_2O_5$ reaction. We reject the T-coefficient derived in ref. [2], see comment (b).

Intermediate Fall-off Range

From the preferred values, one derives $[N_2]_c = 3.5\times10^{18}$ molecule cm^{-3}. For 298 K, a value of $F_c = 0.4$ 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 fall-off range stems from recent experiments by Cox and Tyndall, 1980 [4] who measured $k = 1.6\times10^{-12}$ 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. These data are much less complete than refs. [1] and [2] and are not considered. The apparent observation of pressure independent k over the range 50–580 Torr of Ar, reported by Adachi and Basco, 1980 [5] is not confirmed by refs. [1] and [2].

References

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$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$

$\Delta H^\circ \simeq 80$ kJ mol^{-1}

Rate coefficient data

No available experimental data

Preferred Value

No recommendation.

Comments

Although no recommendation can be made it is clear that $CH_3O_2NO_2$ is quite unstable at room temperature in the gas phase [1–3]. Thermal decomposition of the analogous isopropyl peroxynitrate has been studied quantitatively yielding the Arrhenius expression: $k = 5.0\times10^{14}\exp(-9965/T)\ s^{-1}$, which gives a lifetime of $\simeq$0.3 s at 300 K and 1 atm pressure. A similar decomposition rate is expected for $CH_3O_2NO_2$. However, since the reverse reaction of CH_3O_2 with NO_2 is pressure dependent over the range 25–750 Torr (see data sheet for $CH_3O_2 + NO_2$) the decomposition rate should exhibit a pressure fall-off in this range.

References

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$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2$

$\Delta H^\circ = -143.9$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficient			
$<2.0\times10^{-17}$	298	Simonaitis and Heicklen, 1975 [1]	(a)

Comments

(a) Steady state photolysis of CH_4-O_3-O_2 mixtures. Quantum yield for O_3 decay at high $[O_2]/[O_3]$ was approximately 1.3 showing that secondary attack on O_3 by CH_3O_2 and CH_3O radicals was relatively slow. Upper limit for the ratio $k/k^{1/2}(CH_3O_2 + CH_3O_2) = 3.2\times10^{-11}$ cm$^{3/2}$ molecule$^{-1/2}$ s$^{-1/2}$; k evaluated using $k(CH_3O_2 + CH_3O_2) = 3.7\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (CODATA).

Preferred Value

$k < 2.0\times10^{-17}$ cm^3 molecule^{-1}s^{-1} at 298 K.

Comments on Preferred Value

The recommended upper limit is based on ref. [1]. Similar results have been reported by DeMore [2] for this system which support the upper limit reported for k in ref. [1]. Thus the reaction of CH_3O_2 with O_3 is certainly slow compared to its other removal processes, primarily the $CH_3O_2 + CH_3O_2$ reaction.

References

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$$\mathbf{CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \quad (1)}$$
$$\mathbf{\rightarrow 2CH_3O + O_2 \quad (2)}$$
$$\mathbf{\rightarrow CH_3OOCH_3 + O_2 \quad (3)}$$

$\Delta H°(1) = -340.9\ \text{kJ mol}^{-1}$

$\Delta H°(2) = -2.4\ \text{kJ mol}^{-1}$

$\Delta H°(3) = -157.1\ \text{kJ mol}^{-1}$

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

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.15 \pm 0.04) \times 10^{-13}$	300	Kan and Calvert, 1979 [1]	(a)(b)
$(3.7 \pm 0.3) \times 10^{-13}$	300	Sanhueza, Simonaitis, and Heicklen, 1979 [2]	(a)(c)
$(4.2 \pm 0.5) \times 10^{-13}$	295	Kan et al., 1979 [3]	(a)(d)
$(5.2 \pm 0.9) \times 10^{-13}$	298	Cox and Tyndall, 1980 [4]	(a)(e)
$(3.7 \pm 0.7) \times 10^{-13}$	298	Sander and Watson, 1980 [5]	(a)(f)
$(1.40 \pm 0.20) \times 10^{-13} \exp((223 \pm 41)/T)$	250–420	Sander and Watson, 1981 [6]	(a)(g)
$(3.0 \pm 0.5) \times 10^{-13}$	298		
$(5.8 \pm 0.5) \times 10^{-13}$	300	Adachi, Basco, and James, 1980 [7]	(h)
Branching Ratios			
$k_1/k_2 = 1.32 \pm 0.16$ $k_1/k_3 \geqslant 7$	298	Kan, Calvert, and Shaw, 1980 [8]	(i)
Reviews and Evaluations			
4.6×10^{-13}	298	CODATA, 1980 [9]	(j)
4.0×10^{-13}	298	NASA, 1981 [10]	

Comments

(a) k value is for overall second order decay of CH_3O_2, including secondary removal from products of (2) as defined by $-d[CH_3O_2]/dt = 2k_0[CH_3O_2]^2$.

(b) Flash photolysis of $(CH_3)_2N_2$-O_2-H_2O mixtures; CH_3O_2 measured by uv absorption. Presence of 14 Torr H_2O influences uv spectrum of CH_3O_2, shifting maximum from ca. 240 nm to ca. 250 nm. This indicates complex formation of CH_3O_2 with H_2O. k was, however, unaffected by H_2O and also by changes in monitoring wavelength. $k/\sigma(245\ \text{nm}) = 1.36 \times 10^5\ \text{cm s}^{-1}$, $\sigma(245) = 3.06 \times 10^{-18}\ \text{cm}^2\text{molecule}^{-1}$, ($[H_2O] = 0$); $k/\sigma(265\ \text{nm}) = 1.5 \times 10^{-5}\ \text{cm s}^{-1}$, $\sigma(265) = 2.7 \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}$ (14 Torr H_2O); $k/\sigma(265\ \text{nm}) = 2.13 \times 10^5\ \text{cm s}^{-1}$ $\sigma_{265} = 1.95 \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}$ ($[H_2O] = 0$).

(c) Flash photolysis of Cl_2-CH_4-O_2 mixtures at room temperature and pressure range 60–750 Torr. CH_3O_2 monitored by absorption at 254 nm. Pressure and $[H_2O]$ independence of k reported. $k/\sigma(254\ \text{nm}) = 1.47 \times 10^{-5}\ \text{cm s}^{-1}$ $\sigma(254\ \text{nm}) = 2.52 \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}$ [11].

(d) Flash photolysis of $(CH_3)_2N_2$-O_2, CH_3O_2 monitored in absorption at 265 nm. Second order decay curves showed some deviation at long delay times. Linear portion analyzed for k. $k/\sigma(265) = (2.04 \pm 0.25) \times 10^5\ \text{cm s}^{-1}$, $\sigma(265\ \text{nm}) = (2.03 \pm 0.10) \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}$. Evidence found for reaction of CH_3O_2 with $(CH_3)_2N_2$. Authors also estimate that the true value of the rate coefficient k after allowance for secondary removal of CH_3O_2 is $k \gtrsim 3.8 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$.

(e) Molecular modulation; CH_3O_2 by absorption at 250 nm in photolysis of Cl_2-CH_4-O_2 mixtures $k/\sigma(250) = 1.33 \times 10^5\ \text{cm s}^{-1}$, $\sigma = 3.9 \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}\ \text{s}^{-1}$ at 250 nm.

(f) Flash photolysis $(CH_3)_2N_2 + O_2$ and $Cl_2 + CH_4 + O_2$ mixtures. CH_3O_2 by long path uv absorption. $k/\sigma = (1.06 \pm 0.07) \times 10^5\ \text{cm s}^{-1}$ at 245 nm and $(2.84 \pm 0.36) \times 10^5\ \text{cm s}^{-1}$ at 270 nm. Value quoted is a mean value using σ values obtained by Hochanadel et al. [1]. Small effects of varying O_2 and adding CO are reported.

(g) Flash photolysis of $Cl_2 + CH_4 + O_2$ mixtures. σ determined from absorption at $t = 0$ extrapolated from decay curves and estimate of $[CH_3O_2]_0$ from change in Cl_2 concentration in flash. $\sigma(250\ \text{nm}) = (2.5 \pm 0.4) + 10^{-18}\ \text{cm}^2$ at 298 K. $k/\sigma(250\ \text{nm}) = (5.6 \pm 0.8) \times 10^4 \exp((223 \pm 41)/T)\ \text{cm s}^{-1}$ (250–420 K).

(h) Flash photolysis of diazomethane—CH_3O_2 monitored by uv absorption. Absorption coefficients measured from comparison of yield of N_2 with absorption at $t = 0$ from extrapolation of decay curves. $\sigma(240\ \text{nm}) = 5.58 \times 10^{-18}\ \text{cm}^2\ \text{molecule}^{-1}$ $k/\sigma = (1.04 \pm 0.10) \times 10^5\ \text{cm s}^{-1}$ at 240 nm. Note the k value reported is corrected for secondary removal of CH_3O_2 and is a factor of 1.08 lower than the observed overall second order decay coefficients. The latter showed a small increase with increasing $[O_2]$.

(i) Steady state photolysis of $(CH_3)_2N_2$-O_2 mixtures with product analysis by FTIR spectroscopy. Some unidentified products found indicating a complex mechanism for secondary reactions.

(j) Based on molecular modulation studies of Parkes [12]. Also gave $k_2/k = 0.33$ at 298 K.

Preferred Values

$k = 3.7 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ at 298 K.

$k_2/k = 0.4$; $k_3/k \leqslant 0.075$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta k_2/k = \pm 0.15$.
$\Delta k_2/k = \pm 0.075$.

Comments on Preferred Values

The recently reported values of k at room temperature are only in moderately good agreement, the values tending to fall into two groups depending on the absorption cross section determined. Unfortunately the measured parameter, k/σ cannot be directly compared since measurements were made at different wavelengths. The absorption cross sections obtained from the flash photolysis experiments reported in [1,3,6, and 11] are in good agreement but those from ref. [7] (flash photolysis) and molecular modulation [4,12] are approximately a factor of 1.5–2 higher. The reason for this discrepancy is not apparent and it causes considerable uncertainty in k.

The preferred value for k was obtained as follows: A preferred value of k/σ(240 nm) was obtained from all of the available data in refs. [1–7,11, and 12], using a normalized spectrum based on data reported in refs. [1,11, and 12]. Data from refs. [1,3,4,6,7,11, and 12] was then averaged to give σ(240 nm) $= 3.9 \times 10^{-18}$ cm^2 and the overall second order decay coefficient thus obtained, $k_0 = 4.49 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Interpretation of the kinetic data to obtain k is complicated in this system by possible secondary removal of CH_3O_2 by radical products resulting from channel (2). This is discussed in [3,5] and [11]. It can be shown that k_0/k can have any value between 1 and $1 + k_2/k$, depending on the chemical fate of CH_3O in the system. The branching ratio k_2/k has been determined to lie in the range 0.33–0.43 [3,11,12]. Taking the preferred mean value of 0.4 gives $1.0 < k_0/k < 1.4$. In view of the complex chemistry involving CH_3O, an average value of $k_0/k = 1.2 \pm 0.2$ is preferred giving $k = (3.7 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The preferred value of $k_3/k = 0.075$ is based on the work in [7] which is basically in agreement with earlier work [12].

The recent study of the temperature dependence of k reported in ref. [6] shows a slight negative T dependence over the temperature range 250–420 K. This supports the earlier findings of Parkes [12] and Anastasi et al. [14] of no apparent T dependence of k over a smaller temperature range.

References

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$C_2H_5 + O_2(+M) \rightarrow C_2H_5O_2(+M)$

$\Delta H° = -106.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
<u>Relative Rate Coefficient</u>			
6.9×10^{-12}	295	Dingledy and Calvert, 1963 [1]	(a)
<u>Reviews and Evaluations</u>			
6.8×10^{-12}	300	Demerjian, Kerr, and Calvert, 1974 [2]	(b)

Comments

(a) Flash photolysis of azoethane-O_2 mixtures. Product analysis by mass spectrometry and gas chromatography. C_2H_5 concentration during experiment modelled from flash intensity profile and yield of n-C_4H_{10} formed in the reaction $2C_2H_5 \rightarrow C_4H_{10}$. Hence k relative of $k(C_2H_5 + C_2H_5) = 4.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [3] but complex iterative procedure used to evaluate k. The value was independent of total pressure (4.8–103 Torr). The bath gas was azoethane + diethyl ether.

(b) Based on ref. [1].

Preferred Value

$k = 6.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Value.

The preferred value is based on the single experimental kinetic study of this reaction, which involved a rather indirect determination of k from simulation of the complex chemistry occurring in the flash photolysis of azoethane-O_2 mixtures. The value is, nevertheless, very reasonable for a radical + O_2 association reaction near the high pressure limit (e.g. $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$, $k_\infty = 2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}). The results also show that k is independent of pressure down to 4.8 Torr azomethane, although with air as bath gas, fall-off in k may start at a higher pressure. It is probable, however, that the high pressure value given above is applicable for atmospheric chemistry at least up to the tropopause. The high pressure value is expected to have little or no temperature dependence in the 200–300 K range.

References

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$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H^\circ = -139$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
3.8×10^{-17}	300	Demerjian, Kerr, and Calvert, 1974 [1]	(a)
$1.7\times10^{-12}\exp(-2000/T)$		Batt, 1979 [2]	(b)
1.2×10^{-15}	303	Carter et al., 1979 [3]	(c)

Comments

(a) Based on estimate for the analogous reaction of $CH_3O + O_2$, which was obtained from modelling smog chamber data.

(b) Based on unpublished results (Batt and Patrick) for photolysis of ethyl nitrite in presence of O_2.

(c) Based on analogy with $CH_3O + O_2$.

Preferred Values

No recommendation.

Comments on Preferred Values

The only experimental study reported in [2] of this reaction suffers from lack of sufficient data for a proper interpretation. The ratio k/k ($C_2H_5O + NO_2 \rightarrow C_2H_5NO_3$) was determined from the yields of CH_3CHO and $C_2H_5NO_3$ and the mean concentration of NO_2, which was calculated, not measured. There is consequently considerable uncertainty in the values of k derived, which are, however, very similar to those for the analogous reaction of CH_3O with O_2. No recommendation can be made on this basis, but provisionally it is suggested that the Arrhenius expression recommended for the reaction of CH_3O with O_2 is used for k.

References

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$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$

$\Delta H^\circ = -74.5$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
3.2×10^{-13}	300	Demerjian, Kerr, and Calvert, 1974 [1]	(a)
2.0×10^{-11}	303	Carter et al., 1979 [2]	(b)

Comments

(a) Estimate based on the then current estimate for $k(HO_2 + NO) = 1.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, now known to be a factor of 60 too low.

(b) Estimate based on Smog Chamber modelling studies.

Preferred Value

$k = 7.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Value

There are no experimental measurements of this rate coefficient. The above recommendation is based on the assumption that the reaction of ethylperoxy radicals with NO will be similar to the analogous reaction of CH_3O and NO for which the rate coefficients are moderately well established at 298 K and show very little temperature dependence in the 200–300 K range (see CODATA evaluation). The error limits reflect the uncertainty in drawing this analogy.

References

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[2] Carter, W. P. L., Lloyd, A. C., Sprung, J. L., and Pitts, J. N., Jr., Int. J. Chem. Kinet. **11**, 45 (1979).

$C_2H_5O_2 + NO_2(+M) \rightarrow C_2H_5O_2NO_2(+M)$

$\Delta H^\circ \simeq -80$ kJ mol^{-1}

Rate coefficient data

No experimental data

Preferred Value

5.0×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and 1 atm.

Reliability

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

Comments on Preferred Value.

The preferred value is for 1 atm pressure air and is suggested by analogy with the corresponding reactions of methyl peroxy and acetylperoxy radicals to form peroxynitrates (CODATA). Since the reaction is probably near its high pressure limit at 1 atm, M = air, a zero of small negative temperature coefficient is expected for the 200–300 K range..

$C_2H_5O_2NO_2(+M) \rightarrow C_2H_5O_2 + NO_2(+M)$

$\Delta H^\circ \simeq 80$ kJ mol^{-1}

Rate coefficient data

No experimental data available

Preferred Value

No recommendation.

Comments

Decomposition rate coefficients probably similar to those for isopropylperoxynitrate, for which the following Arrhenius expression is reported: $k = 5.0\times10^{14} \exp(-9965/T)$ s^{-1} [1].

Reference

[1] Edney, E. O., Spence, J. W., and Hanst, P. L., J. Air. Poll. Contr. Assoc. **29**, 741 (1979).

$CH_3CO_3 + NO \rightarrow CH_3 + CO_2 + NO_2$

$\Delta H^\circ = -133.9$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
1.0×10^{-11}	300	Cox et al., 1976 [1]	(a,b)
$(1.1 \pm 0.3)\times10^{-11}$	295	Cox and Roffey, 1977 [2]	(b,c)
$(2.1 + 0.3)\times10^{-11}$	298–318	Hendry and Kenley, 1977 [3]	(b,d)
Reviews and Evaluations			
3.1×10^{-13}	298	Demerjian, Kerr, and Calvert, 1974 [4]	(e)

Comments

(a) Photolysis of dilute HONO-CH_3CHO mixtures in air. Ratio $k/k(CH_3CO_3 + NO_2) = 1.7$ measured from effect of ratio $[NO]/[NO_2]$ on yield of peroxyacetyl nitrate.

(b) k calculated here using $k(CH_3CO_3 + NO_2) = 6\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (CODATA evaluation).

(c) Thermal decomposition of peroxyacetylnitrate in presence of NO. $k/k(CH_3CO_3 + NO_2) = 1.58 \pm 0.61$ determined from effect of ratio $[NO]/[NO_2]$ on the rate of thermal decomposition of $CH_3CO_3NO_2$.

(d) Similar techniques to (c); $k/k(CH_3CO_3 + NO_2) = 3.5 \pm 0.5$ independent of temperature over range 298–318 K.

(e) Estimate based on the then current estimate for $k(HO_2 + NO) = 1.3\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, now known to be a factor of 60 too low.

Preferred Values

$k = 1.4\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$.

Comments on Preferred Values

The determination of this rate coefficient relies entirely on measurement of its rate relative to that for the reaction of CH_3CO_3 with NO_2 to form peroxyacetylnitrate. The results from [1] and [2], using different techniques, agree well, but the data from [3], which give a higher value of $k/k(CH_3CO_3 + NO_2)$ claim to have less experimental error. This preferred value is a mean of all three determinations of k using the CODATA recommended value of $k(CH_3CO_3 + NO_2) = 6\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The error limits reflect errors for both $k(CH_3CO_3 + NO_2)$ and for the relative rate determination. A fast bimolecular reaction of this type is expected to exhibit a zero or slightly negative temperature dependence.

References

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$CH_3CO_3 + NO_2(+M) \rightarrow CH_3CO_3NO_2(+M)$

$\Delta H^\circ = -110$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.4×10^{-12} (1 atm air)	294–328	Cox and Roffey, 1977 [1]	(a)
1.0×10^{-12} (1 atm N_2)	298–313	Hendry and Kenley, 1977 [2]	(a)
$(2.1 \pm 0.4)\times10^{-12}$ (28 Torr O_2)	302	Addison et al., 1980 [3]	(b)
$(6.0 \pm 2.0)\times10^{-12}$ (715 Torr O_2)	302		
Reviews and Evaluations			
3.3×10^{-13} (1 atm air)	298	Demerjian, Kerr, and Calvert, 1974 [4]	(c)

Comments

(a) Based on Arrhenius expression for measured rate coefficients for thermal decomposition for peroxyacetylnitrate and estimated equilibrium constant. Uncertainty quoted was ± a factor of 10.

(b) Molecular modulation—uv absorption for measurement of CH_3CO_3 in absorption band characterised in the same study. Pseudo first order kinetics for CH_3CO_3 in excess NO_2. CH_3CO_3 produced by photolysis of Cl_2-CH_3CHO-O_2 mixtures and monitored at 245 or 255 nm.

(c) Based on analogy with reaction $CH_3O + NO_2 \rightarrow CH_3ONO_2$. The rate constant used for the $CH_3O + NO_2$ reaction has subsequently been revised upwards by a factor of 30.

Preferred Value

$k = 6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 atm pressure and at 298 K.

Reliability

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

Comments on Preferred Value

The preferred value at 1 atm pressure is based on the direct measurements of Addison et al. [3], which supersede all previous estimates which are subject to large uncertainty. The direct measurements also indicate that the reaction is pressure dependent below 1 atm but insufficient data are available to describe the fall-off in k with pressure accurately. Only a value for 1 atm is therefore recommended. Since this value is undoubtedly near the high pressure limit it should exhibit little if any temperature dependence.

References

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$CH_3CO_3NO_2(+M) \rightarrow CH_3CO_3 + NO_2(+M)$

$\Delta H^\circ = 110$ kJ mol^{-1}

Rate coefficient data

k /s^{-1}		Temp./K	Reference	Comments
Absolute Rate Coefficients				
4×10^{-4}	(1 atm)	298	Pate, Atkins, and Pitts, 1976 [1]	(a)
$(8^{+24}_{-6})\times10^{14}\exp(-(12500\pm380)/T)$	(1 atm)	294–328	Cox and Roffey, 1977 [2]	(b)
4.6×10^{-4}		298		
$(2^{+6}_{-1.5})\times10^{16}\exp(-(13510\pm452)/T)$	(1 atm)	298–313	Hendrey and Kenley, 1977 [3]	(c)
3.6×10^{-4}		298		
$3.2\times10^{16}\exp(-13610/T)$	(1 atm)	295–315	Schurath and Wipprecht, 1979 [4]	(a)
4.8×10^{-4}		298		

Comments

(a) Rate of thermal decomposition of peroxyacetylnitrate in presence of excess NO was determined.

(b) Rate of NO oxidation measured in the thermal decomposition of peroxyacetylnitrate in the presence of excess NO in air. NO rate related to k with stoichiometric factor which was only determined at 296 K. 298 K value calculated from Arrhenius expression.

(c) Rate of exchange of ^{15}N between CH_3CO_3 $^{15}NO_2$ and $^{15}NO_2$ measured as well as decay of peroxyacetylnitrate in the presence of excess NO.

Preferred Values

$k = 4.2\times10^{-4}$ s^{-1} at 298 K and 1 atm.

$k = 1.12\times10^{16}\exp(-13330/T)$ s^{-1} over range 295–330 K and 1 atm.

Reliability

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

Comments on Preferred Values

The reported values for k at 298 K are in excellent agreement. The temperature dependence of Hendrey and Kenley's data [3] is in excellent agreement with that of Schurath and Wipprecht [4] but the data of Cox and Roffey [2] which was determined over a slightly wider temperature range, gives a lower E/R. This may arise from a systematic change in the stoichiometry factor relating the measured rate of NO removal with k_1 in the latter study which was only determined at one temperature. However, over the common temperature range, the error bars on the experimetal values in all studies overlap.

The preferred Arrhenius expression is based on the mean value of E/R from the three temperature dependence studies with an A- factor adjusted to give a 298 K value of k equal to the mean from all four studies, i.e., $4\times2\times10^{-4}$ s^{-1}. The preferred values are for a pressure of 1 atm air only; based on experimental results for reverse reaction, k is pressure dependent below 1 atm.

References

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$HCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0°/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HCHO + h\nu \rightarrow H + HCO$ (1)	358.4	334
$\rightarrow H_2 + CO$ (2)	-9.1	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
326.1	Platt, Perner, and Patz, 1979 [1]	(a)
261–355	Bass et al., 1980 [2]	(b)
240–350	Moortgat et al., 1980 [3]	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength/nm	Reference	Comment
$\phi_1/\phi = 0.63$	313	Morrison and Heicklen, 1979 [4]	(d)
$\phi = 1$	290–330	Moortgat et al., 1980 [3]	(e)
$\phi = 0.75$	250		
$\phi_2 < 1$	> 330		
$\phi_1 \simeq 0.4$	320	Tang, Fairchild, and Lee, 1979 [5]	(f)
$\phi_1 \simeq 0.8$	300		

Comments

(a) $\sigma = 7.8 \times 10^{20}$ cm^2 molecule^{-1} for $2^2 4^1$ band measured with resolution of 0.3 nm. Agrees with Moortgat et al. [3].

(b) Cross-sections measured in a long path cell containing 0.5–5 Torr HCHO ($>$ 99.9% pure) with a resolution of 0.05 nm. Temperatures: 296 and 223 K. Effect of lower temperature was a decrease in absorption on the red side of the main bands. Cross-sections averaged over 5 nm and 10 nm intervals given as well as complete spectrum.

(c) Cross-sections measured over the temperature range 211–362 K with resolution of 0.5 nm. Values at 5 nm resolution are also given at 220 and 298 K.

(d) Photo-oxidation of HCHO at 313 nm studied. ϕ(CO) and ϕ(HCOOH) determined as function of [O_2] and [HCHO]. Total Φ (as measured from CO yield) decreased with increasing O_2 pressure. Results in conflict with all previous studies and are interpreted as strong quenching of ϕ_1 and ϕ_2 by O_2.

(e) Quantum yields ϕ (CO) and ϕ (H_2) measured as function of wavelength 240–355 nm for HCHO at low concentration in air. Confirmed results of Moortgat and Warneck [7] including pressure and temperature dependence of ϕ_2 at $\lambda > 330$ nm.

(f) Laser induced photodecomposition at HCHO from the single vibronic levels of the excited $\tilde{A}$ $^1A_2$ state. ϕ_1 determined from H atom yield measured by HNO chemiluminescence in reaction $H + NO \rightarrow HNO + h\nu$.

Preferred Values

Absorption cross-sections and quantum yields for HCHO photolysis at 760 Torr[a]

	$10^{20}\,\sigma/\mathrm{cm}^2$			
Wavelength/nm	286 ± 9 K	218 ± 4 K	Φ_1	Φ_2
240	0.03	0.02	0.20	0.49
250	0.13	0.08	0.26	0.51
260	0.47	0.47	0.33	0.51
270	0.86	0.85	0.43	0.48
280	1.86	1.93	0.60	0.40
290	2.51	2.47	0.72	0.28
300	2.62	2.58	0.79	0.21
310	2.45	2.40	0.79	0.21
320	1.85	1.71	0.64	0.36
330	1.76	1.54	0.31	0.61
340	1.18	1.10	0	0.57
350	0.42	0.39	0	0.33
360	0.06	0.02	0	0.14

[a] All values averaged for 10 nm intervals of wavelength centered on indicated wavelength.

Pressure dependence of quantum yields for HCHO photolysis in air

ϕ_1, independent of pressure; ϕ_2 pressure independent at $\lambda < 329$ nm and 300 K.

Pressure/Torr	ϕ_2				
λ/nm	760	500	250	100	0
340	0.69	0.77	0.87	0.94	1.0
350	0.40	0.50	0.67	0.83	1.0
355	0.26	0.35	0.51	0.73	1.0

Comments on Preferred Values

The new measurements of absorption cross-section for HCHO in the $\tilde{A}\,{}^1A_2 \leftarrow \tilde{X}\,{}^1A_1$ system provide a firmer data base than previously available. The new values are 25 to 50% lower than those previously recommended on the basis of McQuigg and Calvert's [6] measurements. Also the values of Bass et al. [2] are ~25% lower than those of Moortgat et al. [3] at wavelengths > 300 nm. The recommended 10 nm averaged values of σ are based on the data from ref. [2] at 296 and 223 K and from ref. [3] at 277 and 214 K. Figure 7, supplied by G. K. Moortgat, shows the spectrum of HCHO at 0.5 nm resolution and 277.4 K. The absolute values of σ shown are about 3 percent lower than the values tabulated in ref. [3].

The new quantum yield measurements from Moortgat et al. [3] extend the data base to 240 nm. The results of Morrison and Heicklen for HCHO/O$_2$ mixtures are in conflict with those of others, and their conclusions are therefore of uncertain value. The preferred values for HCHO photolysis in air are based primarily on the earlier work of Moortgat and Warneck [7], Horowitz and Calvert [8] and Clark et al. [9], and these results are

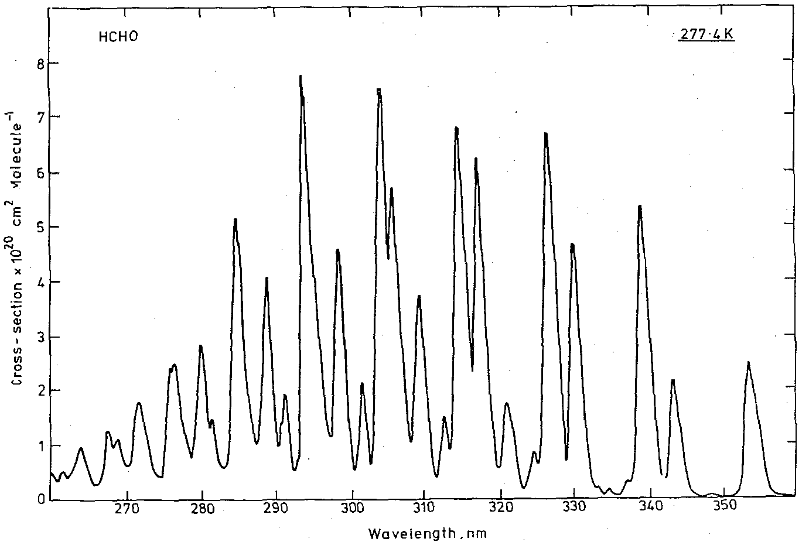

FIGURE 7. Absorption spectrum of HCHO. Resolution of 0.5 nm, $T = 277.4$ K, private communication from G. K. Moortgat.

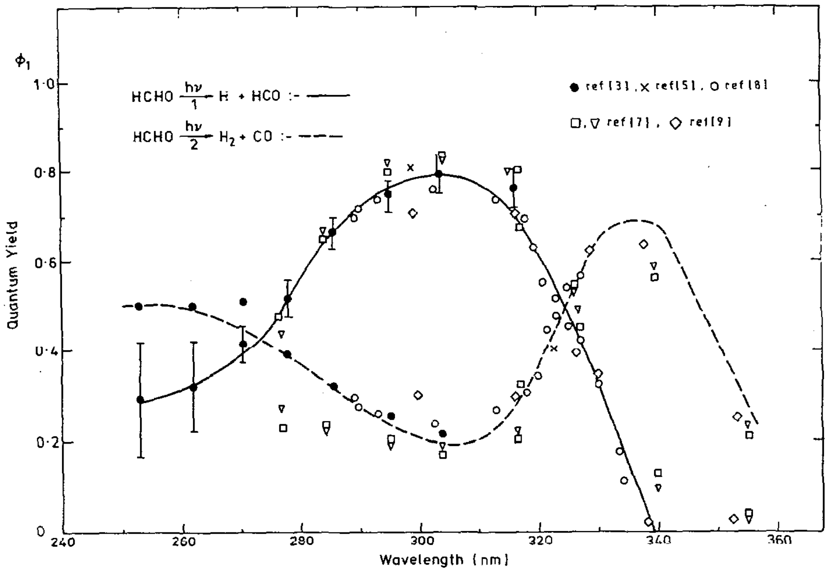

FIGURE 8. Wavelength dependence of HCHO photolysis quantum yields.

plotted together with those from ref. [3] in fig. (8). The new data of Tang et al. [5] also show agreement for ϕ_1. The pressure dependence of ϕ_2 at $\lambda > 329$ nm and 300 K is calculated from the expressions given by Moortgat et al. [3]:

$$\phi_2 = [1 + p(1 - \phi_A(\lambda))/\phi_A(\lambda)]^{-1} \text{ for } \lambda > 340$$

where p = pressure in atm. $\phi_A(\lambda)$ is the total quantum yield ($\phi_1 + \phi_2$) at 1 atm pressure, which is given by the expression

$$\phi_A(\lambda) = 1 - \beta\left(\frac{\lambda - \lambda_0}{\lambda_1 - \lambda_0}\right)$$

where $\lambda_0 = 329$ nm; $\lambda_1 - \lambda_0 = 355\text{–}329 = 26$ nm and $\beta = 1 - \phi_A(355) = 0.74$ (as measured).

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$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1} [a]	$\lambda_{threshold}$/nm
$CH_3OOH + h\nu \rightarrow CH_3O + HO$ (1)	184.6	647
$\rightarrow CH_3 + HO_2$ (2)	287.1	429
$\rightarrow CH_3O_2 + H$ (3)	365.1	335

[a] Calculated assuming $\Delta H_0^\circ - \Delta H^\circ_{298}$, 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)

Comments

(a) CH_3OOH prepared by standard method and absorption measured in long-path cell in 15 separate runs. Beers Law obeyed. Similar spectrum observed on aqueous solution, which agreed with earlier solution work.

(b) Absorption of product of reaction of $CH_3O_2 + HO_2$ in photolysis of Cl_2-CH_4-H_2-O_2 mixtures. Assumed absorption due to CH_3OOH.

Quantum Yield Data

No data.

Preferred Values

Absorption cross sections

λ/mn	$10^{20}\sigma$/cm^2
210	37.5
220	22.0
230	13.8
240	8.8
250	5.8
260	3.8
270	2.5
280	1.5
290	0.90
300	0.58
310	0.34
320	0.19
330	0.11
340	0.06
350	0.04

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred absorption cross section data are those of Molina and Arguello [1], taken directly from their tabulation. The data of Cox and Tyndall can only be considered approximate since it was not established that the absorption was due entirely to CH_3OOH. The values agree well with those in [1] at $\lambda < 230$ nm but are higher at longer wavelengths. No data are available on the quantum yield or branching ratio for CH_3OOH photolysis but, by analogy with other peroxide species, it is probable that $\Phi_1 = 1$ and $\Phi_2 = \Phi_3 = 0$ for all wavelengths $\geqslant$200 nm [3].

References

[1] Molina, M. J., and Arguello, G., Geophys. Res. Letters. 6, 953 (1979).
[2] Cox, R. A., and Tyndall, C. S., Chem. Phys. Lett. 65, 357 (1979).
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$CH_3O_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2$	80	1493
$\rightarrow CH_3O + NO_3$	125	956

Note: Only approximate values of $\Delta H°_{298}$ 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)

Quantum yields: No data.

Comments

(a) $CH_3O_2NO_2$ prepared in photolysis of Cl_2-CH_4-O_2-NO_2 mixtures at 275 K. Absorption cross sections based on assumption that all CH_3O_2 radicals produced in system reacted with NO_2. Correction for absorption due to NO_2 and O_3 was also necessary.

(b) Similar to (a) using 366 nm photolysis and at 296 K.

(c) Residual absorption in flash photolysis of $Cl_2 + CH_4$ or $(CH_3)_2N_2$ in the presence of O_2 and NO_2. σ measured relative to the absorption cross section for CH_3O_2 in range 240–280 nm, and assuming stoichiometric conversion to $CH_3O_2NO_2$. Temp. = 298 K.

Preferred Values

Absorption cross-sections for $CH_3O_2NO_2$

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
200	500	265	20
205	360	270	16
210	240	275	13
215	150	280	10.5
220	105	285	8.4
225	80	290	7.0
230	68	295	6.0
235	60	300	5.0
240	53	305	4.0
245	46	310	3.0
250	39	315	
255	32	320	
260	26	325	

Quantum Yields

No recommendation since no available data to indicate relative importance of Φ_1 and Φ_2.

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$ measurement of cross-section presents considerable experimental problems. Nevertheless the three studies yield values of σ in moderately good agreement at wavelengths <255 nm as will be seen from figure 9. At longer wavelengths the agreement is less good and the experimental data from [1], which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \gtrsim 290$ nm), show large scatter. This is reflected in the increased uncertainty limits at longer wavelengths, for the preferred values given in the table, which were obtained by constructing the best curve through all of the data points from [1–3].

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 (e.g. 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

[1] Cox, R. A., and Tyndall, G. S., Chem. Phys. Lett. **65**, 357 (1979).
[2] Morel, O., Simonaitis, R., and Heicklen, J., Chem. Phys. Lett. **73**, 38 (1980).
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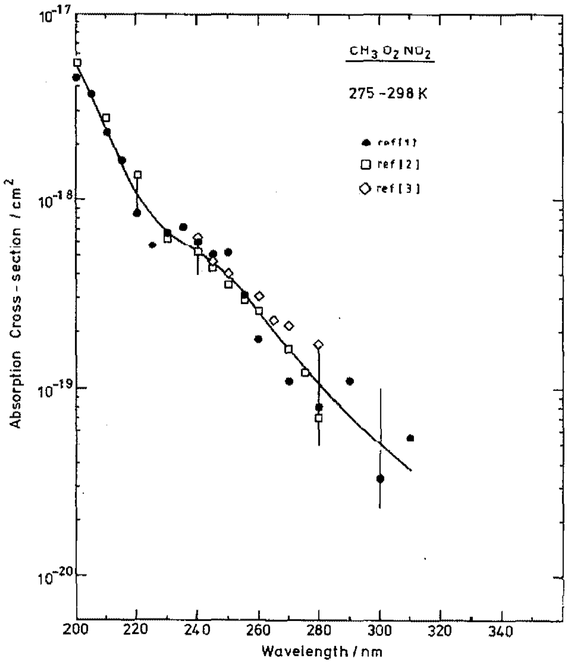

FIGURE 9. Absorption cross section for methyl peroxynitrate, 200–320 nm.

$CH_3CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CHO + h\nu \rightarrow CH_4 + CO$	(1)	-25.4	
$\rightarrow CH_3 + HCO$	(2)	341.4	350.1
$\rightarrow CH_3CO + H$	(3)	354.1	337.5
$\rightarrow {}^3CH_3CHO$	(4)	?	

Absorption cross section

Wavelength range/nm	Reference	Comments
290–340	Leighton, 1971 [1]	(a)
200–350	Calvert and Pitts, 1966 [2]	(b)
290–350	Weaver, Meagher, and Heicklen, 1977 [3]	(c)

Quantum yield data $|\Phi = \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4|$

Measurement	Wavelength	Reference	Comment
$\Phi_2 = 0.20$, $\Phi_1 = 0.013$	313.0	Blacet and Heldman, 1942 [5]	(d)
$\Phi_2 = 0.81$	313.0	Calvert, Pitts, and Thompson, 1956 [6]	(e)
$0.2 \leqslant \Phi_2 \leqslant 0.8$; $\Phi_1 = 0.013$	313.0		(f)
$\Phi_2 = 0.39$; $\Phi_1 = 0.15$	280.4	Leighton, 1961 [1] Calvert and Pitts, 1966 [2]	(f,g)
$\Phi_2 = 0.36$; $\Phi_1 = 0.28$	265.4		
$\Phi_4 = 1.0$	334.0		
$= 0.84$	313.0	Paramenter and Noyes, 1963 [7]	(h)
$= 0.59$	296.7		
$= 0.48$	280.4		
$\Phi_2 \leqslant 0.05$	313.0	Archer, Cundall, and Palmer, 1973 [8]	(i)
$\Phi_2 = 0.05$; $\Phi_4 = 0.84$	313.0	Weaver, Meagher, and Heicklen, 1977 [4]	(j)
$\Phi_2 = 0$	> 321.0	Gill and Atkinson, 1979 [9]	(k)
$\Phi_2 =$ important	266–320		

Comments

(a) Values of ϵ (L mol^{-1} cm^{-1}, base 10) averaged over 10 nm wavelength intervals given. Source: early work of Smith [4].

(b) Graphical presentation of ϵ (L mol^{-1} cm^{-1}, base 10) vs wavelength at 298 K. Spectrum determined in 10 cm path length with various pressures CH_3CHO and undefined spectral resolution.

(c) Table giving σ (cm^2 molecule^{-1}) averaged over 5 nm wavelength intervals. No details given.

(d) Photolysis of CH_3CHO-I_2 mixtures. Φ(CO), Φ(CH_3I), Φ(CH_4) measured at 333–443 K. CH_3I used as a measure of CH_3 production.

(e) CH_3CHO photolysis at 573–623 K. Φ_{H_2} used as a measure of HCO formation, assuming complete dissociation of HCO: $HCO(+M) \rightarrow H + CO(+M)$.

(f) Reviews based on earlier work including [5] and [6].

(g) Role of triplet state also considered.

(h) Product quantum yields and emission studies for CH_3CHO photolysis in presence and absence of NO in an attempt to distinguish the role of excited triplet and single states of CH_3CHO.

(i) Cis-trans isomerisation of 2-butane used as a measure of triplet acetaldehyde production. Limiting high pressure values of Φ(CO) and Φ(CH_4) give Φ_2.

(j) Photooxidation of CH_3CHO at 313 nm studied. Quantum yields for CO and other products measured as function of [O_2], [CH_3CHO], etc. Atmospheric photolysis rates were calculated.

(k) Wavelength dependence of HCO formation in photodissociation of CH_3CHO measured using narrow band laser excitation and time-resolved intra-cavity detection of HCO.

Preferred Values

Wavelength/nm	$10^{20}\sigma$/cm^2	Wavelength/nm	$10^{20}\sigma$/cm^2
200	0.77	295	4.5
210	0.31	300	4.3
220	$\lesssim 0.1$	305	3.4
240	0.42	315	2.1
250	1.0	320	1.8
260	2.0	325	1.1
270	3.4	330	0.69
280	4.5	335	0.38
290	4.9	340	0.15
		345	0.08

Quantum Yields

No recommendation.

Comments on Preferred Values

The absorption cross-sections given in the table are actual values for the wavelengths indicated and are not averaged. Since the spectrum shows very little structure, little error would result from interpolation. The preferred values are based on those from [2] and [3] which are in excellent agreement. Data from [1] appear high by ~50%. No firm recommendation can be made for the quantum yields for the various photochemical transitions. The photolysis of acetaldehyde is complicated by the various excited molecular states which can be populated following absorption of a photon in the uv band. The wavelength dependence of Φ_1 [1,2] and the recent time-resolved study of HCO formation [9] show that the dissociation mechanisms and yields change with excitation wavelength. The emission study [7] and cis-trans isomerisation work [8] clearly show an important role of the triplet CH_3CHO molecules and since triplet carbonyl species exhibit temperature dependent decomposition, extrapolation from the early work at high temperture [5,6] is probably not valid for room temperature, atmospheric pressure values. Furthermore, photochemical decomposition of CH_3CHO could result from reaction of $^3CH_3CHO$ with O_2 as suggested by Weaver et al. [3], from their study of the photo-oxidation of CH_3CHO. Possible uncertainties in the interpretation of the secondary chemistry in their system could, however, affect their conclusions.

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$CH_3CO_3NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CH_3CO_3NO_2 + h\nu \rightarrow CH_3CO_3 + NO_2$	110	1086
$\rightarrow CH_3CO_2 + NO_3$	131	914

Absorption cross section data

Wavelength range/nm	Reference	Comments
220–270	Stephens, 1974 [1]	(a)

Comments

(a) Pure sample of peroxyacetylnitrate in N_2 prepared by standard techniques. Absorption measured in 10 cm cell and given as plot of ϵ vs wavelength.

Quantum Yield Data

No available data.

Preferred Values

The following table shows provisional values for absorption cross sections in the range 220–270 nm.

Absorption cross sections

Wavelength/nm	$10^{20}\sigma$/cm^2	Wavelength/nm	$10^{20}\sigma$/cm^2
220	100	250	15
225	70	255	11
230	50	260	8
235	37	265	6
240	27	270	4
245	20		

Quantum Yields

No recommendation.

Comments

The only published values of the absorption cross-sections are those in ref. [1], although confirmation of these values has been reported [2]. The values given are estimated from the figure in ref. [1]. No information is available concerning the relative importance of ϕ_1 and ϕ_2, but by analogy with other nitrates it is probable that $\phi_1 + \phi_2 = 1$, for absorption in the uv region.

References

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5.5. Sulfur Compounds

$O + H_2S \rightarrow HO + HS$

$\Delta H^\circ = -44$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.15 \times 10^{-11} \exp(-2000/T)$	281–497	Slagle, Baiocchi, and Gutman, 1978 [1]	(a)
$(3.6 \pm 0.72) \times 10^{-14}$	301		
$(2.6 \pm 1.4) \times 10^{-11} \exp(-(2171 \pm 202)/T)$	297–502	Singleton et al., 1979 [2]	(b)
$(1.83 \pm 0.15) \times 10^{-14}$	297		
Reviews and Evaluations			
$2.6 \times 10^{-11} \exp(-2170/T)$	200–300	NASA, 1979 [3]	(c)
$7.2 \times 10^{-12} \exp(-1660/T)$	250–500	CODATA, 1980 [4]	(d)
$2.6 \times 10^{-11} \exp(-2170/T)$	200–300	NASA, 1981 [5]	(c)

Comments

(a) Fast-flow discharge, $[O] \gg [H_2S]$. $[H_2S]$ monitored by photoionization mass spectrometry. Values of k found to be constant for initial $[O]/[H_2S] > 50$. Arrhenius expression quoted is least squares fit to values of k given in [1].

(b) Molecular modulation technique. O generated by Hg photosensitized decomposition of N_2O at 254 nm.

(c) Accepted results of [2].

(d) Based on all available data prior to [1], [2].

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-11} \exp(-1920/T)$ cm^3 molecule^{-1} s^{-1} over range 290–500 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 750$ K.

Comments on Preferred Values

The two recent measurements of k [1], [2] are in reasonable agreement on the temperature coefficient of the rate coefficient but the absolute values differ by approximately a factor of two over the whole temperature range. In the discharge flow study [1] the reactions of O with a number of sulphur containing compounds were studied and where comparison is possible it appears that the rate coefficient values are high compared with results from other laboratories. On the other hand the results from [2] are in better agreement with the most reliable previous results, those of [6] ($k = 7.2 \times 10^{-12} \exp(-1660/T)$ cm^3 molecule^{-1} s^{-1}), than the difference in Arrhenius parameters might suggest. The absolute values of k in the range 330–500 K in these two studies [2], [6] are identical, within experimental error, and it is only at lower temperatures that they diverge considerably so leading to the differences in the Arrhenius expressions.

The preferred values are derived from a least squares fit to the results of [2] and [6] but, because of the divergence of results at lower temperatures the range of validity of our recommendation is limited to $T > 290$ K.

If the results of Hollinden et al. [7] in the range 205–300 K are correct, they suggest a marked and abrupt change in the reaction mechanism, but it would be premature to assume this. Further studies in this temperature region would obviously be of value.

References

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[3] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Read, E. I., editors (1979).

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$O + CH_3SCH_3 \rightarrow CH_3SOCH_3 \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.42 \pm 0.07) \times 10^{-11} \exp((367 \pm 15)/T)$	268–424	Lee, Timmons, and Stief, 1976 [1]	(a)
$(4.85 \pm 0.52) \times 10^{-11}$	298		
6.3×10^{-11}	300	Slagle, Graham, and Gutman, 1976 [2]	(b)
$(1.93 \pm 0.10) \times 10^{-11} \exp((304 \pm 16)/T)$	252–493	Slagle, Baiocchi, and Gutman, 1978 [3]	(c)
5.7×10^{-11}	296		
$(1.28 \pm 0.12) \times 10^{-11} \exp((419 \pm 30)/T)$	272–472	Lee, Tang, and Klemm, 1979 [4]	(d)
$(4.83 \pm 0.46) \times 10^{-11}$	296		

Comments

(a) Flash photolysis; resonance fluorescence detection of O. Flow system to avoid product accumulation. No change in k with flash energy and total pressure (Ar diluent) over range 40–100 Torr.

(b) Fast-flow discharge study. Photoionisation mass spectrometric detection of CH_3SCH_3 removal in excess ($\sim$20 fold) of O.

(c) Method as in (b). Arrhenius expression quoted is least squares fit to points from [3].

(d) Fast-flow discharge study. [O] monitored by resonance fluorescence. $[CH_3SCH_3]$ in large excess.

Preferred Values

$k = 4.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-11} \exp(390/T)$ cm^3 molecule^{-1} s^{-1} over range 270–500 K.

Reliability

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

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

Comments on Preferred Values

Two of the studies using different techniques, but from the same laboratory, are in excellent agreement [1], [4]. The other results [2], [3] are $\sim$30% higher over most of the temperature range. The values of k ($O + H_2S$) in the same study [2] also appear to be higher than those from other laboratories. The preferred values are therefore obtained from [1] and [4] by averaging the values of E/R and fitting the Arrhenius expression to the preferred value of k at 298 K. The error limits are sufficiently wide to encompass the results of [2], [3]. The rate coefficient appears to be independent of pressure over the range 0.7–100 Torr Ar.

It is suggested [1], [2] that the reaction proceeds by O atom addition to S. There is evidence for this from the high values of k, the trend in rate coefficients for O atom reactions with RSR species (where R = H, methyl) [3] and from a crossed molecular beam study at very low pressure in which product fragments could be observed [2]. However the reaction products at higher pressures have not been identified.

References

[1] Lee, J. H. Timmons, R. B., and Stief, L. J., J. Chem. Phys. **64**, 300 (1976).
[2] Slagle, I. R., Graham, R. E., and Gutman, D., Int. J. Chem. Kinet. **8**, 451 (1976).
[3] Slagle, I. R., Baiocchi, F., and Gutman, D., J. Phys. Chem. **82**, 1333 (1978).
[4] Lee, J. H., Tang, I. N., and Klemm, R. B., J. Chem. Phys. **72**, 1793 (1980).

$$\mathbf{O + CS_2 \rightarrow SO + CS \quad (1)}$$
$$\mathbf{\rightarrow CO + S_2 \quad (2)}$$
$$\mathbf{\rightarrow OCS + S \quad (3)}$$

$\Delta H^\circ(1) = -89$ kJ mol^{-1}
$\Delta H^\circ(2) = -348$ kJ mol^{-1}
$\Delta H^\circ(3) = -231$ 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			
2.9×10^{-12}	249	Graham and Gutman, 1977 [1]	(a)
3.6×10^{-12}	273		
4.1×10^{-12}	295		
5.1×10^{-12}	335		
6.1×10^{-12}	376		
8.5×10^{-12}	431		
11.2×10^{-12}	500		
Relative Rate Coefficients			
$k_2 = (5.82 \pm 0.75)\times10^{-14}$	298	Hsu et al., 1979 [2]	(b)
Reviews and Evaluations			
$k_1 = 3.1\times10^{-11}\exp(-640/T)$	200–300	NASA, 1979 [3]	(c)
$5.8\times10^{-11}\exp(-700/T)$	200–300	CODATA, 1980 [4]	(d)
$k_1 = 3.1\times10^{-11}\exp(-640/T)$	200–300	NASA, 1981 [5]	(c)

Comments

(a) This data incorrectly tabulated in CODATA, 1980 [4].

(b) Flash photolysis of NO/CS$_2$ mixtures. [CO] monitored by CO laser absorption. Relative yields of CO extrapolated to $t = 0$ to give $k/k(\mathrm{O + C_2H_2}) = 0.373 \pm 0.48$. $k(\mathrm{O + C_2H_2}) = 1.57\times10^{-13}$ cm^3 molecule^{-1} s^{-1} [6] used to obtain k_2.

(c) Reaction attributed to channel (1).

(d) Based on data from [1], [7–10]. See note (a).

Preferred Values

$k = 3.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 3.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 5.8\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 3.3\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0\times10^{-11}\exp(-530/T)$ over range 200–500 K.
$k_1/k = 0.91$ over range 200–500 K.
$k_3/k = 0.09$ over range 200–500 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta \log k_1 = \pm 0.2$ at 298 K.
$\Delta \log k_2 = \pm 0.2$ at 298 K.
$\Delta \log k_3 = \pm 0.25$ at 298 K.
$\Delta (E/R) = \pm 100$ K.
$\Delta (k_1/k) = \pm 0.02$ over range 200–500 K.
$\Delta (k_3/k) = \pm 0.02$ over range 200–500 K.

Comments on Preferred Values

The preferred value of k in CODATA, 1980 [4] was based upon incorrectly tabulated values from [1]. The preferred value of k now given is obtained by a least squares fit to the correct data from [1] and data from [7–10]. The value of k_2 is the only available measurement [2]; it is recommended but with substantially increased error limits. k_3 at 298 K is calculated from the preferred value of k and the measured branching ratio k_3/k [1]. k_1 at 298 K is obtained from k, k_2, and k_3 by difference.

Measurements of k_3/k [1] over the range 200–500 K indicate a very slight temperature dependence but until this is confirmed we have chosen to recommend a temperature independent ratio with wider error limits. At 298 K, $k_2 \ll k_1$ and assuming this to persist over the range 200–500 K, the preferred value for k_1/k for this temperature range is obtained, by difference, from k and k_3.

References

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[4] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
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[9] Slagle, I. R., Gilbert, J. R., and Gutman, D., J. Chem. Phys. **61**, 704 (1974).
[10] Wei, C. N., and Timmons, R. B., J. Chem. Phys. **62**, 3240 (1975).

$O + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.12 \pm 0.22) \times 10^{-10}$	270–329	Lee and Tang, 1980 [1]	(a)

Comments

(a) Fast-flow discharge study; resonance fluorescence detection of O atoms. $[CH_3SSCH_3]/[O] \sim 10$–40. Rate coefficient independent of pressure over range studied (0.52–2.60 Torr).

Preferred Value

$k = 2.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 270–330 K.

Reliability

$\Delta \log k = \pm 0.3$ over range 270–330 K.

Comments on Preferred Value

Although there is only one available study, the method used was direct and appears to give reliable results for the $O + CH_3SCH_3$ reaction. The value of k is very high but not unacceptably so in comparison with that established for the $O + CH_3SCH_3$ reaction. This one value is therefore recommended but with wider error limits until confirmed by other studies. The reaction products have not been identified.

References

[1] Lee, J. H., and Tang, I. N., J. Chem. Phys. **72**, 5718 (1980).

$S + O_2 \rightarrow SO + O$

$\Delta H^\circ = -22.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.5) \times 10^{-12} \exp((153 \pm 108)/T)$ $(2.6 \pm 0.3) \times 10^{-12}$	296–393	Clyne and Whitefield, 1979 [1]	(a)
Reviews and Evaluations			
2.0×10^{-12}	230–400	CODATA, 1980 [2]	(b)

Comments

(a) Discharge flow; S atoms generated by discharge in Ar/SO_2 mixtures. $[S] \ll [O_2]$. [S] monitored by resonance fluorescence.

(b) Based on [3–7].

Preferred Value

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 230–400 K.

Reliability

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

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

Comments on Preferred Value

The most recent measurements [1] agree well with most of the earlier results and the previously recommended value [2]. A small decrease in k with increase in temperature was found, but the error limits comfortably encompass the value suggested in CODATA [2] and we modify only slightly this previous recommendation. The present recommendation is based on [1], [3–6].

References

[1] Clyne, M. A. A., and Whitefield, P. D., J. Chem. Soc. Faraday Trans. 2 **75**, 1327 (1979).
[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
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$HO + H_2S \rightarrow H_2O + HS$

$\Delta H^\circ = -114$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.0 \pm 0.3) \times 10^{-12}$	298	Cox and Sheppard, 1980 [1]	(a)
Reviews and Evaluations			
5.3×10^{-12}	200–300	NASA, 1979 [2]	(b)
$1.1 \times 10^{-11} \exp(-225/T)$	250–400	CODATA, 1980 [3]	(c)
$1.1 \times 10^{-11} \exp(-220/T)$	200–300	NASA, 1981 [4]	(c)

Comments

(a) Photolysis of ~5 ppm of HONO in synthetic air mixture, at one atmosphere pressure, containing a few ppm of C_2H_4 and H_2S. $[C_2H_4]$ and $[H_2S]_3$ monitored by gas chromatography. $k/k(HO + C_2H_4) = 0.62 \pm 0.04$ obtained. $k(HO + C_2H_4) = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} used (CODATA evaluation).

(b) Mean of values from [5] and [6].

(c) Based on [5], [6].

Preferred Values

$k = 5.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-11} \exp(-225/T)$ cm^3 molecule^{-1} s^{-1} over range 250–400 K.

Reliability

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

$\Delta (E/R) = \pm 225$ K.

Comments on Preferred Values

The only recent measurement is in good agreement with the previous CODATA evaluation [3] which is therefore unchanged.

References

[1] Cox, R. A., and Sheppard, D., Nature (London) **284**, 330 (1980).

[2] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Reed, E. I., editors (1979).

[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

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[5] Westenberg, A. A., and de Haas, N., J. Chem. Phys. **59**, 6685 (1973).

[6] Perry, R.A., Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys. **64**, 3237 (1976).

$HO + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.47 \times 10^{-12} \exp((179 \pm 150)/T)$	300–427	Atkinson, Perry, and Pitts, 1978 [1]	(a)
$(9.8 \pm 1.2) \times 10^{-12}$	300		
$(6.25 \pm 4.19) \times 10^{-12} \exp((131 \pm 215)/T)$	273–400	Kurylo, 1978 [2]	(a)
$(8.28 \pm 0.87) \times 10^{-12}$	296		
Relative Rate Coefficients			
$(9.1 \pm 1.4) \times 10^{-12}$	297	Cox and Sheppard, 1980 [3]	(b)

Comments

(a) Vacuum uv photolysis of $H_2O/Ar/CH_3SCH_3$ mixtures. [HO] monitored by resonance fluorescence. Large excess of CH_3SCH_3 over HO. Flow system used to prevent accumulation of reaction products.

(b) HO generated by photolysis of ~5 ppm of HONO in synthetic air mixture at atmospheric pressure, containing a few ppm of C_2H_4 and CH_3SCH_3. $[C_2H_4]$ and $[CH_3SCH_3]$ monitored by gas chromatography. $k/k(HO + C_2H_4) = 1.14$ obtained. Value of k obtained using $k(HO + C_2H_4) = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

Preferred Values

$k = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.5 \times 10^{-12} \exp(150/T)$ cm^3 molecule^{-1} s^{-1} over range 200–500 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

Results from the two independent flash photolysis studies [1], [2], and the relative rate study [3] are in excellent agreement. The preferred values are based on these three studies. The reaction products have not been identified and it is not certain whether the reaction proceeds by abstraction or addition.

References

[1] Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., Chem. Phys. Lett. **54**, 14 (1978).
[2] Kurylo, M. J., Chem. Phys. Lett. **58**, 233 (1978).
[3] Cox, R. A., and Sheppard, D., Nature (London) **284**, 330 (1980).

HO + CS_2→products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<9.9\times10^{-15}$	251	Wine, Shah, and Ravishankara, 1980 [1]	(a)
$<1.5\times10^{-15}$	297		
$<1.6\times10^{-15}$	363		
Relative Rate Coefficients			
$<3\times10^{-15}$	298	Subramonia Iyer and Rowland, 1980 [2]	(b)
$(4.3\pm1.6)\times10^{-13}$	295	Cox and Sheppard, 1980 [3]	(c)
Reviews and Evaluations			
1.9×10^{-13}	298	NASA, 1979 [4]	(d)
$\leqslant2\times10^{-13}$	298	CODATA, 1980 [5]	(e)
$\leqslant1.5\times10^{-15}$	200–300	NASA, 1981 [6]	(f)

Comments

(a) Flash photolysis of H_2O/CS_2/diluent mixtures in flow system. [HO] monitored by resonance fluorescence. Decay of [HO] over whole time scale found to be first-order only when CS_2 used to filter flash and SF_6 used as diluent. Suggest that large values of k reported in previous studies [7], [8] due to CS_2 photolysis product reacting with HO.

(b) Photolysis at 254 nm of $H_2O_2/CS_2/X$ mixtures (where X = CO, C_3H_8, iso-C_4H_{10}). Gas chromatographic and radiochemical assay of products. Rate of COS formation determined. Values obtained for $k/k(HO + CO) = 0.02$–0.0067, $k/k(HO + C_3H_8) = 0.0059$, $k/k(HO + \text{iso-}C_4H_{10}) = 0.0038$, which give values of k in the range $(0.01$–$1.0)\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, using $k(HO + CO) = 1.5\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation), $k(HO + C_3H_8) = 1.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (authors' value), and $k(HO + \text{iso-}C_4H_{10} = 2.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (authors' value).

(c) Photolysis of ~5 ppm of HONO in synthetic air mixture, one atmosphere pressure, containing a few ppm of ethylene and CS_2. [C_2H_4] and [CS_2] monitored by gas chromatography. $k/k(HO + C_2H_4) = 0.06 \pm 0.02$ obtained. $k(HO + C_2H_4) = 8\times10^{-12}$ cm molecule^{-1} s^{-1} used (CODATA evaluation).

(d) Accepts value of [7].

(e) Value of [7] taken as upper limit.

(f) Accepts value of [1] as upper limit.

Preferred Value

$k \leqslant 1.5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

Two recent studies [1], [2] suggest strongly that previous measurements [7], [8] of k are far too high. A possible reason in the case of earlier flash photolysis work on CS_2/H_2O mixtures is that the HO is rapidly moved by reaction with CS_2 photolysis products rather than CS_2 itself. In the relative rate work there are several factors which could have lead to the high values obtained, including CS_2^* formation and the presence of oxygen. The recent results [1], [2] are preferred but should be used with caution for atmospheric modelling.

References

[1] Wine, P. H., Shah, R. C., and Ravishankara, A. R., J. Phys. Chem. **84**, 2499 (1980).
[2] Subramonia Iyer, R., and Rowland, F. S., Geophys. Res. Lett. **7**, 797 (1980).
[3] Cox, R. A., and Sheppard, D., Nature (London) **284**, 330 (1980).
[4] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Reed, E. I., editors (1979)
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HO + CH_3SSCH_3→Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.23 \pm 0.80)\times10^{-10}$	298	Cox and Sheppard, 1980 [1]	(a)

Comments

(a) Photolysis of ~5 ppm of HONO in synthetic air mixture at atmospheric pressure, containing a few ppm of C_2H_4 and CH_3SSCH_3. $[C_2H_4]$ and $[CH_3SSCH_3]$ monitored by gas chromatography. $k/k(HO + C_2H_4) = 28 \pm 10$ obtained. $k(HO + C_2H_4)$ taken as 8.0×10^{-12} cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

Preferred Value

$k = 2.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The only available value of k comes from a study in which a number of rate constants for related compounds were all determined by the same technique, which gave values in good agreement with other measurements.

This value of k is therefore recommended but with wider error limits until confirmatory studies are undertaken. The reaction products have not been identified. The magnitude of the rate constant suggests that the initial step in the reaction is one of additions.

References

[1] Cox, R. A., and Sheppard, D., Nature (London) **284**, 330 (1980).

HO + OCS→products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(0.88 \pm 0.01)\times10^{-14}$	298	Ravishankara et al., 1980 [1]	(a)
$(1.89 \pm 0.25)\times10^{-14}$	343		
$(3.27 \pm 0.56)\times10^{-14}$	369		
Relative Rate Coefficients			
$\leqslant 4\times10^{-14}$	295	Cox and Sheppard, 1980 [2]	(b)
Reviews and Evaluations			
5.6×10^{-14}	298	NASA, 1979 [3]	(c)
$\leqslant 6\times10^{-14}$	298	CODATA, 1980 [4]	(d)
$< 1.0\times10^{-14}$	298	NASA, 1981 [5]	(e)

Comments

(a) Flash photolysis-resonance fluorescence study. With H_2O as HO source photolysis of OCS cannot be avoided and introduces interfering secondary reactions. Use of laser photolysis of HNO_3 at 193 nm eliminates this problem.

(b) Photolysis of ~5 ppm of HONO in synthetic air mixtures at 1 atmosphere pressure containing a few ppm of ethylene and OCS. $[C_2H_4]$ and [OCS] monitored by gas chromatography. $k/k(HO + C_2H_4) \leqslant 0.005$ obtained. $k(HO + C_2H_4) = 8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} used (CODATA evaluation).

(c) Accepts, with some reservations, the value of [6].

(d) Value of [6] taken as upper limit.

(e) Accepts value of [1] as upper limit.

Preferred Value

$k \leqslant 9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

Flash photolysis studies of this reaction suffer from the difficulty of obtaining a clean source of HO radicals in the presence of OCS. OCS is readily photolysed and, because of the slowness of its reaction with HO radicals, small traces of photolytic impurities may compete effectively with OCS for HO radicals. Earlier measurements [6–8] probably suffered from this. The recent study [1] appears to have largely overcome the problem and the preferred value is taken from this work but, conservatively, we take it as an upper limit until it is confirmed by other studies. The results of [1] suggest a significant temperature dependence of the rate coefficient.

References

[1] Ravishankara, A. R., Kreutter, N. M., Shah, R. C., and Wine, P. H., Geophys. Res. Lett. **7**, 861 (1980).

[2] Cox, R. A., and Sheppard, D., Nature (London) **284**, 330 (1980).

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[6] Kurylo, M., Chem. Phys. Lett. **58**, 238 (1978).

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$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H^\circ \simeq -223$ 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			
$3.0\times10^{-31}(T/300)^{-2.9}[N_2]$	200–400	NASA, 1979 [1], 1981 [3]	(a)
$3.0\times10^{-31}(T/300)^{-2.9}[N_2]$	200–400	CODATA, 1980 [2]	(b)

Comments

(a) Values from ref. [2].

(b) From fall-off curves in the pressure range 5–1000 Torr, evaluated with $F_c \simeq 0.7$. Values in agreement with the evaluation by Zellner, 1978 [4].

Preferred Value

$k_0 = 3.0\times10^{-31}(T/300)^{-2.9}[N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 200–400 K.

Comments on Preferred Value.

No new data in the low pressure part of the fall-off curve. New data at very low pressures and a new evaluation are needed.

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2×10^{-12}	200–400	NASA, 1979 [1], 1981 [3]	(a)
2×10^{-12}	200–400	CODATA, 1908 [2]	(b)

Comments

(a) and (b): see comments for k_0.

Preferred Value

$k_\infty = 2.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$

Comments on Preferred Value

The earlier evaluation of ref. [2] was made with $F_c = 0.7$, which now appears to be too large. If one chooses an average of the F_c values of the HNO_3 and $ClNO_3$ systems one obtains $F_c = 0.55$ and hence the given k_∞ value. The shape of the fall-off curve must remain uncertain until new high pressure measurements are made.

Intermediate fall-off range

Rate coefficient data at 1 atm

k (1 atm)/cm^3 molecule^{-1} s^{-1}	M	Temp./K	Reference	Comments
Absolute Rate Coefficients				
9×10^{-13}	N_2	298	Davis, Ravishankara, and Fischer, 1979 [5]	(a)
1.0×10^{-12}	N_2	298	Harris, Atkinson, and Pitts, 1980 [6]	(b)
Relative Rate Coefficients				
$(7.2\pm1.6)\times10^{-13}$	N_2	297	Cox and Sheppard, 1980 [7]	(c)
Reviews and Evaluations				
1.2×10^{-12}	N_2	298	CODATA, 1980 [2]	(d)

Comments

(a) Flash photolysis-resonance fluorescence. Measurements in N_2 (5–20 Torr), Ar (20–500 Torr) and He (50–200 Torr). Data too incomplete to allow for a construction of the fall-off curve. Value given by combination of these data with results from other laboratories.

(b) Flash photolysis-resonance fluorescence. Measurements in Ar (404–653 Torr, 298–424 K) and SF_6 (98–650 Torr, 298–424 K). Data too incomplete to construct fall-off curves. Value given for N_2 estimted with the help of $Ar:N_2:SF_6$ relative efficiencies from the $HO + NO_2$ reaction.

(c) Photolysis of HONO to generate HO radicals, detection by consumption of added C_2H_4. Only atmospheric pressure studied. Measured ratio $k/k(HO + C_2H_4)$ evaluated with $k(HO + C_2H_4) = 8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation).

(d) Calculated from preferred k_0, k_∞, and F_c from ref. [2].

Preferred Value

$F_c = 0.55$ at 298 K.

Comments on Preferred Value

Within the relative large scatter the new data at 1 atm agree with the preferred values from ref. [2]. A slightly smaller F_c and larger k_∞ are suggested tentatively. New fall-off measurements are needed.

References

[1] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Reed, E. I. editors (1979).

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

[3] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," DeMore, W. B., Stief, L. J., Golden, D. M., Hampson, R. F., Jr., Kurylo, M. J., Margitan, J. J., Molina, M. J., Watson, R. T., JPL Publ. 81-3 (1981).

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[6] Harris, G. W., Atkinson, R., and Pitts, J. N., Chem. Phys. Lett. **69**, 378 (1980).

[7] Cox, R. A., and Sheppard, D., Nature **284**, 330 (1980).

$HO_2 + SO_2 \rightarrow$ Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$\leqslant4.3\times10^{-17}$	~298	Burrows et al., 1979 [1]	(a)

Comments

(a) Fast-flow discharge. HO_2 generated by discharge in H_2O_2 and by reaction of F atoms with H_2O_2. $[HO_2]$ and [HO] monitored by laser magnetic resonance to yield $k/k(HO + H_2O_2)$. Value of $k/k(HO + H_2O_2)$ not quoted but from their value of $k\leqslant2\times10^{-17}$ cm^3 molecule^{-1} s^{-1} and the value of $k(HO + H_2O_2) = 8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} used we obtain $k/k(HO + H_2O_2)\leqslant2.5\times10^{-3}$. We use $k(HO + H_2O_2) = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (CODATA evaluation). Quoted value of k assigned to $HO_2 + SO_2 \rightarrow HO + SO_3$ but results suggest other channels are also slow.

Preferred Value

$k\leqslant1\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

The only recent determination [1] confirms that the reaction is slower than some earlier results [2] suggest and supports the even lower limit set by Graham et al. [3], which we take as the preferred value.

References

[1] Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. T., Proc. R. Soc. London, Ser. A **368**, 463 (1979).

[2] Payne, W. A., Stief, L. J., and Davis, D. D., J. Am. Chem. Soc. **95**, 7614 (1973).

[3] Graham, R. A., Winer, A. M., Atkinson, R., and Pitts, J. N., Jr., J. Phys. Chem. **83**, 1563 (1979).

$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ (1)
$\rightarrow CH_3O_2SO_2$ (2)

$\Delta H°(1) = -92$ 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			
$(8.2 \pm 0.5) \times 10^{-15}$	298	Sanhueza, Simonaitis, and Heicklen, 1979 [1]	(a)
$<5 \times 10^{-17}$	298–423	Sander and Watson, 1981 [2]	(b)
Reviews and Evaluations			
$\leqslant 5 \times 10^{-17}$	298	NASA, 1981 [3]	(c)

Comments

(a) Flash photolysis of $Cl_2/CH_4/O_2/SO_2$ mixtures in static system, single flash. Decay of $[CH_3O_2]$ followed by absorption at 254 nm. Reaction products not identified. Authors recognise possibility of competitive removal of CH_3O_2 by reaction products affecting measurement.

(b) Flash photolysis of flowing $Cl_2/CH_4/O_2/SO_2$ mixtures. Low energy multiple flash used to ensure that $[CH_3O_2]$ much smaller (10^2–10^3) than $[SO_2]$. $[CH_3O_2]$ monitored by absorption at 242.5 nm.

(c) Accepts [2].

Preferred Value

$k \leqslant 5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

Of the two recent measurements that of [2] was carried out under conditions less prone to perturbation by secondary reactions, and the result is in accord with measurements on the HO_2 radical which also appears to react very slowly with SO_2 [4], [5]. Accordingly [2] is preferred to earlier results [1], [6] which are approximately a factor of 100 higher.

References

[1] Sanhueza, S., Simonaitis, R., and Heicklen, J., Int. J. Chem. Kinet. **11**, 907 (1979).

[2] Sander, S. P., and Watson, R. T., Chem. Phys. Lett. **77**, 473 (1981).

[3] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," DeMore, W. B., Stief, L. J., Golden, D. M., Hampton, R. F., Jr., Kurylo, M. J., Margitan, J. J., Molina, M. J., and Watson, R. T., JPL Publ. 81-3 (1981).

[4] Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. J., Proc. R. Soc. London, Ser. A **368**, 463 (1979).

[5] Graham, R. A., Winer, A. M., Atkinson, R., and Pitts, J. N., Jr., J. Phys. Chem. **83**, 1563 (1979).

[6] Kan, C. S., McQuigg, R. D., Whitbeck, M. R., and Calvert, J. G., Int. J. Chem. Kinet. **11**, 921 (1979).

$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H° = -645$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.7 \pm 1.6) \times 10^{-14}$	298	Robertshaw and Smith, 1980 [1]	(a)
Reviews and Evaluations			
$2.5 \times 10^{-12} \exp(-1100/T)$	220–300	CODATA, 1980 [2]	(b)

Comments

(a) Pulsed laser photolysis of O_3 in presence of OCS and large excess of N_2. SO generated by $O + OCS \rightarrow SO + CO$. Formation of SO_2 followed by detection of chemiluminescence of electronically excited SO_2.

(b) Accepts value of [3].

Preferred Values

$k = 7.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.2 \times 10^{-12} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over range 220–300 K.

Reliability

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

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

Comments on Preferred Values

The recent study [1], using a quite different technique from the only other measurement [3], gives a value of k in good agreement with the previous study. The recommended value at 298 K is the mean of [1] and [3]. The temperature coefficient is that of [3] and the pre-exponential factor is chosen to fit the value of k at 298 K.

References

[1] Robertshaw, J. S., and Smith, I. W. M., Int. J. Chem. Kinet. **12**, 729 (1980).
[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson. R. F., Jr., Kerr, I. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
[3] Halstead, C. J., and Thrush, B. A., Proc. R. Soc. London, Ser. A **295**, 380 (1966).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H^\circ = -245$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.10) \times 10^{-11}$	295	Clyne and MacRobert, 1980 [1]	(a)
Reviews and Evaluations			
1.4×10^{-11}	298	CODATA, 1980 [2]	(b)

Comments

(a) Fast-flow discharge study. SO from discharge in SO_2/He mixtures, O and S produced was preferentially removed by combination reactions leaving SO. [SO], in large excess of NO_2, monitored by mass spectrometry.

(b) Evaluation. Accepts value of [3].

Preferred Value

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The recent measurement of k [1] is in excellent agreement with the previous CODATA recommendation [2]. The new determination was by a more direct method and is likely to be more reliable than the earlier measurements [3] and hence the previously recommended error limits are reduced.

References

[1] Clyne, M. A. A., and MacRobert, A. J., Int. J. Chem. Kinet. **12**, 79 (1980).
[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson. R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
[3] Clyne, M. A. A., Halstead, C. J., and Thrush, B. A., Proc. R. Soc. London. Ser. A **295**. 355 (1966).

$CS_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CS_2 + h\nu \rightarrow CS + S(^3P)$	426	281
$\rightarrow CS - S(^1D)$	537	223

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma$/cm^2
295	9.6
305	46.1
315	71.7
325	48.2
335	5.3
345	2.6
355	0.51

Comments on Preferrd Values

The absorption spectrum of CS_2 at wavelengths greater than 200 nm consists of two strongly structured bands (190–220 nm and 290–350 nm), the former having absorption cross-sections approximately (5–10) × 10^3 times the latter. The values tabulated were supplied by Dr. R. A. Cox, A. E. R. E., Harwell, U.K. More detailed measurements have been published but not in a form lending itself to tabulation [1]. These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [2].

Photolysis at wavelengths $>$230 nm appears only to produce electronically excited CS_2 molecules. At $\lambda < 220$ nm formation of $S(^3P)$ is observed [3] but not $S(^1D)$. No quantum yield measurements have been reported.

References

[1] Rabelais, J. W., McDonald, J. M. Scherr, V., and McGlynn, S. P., Chem. Rev. **71**, 73 (1971).
[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L. Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
[3] Callear, A. B., Proc. R. Soc. London, Ser. A **276**, 401 (1963).

$CH_3SSCH_3 + h\nu \rightarrow$ Products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1} [a]	$\lambda_{threshold}$/nm[a]
$CH_3SSCH_3 \rightarrow CH_3SS + CH_3$	242	494
$\rightarrow 2CH_3S$	309	387

[a] Data for 298 K quoted since no data available for 0 K.

Absorption cross section data

Wavelength range/nm	Reference	Comments
200–310	Calvert and Pitts, 1966 [1]	(a)

Comments

(a) Results of McMillan, V., reported in [1]. Temperature 298 K. Continuum, no sign of structure in published spectrum.

Quantum Yield Data

No data available.

Preferred Values

Absorption cross sections

λ /nm	$10^{20}\sigma$/cm^2	λ /nm	$10^{20}\sigma$/cm^2
200	1300	260	100
210	530	270	80
220	130	280	50
230	80	290	30
240	100	300	15
250	120	310	6

Comments on Preferred Values

The only available data are in the form of a spectrum published in [1]. The cross sections quoted are taken from that figure but in view of this and lack of experimental details no error limits are suggested. There have been no quantum yield measurements and the primary photolytic pathways have not been identified.

References

[1] Calvert, J. G., and Pitts, J. N., Jr., "Photochemistry," (Wiley), 1966, p. 490.

OCS + $h\nu \rightarrow$ Products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
OCS + $h\nu \rightarrow$ CO + S(^{3}P) (1)	303	394
$\rightarrow$ CO + S(^{1}D) (2)	414	288

Absorption cross section data

Wavelength range/nm	Reference	Comments
186–226	Chou, Vera-Ruiz, and Rowland, 1979 [1]	(a)

Comments

(a) Temperatures, 232, 252, 296 K. Results quoted in NASA Panel review [1] but original work does not seem to have been published.

Preferred Values

Absorption cross sections

λ/nm \ Temp/K	232	251	296
	$10^{20}\sigma$/cm^2		
185	12.1	12.8	16.0
190	1.8	2.2	3.0
195	1.2	1.5	1.4
200	3.2	3.4	3.2
205	7.0	7.2	7.2
210	13.1	13.2	13.2
215	21.3	21.5	21.8
220	26.2	26.1	26.2
225	28.0	28.6	29.2
230			24.6
235			15.9
240			8.8
245			4.1
250			1.84
255			0.78

Comments on Preferred Values

There is good agreement between the recent measurements [1] and the values given in [2] for the region of overlap (205–225 nm at 296 K). The preferred values are based on those two sets of data. Values in the range 185–225 nm are obtained by linear interpolation between values tabulated in [1]. Values in the range 230–255 nm are taken from [3].

References

[1] Chou, C. C., Vera-Ruiz, H., and Rowland, F. S., unpublished results quoted in NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Hudson, R. D., and Reed, E. I., editors (1979).

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

[3] Breckenridge, W. H., and Taube, H., J. Chem. Phys. **53**, 1750 (1970).

5.6. Fluorine Compounds

$F + H_2 \rightarrow HF + H$

$\Delta H^\circ = -134.8$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.8\times10^{-10}\exp(-775/T)$	298–400	Homann et al., 1970 [1]	(a)
2.75×10^{-11}	295		
$2.7\times10^{-10}\exp(-599/T)$	250–375	Warnatz, Wagner, and Zetzsch, 1972 [2]	(b)
3.5×10^{-11}	295		
$1.8\times10^{-10}\exp(-528/T)$	260–370		
3.0×10^{-11}	295		
$(3.0\pm0.5)\times10^{-11}$	293	Zhitneva and Pshezhetskii, 1978 [3]	(c)
$(3.0\pm0.5)\times10^{-11}$	295	Heidner et al., 1979 [4]	(d)
$(2.2\pm0.4)\times10^{-10}\exp(-(595\pm50)/T)$	295–765	Heidner et al., 1980 [5]	(d)
$(3.0\pm0.5)\times10^{-11}$	295		
$1.0\times10^{-10}\exp(-(433\pm50)/T)$	190–373	Wurzberg and Houston, 1980 [6]	(d)
$(2.27\pm0.18)\times0^{-11}$	296		
Reviews and Evaluations			
$2.0\times10^{-10}\exp(-620/T)$	200–400	NASA, 1979 [7]	(e)
$2.0\times10^{-10}\exp(-620/T)$	200–400	CODATA, 1980 [8]	(e)
$2.0\times10^{-10}\exp(-620/T)$	200–400	NASA, 1981 [9]	(e)

Comments

(a) These values were recalculated from the original data by Warnatz et al. [2].

(b) No experimental details as the report was unobtainable.

(c) Chain reaction between ClF and H_2 initiated by uv light (250–320 nm). k_1 determined by monitoring the rate of change of ClF spectrophotometrically when $[ClF]_0 > [H_2]_0$.

(d) Atomic fluorine generated from the infra-red multiphoton dissociation of SF_6. The reaction monitored by means of the time-resolved infra-red emission from HF*.

(e) Based on the data reported by Homann et al., 1970 [1] (uncorrected), Dodonov et al., 1971 [10], Clyne et al., 1973 [11], Bozzelli, 1973 [12], and Igoshin et al., 1974 [13].

Preferred Values

$k = 2.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9\times10^{-10}\exp(-570/T)$ cm^3 molecule^{-1} s^{-1} over range 190–770 K.

Reliability

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

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

Comments on Preferred Values

The value of k at 298 K seems to be well established with the results reported by Homann et al. [1], Warnatz et al. [2], Zhitneva and Pshezheskii [3], Heidner et al. [4], Wurzberg and Houston. [5], Dodonov et al. [10], Clyne et al. [11], Bozzelli [12] and Igoshin et al. [13], being in excellent agreement (range of k being 2.3–3.3×10^{-11} cm^3 molecule^{-1} s^{-1}). The preferred value at 298 K is taken to be the mean of the values reported in these references. The magnitude of the temperature dependence is not quite as well established with values of E/R ranging from 433–775 K (references [1], [2], [5], [6], [13]). The preferred value of E/R is taken to be the mean of the results from all of the studies. The A factor was calculated by taking E/R to be 570 K, and k at 298 K to be 2.8×10^{-11} cm^3 molecule^{-1} s^{-1}.

References

[1] Homann, K. H., Solomon, W. E., Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Ber. Bunsenges. Phys. Chem. **74**, 585 (1970).

[2] Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Report T-0240/92410/01017, Fraunhofer Gesellschaft, (1972).

[3] Zhitneva, G. P., and Pshezhetskii, S. Ya., Kinetika i Kataliz **19**, 296 (1978).

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[12] Bozzelli, J. Thesis, Dept. of Chemistry, Princeton University, Diss. Abstr. Int. B 34 (2), 608 (1973).

[13] Igoshin, V. I., Kulakov, L. V., and Nikitin, A. I., Sov. J. Quantum Electron. 3, 306 (1974).

$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H^\circ = -29$ 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			
$(2.8 \pm 0.8)\times 10^{-34} \exp(906/T)$ [Ar]	223–293	Shamonima and Kotov, 1979 [1]	(a)
6.1×10^{-33}	293		
Reviews and Evaluations			
$1.1\times 10^{-32}(T/300)^{-2}$ [N_2]	270–360	CODATA, 1980 [2]	(b)

Comments

(a) Discharge flow-ESR detection of atomic fluorine in the presence of excess O_2 and Ar. Limited experimental conditions, e.g. [O_2] only varied by a factor of 2, and total pressure was fixed. The third order rate constant reported for Ar as the diluent gas may be somewhat overestimated as the O_2 ranged from ~12–25% of the total pressure. Stoichiometry assumed to be 2, i.e., $-d[F]dt - 2k[F][O_2][M]$ due to secondary removal of atomic fluorine by the primary product FO_2.

(b) Based on experimental data (both He and N_2 data) reported by Zetzsch, 1973 [3], Arutyunov et al., 1976 [4] and Chen et al., 1977 [5].

Preferred Values

$k_0 = 1.6\times 10^{-32}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 1.6\times 10^{-32}(T/300)^{-2.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 223–360 K.

Reliability

$\Delta k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1.0$.

Comments on Preferred Values

The preferred value at 298 K is based upon the following factors: (a) the average of the three determinations of k_0(M = He) reported by Zetzsch [3], Arutyunov et al., [4] and Chen et al., [5]; (b) the average of the three determinations of k_0(M = Ar) reported by Arutyunov et al. [4], Chen et al., [5] and Shamonima and Kotov [1]; (c) the relative efficiencies of N_2: He and N_2: Ar reported by Arutyunov et al. [4]. The temperature dependence of k_0 has not been determined for M = N_2, therefore, the value of n is an average of that determined for M = He ($n \simeq 2$) and that determined for M = Ar ($n \simeq 3$).

High Pressure Rate Coefficients

No experimental data available. A value of $k_\infty = 3\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is estimated as calculated for F + NO + M→FNO + M [6]. This gives [N_2]$_c \cong 2.7\times 10^{21}$ molecule cm^{-3} at 300 K.

Preferred Value

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

Reliability

$\Delta \log k = \pm 0.5$ over range 200–400 K.

Comments on Preferred Value

Rough estimate indicating fall-off effects only to occur in the 10–100 atm range.

References

[1] Shamonima, N. F., and Kotov, A. G., Kinetika i Kataliz **20**, 233 (1979).

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

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[6] Quack, M., and Troe, J., Ber. Bunsenges. Phys. Chem. **81**, 329 (1977).

$FO + NO \rightarrow F + NO_2$

$\Delta H^\circ = -239$ 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			
2.0×10^{-11}	298	NASA, 1979 [2]	(b)
2.0×10^{-11}	298	CODATA, 1980 [3]	(b)
2.6×10^{-11}	298	NASA, 1981 [4]	(c)

Comments

(a) Discharge flow: mass spectrometric detection of FO. Psuedo-first order conditions, $[NO]_0 > [FO]_0$.

(b) Estimated.

(c) Based on reference [1].

Preferred Value

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

Reliability

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

Comments on Preferred Value

The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions have been reported to be negative with E/R values of -294 K and -260 K, respectively (CODATA preferred values).

References

[1] Ray, G. W., and Watson, R. T., J. Phys. Chem. **85**, 2955 (1981).
[2] NASA Ref. Publ. 1049, "The Stratosphere: Present and Future," Chapter 1, R. D. Hudson and E. R. Reed, editors (1979).
[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
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$HF + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HF + h\nu \rightarrow H + F$	566.57	211

HF is optically transparent within the wavelength region of interest is this review, i.e., $\lambda > 165$ nm. Safary et al. [1] observed the onset of a weak absorption continuum at 161.3 nm where the absorption cross section had a value of $\sim 1.5 \times 10^{-22}$ cm^2 molecule^{-1}.

References

[1] Safary, E., Romand, J., and Vodar, B., J. Chem. Phys. **19**, 379 (1951).

$COF_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$COF_2 + h\nu \rightarrow CO + F_2$	(1)	518	231
$\rightarrow COF + F$	(2)	539	222
$\rightarrow CO + 2F$	(3)	672	178
$\rightarrow CF_2 + O(^3P)$	(4)	697	172

Preferred Values

Absorption cross sections for COF_2 photolysis at 298 K

λ (nm)	$10^{20}\sigma/cm^2$	λ (nm)	$10^{20}\sigma/cm^2$
184.9	4.7	205.1	0.86
186.0	5.5	207.3	0.65
187.8	5.2	209.4	0.48
189.6	4.5	211.6	0.36
191.4	3.3	213.9	0.26
193.2	3.3	216.2	0.21
195.1	2.8	218.6	0.15
197.0	2.3	221.0	0.12
199.0	1.9	223.5	0.10
201.0	1.4	226.0	0.08
203.0	1.1		

Quantum yields for COF_2 photolysis at 298 K.
No recommendation.

Comments on Preferred Values

The preferred values of the absorption cross sections are those of Chou et al. [1], and by analogy with $COCl_2$ photolysis process (2) would be expected to be the primary photolytic process within the wavelength region of interest, 185 nm$\leqslant\lambda\leqslant$226 nm. These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [2] where detailed discussion can be found.

References

[1] Chou, C. C., Crescentini, G., Vera-Ruiz, H., Smith, W. S., and Rowland, F. S., Presented at the 173rd American Chemical Society National Meeting, New Orleans, March 1977.

[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data 9, 295 (1980).

$FONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}/kJ\ mol^{-1}$	$\lambda_{threshold}/nm$
$FONO_2 + h\nu \rightarrow FO + NO_2$	(1)	182	906
$\rightarrow F + NO_3$	(2)	140	854
$\rightarrow FONO + O(^3P)$	(3)	306	391
$\rightarrow FONO + O(^1D)$	(4)	496	241

Note: $\Delta H°_{298}$ values are given since the heat of formation of FONO at 0 K is not known. No experimental data are available for either the absorption cross sections or quantum yields for photodissociation of fluorine nitrate.

Preferred Values

No preferred values can be given in the absence of experimental data. In all probability, the absorption cross sections will be significantly lower than those of $ClONO_2$, resulting in low atmospheric J values.

5.7. Chlorine Compounds

$O + HOCl \rightarrow HO + ClO$

$\Delta H° = -30$ kJ mol^{-1}

Rate Coefficient Data: no experimental data available.

Preferred Values

$k = 6\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1\times10^{-11}\exp(-2200/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

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

Comments on Preferred Values

There are no experimental data. This is an estimated va based on rates of O-atom reactions with similar compounds, e.g., H_2O_2 (CODATA evaluation).

$$\begin{array}{lr} O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl & (1) \\ \rightarrow O(^3P) + CF_2Cl_2 & (2) \\ \rightarrow COF_2 + Cl_2 & (3) \\ \rightarrow COFCl + FCl & (4) \end{array}$$

$\Delta H^\circ(1) = -112.2$ kJ mol^{-1}

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

$\Delta H^\circ(3) = -580.3$ kJ mol^{-1}

$\Delta H^\circ(4) = -423$ 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	Addison, Donovan, and Garraway, 1981 [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	NASA, 1979 [4]	(e)
2.8×10^{-10}	298	CODATA, 1980 [5]	(f)
1.4×10^{-10}	298	NASA, 1981 [6]	(e)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time resolved production of $O(^3P)$ monitored by resonance absorption via the 3 $^3S_1$2 ^3P_J triplet at 130.2–130.6 nm.

(b) Flash photolysis: plate photometric detection (ultraviolet absorption) of ClO and O_3. Δ [ClO]$_{produced}$ / Δ [O_3]$_{removed}$ monitored. This value is a lower limit as Δ [ClO] may have been underestimated due to removal by any $O(^3P)$ formed in reaction (2).

(c) Flash photolysis. Plate photometric detection of ClO, and resonance absorption detection of $O(^3P)$ at ~130 nm. Corrections required for ClO formation via possible secondary reactions such as $CF_2Cl + O_3 \rightarrow ClO + CF_2O_2$. Channels (1) and (2) have been shown to be the dominant, but not necessarily exclusive, pathways.

(d) The rate constant for the quenching channel, k_2, was determined to be $(0.2 \pm 0.1)\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The overall rate constant for the reactive removal of $O^1D(k_1 + k_3 + k_4) = (1.2 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(e) Based on Davidson et al., 1978 [7].

(f) Based on Fletcher and Husain, 1976 [8], Davidson et al., 1978 [7], Jayanty et al., 1975 [9], Atkinson et al., 1976 [10], and Green and Wayne, 1977 [11].

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

Based on Force and Wiesenfeld [1] and Davidson et al. [7], the results of which are in excellent agreement. This is consistent with the recent data [12–14] on the reactions of $O(^1D)$ with atmospheric gases (N_2, O_2, N_2O, CO_2, etc.) which have supported the results from the NOAA Laboratories in preference to the results from the Cambridge Laboratory (Fletcher and Husain [8]). 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 CODATA preferred value for $k(O^1D + N_2O)$, i.e. 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}, yields values of k in excellent agreement with the preferred value. Both Addison et al. [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] Force, A. P., and Wiesenfeld, J. R., J. Phys. Chem. 85, 782 (1981).
[2] Gillespie, H. M., Garraway, J., and Donovan, R. J., J. Photochemistry 7, 29 (1977).
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[13] Brock, J., and Watson, R. T., Reported at the NATO Advanced Study Institute on Atmospheric Ozone, Protugal (1979). See Moortgat's review paper, Report No. FAA-EE-80-20 (1980).
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$$\begin{aligned} O(^1D) + CFCl_3 &\rightarrow ClO + CFCl_2 && (1)\\ &\rightarrow O(^3P) + CFCl_3 && (2)\\ &\rightarrow COFCl + Cl_2 && (3)\\ &\rightarrow COCl_2 + FCl && (4) \end{aligned}$$

$\Delta H°(1) = -148$ kJ mol^{-1}
$\Delta H°(2) = -189.4$ kJ mol^{-1}
$\Delta H°(3) = -581$ kJ mol^{-1}
$\Delta H°(4) = -424.8$ 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	Addision, Donovan, and Garraway, 1981 [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			
2.2×10^{-10}	298	NASA, 1979 [4]	(e)
3.5×10^{-10}	298	CODATA, 1980 [5]	(f)
2.2×10^{-10}	298	NASA, 1981 [6]	(e)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time resolved production of $O(^3P)$ monitored by resonance absorption via the $3^3S_1 - 2^3P_J$ triplet at 130.2–130.6 nm.

(b) Flash photolysis plate photometric detection (ultraviolet absorption) of ClO and O_3. $\Delta[ClO]_{produced} / \Delta[O_3]_{removed}$ monitored. This value is a lower limit as Δ [ClO] may have been underestimated due to removal by any $O(^3P)$ formed in reaction (2).

(c) Flash photolysis. Plate photometric detection of ClO, and resonance absorption detection of $O(^3P)$ at ~130 nm. Corrections required for ClO formation via possible secondary reactions such as $CFCl_2 + O_3 \rightarrow ClO + CFClO_2$. Channels (1) and (2) have been shown to be the dominant, but not necessarily exclusive, pathways.

(d) The quenching rate constant, k_2, was determined to be $(0.3 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The overall rate constant for the reactive removal of $O^1D(k_1 + k_3 + k_4) = (2.1 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(e) Based on Davidson et al., 1978 [7].

(f) Based on Fletcher and Husain, 1976 [8], Davidson et al., 1978 [7], Jayanty et al., 1975 [9], and Atkinson et al., 1976 [10].

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

Based on Force and Wiesenfeld [1] and Davidson et al. [7], the results of which are in excellent agreement. This is consistent with the recent data [11–13] on the reactions of O^1D with atmospheric gases (N_2, O_2, N_2O, CO_2, etc.) which have supported the results from the NOAA Laboratories in preference to the results from the Cambridge Laboratory. The results from the relative rate coefficient studies [9] and [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 CODATA preferred value for $k\,(O^1D + N_2O)$, i.e. 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}, yields values which are ~25% smaller and greater, respectively, than the preferred value. Both Addison et al. [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] Force, A. P., and Wiesenfeld, J. R., J. Phys. Chem. **85**, 782 (1981).

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$$
\begin{array}{lr}
\mathbf{O(^1D) + CCl_4 \rightarrow ClO + CCl_3} & \mathbf{(1)} \\
\mathbf{\rightarrow O(^3P) + CCl_4} & \mathbf{(2)} \\
\mathbf{\rightarrow COCl_2 + Cl_2} & \mathbf{(3)}
\end{array}
$$

$\Delta H°(1) = -161$ kJ mol^{-1}

$\Delta H°(2) = -189.7$ kJ mol^{-1}

$\Delta H°(3) = -563.2$ 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]	(a,b)
Reviews and Evaluations			
4.8×10^{-10}	298	CODATA, 1980 [2]	(c)

Comments

(a) Laser flash photolysis of O_3 at 248 nm. The time production of $O(^3P)$ monitored by resonance absorption $3^3S_1 - 2^3P_J$ triplet at 130.2–130.6 nm.

(b) The quenching rate constant, k_2, was determined to be $(0.49 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The overall rate constant for the reactive removal of $O^1D(k_1 + k_3) = (3.0 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

(c) Based on Fletcher and Husain, 1976 [3], Davidson et al., 1978 [4], and Jayanty et al., 1975 [5].

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

Based on Force and Wiesenfeld [1] and Davidson et al. [4], the results of which are in excellent agreement. This is consistent with the recent data [6–8] on the reactions of O^1D with atmospheric gases (N_2, O_2, N_2O, CO_2, etc.) which have supported the results from the NOAA laboratories in preference to the results from the Cambridge Laboratory. The results from the relative rate coefficient study [5] was not considered in this evaluation. Combining the value of k/k ($O^1D + N_2O$) reported in reference [5] with the CODATA preferred value of k ($O^1D + N_2O$), *i.e.* 1.2×10^{-10} cm^3 molecule^{-1} s^{-1}, 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 $O(^1D)$ with CF_2Cl_2 and $CFCl_3$ reactions. Consequently preferred values are given for both the overall rate constant, k, and for the branching ratio k_2/k.

References

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$Cl + HO_2 \rightarrow HCl + O_2$ (1)
$\rightarrow ClO + HO$ (2)

$\Delta H°(1) = -224$ kJ mol^{-1}

$\Delta H°(2) = +9$ 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			
$(6.9 \pm 3.5) \times 10^{-11}$	274–338	Cox, 1980 [1]	(a)
Reviews and Evaluations			
4.5×10^{-11}	298	NASA, 1979 [2]	(b)
4.1×10^{-11}	298	CODATA, 1980 [3]	(b)
4.8×10^{-11}	298	NASA, 1981 [4]	(c)

Comments

(a) Molecular modulation: ultraviolet detection of HO_2. k determined relative to $k(Cl + H_2)$. $k/k(Cl + H_2) = (3.0^{+5.1}_{-1.8})$ $\exp(+(2120 \pm 370/T))$. Combining the experimentally determined ratio of $k/k(Cl + H_2)$ with the CODATA preferred value of $k(Cl + H_2)$, i.e. $4.7 \times 10^{-11} \exp(-2340/T)$ cm^3 molecule^{-1} s^{-1} yields the expression, $k = 1.41 \times 10^{-10} \exp(-220/T)$ cm^3 molecule^{-1} s^{-1}. However, considering the uncertainties in both $k/k(Cl + H_2)$ and $k(Cl + H_2)$ a temperature invariant value was reported for k.

(b) Based on the relative rate coefficient studies of Leu and DeMore, 1976 [5], Cox and Derwent, 1977 [6], Poulet et al., 1978 [7] and Burrows et al., 1979 [8].

(c) Based on the relative rate coefficient data of Leu and DeMore, 1976 [5], Poulet et al., 1978 [7], Burrows et al., 1978 [8], and Cox, 1980 [1], but not Cox and Derwent, 1977 [6].

Preferred Value

$k_1 = 4.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 274–338 K.

Reliability

$$\Delta \log k = {}^{+0.3}_{-0.5} \text{ at } 298 \text{ K.}$$
$$\Delta (E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Value

The preferred value of 4.8×10^{-11} cm^3 molecule^{-1} s^{-1} for k at 298 K was obtained by averaging the reevaluated values of Leu and DeMore, 1976 [5], Poulet et al., 1978 [7], Burrows et al., 1978 [8], and the value of Cox, 1980 [1]. Cox, 1980 [1] reevaluated the earlier work of Cox and Derwent, 1977 [6], to determine a value of $\geqslant 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for k (due predominantly to a revised value for $k(Cl + H_2)$) which is consistent with the preferred value. The lack of a temperature dependence (reference [1]) is consistent with that expected for an atom-radical reaction. Based upon the data of Burrows et al., 1979 [8] an upper limit of 4.8×10^{-13} cm^3 molecule^{-1} s^{-1} can be placed on k_2 ($\geqslant 1\%$ of the total rate constant). However, this value is not given as a preferred value as there is an inconsistency between the values of $k_2(Cl + HO_2 \rightarrow ClO + HO)$, $k_{-2}(HO + ClO \rightarrow HO_2 + Cl)$ and the thermodynamic equilibrium constant, $K_{eq} = k_2/k_{-2}$ (see the HO + ClO data sheet for a more detailed discussion).

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$Cl + CH_4 \rightarrow HCl + CH_3$

$\Delta H° = +6.7$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.2 \pm 0.44) \times 10^{-12} \exp(-(1063 \pm 34)/T)$	221-298	Ravishankara and Wine, 1980 [1]	(a)
$(9.65 \pm 0.55) \times 10^{-13}$	298		
$(1.67 \pm 0.45) \times 10^{-12} \exp(-(1542 \pm 88)/T)$	298-375		
Reviews and Evaluations			
$9.9 \times 10^{-12} \exp(-1359/T)$	200-300	NASA, 1979 [2]	(b)
$9.9 \times 10^{-12} \exp(-1360/T)$	200-300	CODATA, 1980 [3]	(b)
$9.6 \times 10^{-12} \exp(-1350/T)$	200-300	NASA, 1981 [4]	(c)

Comments

(a) Flash photolysis: resonance fluorescence detection of atomic chlorine. Non-linear Arrhenius behavior was observed. At temperatures at and below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture. Ravishankara and Wine suggested that this was due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ spin states of atomic chlorine at high values of the pseudo-first order rate constant, k', i.e. if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations, i.e. high values of k'. The Arrhenius expressions for k between 221 and 298 K, and between 298 and 375 K were derived from the data shown in their table II (excluding the high CH_4 data in the $He/Cl_2/CH_4$ system).

(b) Based on the absolute rate coefficient data of Watson et al., 1976 [5], Whytock et al., 1977 [6], Michael and Lee, 1977 [7], Manning and Kurylo, 1977 [8], Zahniser et al., 1978 [9], Lin et al., 1978 [10], and Keyser, 1978 [11], and the relative rate coefficient data of Pritchard et al., 1954 [12], Knox, 1955 [13], Pritchard et al., 1955 [14], Knox and Nelson, 1959 [5], and Lin et al., 1978 [10].

(c) Based on the same data as for NASA, 1979 [2] (see note (b)) and Ravishankara and Wine, 1980 [1].

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 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 reaction was discussed in detail in the previous CODATA evaluation [3], i.e. the non-linear Arrhenius behavior and the differences between the results from the absolute rate coefficient studies and the relative rate coefficient studies. Inclusion of the data of Ravishankara and Wine [1] results in minor modifications to the earlier preferred CODATA values [3].

The preferred value at 298 K was obtained by taking the mean from the most reliable absolute (Watson et al. [5], Whytock et al. [6], Michael and Lee [7], Manning and Kurylo [8], Zahniser et al. [9], Lin et al. [10], Keyser [11], and Ravishankara and Wine [1]) and the most reliable relative (Pritchard et al. [12], Knox [13], Pritchard et al. [14], Knox and Nelson [15] and Lin et al. [9]) rate coefficient studies.

The preferred Arrhenius expression was derived to best fit all the reliable experimental data between 200 and 300 K. Data obtained above 300 K were not considered due to the non-linear Arrhenius behavior observed in the absolute rate coefficient studies ([1], [6], [10] and [11]). The average values of k at 230 K are: 3.19×10^{-14} cm^3 molecule^{-1} s^{-1} (flash photolysis [1,5,6,8]); 2.67×10^{-14} cm^3 molecule^{-1} s^{-1} (discharge flow [9,11]); and 2.27×10^{-14} cm^3 molecule^{-1} s^{-1} (competitive chlorination [10,12–15]). These differences increase at lower temperatures. Ravishankara and Wine 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 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 values of k 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 $= 1.07 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}), and (k at 230 K $= 3.19 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}).

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$Cl + H_2CO \rightarrow HCl + HCO$

$\Delta H^\circ = -67.4$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.7 \pm 1.0)\times10^{-11}$	298	Foon, LeBras, and Combourieu, 1979 [1]	(a)
$(7.4 \pm 0.7)\times10^{-11}$	295	Fasano and Nogar, 1981 [2]	(b)
Reviews and Evaluations			
$9.2\times10^{-11}\exp(-68/T)$	200–500	NASA, 1979 [3]	(c)
$7.9\times10^{-11}\exp(-34/T)$	200–500	CODATA, 1980 [4]	(c)
$9.2\times10^{-11}\exp(-68/T)$	200–500	NASA, 1981 [5]	(c)

Comments

(a) Discharge flow: EPR detection of atomic chlorine.

(b) Pulsed CO_2 laser induced photodissociation of $CFCl_3$ to produce Cl. HCl infrared chemiluminescence used to monitor the reaction.

(c) Based on the absolute rate coefficient studies of Michael et al., 1979 [6] and Anderson and Kurylo, 1979 [7], and the relative rate coefficient study of Niki et al., 1978 [8].

Preferred Values

$k = 7.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.9\times10^{-11}\exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over range 200–500 K.

Reliability

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

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

Comments on Preferred Values

The results from Michael et al., 1979 [6], Anderson and Kurylo, 1979 [7], Niki et al., 1978 [8], and Fasano and Nogar, 1981 [2] are in good agreement at ~298 K, but ~50% greater than the value reported by Foon et al., 1979 [1]. Therefore, the data of Foon et al. is rejected, and the preferred values remain unchanged from the previous CODATA evaluation.

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$HO + HOCl \rightarrow H_2O + ClO$

$\Delta H^\circ = -101$ kJ mol^{-1}

Rate Coefficient Data: no experimental data available.

Preferred Values

$k = 1.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3 \times 10^{-12} \exp(-150/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

$\Delta (E/R) = ^{+850\ \mathrm{K}}_{-150\ \mathrm{K}}$.

Comments on Preferred Values

There are no experimental data for this reaction. This is an estimated value based on the rate coefficient for the HO + H_2O_2 reaction (CODATA evaluation).

$HO + ClO \rightarrow HO_2 + Cl$ (1)

$\rightarrow HCl + O_2$ (2)

$HO + ClO + (M) \rightarrow HOClO + (M)$ (3)

$\Delta H^\circ(1) = -9$ kJ mol^{-1}

$\Delta H^\circ(2) = -234$ 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			
$(3.9 \pm 0.6) \times 10^{-12}$	295	Garraway and Donovan, 1980 [1]	(a)
Reviews and Evaluations			
9.1×10^{-12}	298	NASA, 1979 [2]	(b)
9.1×10^{-12}	298	CODATA, 1980 [3]	(b)
9.1×10^{-12}	298	NASA, 1981 [4]	(b)

Comments

(a) Flash photolysis: resonance absorption detection of HO. Total pressure was varied from 10–240 Torr (M = SF_6), and k was observed to increase from $(3.4–4.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, possibly indicating the presence of a third-order complex forming process.

(b) Based on the data of Leu and Lin, 1979 [5].

Preferred Value

$k = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The preferred value is that reported by Leu and Lin [5]. The results are not in particularly good agreement (a factor of 2.7 in the low pressure regime), but this may be partly accounted for insofar as Garraway and Donovan only claimed a factor of two accuracy in their determination of k due to the complexity of their reaction system. A lower limit of 0.65 was determined by Leu and Lin for k_1/k at 298 K. The approach was somewhat indirect and the actual value of k_1/k may possibly be unity. It should be noted that the lower limit of 5.9×10^{-12} cm^3 molecule^{-1} s^{-1} reported for k_1 by Leu and Lin is not compatible with the thermodynamic equilibrium constant, $K_{eq} = k_1(HO + ClO \rightarrow HO_2 + Cl)/k_{-1}(HO_2 + Cl \rightarrow HO + ClO)$, and the upper limit of 3×10^{-13} cm^3 molecule^{-1} s^{-1} placed on k_{-1} by Burrows et al. [6]. For all the data to be consistent it requires that either: (a) k_1 is lower than reported by Leu and Lin (i.e. $< 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) or (b) k_{-1} is greater than 3×10^{-13} cm^3 molecule^{-1} s^{-1} or (c) ΔH°_{f298} (HO_2) < 10.5 kJ mol^{-1} (i.e. $\leqslant 7.5$ kJ mol^{-1}). With the results of Garraway and Donovan indicating a possible pressure dependence in k, it is clear that additional studies of the rate constant and mechanism of this reaction as a function of pressure and temperature are required.

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$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$

$\Delta H^\circ = -74$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.51 \pm 1.10)\times10^{-12}\exp((-1313 \pm 111)/T)$	247–483	Jeong and Kaufman, 1981 [1]	(a)
$(3.95 \pm 0.52)\times10^{-14}$	293		
$(4.10 \pm 0.68)\times10^{-14}$	297	Paraskevopoulos, Singleton, and Irwin, 1981 [2]	(b)
Reviews and Evaluations			
$2.2\times10^{-12}\exp(-1142/T)$	240–422	NASA, 1979 [3]	(c)
$2.2\times10^{-12}\exp(-1140/T)$	240–422	CODATA, 1980 [4]	(c)
$1.8\times10^{-12}\exp(-1112/T)$	~220–300	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow: resonance fluorescence detection of HO. Although an Arrhenius expression has been entered in the table, the experimental data was observed to exhibit a non-linear Arrhenius behavior and was best described by a three parameter equation of the form, $k = AT^n \exp(-B/T)$, where $n \simeq 2$, i.e. $k = 4.22\times10^{-18}\,T^{1.97}\exp(-599/T)$ cm^3 molecule^{-1} s^{-1}.

(b) Flash photolysis-resonance absorption detection of HO.

(c) These expressions were derived from the absolute rate coefficient data of Howard and Evenson, 1976 [6], Davis et al., 1976 [7], and Perry et al., 1976 [8].

(d) Derived using the absolute rate coefficient data of Jeong and Kaufman [1], Howard and Evenson [6], Davis et al. [7], and Perry et al. [8]. Data fit to an expression of the form, $k = BT^2\exp(-C/T)$, and then an Arrhenius expression ($k = A\exp(-E/T)$) centered at 265 K was derived, where $A = B\times e^2\times T^2$ and $E = C + 2T$.

Preferred Values

$k = 4.2\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9\times10^{-12}\exp(-1120/T)$ cm^3 molecule^{-1} s^{-1} over range 247–350 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values were obtained using the absolute rate coefficient data of Howard and Evenson [6], Davis et al., [7], Perry et al., [8], Jeong and Kaufman [1] and Paraskevopoulos et al. [2] which are in good agreement. Although the E/R values vary from 1097 K (reference [7]) to 1359 K (reference [8]), the discrepancy can possible be attributed to the reaction exhibiting non-linear Arrhenius behavior (reference [1]) and being studied over different temperature ranges, i.e. 250–350 K (reference [7]) and 298–422 K (reference [8]). The preferred value of k at 298 K was obtained by taking the mean of the values reported at ~298 K in references [1] (normalized to 298 K) and [2,6–8]. Owing to the possible non-linear Arrhenius behavior of the reaction the preferred Arrhenius expression was derived using only data obtained at and below 350 K. An alternate expression which allows for the possible non-linear Arrhenius behavior can be obtained by fitting all of the absolute rate data from references [1,2,6–8] to a three parameter equation of the form, $k = AT^2\exp(-B/T)$. This results in the equation $3.49\times10^{-18}\,T^2\exp(-582/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 247–483 K.

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$HO + CH_2FCl \rightarrow H_2O + CHFCl$

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		
$(2.44 \pm 0.64)\times 10^{-12}\exp(-(1147 \pm 91)/T)$	250–486	Jeong and Kaufman, 1981 [4]	(d)
$(4.94 \pm 0.60)\times 10^{-14}$	295		
$(4.45 \pm 0.66)\times 10^{-14}$	297	Paraskevopoulos, Singleton, and Irwin, 1981 [5]	(e)
Reviews and Evaluations			
$3.5\times 10^{-12}\exp(-1322/T)$	245–375	NASA, 1979 [6]	(f)
$2.0\times 10^{-12}\exp(-1134/T)$	~220–300	NASA, 1980 [7]	(g)

Comments

(a) Discharge flow: laser magnetic resonance detection of HO.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) Flash photolysis: resonance absorption detection of HO.

(d) Discharge flow: resonance fluorescence detection of HO. Although an Arrhenius expression has been entered in the table, the experimental data was observed to exhibit a non-linear Arrhenius behavior and was best described by a three parameter equation of the form $k = AT^n \exp(-B/T)$, where $n \simeq 2$, i.e. $k = 2.6\times 10^{-18}\, T^2 \exp(-459/T)$ cm^3 molecule^{-1} s^{-1}.

(e) Flash photolysis-resonance absorption detection of HO.

(f) This expression was derived from the absolute rate coefficient data reported in references [1–3].

(g) Derived using the data reported in references [1–4]. Data fit to an expression of the form, $k = BT^2 \exp(-C/T)$, and then an Arrhenius expression, $k = A \exp(-E/T)$, centered at 265 K was derived, where $A = B \times e^2 \times T^2$ and $E = C + 2T$.

Preferred Values

$k = 4.4\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6\times 10^{-12}\exp(-1210/T)$ cm^3 molecule^{-1} s^{-1} over range 245–350 K.

Reliability

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

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

Comments on Preferred Values

The preferred values were obtained using the absolute rate coefficient data from references [1–5] which are in good agreement. Owing to the possible non-linear Arrhenius behavior of the reaction [1] the preferred Arrhenius expression was derived using only data obtained at and below 350 K. An alternate expression which allows for the possible non-linear Arrhenius behavior can be obtained by fitting all the absolute rate data to a three parameter equation of the form, $k = AT^2 \exp(-B/T)$. This results in the equation $3.8\times 10^{-18}\, T^2 \exp(-604/T)$ cm^3 molecule^{-1} s^{-1} over range 245–486 K.

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$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$

$\Delta H° = -66$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Comments
Absolute Rate Coefficients			
$(1.28 \pm 0.66) \times 10^{-12} \exp(-(1671 \pm 191)/T)$	293–482	Jeong and Kaufman, 1981 [1]	(a)
$(4.83 \pm 0.63) \times 10^{-15}$	293		
$(4.58 \pm 0.58) \times 10^{-15}$	297	Paraskevopoulos, Singleton, and Irwin, 1981 [2]	(b)
Reviews and Evaluations			
$1.2 \times 10^{-12} \exp(-1666/T)$	250–430	NASA, 1979 [3]	(c)
$1.3 \times 10^{-12} \exp(-1670/T)$	240–400	CODATA, 1980 [4]	(c)
$7.8 \times 10^{-13} \exp(-1530/T)$	~220–300	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow-resonance fluorescence detection of HO. Although an Arrhenius expression has been entered in the table, the experimental data was observed to exhibit a non-linear Arrhenius behavior and was best described by a three parameter equation of the form, $k = AT^n \exp(-B/T)$, where $n \simeq 2$, i.e. $k = 1.28 \times 10^{-18}\ T^{2.0} \exp(-946/T)$ cm^3 molecule^{-1} s^{-1}.

(b) Flash photolysis-resonance absorption detection of HO.

(c) These expressions were derived from the absolute rate coefficient data of Atkinson et al., 1975 [6], Howard and Evenson, 1976 [7], Watson et al., 1977 [8], Chang and Kaufman, 197 [9], and Handwerk and Zellner, 1978 [10], but not Clyne and Holt, 1979 [11].

(d) Derived using the absolute rate coefficient data of Jeong and Kaufman [1], Atkinson et al., [6], Howard and Evenson [7], Watson et al., [8], Chang and Kaufman [9], Handwerk and Zellner [10]. Data fit to an expression of the form, $k = BT^2 \exp(-C/T)$, and then an Arrhenius expression, $k = A \exp(-E/T)$, centered at 265 K was derived, where $A = B \times e^2 \times T^2$ and $E = C + 2T$.

Preferred Values

$k = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-12} \exp(-1620/T)$ cm^3 molecule^{-1} s^{-1} over range 250–360 K.

Reliability

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

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

Comments on Preferred Values

The preferred values were obtained using the absolute rate coefficient data of Atkinson et al. [6], Howard and Evenson [7], Watson et al. [8], Chang and Kaufman [9], Handwerk and Zellner [10], Jeong and Kaufman [1] and Paraskevopoulos et al. [2] which are in good agreement. Owing to the possible non-linear Arrhenius behavior of the reaction [1] the preferred Arrhenius expression was derived using only data obtained at and below 360 K (if the data used were restricted to $T \leqslant 350$ K then the expression derived was $1.2 \times 10^{-12} \exp(-1653/T)$ cm^3 molecule^{-1} s^{-1}). An alternate expression which allows for the possible non-linear Arrhenius behavior can be obtained by fitting all the absolute rate data from references [1,2,6–10] to a three parameter equation of the form, $k = AT^2 \exp(-B/T)$. This results in the equation $1.5 \times 10^{-18}\ T^2 \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over range 250–482 K.

References

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$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$

$\Delta H^\circ = -92$ kJ mol^{-1}

Rate coefficient data

k /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.21 \pm 0.26)\times10^{-12} \exp(-(1057 \pm 76)/T)$	250–483	Jeong and Kaufman, 1980 [1]	(a)
$(3.37 \pm 0.44)\times10^{-14}$	295		
$(3.39 \pm 0.86)\times10^{-14}$	297	Paraskevopoulos, Singleton, and Irwin, 1981 [2]	(b)
Reviews and Evaluations			
$1.5\times10^{-12} \exp(-1184/T)$	240–420	NASA, 1979 [3]	(c)
$1.5\times10^{-12} \exp(-1180/T)$	240–400	CODATA, 1980 [4]	(c)
$8.9\times10^{-13} \exp(-1013/T)$	~220–300	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow-resonance fluorescence detection of HO. Although an Arrhenius expression has been entered in the table, the experimental data was observed to exhibit a non-linear Arrhenius behavior and was best described by a three parameter equation of the form $k = AT^n \exp(-B/T)$, where $n \simeq 2$, i.e. $k = 1.22\times10^{-18}\, T^{2.0} \exp(-338/T)$ cm^3 $molecule^{-1}$ s^{-1}.

(b) Flash photolysis-resonance absorption detection of HO.

(c) These expressions were derived from the absolute rate coefficient data of Howard and Evenson, 1978 [6], Perry et al., 1976 [7], Watson et al., 1977 [9], but not Clyne and Holt, 1979 [10].

(d) Derived using the absolute rate coefficient data of Jeong and Kaufman [1], Howard and Evenson [6], Perry et al. [7], Watson et al. [8], and Chang and Kaufman [9], but not Clyne and Holt [10]. Data fit to an expression of the form, $k = BT^2 \exp(-C/T)$, and then an Arrhenius expression, $k = A \exp(-E/T)$ centered at 265 K was derived, where $A = B \times e^2 \times T^2$ and $E = C + 2T$

Preferred Values

$k = 3.0\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 1.1\times10^{-12} \exp(-1070/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 240–350 K.

Reliability

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

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

Comments on Preferred Values

The preferred value of k at 298 K was obtained by taking the mean of the absolute rate coefficients reported by Howard and Evenson [6], Perry et al. [7], Watson et al. [8], Chang and Kaufman [9], Jeong and Kaufman [1], and Paraskevopoulos et al. [2] which are in good agreement. Owing to the possible non-linear Arrhenius behavior of the reaction [1] the preferred Arrhenius expression was derived using only data obtained at and below 350 K. An alternate expression which allows for the possible non-linear Arrhenius behavior can be obtained by fitting all of the absolute rate data from references [1,2,6–9] to a three parameter equation of the form, $k = AT^2 \exp(-B/T)$. This results in the equation $1.7\times10^{-18}\, T^{2.0} \exp(-483/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 241–483 K.

References

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HO + C_2HCl_3→Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.4) \times 10^{-12}$	296	Howard, 1976 [1]	(a)
$(5.32 \pm 0.71) \times 10^{-13} \exp(+(445 \pm 41)/T)$	234–420	Chang and Kaufman, 1977 [2]	(b)
$(2.37 \pm 0.10) \times 10^{-12}$	296		
Relative Rate Coefficients			
$(4.5 \pm 1.3) \times 10^{-12}$	298	Winer et al., 1976 [3]	(c)
Reviews and Evaluations			
$5.0 \times 10^{-13} \exp(445/T)$	234–420	NASA, 1979 [4]	(d)
$5.0 \times 10^{-13} \exp(445/T)$	234–420	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow-laser magnetic resonance detection of HO.

(b) Discharge flow-resonance fluorescence detection of HO.

(c) Photochemical smog chamber. k/k(HO + iso-butene) = 0.088. Combining this ratio with the value of 5.1×10^{-11} cm^3 molecule^{-1} s^{-1} for k (HO + iso-butene) yields the value of k entered in the table [6].

(d) Based on references [1] and [2].

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 range 234–420 K.

Reliability

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

$\Delta (E/R) = \pm 445$ K.

Comments on Preferred Values

The preferred value at 298 K is a mean of the value reported by Howard, and Chang and Kaufman. The value reported by Winer et al. is a factor of 2 greater than the other values and is not considered in deriving the preferred value at 298 K. The preferred Arrhenius parameters are based on those reported by Chang and Kaufman (the A-factor is reduced to yield the preferred value at 298 K).

References

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HO + C_2Cl_4→Products

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.70 \pm 034) \times 10^{-13}$	296	Howard, 1976 [1]	(a)
$(9.44 \pm 1.34) \times 10^{-14} \exp(-(1199 \pm 55)/T)$	297–420	Chang and Kaufman, 1977 [2]	(b)
$(1.69 \pm 0.07) \times 10^{-13}$	297		
Relative Rate Coefficients			
$(2.2 \pm 0.7) \times 10^{-12}$	298	Winer et al., 1976 [3]	(c)
Reviews and Evaluations			
$9.4 \times 10^{-12} \exp(-1200/T)$	250–420	NASA, 1979 [4]	(d)
$9.4 \times 10^{-12} \exp(-1200/T)$	250–420	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow-laser magnetic resonance detection of HO.

(b) Discharge flow-resonance fluorescence detection of HO.

(c) Photochemical smog chamber. $k/k(\mathrm{HO} + \text{iso-butene}) = 0.044$. Combining this ratio with the value of $5.1\times10^{-11}\,\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ for $k(\mathrm{HO} + \text{iso-butene})$ yields the value of k entered in the table [6].

(d) Based on reference [2].

Preferred Values

$k = 1.7\times10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ at 298 K.

$k = 9.4\times10^{-12}\exp(-1200/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ over range 297–420 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K is a mean of the values reported by Howard, and Chang and Evenson. The value reported by Winer et al., which is more than a factor of 10 greater, is rejected. The preferred Arrhenius parameters are those of Chang and Kaufman.

References

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$\mathrm{ClO + HO_2 \rightarrow HOCl + O_2}$ (1)

$\mathrm{\rightarrow HCl + O_3}$ (2)

$\mathrm{ClO + HO_2 + (M) \rightarrow HOOClO + (M)}$ (3)

$\Delta H^\circ(1) = -191\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^\circ(2) = -62\ \mathrm{kJ\ mol^{-1}}$

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

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$3.3\times10^{-11}\exp(-850/T) + 4.5\times10^{-12}(T/300)^{-3.7}$	235–393	Stimpfle, Perry, and Howard, 1979 [1]	(a)
$(6.3\pm1.3)\times10^{-12}$	298		
$(4.5\pm0.9)\times10^{-12}$	298	Leck, Cook, and Birks, 1980 [2]	(b)
$(5.4^{+1}_{-2})\times10^{-12}$	298	Burrows and Cox, 1981 [3]	(c)
Branching Ratio			
$k_2/k \leqslant 0.02$	298	Leck, Cook, and Birks, 1980 [2]	(d)
$k_2/k \leqslant 0.015$	298	Leu, 1980 [4]	(d)
$k_2/k \leqslant 0.03$	248		
$k_2/k \leqslant 0.003$	298	Burrows and Cox, 1981 [3]	(c)
Reviews and Evaluations			
5.2×10^{-12}	298	NASA, 1979 [5]	(e)
5.2×10^{-12}	298	CODATA, 1980 [6]	(e)
$4.6\times10^{-13}\exp(+710/T)$	235–298	NASA, 1981 [7]	(f)

Comments

(a) Discharge flow: laser magnetic resonance detection of $\mathrm{HO_2}$. Non-linear Arrhenius behavior was observed. The experimental data were best fit by the four parameter expression shown in the table. The value of k at 298 K shown in the previous CODATA review is superseded by that entered in this table.

(b) Discharge flow: mass spectrometric detection of ClO and HOCl. The value shown in the previous CODATA review is superseded by that entered in this table.

(c) Molecular modulation: ultraviolet absorption detection of ClO and $\mathrm{HO_2}$, chemiluminescence detection of $\mathrm{O_3}$ at 1 atmosphere total pressure.

(d) Upper limits of k_2/k based on the discharge flow: mass spectrometric detection of $\mathrm{O_3}$.

(e) Based on the absolute rate coefficient data of Reimann and Kaufman, 1978 [8], Stimpfle et al., 1979 [1], (provisional value), and Leck et al., 1980 [2] (provisional value), but not Poulet et al., 1978 [9].

(f) Based on the 298 K data of Reimann and Kaufman, 1978 [7], Leck et al., 1980 [2], and Burrows et al., 1980 [3], and the low-temperature data ($T \leqslant 298$ K) of Stimpfle et al., 1979 [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 range 235–298 K.
$k_2 \leqslant 2.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = {}^{+250\ \mathrm{K}}_{-700\ \mathrm{K}}$.

Comments on Preferred Values

The preferred value at 298 K is based on the data of Reimann and Kaufman, 1978 [8], Stimpfle et al., 1979 [1], Leck et al., 1980 [2] and Burrows et al., 1980 [3] which are in good agreement. The only temperature dependence study (Stimpfle et al.) observed a non-linear Arrhenius behavior. Their data were best described by a four parameter equation of the form, $k = A\mathrm{e}^{-B/T} + CT^n$, possibly suggesting that two different mechanisms may be occuring. Two possible preferred values can be forwarded for the temperature dependence of k, (a) an expression of the form suggested by Stimpfle et al., but where the values of A and C are adjusted to yield a value of 5.0×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K, or a simple Arrhenius expression which fits the data obtained at and below 298 K (normalized to 5.0×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K). The latter expression is preferred. The upper limit of 2.0×10^{-14} cm^3 molecule^{-1} s^{-1} for k_2 at 298 K is based on the data of Burrows and Cox [3]. The agreement between the low-pressure values (references [1], [2], and [7]) and the one atmosphere value (reference [3]) suggests the absence of a third-order complex forming process.

References

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$ClO + H_2CO \rightarrow HOCl + HCO$

$\Delta H^\circ = -34$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$< 10^{-15}$	298	Poulet, LeBras, and Combourieu, 1980 [1]	(a)

Comments

(a) Discharge flow-ESR detection of ClO.

Preferred Value

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

Comments on Preferred Value

Preferred value is that given by the only published study of this reaction. On the basis of the upper limiting value of the rate constant, this reaction cannot be of any importance in stratospheric chemistry.

References

[1] Poulet, G., LeBras, G., and Combourieu, J., Geophys. Res. Lett. 7, 413 (1980).

$ClO + NO \rightarrow Cl + NO_2$

$\Delta H^\circ = -38.1$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.61 \pm 0.16) \times 10^{-11}$	295	Clyne and MacRobert, 1980 [1]	(a)
$(7.1 \pm 1.4) \times 10^{-12} \exp(+(270 \pm 50)/T)$	202–393	Lee et al., 1982 [2]	(b)
$(1.78 \pm 0.06) \times 10^{-11}$	296		
Reviews and Evaluations			
$7.8 \times 10^{-12} \exp(250/T)$	227–415	NASA, 1979 [3]	(c)
$8.9 \times 10^{-12} \exp(210/T)$	227–415	CODATA, 1980 [4]	(d)
$6.5 \times 10^{-12} \exp(283/T)$	202–415	NASA, 1981 [5]	(e)

Comments

(a) Discharge flow: mass spectrometric detection of ClO.

(b) Discharge flow: laser magnetic detection of ClO.

(c) Based on the absolute rate coefficient data of Clyne and Watson, 1974 [6], Leu and DeMore, 1978 [7], and Ray and Watson, 1981 [8], and the relative rate coefficient data of Zahniser and Kaufman, 1977 [9]. The E/R value was derived by taking the average of the E/R values reported in references [7] and [9].

(d) Based on the same data used for NASA, 1979 [3] (see note (c)). However, the E/R value of Zahniser and Kaufman, 1977 [9] was re-evaluated prior to using it to derive the preferred E/R value.

(e) Based on the absolute rate coefficient data of Clyne and Watson, 1974 [6], Leu and DeMore, 1978 [7], Ray and Watson, 1981 [8], Clyne and MacRobert, 1980 [1], and Lee et al., 1982 [2].

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 range 202–415 K.

Reliability

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

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

Comments on Preferred Values

The absolute rate coefficient data reported by Clyne and Watson, 1974 [6], Leu and DeMore, 1978 [7], Ray and Watson, 1981 [8], Clyne and MacRobert, 1980 [1], and Lee et al., 1982 [2] are in excellent agreement at ~298 K and are averaged to yield the preferred value. The value reported by Zahniser and Kaufman, 1977 [9] from a competitive study is not used in the derivation of the preferred value at 298 K as it is ~33% higher than the other values. The E/R values reported by Leu and DeMore, 1978 [7] and Lee et al., 1982 [2] are in excellent agreement. Although the E/R value reported by Zahniser and Kaufman, 1977 [9] is in fair agreement with the other values, it was not considered as it is dependent upon the E/R value assumed for the $Cl + O_3$ reaction. The Arrhenius expression was derived from a least squares fit to the data reported in references [1,2,6–8].

References

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$$\begin{aligned} \mathrm{ClO + NO_2 + M} &\rightarrow \mathrm{ClONO_2 + M} \quad (1)\\ &\rightarrow \mathrm{OClONO + M} \quad (2)\\ &\rightarrow \mathrm{ClOONO + M} \quad (3)\end{aligned}$$

$\Delta H°(1) = -109$ kJ mol^{-1}

Low pressure rate coefficients

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

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.50 \pm 0.12)\times10^{-31}$ [N$_2$]	298	Molina, Molina, and Ishiwata, 1980 [1]	(a)
Reviews and Evaluations			
$1.6\times10^{-31}(T/300)^{-3.4}$ [N$_2$]	200–300	NASA, 1979 [5], 1981 [7]	(b)
$3.5\times10^{-32}(T/300)^{-3.8}$ [N$_2$] (k_1)	200–300		(b)
$1.7\times10^{-31}(T/300)^{-3.0}$ [N$_2$]	250–450	CODATA, 1980 [6]	(c)

Comments

(a) Flash photolysis-uv absorption technique monitoring the ClO decay. Fourier transform infrared spectroscopy was also used to monitor reaction products. The rate coefficient was found to decrease by about a factor of 3 when OClO was added. OClO was postulated to be a scavenger for ClNO$_3$ isomers other than ClONO$_2$ which regenerates ClO. The results confirm the earlier suggestion, that several isomers are formed, which was based on inconsistencies between recombination and thermal dissociation data (refs. [2] and [3]). A theoretical analysis in ref. [4] supports this conclusion by indicating that less stable product isomers can be formed preferentially.

(b) Two recommendations for channel 1 to account for the suggested isomer formation (refs. [2] and [3]).

(c) Average of several results which were in good agreement.

Preferred Values

$k_0 = 1.6\times10^{-31}$ [N$_2$] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 1.6\times10^{-31}(T/300)^{-3.4}$ [N$_2$] over range 250–420 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$ over range 250–420 K.

Comments on Preferred Values

The preferred value of k_0 is an average of the present and earlier data which all agree quite well. The k_0 value is based on measurements of the disappearance of ClO. Based on the studies of Molina et al. [1] and Knauth [2] there is evidence for more than one reaction pathway. However, it is difficult to give a firm recommendation for the branching ratio on the basis of the data available.

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
$1.5\times10^{-11}(T/300)^{-1.9}$	200–300	NASA, 1979 [1], 1981 [3]	
1.2×10^{-11}	200–300	CODATA, 1980 [6]	
2.0×10^{-11}	298	Sander, Ray and Watson, 1981 [8]	(a)

Comments

(a) New evaluation of earlier fall-off data from Cox and Lewis [9] with theoretically calculated and empirically fitted F_c values.

Preferred Value

$k_\infty = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

Comments on Preferred Value

The k_∞ value derived here is preferred to the earlier value since it was derived from a proper fit of the fall-off curve. The temperature dependence chosen here corresponds to the normal behaviour of analogous reactions.

Intermediate Fall-off Range

From the preferred values one derives [N$_2$]$_c$ $= 1.25\times10^{20}$ molecule cm^{-3} at 298 K. The theoretically predicted F_c value of 0.45 ± 0.11 is in good agreement with the fitted F_c of 0.5 ± 0.1 [8] at 298 K. For typical T-dependences of F_c, see the $N_2O_5 \rightarrow NO_2 + NO_3$ data sheet.

References

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HOCl + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HOCl + h\nu \rightarrow HCl + O(^3P)$	(1)	230	520
$\rightarrow HO + Cl$	(2)	233	513
$\rightarrow ClO + H$	(3)	393	304
$\rightarrow HCl + O(^1D)$	(4)	420	285

Absorption cross section data

Wavelength range/nm	Reference	Comments
311–352	Spence, Edney and Hanst, 1980 [1]	(a)

Comments

(a) HOCl formed by irradiation of $H_2O_2/Cl_2/O_3$ mixtures by light of wavelengths > 300 nm at $T = 295$ K. Optical pathlength of 13.5 m was used for the uv measurements. HOCl concentrations determined from the 1226 cm^{-1} infra-red band using an absorption coefficient of 45 atm^{-1} (Su et al., 1979 [2]).

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
200	5.2	310	6.2
210	6.1	320	5.0
220	11.0	330	3.7
230	18.6	340	2.4
240	22.3	350	1.4
250	18.0	360	0.8
260	10.8	370	0.45
270	6.2	380	0.24
280	4.8	390	0.15
290	5.3	400	0.05
300	6.1	410	0.04

Quantum yields for HOCl photolysis at 298 K.
$\Phi_2 = 1.0$ for $\lambda > 200$ nm.

Comments on Preferred Values

The preferred absorption cross sections are taken directly from the study of Knauth et al. 1979 [3]. The studies of Jaffe and DeMore, 1977 [4], Molina and Molina, 1978 [5], and Knauth e al. [3] all derived absorption cross sections for HOCl from gas phase spectra of equilibrium mixtures of H_2O-Cl_2O-HOCl. In order to derive accurate absorption cross sections for HOCl the value of K_{eq} is required. The equilibrium constants determined by Knauth et al., Jaffe and DeMore, and Niki et al., 1979 [6] are in excellent agreement with a value of ~ 0.08 at 298 K. The cross sections derived from Molina and Molina's data recalculated using a value of ~ 0.08 for K_{eq} are in excellent agreement with the results of Knauth et al. (Molina and Molina's reported values were derived using a value of 0.25 for K_{eq}.) The values of the absorption cross sections reported by Spence et al. are approximately a factor of 2 greater than those preferred. These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [7] where detailed discussion can be found regarding all experimental and theoretical studies of the HOCl ultraviolet spectrum. The preferred quantum yield values are based on the data reported by Molina et al., 1980 [8].

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$COFCl + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$COFCl + h\nu \rightarrow CO + FCl$	(1)	266	450
$\rightarrow COF + Cl$	(2)	378	316
$\rightarrow COCl + F$	(3)	489	244
$\rightarrow CO + F + Cl$	(4)	517	231
$\rightarrow CFCl + O(^3P)$	(5)	706	169

Note: $\Delta H°_{298}$ values are given since the heat of fomration of COFCl at 0 K is not known.

Preferred Values

Absorption cross sections for COFCl photolysis at 298 K

λ (nm)	$10^{20}\sigma$/cm^2	λ (nm)	$10^{20}\sigma$/cm^2
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

Quantum yields for COFCl photolysis at 298 K.
No recommendation.

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Chou et al. [1]. Data attributed to Chou et al. in Watson [2] has since been revised. Although there have been no quantum yield studies of COFCl photolysis it is reasonable to assume that by analogy with $COCl_2$ photolysis process (2) dominates. These recommendations are unchanged from those give in the previous evaluation, CODATA, 1980 [3].

References

[1] Chou, C. C., Crescentini, G., Vera-Ruiz, H., Smith, W. S., and Rowland, F. W., Presented at the 173rd American Chemical Society National Meeting, New Orleans, March 1977.
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$ClONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	(1)	109	1100
$\rightarrow Cl + NO_3$	(2)	166	721
$\rightarrow ClONO + O(^3P)$	(3)	306	391
$\rightarrow ClONO + O(^1D)$	(4)	496	241

Note: $\Delta H°_{298}$ values are given since the heats of formation of $ClONO_2$ and ClONO at 0 K are not known.

Preferred Values

Absorption cross sections for $ClONO_2$ photolysis at 296 K, 243 K, and 227 K

	$10^{20}\sigma/cm^2$				$10^{20}\sigma/cm^2$		
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 at 298 K.
$\Phi_2 = 1.0$ for $\lambda > 260$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those of Molina and Molina, 1979 [1], and the preferred quantum yields are based on the data of Chang et al., 1979 [2]. These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [3] where detailed discussion can be found.

References

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$COCl_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$COCl_2 + h\nu \rightarrow CO + Cl_2$	(1)	110	1087
$\rightarrow COCl + Cl$	(2)	324	369
$\rightarrow CO + 2Cl$	(3)	352	340
$\rightarrow CCl_2 + O(^3P)$	(4)	707	169

Note: ΔH°_{298} values are given since the heat of formation of COCl at 0 K is not known.

Preferred Values

Absorption cross sections for $COCl_2$ photolysis at 298 K

λ (nm)	$10^{20}\sigma/cm^2$	λ (nm)	$10^{20}\sigma/cm^2$
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.
$\Phi_2 = 1$ for $\lambda > 184.9$ nm.

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Chou et al. [4] for 184.9 nm$\leqslant\lambda\leqslant$226 nm, and Okabe [3] for 240 nm$\leqslant\lambda\leqslant$280 nm. The values reported by Heicklen [1] and Okabe [3] for the absorption cross section at 253.7 nm agree to within ~4%. The relative values of the absorption cross sections with wavelength reported by Moule and Foo [2] are in good agreement with the preferred values. Giddings and Innes [6] reported an absorption maximum at 232 nm which is in excellent agreement with the set of preferred values.

From the observations of Wijnen [5], Heicklen [1] and earlier investigators [7], it can be assumed that process (2) is the primary photolysis pathway. The photolytic product COCl is assumed to undergo rapid thermal dissociation into CO and Cl due to the weak Cl–CO bond (~25 kJ [8]). Both Giddings and Innes [6] and Henri and Howell [9] noted diffuseness in their spectra of $COCl_2$.

These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [10] where detailed discussion can be found.

References

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$CF_2Cl_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CF_2Cl_2 + h\nu \rightarrow CF_2 + Cl_2$	(1)	311	385
$\rightarrow CF_2Cl + Cl$	(2)	346	346
$\rightarrow CFCl + FCl$	(3)	473	253
$\rightarrow CFCl_2 + F$	(4)	477	251
$\rightarrow CF_2 + 2Cl$	(5)	554	216
$\rightarrow CFCl + F + Cl$	(6)	724	165

Note: ΔH°_{298} values are given since the heats of formation of $CFCl_2$ and CF_2Cl at 0 K are not known.

Preferred Values

Absorption cross sections for CF_2Cl_2 photolysis at 298 K

λ (nm)	$10^{20}\sigma/\mathrm{cm}^2$	λ (nm)	$10^{20}\sigma/\mathrm{cm}^2$
170	124	200	8.84
172	151	202	5.60
174	171	204	3.47
176	183	206	2.16
178	189	208	1.32
180	173	210	0.80
182	157	212	0.48
184	137	214	0.29
186	104	216	0.18
188	84.1	218	0.12
190	62.8	220	0.068
192	44.5	225	0.022
194	30.6	230	0.0055
196	20.8	235	0.0016
198	13.2	240	0.00029

Absorption cross sections for CF_2Cl_2 photolysis at temperatures below 298 K. $\sigma_T = \sigma_{298}\exp(B(\lambda - 1849)(T - 298))$ for wavelength λ (in Ångstron units) and absolute temperature, T. The value of B is 4.1×10^{-5}.

Quantum Yields for CF_2Cl_2 photolysis at 298 K

λ (nm)	Φ_2	Φ_5	λ (nm)	Φ_2	Φ_5
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 absorption cross sections at 298 K are derived by taking the mean of the values reported by Rowland and Molina, 1975 [1], Robbins et al., 1975 [2], Bass and Ledford, 1976 [3], Chou et al., 1977 [4], Hubrich et al., 1977 [5] and Vanlaethem-Meurre et al., 1978 [6]. The temperature dependence of the absorption cross sections can be adequately described by the expression shown with a preferred value of 4.1×10^{-5} for B which is a weighted average of all the derived values from references [3–6], and Rebbert and Ausloos, 1975 [7]. At wavelengths shorter than 184.9 nm the absorption cross sections are not expected to exhibit any significant temperature dependence, indeed, Hubrich et al. [5] show slightly higher values for below 184.9 nm at 208 K.

The preferred values for Φ_2, the quantum yield for CF_2Cl production, were derived by fitting a smooth curve (s-shaped) to the data points reported by Rebbert and Ausloos [7] at 163.3 nm ($\Phi_2 = 0.56$), 184.9 nm ($\Phi_2 = 0.64$), 213.9 nm ($\Phi_2 = 0.91$), and $\geqslant$230 nm (Φ_2 assumed to be unity) and interpolating between these points. The values shown for Φ_5, the quantum yield for CCl_2 production are calculated assuming that $\Phi_2 + \Phi_5 = 1$.

These recommendations are unchanged from those given in the previous evaluation, CODATA, 1980 [8], where detailed discussion can be found.

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$CFCl_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$	(1)	310	386
$\rightarrow CFCl + Cl_2$	(2)	315	380
$\rightarrow CCl_3 + F$	(3)	444	269
$\rightarrow CCl_2 + FCl$	(4)	472	253
$\rightarrow CFCl + 2Cl$	(5)	558	214
$\rightarrow CCl_2 + F + Cl$	(6)	724	165

Note: ΔH°_{298} values are given since the heat of formation of $CFCl_2$ at 0 K is not known.

Absorption cross section data

Wavelenth range/nm	Reference	Comments
230–260	Hubrich and Stuhl, 1980 [1]	(a)

Comments

(a) Absorption cross sections determined at 5 nm intervals using both 10 and 100 cm long cells at 298 K. In addition, absorption cross sections relative to those for CCl_4, were determined using a photochemical technique (rate of decay of NO in $NO/N_2/CX_4$ mixtures) at 253.7 nm and for the wavelength range 280–375 nm. The photochemical technique produced results at $\lambda = 253.7$ nm consistent with the results obtained using the conventional approach, and it was shown that σ was $< 10^{-26}$ cm^2 molecule^{-1} between 280 and 375 nm.

Preferred Values

Absorption cross sections for $CFCl_3$ photolysis at 298 K

λ (nm)	$10^{20}\sigma/\text{cm}^2$	λ (nm)	$10^{20}\sigma/\text{cm}^2$
170	316	210	15.4
172	319	212	10.9
174	315	214	7.52
176	311	216	5.28
178	304	218	3.56
180	308	220	2.42
182	285	222	1.60
184	260	224	1.10
186	233	226	0.80
188	208	228	0.55
190	178	230	0.35
192	149	235	0.126
194	123	240	0.0464
196	99	245	0.0173
198	80.1	250	0.00661
200	64.7	255	0.00337
202	50.8	260	0.00147
204	38.8		
206	29.3		
208	21.2		

Absorption cross sections for $CFCl_3$ photolysis at temperatures below 298 K

λ (nm)	$10^{20}\sigma/\text{cm}^2$			
	210 K	225 K	240 K	255 K
190	178	178	278	178
195	105	107	108	109
200	58	60	61	62
205	28	30	31	32
210	10.8	11.9	13.1	13.6
215	3.8	4.2	4.8	5.2
220	1.2	1.4	1.5	1.7
225	0.48	0.48		
230	0.18	0.18		

Quantum yields for $CFCl_3$ photolysis at 298 K

λ (nm)	Φ_1	Φ_5	λ (nm)	Φ_1	Φ_5
160	0.48	0.52	200	0.84	0.16
170	0.57	0.43	210	0.94	0.06
180	0.66	0.34	220	1.0	
190	0.74	0.26	230	1.0	

Comments on Preferred Values

The preferred absorption cross sections at 298 K are derived by taking the mean values reported by Rowland and Molina, 1975 [2], Robbins et al., 1975 [3], Bass and Ledford, 1976 [4], Chou et al., 1977 [5], Hubrich et al., 1977 [6], Vanlaethem-Meuree et al., 1978 [7] and Hubrich and Stuhl, 1980 [1] for the wavelength range $\sim 180\ \text{nm} \leqslant \lambda \leqslant 230$ nm. The values shown for $\lambda = 230$–240 nm are those reported by Hubrich et al. [6] and Hubrich and Stuhl [1]. The recent results of Hubrich and Stuhl [1] are preferred for $\lambda \geqslant 240$ nm. The temperature dependence of the absorption cross sections cannot be fitted to a simple expression relating σ and T as was the case for CF_2Cl_2. However, the magnitude of the temperature dependence of the $CFCl_3$ absorption cross sections near 200 nm is much smaller than for CF_2Cl_2. The temperature dependences reported by Bass and Ledford [4], Chou et al. [5] and Hubrich et al. [6] are in good agreement and are used to derive the preferred values below 298 K. However, the low temperature data of Vanlaethem-Meurre et al. [7] is in less satisfactory agreement and they reported a temperature dependence for σ even at short wavelengths, i.e., $\lambda \leqslant 200$ nm which is inconsistent with the data reported in the other studies [4–6].

The preferred values for Φ_1, the quantum yield for $CFCl_2$ production, were derived by fitting a smooth line to the data points reported by Rebbert and Ausloos [8] at 163.3 nm ($\Phi_1 = 0.5$), 184.9 nm ($\Phi_1 = 0.7$), 213.9 nm ($\Phi_1 = 0.98$), and 230 nm (Φ_1 assumed to be unity), and interpolating between these points. The values shown for Φ_5, the quantum yield for CFCl production, are calculated assuming that $\Phi_1 + \Phi_5 = 1$.

These recommendations are unchanged (except for $\lambda \geqslant 240$ nm) from those given in the previous evaluation, CODATA, 1980 [9], where detailed discussion can be found.

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$CCl_4 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CCl_4 + h\nu \rightarrow CCl_3 + Cl$ (1)	294	407
$\rightarrow CCl_2 + Cl_2$ (2)	332	360
$\rightarrow CCl_2 + 2Cl$ (3)	572	209
$\rightarrow CCl + Cl_2 + Cl$ (4)	716	167

Absorption cross section data

Wavelength range/nm	Reference	Comments
160–275	Hubrich and Stuhl, 1980 [1]	(a)

Comments

(a) Absorption cross sections determined at 5 nm intervals at 298 K.

Preferred Values

Absorption cross sections for CCl_4 photolysis at 298 K

λ (nm)	$10^{20}\sigma/cm^2$	λ (nm)	$10^{20}\sigma/cm^2$
174	995	218	21.8
176	1007	220	17.0
178	976	222	13.0
180	772	224	9.61
182	589	226	7.19
184	450	228	5.49
186	318	230	4.07
188	218	232	3.01
190	144	234	2.16
192	98.9	236	1.51
194	74.4	238	1.13
196	68.2	240	0.784
198	66.0	242	0.579
200	64.8	244	0.414
202	62.2	246	0.314
204	60.4	248	0.240
206	56.5	250	0.183
208	52.0	255	0.0661
210	46.6	260	0.0253
212	39.7	265	0.0126
214	33.3	270	0.0061
216	27.2	275	0.0024

Absorption cross sections for CCl_4 photolysis at 279 K

λ (nm)	$10^{20}\sigma/cm^2$	λ (nm)	$10^{20}\sigma/cm^2$
190	146.9	216	27.4
192	99.2	218	22.0
194	76.7	220	17.5
196	69.5	222	13.4
198	68.0	224	9.72
200	66.0	226	6.90
202	63.8	228	5.13
204	60.9	230	3.67
206	57.4	232	2.52
208	52.9	234	1.67
210	47.1	236	1.17
212	40.8	238	0.79
214	33.9		

Quantum yeilds for CCl_4 photolysis at 298 K.

λ (nm)	Φ_1	Φ_3	λ (nm)	Φ_1	Φ_3
170	0.3	0.7	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 298 K are derived by taking the mean of the values reported by Gordus and Bernstein, 1954 [2], Rowland and Molina, 1975 [3], Robbins et al., 1975 [4], and Vanlaethem-Meurre et al., 1978 [5]. The agreement between the values reported in these studies and that of Hubrich and Stuhl [1] is excellent, better than 10%, over the entire wavelength range. The values of σ at $\lambda > 250$ nm are from the study of Hubrich and Stuhl [1] alone (at $\lambda = 253.7$ nm the value of σ is in good agreement with that reported by Davis et al., 1975 [6]). The preferred values of the absorption cross sections at 279 K are those reported by Vanlaethem-Meurre et al. [9] and represent the only data below ~298 K. A comparison of the two sets of preferred values illustrates that σ exhibits no temperature dependence within the stratospheric window, i.e., ~180–220 nm. At wavelengths greater than 230 nm the results of Vanlaethem-Meurre et al. [5], Curie et al., 1974 [7], and Rebbert and Ausloos, 1976 [8] all suggest that σ exhibits a strong temperature dependence.

The preferred values for Φ_1, the quantum yield for CCl_3 production, were derived by fitting a smooth *s*-shaped curve to the data points reported by Davis et al. [6] at 184.9 nm ($\Phi_1 = 0.4$) and 253.7 nm ($\Phi_1 = 1$), and by Rebbert and Ausloos [8] at 163.3 nm ($\Phi_1 = 0.25$) and 213.9 nm ($\Phi_1 = 0.9$), and interpolating between these points. The values shown for Φ_3, the quantum yield for CCl_2 production, are calculated assuming that $\Phi_1 + \Phi_3 = 1$.

The recommended values are unchanged from these given in the previous evaluation, CODATA, 1980 [9], where detailed discussion can be found (the table has been expanded to include the wavelength region, 250 nm$\leqslant\lambda\leqslant$275 nm).

References

[1] Hubrich, C., and Stuhl, F., J. Photochem. **12** 93 (1980).
[2] Gordus, A. A., and Bernstein, R. B., J. Chem. Phys. **22**, 790 (1954).
[3] Rowland, F. S., and Molina, M. J., Rev. Geophys. Space Phys. **113**, 1 (1975).
[4] Robbins, D. E., Rose, L. T., and Boykin, W. R., Johnson Space Center Internal Note JSC-09937 (1975).
[5] Vanlaethem-Meuree, N., Wisemberg, J., and Simon, P. C., Bull. Acad. R. Belgique, Cl. Sci. **64**, 23 (1978).
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[7] Curie, J., Sidebottom, H. W., and Tedder, J. M., Int. J. Chem. Kinet. **6**, 481 (1974).
[8] Rebbert, R. E., and Ausloos, P. J., J. Photochem. **6**, 265 (1976/77).
[9] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

5.8. Bromine Compounds

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H^\circ = -159$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.2×10^{-13} ($\pm$ factor 2)	298	Posey, Sherwell, and Kaufman, 1981 [1]	(a)
Relative Rate Coefficients			
$(4.0\pm0.8)\times10^{-12}$	773	Clark, Simmons, and Smith, 1969 [2]	(b)
Reviews and Evaluations			
2.0×10^{-11}	298	NASA, 1979 [3]	(c)
1.0×10^{-11}	298	CODATA, 1980 [4]	(c)
No recommendation	298	NASA, 1981 [5]	(d)

Comments

(a) Discharge flow: mass spectrometric detection of HO_2.

(b) Inhibition of the second limit in the thermal reaction between hydrogen and oxygen in the presence of hydrogen bromide. $k/k(H + HO_2 \rightarrow 2HO)$ reported to be (0.125 ± 0.025) at 773 K. Combining this ratio with the CODATA preferred value of 3.2×10^{-11} cm^3 molecule^{-1} s^{-1} for $k(H + HO_2 \rightarrow 2HO)$ at 298 K results in a value of 4.0×10^{-12} cm^3 molecule^{-1} s^{-1} for k at 773 K (this obviously assumes that the $H + HO_2 \rightarrow 2HO$ rate constant is temperature invarient). The system is complex and several of the rate constants of key reactions used to analyze the data are now thought to be incorrect, e.g., $k(HO_2 + HO_2)$ and $k(HO + H_2O_2)$. Besides varying the $k/k(H + HO_2 \rightarrow 2HO)$ ratio, the value of $k(Br + H_2O_2)$ was treated as an unknown (a value of $(1.7\pm0.8)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} for $k(Br + H_2O_2)$ at 773 K was reported).

(c) Estimate.

(d) No recommendation. Suggested range $(1\text{–}500)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

No recommendation.

Comments on Preferred Values

No recommendation until there are further experimental data. The previous CODATA [4] value was an estimate which assumed that the reactivity of HO_2 with atomic chlorine and atomic bromine would be similar, i.e., close to gas kinetic. The experimental value reported by Posey et al. at 298 K seems surprisingly low for such an atom-radical reaction although it is not inconsistent with the value reported by Clark et al. for k at 773 K assuming that the E/R value is $\sim$1400 K, i.e. $k\simeq2.5\times10^{-11}\exp(-1400/T)$ cm^3 molecule^{-1} s^{-1}. However, the value reported by Clark et al. is questionable due to the uncertainty in several of the key rate constants needed to analyze the complex reaction system. The value of k reported by Posey et al. may be approximately correct as their provisional value for $k(Cl + HO_2)$ is within a factor of 3 of the CODATA preferred value.

References

[1] Posey, J., Sherwell, J., and Kaufman, M., Chem. Phys. Lett. **77**, 476 (1981).
[2] Clark, D. R., Simmons, R. F., and Smith, D. A., Trans. Faraday Soc. **66**, 1423 (1969).
[3] NASA Ref. Publ. #1049, "The Stratosphere: Present and Future," Chapter 1, R. D. Hudson and E. I. Reed, editors (1979).
[4] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
[5] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," W. B. DeMore, L. J. Stief, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, JPL Pub. #81-3 (1981).

$Br + H_2O_2 \rightarrow HBr + HO_2$

$\Delta H^\circ = -2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<1.5\times10^{-15}$	298	Leu, 1980 [1]	(a)
$<3.0\times10^{-15}$	417		
$<2.0\times10^{-15}$	298	Posey, Sherwell, and Kaufman, 1981 [2]	(a)
Relative Rate Coefficients			
$(1.7\pm0.8)\times10^{-13}$	773	Clark, Simmons, and Smith, 1969 [3]	(b)
Reviews and Evaluations			
$2.0\times10^{-12}\exp(-(>1400/T))$	200–300	NASA, 1979 [4]	(c)
$<2\times10^{-14}$	298	CODATA, 1980 [5]	(c)
$1.0\times10^{-11}\exp(-(>2650/T))$	200–300	NASA, 1981 [6]	(d)

Comments

(a) Discharge flow: mass spectrometric detection of H_2O_2.

(b) Derived from a complex system. Inhibition of the second limit in the thermal reaction between hydrogen and oxygen in the presence of hydrogen bromide. See comment (b) on the $Br + HO_2$ data sheet.

(c) Upper limits based upon provisional data reported by Leu.

(d) Based on the data of references [1] and [2].

Preferred Value

$k < 2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Value

Based on the data of references [1] and [2]. This upper limit at 298 K is consistent with value of 1.7×10^{-13} cm^3 molecule^{-1} s^{-1} at 773 K assuming a pre-exponential of $\sim1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} for the reaction.

References

[1] Leu, M. T., Chem. Phys. Lett. **69**, 37 (1980).

[2] Posey, J., and Sherwell, J., and Kaufman, M., Chem. Phys. Lett. **77**, 476 (1981).

[3] Clark, D. R., Simmons, S. F., and Smith, D. A., Trans. Faraday Soc. **66**, 1423 (1969).

[4] NASA Ref. Publ. #1049, "The Stratosphere: Present and Future," Chapter 1, R. D., Hudson and E. I. Reed, editors (1979).

[5] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

[6] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," W. B. DeMore, L. J. Stief, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, JPL Publ. #81-3 (1981).

$Br + H_2CO \rightarrow HBr + HCO$

$\Delta H^\circ = -2.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6\pm0.3)\times10^{-12}$	298	LeBras et al., 1980 [1]	(a)
$(1.44\pm0.62)\times10^{-11}\exp(-(750\pm112)/T)$	223–480	Nava, Michael, and Stief, 1981 [2]	(b)
$(1.08\pm0.10)\times10^{-12}$	298		
Reviews and Evaluations			
$1.4\times10^{-11}\exp(-750/T)$	223–480	NASA, 1981 [3]	(c)

Comments

(a) Discharge flow-ESR detection of atomic bromine.

(b) Flash photolysis-resonance fluorescence detection of atomic bromine.

(c) Based on reference [2].

Preferred Values

$k = 1.1\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4\times10^{-11}\exp(-750/T)$ cm^3 molecule^{-1} s^{-1} over range 223–480 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

There have been two determinations of k at 298 K which are not in good agreement. The preferred values are taken from the study of Nava et al., as the value of $k(\mathrm{Cl} + \mathrm{H_2CO} \rightarrow \mathrm{HCl} + \mathrm{HCO})$ determined by LeBras et al., in the same study was ~35% lower than the CODATA preferred value.

References

[1] LeBras, G., Foon, R., Poulet, G., and Combourieu, J., Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report FAA-EE-80-20, 497 (1980).
[2] Nava, D. F., Michael, J. V., and Stief, L. J., J. Phys. Chem. **85**, 1896 (1981).
[3] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," W. B. DeMore, L. J. Stief, D. M. Golden, R. F. Hampson, M.J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, JPL Publ. #81-3 (1981).

$\mathrm{BrO} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{BrONO_2} + \mathrm{M}$

$\Delta H^\circ = -138$ 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)
Reviews and Evaluations			
$3 \times 10^{-31} (T/300)^{-3.0}$ [N$_2$]	200–400	CODATA, 1980 [3]	(b)
$5 \times 10^{-31} (T/300)^{-4.0}$ [N$_2$]	200–300	NASA, 1981 [4]	(c)

Comments

(a) Two independent studies, one using a discharge flow-mass spectrometric 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 $\mathrm{Br} + \mathrm{O_3} \rightarrow \mathrm{BrO} + \mathrm{O_2}$. A major part of the fall-off curve was observed and analyzed by the technique of ref. [2], a fit of F_c giving the same value as the theoretical prediction.

(b) Based on preliminary data by the authors of ref. [1].

(c) Based on ref. [1].

Preferred Values

$k_0 = 5.0 \times 10^{-31}$ [N$_2$] cm^3 molecule^{-1}s^{-1} at 298 K.
$k_0 = 5.0 \times 10^{-31} (T/300)^{-3.0}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$ over range 200–400 K.

Comments on Preferred Values

This value is the result of two independent measurements from the same authors. Therefore, independent confirmation is required. The temperature coefficient is estimated by analogy with the $\mathrm{ClO} + \mathrm{NO_2}$ reaction. A measurement or a theoretical calculation of the T-dependence as described in ref. [2] is required.

High pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2 \pm^{0.5}_{1.0}) \times 10^{-11}$	298	Sander, Ray, and Watson, 1981 [1]	(a)
Reviews and Evaluations			
1.2×10^{-11}	200–400	CODATA, 1980 [3]	(b)

Comments

(a) See comment (a) for k_0. Value obtained from a fit of the fall-off curve.

(b) Estimated by analogy with the ClO + NO_2 reaction.

Preferred Value

$k_\infty = 2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over range 200–400 K.

Reliability

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

Comments on Preferred Value

This is a reasonable value for a reaction of this type; however, an independent confirmation is required.

Intermediate Fall-off Range

From the preferred values one calculates $[N_2]_c = 4.0 \times 10^{19}$ molecule cm^{-3} at 298 K. The fitted $F_c = 0.4^{+0.1}_{-0.05}$ and the theoretically predicted value of $F_c = 0.41 \pm 0.11$ at 298 K from the analysis of ref. [1] agree very well. Since no special analysis for the $BrNO_3$ system itself is available, the temperature dependence of F_c should be estimated by analogy with the $N_2O_5 \rightarrow NO_2 + NO_3$ reaction (see data sheet).

References

[1] Sander, S. P., Ray, G. W., and Watson, R. T., J. Phys. Chem. **85**, 199 (1981).
[2] Troe, J., J. Phys. Chem. **83**, 114 (1979).
[3] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).
[4] NASA Panel for Data Evaluation, "Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling," DeMore, W. B., Stief, L. J., Golden, D. M., Hampson, R. F., Jr., Kurylo, M. J., Margitan, J. J., Molina, M. J., and Watson, R. T., JPL Publ. 81-3 (1981).

BrO + *hν*→products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$BrO + h\nu \rightarrow Br + O(^3P)$ (1)	232	515
$\rightarrow Br + O(^1D)$ (2)	422	283

Preferred Values

Absorption cross sections for BrO photolysis at 298 K.
No recommendation.
Quantum yields for BrO photolysis at 298 K.
$\Phi_1 = 1.0$ for $\lambda > 289$ nm.

Comments on Preferred Values

This recommendation is unchanged from the previous evaluation, CODATA, 1980 [1] where detailed discussion of all experimental absorption cross section studies can be found, i.e., Clyne and Cruse, 1970 [2], Brown and Burns, 1970 [3], Basco and Dogra, 1971 [4], and Sander and Watson, 1981 [5]. The extensive predissociation observed by Durie and Ramsay [6] indicates that the value of Φ_1 should be taken to be unity for all vibrational bands within the *A–X* system.

References

[1] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data 9, 295 (1980).
[2] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66**, 2214 (1970).
[3] Brown, J., and Burns, G., Can. J. Chem. **48**, 3487 (1970).
[4] Basco, N., and Dogra, S. D., Proc. R. Soc. London Ser. A **323**, 41 (1971).
[5] Sander, S. P., and Watson, R. T., In press, J. Phys. Chem., (1981).
[6] Durie, R. A., and Ramsay, D. A., Can. J. Phys. **36**, 35 (1958).

HOBr + *hν*→products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HOBr + h\nu \rightarrow HO + Br$ (1)	231	518
$\rightarrow HBr + O(^3P)$ (2)	293	409
$\rightarrow BrO + H$ (3)	423	283
$\rightarrow HBr + O(^1D)$ (4)	483	248

Note: ΔH°_{298} values are given since the heat of formation of HOBr at 0 K is not known.

Preferred Values

In the absence of experimental data for HOBr in the gas phase, it is suggested that the modellers use the absorption cross section data for HOCl (see table of preferred values) red-shifted by 30 nm. Anbar and Dostrovski reported aqueous phase spectra for both HOBr and HOCl. From this data it can be seen that 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 $\geqslant$200 nm.

References

[1] Anbar, M., and Dostrovski, I., J. Chem. Soc., London, Part I, 1105 (1954).

$BrONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$BrONO_2 + h\nu \rightarrow BrO + NO_2$	(1)	138	866
$\rightarrow Br + NO_3$	(2)	163	734
$\rightarrow BrONO + O(^3P)$	(3)	306	391
$\rightarrow BrONO + O(^1D)$	(4)	496	241

Note: $\Delta H°_{298}$ values are given since the heat of formation of $BrONO_2$ and BrONO at 0 K are not known.

Preferred Values

Absorption cross sections for $BrONO_2$ photolysis at 298 K

λ (nm)	$10^{20}\ \sigma$/cm^2	λ (nm)	$10^{20}\ \sigma$/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

The recommended values are taken from Spencer and Rowland, 1978 [1] and are unchanged from those given in the previous evaluation, CODATA, 1980 [2] where detailed discussion can be found.

References

[1] Spencer, J. E., and Rowland, F. S., J. Phys. Chem. **82**, 7 (1978).
[2] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

5.9. Iodine Compounds

$O + IO \rightarrow O_2 + I$

$\Delta H° = -314$ kJ mol^{-1}

Rate coefficient data: no experimental data available.

Preferred Value

$k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

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 experimentally determined rate constants for ClO and BrO at ~298 K are 5×10^{-11} cm^3 molecule^{-1} s^{-1} and 3×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively [1]. The temperature dependence of the rate constant is expected to be small.

References

[1] CODATA Task Group on Chemical Kinetics, Baulch, D. L., Cox, R. A., Hampson, R. F.. Jr., Kerr, J. A., Troe, J., and Watson, R. T., J. Phys. Chem. Ref. Data **9**, 295 (1980).

$HO + HI \rightarrow H_2O + I$

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

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.5)\times10^{-11}$	295	Takacs and Glass, 1973 [1]	(a)

Comments

(a) Discharge flow: EPR detection of HO. Psuedo first-order conditions, $[HI]_0 > [HO]_0$.

Preferred Value

$k = 1.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

In addition to determining k (HO + HI), Takacs and Glass also determined values for k (HO + HCl) [1] and k (HO + HBr) [2]. While the value determined for k (HO + HCl) is in excellent agreement with several other values, and is used in the determination of the CODATA preferred value, their value for k (HO + HBr) is a factor of ~2.5 lower than that reported in the only other study (Ravishankara et al., 1979 [3]) of HO + HBr. At present the difference between the two values reported for k (HO + HBr) cannot be explained and as such cast doubts about the reliability of the value of HO + HI reported in ref. [1].

References

[1] Takacs, G. A., and Glass, G. P., J. Phys. Chem. **77**, 1948 (1973).
[2] Takacs, G. A., and Glass, G. P., J. Phys. Chem. **77**, 1060 (1973).
[3] Ravishankara, A. R., Wine, P. H., and Langford, A. O., Chem. Phys. Lett. **63**, 479 (1979).

$I + HO_2 \rightarrow HI + O_2$

$\Delta H^\circ = -91$ kJ mol^{-1}

Rate coefficient data: no experimental data available.

Preferred Value

No recommendation.

Comments on Preferred Value

No study of this reaction has been reported. Unfortunately it is difficult even to estimate this rate constant roughly. For such an atom-radical reaction the rate constant might be expected to be quite rapid, i.e., close to gas kinetic. However, while the rate constant for the $Cl + HO_2$ reaction is rapid, i.e., $k = 4.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (CODATA preferred value), the only experimental study of the $Br + HO_2$ reaction at 298 K suggests a value of $\sim 2\times10^{-13}$ cm^3 molecule^{-1} s^{-1} for k (Posey et al. [1]). Consequently, there is no recommendation for k ($I + HO_2$). Clearly studies of this reaction are needed.

References

[1] Posey, J., Sherwell, J., and Kaufman, M., Chem. Phys. Lett. 77, 476 (1981).

$I + O_3 \rightarrow IO + O_2$

$\Delta H^\circ = -78$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.3^{+8.3}_{-4.1})\times 10^{-13}$	293	Clyne and Cruse, 1970 [1]	(a)

Comments

(a) Discharge flow-ultraviolet absorption detection of O_3. Minimal discussion of experimental conditions. Data analysis used the initial rate of decay of O_3 as the atomic iodine concentrations decreased with reaction time due to heterogeneous loss of I on the flow tube walls.

Preferred Value

$k = 1.0\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Value

Limited experimental accuracy. The value of k (Br + O_3) determined in the same system [2] was underestimated by a factor of ~3 from the CODATA preferred value. Consequently the accuracy of this determination of k is questionable considering it presented additional experimental problems in this system over those in the Br + O_3 system. Obviously additional studies are required both at 298 K and as a function of temperature.

References

[1] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66**, 2227 (1970).
[2] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66**, 2214 (1970).

$IO + HO_2 \rightarrow$ Products

Rate coefficient data: no experimental data available.

Preferred Value

No recommendation.

Comments on Preferred Value

No study of this reaction has been reported. The rate constant can only be very roughly estimated from consideration of similar reactions. There may be multiple reaction pathways (bimolecular and termolecular) as have been suggested for the ClO + HO_2 reaction. A rate constant similar to that for ClO + HO_2, i.e., $k \sim 5\times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K may be expected. This value must be considered to be very uncertain (to at least an order of magnitude). Clearly studies of this reaction are needed.

$I + NO + M \rightarrow INO + M$

$\Delta H^\circ = -75.0$ 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		
$(10.5 \pm 3)\times 10^{-33}$ [Ar]	298*		
$(6.0 \pm 2)\times 10^{-33}$ [He]	330		
$(10.3 \pm 0.6)\times 10^{-33}\,(T/300)^{-1.1}$ [Ar]	298–328	Basco and Hunt, 1978 [3]	(c)

Comments

(a) Laser flash photolysis of I_2 at 694 nm in the presence of NO and He. He pressures between 1 and 200 atm. Observation of I_2 and INO spectra.

(b) As comment (a). Study of the effect of 14 different bath gases. Value for M = Ar at 298 K calculated with the value for 330 K and the temperature coefficient from ref. [1].

(c) Flash photolysis of I_2 in the presence of NO and Ar.

Preferred Values

$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0} [N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_0 = 1.0 \times 10^{-32} (T/300)^{-1.0} [Ar]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1.$
$\Delta n = \pm 0.5.$

Comments on Preferred Values

Values for M = Ar from refs. [2] and [3] agree remarkably well and are taken as preferred values. Collision efficiencies for He, Ar, and N_2 follow the usual trends.

High pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.7 \times 10^{-11}$	330	Van den Bergh and Troe, 1976 [1]	(a)

Comments

(a) As comment (a) for k_0. At He pressures of 200 atm, $k \simeq 0.4 k_\infty$ so that extrapolation of the fall-off curve is required. The k_∞ value given represents a lower limit of k_∞, it could be at most a factor of 2 higher than given here.

Preferred Value

$k_\infty = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

Comments on Preferred Value

Although there is only a single measurement of the fall-off curve, we are reasonably confident that the preferred value is close to the lower limit from ref. [1].

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c = 1.0 \times 10^{21}$ molecule cm^{-3} at 298 K. The measured fall-off curve does not allow F_c to be derived with certainty. However, it should be near to 0.75 ± 0.15 at 298 K.

References

[1] Van de Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).
[2] Van der Bergh, H., Benoit-Guyot, N., and Troe, J., Int. J. Chem. Kinet. **9**, 223 (1977).
[3] Basco, N., and Hunt, J. E., Int. J. Chem. Kinet. **10**, 733 (1978).

$I + NO_2 + M \rightarrow INO_2 + M$

$\Delta H^\circ = -79.7$ 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			
$1.52 \times 10^{-31} (T/300)^{-1 \pm 0.5} [He]$	320–450	Van den Bergh and Troe, 1976 [1]	(a)
$1.62 \times 10^{-31} [He]$	330	Van den Bergh, Benoit-Guyot, and Troe, 1977 [2]	(b)
$2.60 \times 10^{-31} [N_2]$	330		

Comments

(a) From NO_2 catalyzed recombination of iodine atoms, iodine atoms being produced by laser flash photolysis at 694 nm. Fall-off curve measured from 1 to 200 atm of He. Only a short extrapolation to k_0 was required.

(b) As comment (a). Efficiences of 26 bath gases studied.

Preferred Values

$k_0 = 2.9\times10^{-31}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 2.9\times10^{-31}$ $(T/300)^{-1}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over range 298–450 K.

Reliability

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

$\Delta n = \pm 0.5$ over range 298–450 K.

Comments on Preferred Values

Results from a single laboratory only. Independent confirmation is required. The value for M = N_2 at 298 K was derived from the measurements at 330 K and the T-dependence for M = He. The value of n is assumed to be identical for He and N_2.

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)

Comments

(a) See comment (a) for k_0. Only a short extrapolation of the fall-off curve toward the high pressure limit was required.

Preferred Value

$k_\infty = 6.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 300–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over range 300–400 K.

Comments on Preferred Value

Results from a single laboratory only. Independent confirmation is required.

Intermediate Fall-off Range

From the preferred values for k_0 and k_∞, at 298 K one derives $[N_2]_c = 2.3\times10^{20}$ molecule cm^{-3}. The measurements of ref. [1] gave $F_c = 0.63$ at 330 K.

References

[1] Van den Bergh, H. and Troe, J., J. Chem. Phys. **64**, 736 (1976).

[2] Van den Bergh, H., Benoit-Guyot, N., and Troe, J., Int. J. Chem. Kin. **9**, 223 (1977).

$IO + NO \rightarrow I + NO_2$

$\Delta H^\circ = -122$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7\pm0.2)\times10^{-11}$	298	Ray and Watson, 1981 [1]	(a)

Comments

(a) Discharge flow: mass spectrometric detection of IO. Psuedo-first order conditions, $[NO]\gg[IO]$.

Preferred Value

$k = 1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions have been reported to be negative with E/R values of -294 K and -260 K, respectively (CODATA preferred values).

References

[1] Ray, G. W., and Watson, R. T., J. Phys. Chem. **85**, 2955 (1981).

$IO + NO_2 + M \rightarrow IONO_2 + M$

Rate coefficient data: no available experimental data.

Preferred Values

$k_0 = 5.0 \times 10^{-31} (T/300)^{-3.0} [N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_\infty = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$F_c = 0.4$ at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.5$.

$\Delta \log k_\infty = \pm 0.5$.

$\Delta n = +1$.

Comments on Preferred Values

The preferred values are those from the $BrO + NO_2 \rightarrow BrONO_2$ reaction. On theoretical grounds the $BrONO_2$ and the $IONO_2$ reactions should have similar properties.

$IO + IO \rightarrow 2I + O_2$ (1)
$\rightarrow I_2 + O_2$ (2)

$\Delta H°(1) = -130$ 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			
$(2.6^{+2.6}_{-1.3}) \times 10^{-12}$	293	Clyne and Cruse, 1970 [1]	(a)

Comments

(a) The value of k shown in this table is derived using the following equation: $-d[IO]/dt = 2k[IO]^2$. In the original publication the authors used the following expression: $-d[IO]/dt = k[IO]^2$. Discharge flow: uv absorption detection of IO using the band head of the $A\,(^2\Pi, v' = 4) \rightarrow X\,(^2\Pi, v'' = 0)$ transition at ~428 nm (the numbering of this transition may be in error as the analogous ClO and BrO systems had to be re-assigned with recent improved spectroscopic data). A value of 1×10^6 cm s^{-1} was reported for k/σ, which when combined with the estimated value of 5×10^{-18} cm^2 molecule^{-1} for σ (based on σ for BrO) yielded the reported value. The value of σ can only be considered to be known to within a factor of ~5.

Preferred Value

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

Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Value

This value is consistent with the preferred values for the BrO + BrO and FO + FO reactions. No experimental information is available concerning the branching ratio. However, if the reaction mechanism is similar to the BrO + BrO and FO + FO reactions then channel (1) may be expected to be the dominant reaction pathway.

References

[1] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. 66, 2227 (1970).

$INO + INO \rightarrow I_2 + 2NO$

$\Delta H° = -8.4$ 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		

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.

Preferred Value

$k = 1.3\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.4\times10^{-11} \exp(-2620/T)$ cm^3 molecule^{-1} s^{-1} over range 300–450 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta (E/R) = \pm 600$ K.

Comments on Preferred Values

Results from ref. [2] preferred over those from ref. [3] because of a much wider range of conditions studied.

References

[1] Porter, G., Szabo, Z. G., and Townsend, M. G., Proc. Roy. Soc. **A270**, 493 (1962).
[2] Van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).
[3] Basco, N., and Hunt, J. E., Int. J. Chem. Kinet. **10**, 733 (1978).

$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$

$\Delta H^\circ = -8.1$ 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)

Comments

(a) From NO_2 catalyzed recombination of iodine atoms, iodine atoms being produced by laser flash photolysis of I_2. Temperature dependence probably similar as for INO + INO.

Preferred Values

$k = 4.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9\times10^{-11} \exp(-2600/T)$ cm^3 molecule^{-1} s^{-1} over range 298–400 K.

Reliability

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

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

Comments on Preferred Values

Preferred value based on 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] Van den Bergh, H. and Troe, J., J. Chem. Phys. **64**, 736 (1976).

$IO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$IO + h\nu \rightarrow I + O(^3P)$	(1)	184	651
$\rightarrow I + O(^1D)$	(2)	374	320

Note: ΔH°_{298} values are given since the heat of formation of IO at 0 K is not known.

Absorption cross section data: no experimental data available.

Quantum yield data: no experimental data available.

Preferred Values

There are no quantative experimental absorption cross section or quantum yield data. A number of red degraded bands have been observed in emission, which are attributed to the $A\,^2\Pi \rightarrow X\,^2\Pi$ transition of the IO radical by Vaidya, 1937 [1], 1938 [2], Coleman, Gaydon, and Vaidya, 1948 [3], and Durie, Legay, and Ramsay, 1960 [4]. Absorption spectra of IO have been reported by Durie and Ramsay, 1958 [5] and Clyne and Cruse, 1970 [6], but no absorption cross section data was obtained. Extensive predissociation was noted in the each of the bands observed in the $X\,^2\Pi\,(v''=0) \rightarrow A\,^2\Pi\,(v' \geqslant 0)$ progression [5]. The magnitude of the absorption cross sections at the band heads are probably similar to those for equivalent transitions of BrO.

HOI + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/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: no experimental data available.

Quantum yield data: no experimental data available.

Preferred Values

Neither qualitative absorption spectra nor absolute cross-sections have been measured for HOI. It is suggested that in the absence of any experimental data that the modellers use the absorption cross section data for HOCl (see table of preferred values) red-shifted by 100 nm. By analogy with HOCl it is probable that $\Phi \sim$ unity for all wavelengths $\geqslant$200 nm.

INO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
INO + $h\nu \rightarrow$ 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)

No quantum yield data.

Comments

(a) Flash photolysis of I_2 in the presence of NO. Inadequate interpretation of the mechanism, σ-values therefore uncertain.

(b) Laser flash photolysis of I_2 in the presence of NO. σ-values have been confirmed by later work of refs. [3] and [4].

(c) Flash photolysis of I_2 in the presence of NO. σ-values derived from analysis of the mechanism.

(d) Spectroscopic investigation of the $I_2 + 2NO \rightleftharpoons 2INO$ equilibrium. Results in very good agreement with refs. [2] and [3].

Preferred Values

λ/nm	$10^{17}\sigma$/cm^2	λ/nm	$10^{17}\sigma$/cm^2
230	1.4	360	0.045
235	5.3	370	0.059
238	7.0	380	0.065
245	6.5	390	0.078
251	5.9	400	0.92
260	2.4	410	0.10
270	1.0	420	0.10
300	0.09	430	0.094
		440	0.080
		450	0.060
		460	0.040

Preferred Values for Absorption Cross Sections

The values are averages of 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.

References

[1] Porter, G., Szabo, Z. G., and Townsend, M. G., Proc. Roy. Soc. (London) **A270**, 493 (1962).
[2] Van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).
[3] Basco, N., and Hunt, J. E., Int. J. Chem. Kinet. **10**, 733 (1978).
[4] Forte, E., Hippler, H., and Van den Bergh, H., Int. J. Chem. Kinet. **13**, 1227 (1981).

$INO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$INO_2 + h\nu \rightarrow I + NO_2$	77	1560

Absorption cross-section data.

No absorption spectrum has been so far detected, although the spectrum has been searched for in the NO_2-catalyzed recombination of iodine atoms. Presumably $\sigma(ION_2) < \sigma(NO_2)$ over the range 250–600 nm (ref. [1]).

Reference

[1] Van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

$IONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ mol^{-1}	$\lambda_{\mathrm{threshold}}$/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 available.

Quantum yield data: no experimental data available.

Preferred Values

Neither qualitative absorption spectra nor absolute cross-sections have been measured for $IONO_2$. It is suggested that in the absence of experimental data the absorption cross-sections data for $BrONO_2$ be used (this will probably lead to an underestimate of J as the $IONO_2$ spectrum will probably be red-shifted relative to the $BrONO_2$ spectrum by ~50 nm).

Appendix I

Enthalpy data

(Substance)	ΔH_f° (298) kJ mol^{-1}	ΔH_f° (0) kJ mol^{-1}	Notes
H	217.997	216.03	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	39.0	38.7	3
HO_2	10.5 ± 4.2		30
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	343	343	2
NH_2	185	188	7
NH_3	− 45.94	− 38.95	1
NO	90.25	89.75	3
NO_2	33.2	36.0	3
NO_3	71 ± 20	77 ± 20	4
N_2O	82.05	85.50	3
N_2O_4	9.1	18.7	4
N_2O_5	11.3	23.8	3
HNO	99.6	102.5	4
HNO_2	− 79.5	− 74	3
HNO_3	− 135.06	− 125.27	3
HO_2NO_2	− 54 ± 20		8
CH	594.1	590.8	4
CH_2	386	386	6
CH_3	145.6	149.0	4
CH_4	− 74.81	− 66.82	3
CO	− 110.53	− 113.81	1
CO_2	− 393.51	− 393.14	1
HCO	37.6	37.2	9
CH_2O	− 108.6	− 104.7	2
HCOOH	− 378.6	− 371.6	3
CH_3O	14.6	22.6	9
CH_3O_2	16 ± 8		10
CH_2OH	− 25.9		20
CH_3OH	− 200.7	− 189.7	3
CH_3OOH	− 131		9
CH_3ONO	− 65.3	− 52.6	9
CH_3ONO_2	− 119.7	− 103.4	9
C_2H	536		20
C_2H_2	227.36		27
C_2H_4	52.09		27
C_2H_5	107.5		2
C_2H_6	− 83.8	− 68.3	2
CH_2CO	− 59.54		27
CH_3CO	− 24.3		20
CH_3CHO	− 166.2		27
C_2H_5O	− 17.2		20
CH_3CO_2	− 207.5		20
$C_2H_5O_2$	− 7.5		9
CH_3OOCH_3	− 125.5		9
S	276.98	274.72	1
S_2	128.49	128.20	1
HS	146 ± 4	145 ± 4	11
H_2S	− 20.63	− 17.70	3
SO	5.0	5.0	5
SO_2	− 296.81	− 294.26	1
SO_3	− 395.7	− 390	3
SOH	21 ± 17		11
HSO_3	− 481 ± 25		12
CS	272	268	11
CS_2	117.2	116.6	3
CH_3SCH_3	− 37.2		11
CH_3SSCH_3	− 24.3		11

Appendix I—con't

(Substance)	ΔH°_f (298) kJ mol^{-1}	ΔH°_f (0) kJ mol^{-1}	Notes
OCS	−142	−142	3
F	79.39	77.28	1
F_2	0	0	1
HF	−273.30	−273.26	1
HOF	−98 ± 4	−95 ± 4	6
FO	109 ± 8	109 ± 8	9
FO_2	50 ± 12	52 ± 12	9
FONO	67		13
$FONO_2$	10	18	4
CF_2	−182 ± 8	−182 ± 8	4
CF_3	−470 ± 4	−468 ± 4	4
CF_4	−933	−927	18
FCO	−170 ± 60	−170 ± 60	4
COF_2	−634.7	−631.6	3
Cl	121.30	119.62	1
Cl_2	0	0	1
HCl	−92.31	−92.13	1
ClO	102	102	2,14
ClOO	89 ± 5	91	2,14
OClO	97 ± 8	100 ± 8	14,15
Cl_2O	81.4	83.2	15
HOCl	−78	−75	2,16
ClNO	51.7	53.6	6
$ClNO_2$	12.5	18.0	3
ClONO	83		17
$ClONO_2$	26.4		15
FCl	−50.7	−50.8	4
CCl	502 ± 20	498 ± 20	4
CCl_2	238 ± 20	237 ± 20	4
CCl_3	79.5	80.1	4
CCl_4	−95.8	−93.6	18
$CHCl_3$	−102.9	−98.0	18
CH_3Cl	125		19
CH_2Cl_2	−95.4	−88.5	18
CH_3Cl	−82.0	−74.0	
ClCO	−17		9
$COCl_2$	−220.1	−218.4	2
CFCl	30 ± 25	30 ± 25	24
$CFCl_2$	−96		20
$CFCl_3$	−284.9	−281.8	21
CF_2Cl	−269		20
CF_2Cl_2	−493.3	−489.1	21
CF_3Cl	−707.9	−702.9	21
$CHFCl_2$	−284.9	−279.5	21
CHF_2Cl	−483.7	−477.4	21
COFCl	−427 ± 33	−423 ± 33	4
C_2Cl_4	−12.4	−11.9	4
C_2HCl_3	−7.8	−4.3	3
CH_2CCl_3	45 ± 30		25
CH_3CCl_3	−142.3	−145.0	22
Br	111.86	117.90	1
Br_2	30.91	45.69	1
HBr	−36.38	−28.54	1
HOBr	−80 ± 8		9
BrO	125	133	3
BrNO	82.2	91.5	3
$BrONO_2$	20 ± 30		26
BrCl	14.6	22.1	4
CH_2Br	163		19
CH_3Br	−37.7	−22.3	23
I	106.762		1
I_2(g)	62.421		1
HI	26.36		1
IO	172		28
INO	121.3	124.3	29
INO_2	60.2	66.5	29

Notes

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Appendix II

Conversion Tables

Equivalent second order rate constants

B A	cm^3 mol^{-1} s^{-1}	dm^3 mol^{-1} s^{-1}	m^3 mol^{-1} s^{-1}	cm^3 $molecule^{-1}$ s^{-1}	$(mm\ Hg)^{-1}$ s^{-1}	atm^{-1} s^{-1}	ppm^{-1} min^{-1}	$m^2\ kN^{-1}\ s^{-1}$
1 cm^3 mol^{-1} s^{-1} =	1	10^{-3}	10^{-6}	1.66×10^{-24}	$1.604 \times 10^{-5} T^{-1}$	$1.219 \times 10^{-2} T^{-1}$	2.453×10^{-9}	$1.203 \times 10^{-4} T^{-1}$
1 dm^3 mol^{-1} s^{-1} =	10^3	1	10^{-3}	1.66×10^{-21}	$1.604 \times 10^{-2} T^{-1}$	$12.19\ T^{-1}$	2.453×10^{-6}	$1.203 \times 10^{-1} T^{-1}$
1 m^3 mol^{-1} s^{-1} =	10^6	10^3	1	1.66×10^{-18}	$16.04\ T^{-1}$	$1.219 \times 10^4 T^{-1}$	2.453×10^{-3}	$120.3\ T^{-1}$
1 cm^3 $molecule^{-1}$ s^{-1} =	6.023×10^{23}	6.023×10^{20}	6.023×10^{17}	1	$9.658 \times 10^{18} T^{-1}$	$7.34 \times 10^{21} T^{-1}$	1.478×10^{15}	$7.244 \times 10^{19} T^{-1}$
1 $(mm\ Hg)^{-1}$ s^{-1} =	$6.236 \times 10^4 T$	$62.36\ T$	$6.236 \times 10^{-2} T$	$1.035 \times 10^{-19} T$	1	760	4.56×10^{-2}	7.500
1 atm^{-1} s^{-1}	$82.06\ T$	$8.206 \times 10^{-2} T$	$8.206 \times 10^{-5} T$	$1.362 \times 10^{-22} T$	1.316×10^{-3}	1	6×10^{-5}	9.869×10^{-3}
1 ppm^{-1} min^{-1} = at 298 K, 1 atm total pressure	4.077×10^8	4.077×10^5	407.7	6.76×10^{-16}	21.93	1.667×10^4	1	164.5
1 m^2 kN^{-1} s^{-1} =	$8314\ T$	$8.314\ T$	$8.314 \times 10^{-3} T$	$1.38 \times 10^{-20} T$	0.1333	101.325	6.079×10^{-3}	1

To convert a rate constant from one set of units A to a new set B find the conversion factor for the row A under column B and multiply the old value by it, e.g. to convert cm^3 $molecule^{-1}$ s^{-1} to m^3 mol^{-1} s^{-1} multiply by 6.023×10^{17}.

Table adapted from High Temperature Reaction Rate Data No. 5, The University, Leeds (1970).

Equivalent third order rate constants

B / A	$cm^6\ mol^{-2}\ s^{-1}$	$dm^6\ mol^{-2}\ s^{-1}$	$m^6\ mol^{-2}\ s^{-1}$	$cm^6\ molecule^{-2}\ s^{-1}$	$(mm\ Hg)^{-2}\ s^{-1}$	$atm^{-2}\ s^{-1}$	$ppm^{-2}\ min^{-1}$	$m^4\ kN^{-2}\ s^{-1}$
$1\ cm^6\ mol^{-2}\ s^{-1} =$	1	10^{-6}	10^{-12}	2.76×10^{-48}	$2.57 \times 10^{-10}\ T^{-2}$	$1.48 \times 10^{-4}\ T^{-2}$	1.003×10^{-19}	$1.447 \times 10^{-8}\ T^{-2}$
$1\ dm^6\ mol^{-2}\ s^{-1} =$	10^6	1	10^{-6}	2.76×10^{-42}	$2.57 \times 10^{-4}\ T^{-2}$	$148\ T^{-2}$	1.003×10^{-13}	$1.447 \times 10^{-2}\ T^{-2}$
$1\ m^6\ mol^{-2}\ s^{-1} =$	10^{12}	10^6	1	2.76×10^{-36}	$257\ T^{-2}$	$1.48 \times 10^8\ T^{-2}$	1.003×10^{-7}	$1.447 \times 10^4\ T^{-2}$
$1\ cm^6 molecule^{-2}\ s^{-1} =$	3.628×10^{47}	3.628×10^{41}	3.628×10^{35}	1	$9.328 \times 10^{37}\ T^{-2}$	$5.388 \times 10^{43}\ T^{-2}$	3.64×10^{28}	$5.248 \times 10^{39}\ T^{-2}$
$1\ (mm\ Hg)^{-2}\ s^{-1} =$	$3.89 \times 10^9\ T^2$	$3.89 \times 10^3\ T^2$	$3.89 \times 10^{-3}\ T^2$	$1.07 \times 10^{-38}\ T^2$	1	5.776×10^5	3.46×10^{-5}	56.25
$1\ atm^{-2}\ s^{-1} =$	$6.733 \times 10^3\ T^2$	$6.733 \times 10^{-3}\ T^2$	$6.733 \times 10^{-9}\ T^2$	$1.86 \times 10^{-44}\ T^2$	1.73×10^{-6}	1	6×10^{-11}	9.74×10^{-5}
$1\ ppm^{-2}\ min^{-1} =$ at 298 K, 1 atm total pressure	9.97×10^{18}	9.97×10^{12}	9.97×10^6	2.75×10^{-29}	2.89×10^4	1.667×10^{10}	1	1.623×10^6
$1\ m^4\ kN^{-2}\ s^{-1} =$	$6.91 \times 10^7\ T^2$	$69.1\ T^2$	$6.91 \times 10^{-5}\ T^2$	$1.904 \times 10^{-40}\ T^2$	0.0178	1.027×10^4	6.16×10^{-7}	1

See note to table for second order rate constants.

Conversion factors for units of optical absorption coefficients

B / A	(Cross section σ) $cm^2\ molecule^{-1}$ base *e*	$(atm\ at\ 273)^{-1}\ cm^{-1}$ base *e*	$dm^3\ mol^{-1}\ cm^{-1}$ base 10	$cm^2\ mol^{-1}$ base 10
1 $(atm\ at\ 298)^{-1}\ cm^{-1}$ base *e* =	4.06×10^{-20}	1.09	10.6	1.06×10^4
1 $(atm\ at\ 298)^{-1}\ cm^{-1}$ base 10 =	9.35×10^{-20}	2.51	24.4	2.44×10^4
1 $(mm\ Hg\ at\ 298)^{-1}\ cm^{-1}$ base 10 =	7.11×10^{-17}	1.91×10^3	1.86×10^4	1.86×10^7
1 $(atm\ at\ 273)^{-1}\ cm^{-1}$ base *e* =	3.72×10^{-20}	1	9.73	9.73×10^3
1 $(atm\ at\ 273)^{-1}\ cm^{-1}$ base 10 =	8.57×10^{-20}	2.303	22.4	2.24×10^4
1 $dm^3\ mol^{-1}\ cm^{-1}$ base 10 =	3.82×10^{-21}	0.103	1	10^3
1 $cm^2\ mol^{-1}$ base 10 =	3.82×10^{-24}	1.03×10^{-4}	10^{-3}	1
1 $cm^2\ molecule^{-1}$ base *e* =	1	2.69×10^{19}	2.62×10^{20}	2.62×10^{23}

To convert an absorption coefficient from one set of units A to a new set B, *multiply by the value tabulated for row A under column B, e.g.* to convert the value of the absorption coefficient expressed in $dm^3\ mol^{-1}\ cm^{-1}$ base 10 to $(atm\ at\ 273)^{-1}\ cm^{-1}$ base *e*, multiply by 0.103.

Units for Expressing Pressure

In this evaluation we have expressed pressures in terms of Torr and atmosphere. These are defined in terms of SI units by the following equations:

1 Torr = 133.322 Pa

1 Atm = 101,325 Pa.