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Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry

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This paper contains a critical evaluation of the kinetics and photochemistry of gas phase chemical reactions of neutral species involved in middle atmosphere chemistry (10–55 km altitude). 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 148 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 dependency where possible. The selection of the preferred value is discussed, and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an Appendix listing the available data on enthalpies of formation of the reactant and product species.

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

Contents

1. Preface

In 1977 the CODATA Task Group on Chemical Kinetics was charged with producing a set of critically evaluated rate parameters for reactions pertaining to atmospheric chemistry. Emphasis was given to those reactions bearing on the problems associated with the possible depletion of ozone in the stratosphere, and the primary aim was to furnish the kinetic data for atmospheric modelers.

In compiling the list of reactions for consideration, we have drawn heavily from previous evaluations and compilations, notably from (i) the NASA Reference Publication 1010 [1],[1] (ii) N.B.S. Technical Note 866 [2], (iii) N.B.S. Special Publication 513 [3] and the recent evaluation of ClO_x reactions by Watson [4].

The list of reactions is limited to those of neutral species in the stratosphere and the natural (i.e., unpolluted) troposphere. Reactions of hydrocarbons are limited to those species containing one carbon atom only. Background notes on the types and classification of atmospheric reactions are given in a subsequent section dealing with atmospheric chemistry.

We have prepared data sheets on the kinetics of the chemical reactions and on the photochemistry of the neutral species which are presently considered to be important or which should be looked at in middle atmosphere chemistry. The format of the data sheets is intermediate in detail between the types of data sheet produced by Baulch and co-workers [5] at Leeds and those by Johnston and Garvin [6] at the National Bureau of Standards.

The Task Group met in a series of working sessions, the last held in May 1979, to put the manuscript in final form prior to its submission for publication. The last meeting at which new data were considered was held in December 1978. At that time the Task Group considered only data published in the scientific literature, preprints of journal articles, and significant new results presented at open scientific meetings.

2. 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.

2.1. 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. Some of the earlier data summarized in previous evaluations have been omitted, except where the data have a direct bearing on the preferred data selected here. 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 expressed in the normal Arrhenius form, $k = A \exp(-C/T)$ where $C = E/R$. For pressure-dependent combination and dissociation reactions an alternative non-Arrhenius temperature dependence is used which is discussed more fully in a subsequent section of the introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at 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 data listed under Reviews and Evaluations are from the most recent source if that source contains the same recommendations as earlier reviews.

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.

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[1] Numbers in brackets indicate literature references.

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 in (E/R) for the temperature range of the preferred rate coefficient. 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 give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question.

The data sheets are concluded with a list of the relevant references.

2.2. 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.

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

$$-(½)d[A]/dt = d[B]/dt = d[C]/dt = k[A]^2.$$

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

2.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$A + B + M \rightleftarrows AB + M,$$

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 psuedo second-order rate law

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

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

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

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

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

which is independent of [M]. 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 $k_0/k_\infty = [M]/[M]_c$ where the "center of the fall-off curve" $[M]_c$ 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 relation holds:

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

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

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

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

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. At low temperatures the broadening factors at the center, F_c, do not deviate too much from unity, values in the range 0.7 to 0.9 being typical for the present reactions (for theoretical predictions of F_c, and modification of the expression $F(k_0/k_\infty)$ at higher temperatures, see ref. [7]). The dependence of k_0 and k_∞ on the temperature T is represented by 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

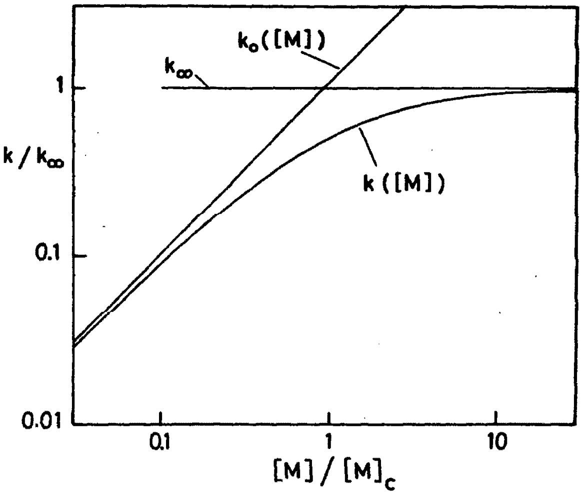

FIGURE 1. Reduced fall-off curve of k/k_∞ as a function of $[M]/[M]_c$.

dependence because it gives a better fit to the data over a wider range of temperatures 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 $k([M])$.

2.4. 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 yields 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.

2.5. 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

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

$$\sigma = (1/([N]\ell))\ell n(I_0/I)$$

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

2.6. 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 ±100% are appropriate.

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

2.7. $O(^1D)$ Rate Coefficients

There exist in the literature two large, disparate sets of $O(^1D)$ reaction rate data. One set is based on measurements of the National Oceanic and Atmospheric Administration Laboratories in which $O(^1D)$ is monitored by the time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm [8a–8f]. These measurements appear in principle to be quite straightforward—the main complication is interfering secondary chemiluminescent emissions, which were minimized by addition of SF_6. The other set of rate data is based on measurements at the University of Cambridge Laboratory in which $O(^1D)$ is monitored in absorption by the time resolved attenuation of the atomic resonance radiation at 115.2 nm, $O(3D_2) \leftarrow O(2D_2)$ [9a–9g]. Data analysis of these results uses the modified Beer-Lambert absorption law: $I_t/I_0 = \exp(-\epsilon(c\ell)^\gamma)$. This method requires an independent calibration of the value of γ, resulting in the reported value $\gamma = 0.41$. Disagreement over the interpretation of these results has focused on the correct value of γ to be used in the absorption law. There exists also a large body of relative rate data resulting from studies of $O(^1D)$ reactions in competitive systems. From an analysis of the data Cvetanović [10] developed a consistent set of relative rate data by reducing these values to a common base with the rate for CO_2 set equal to unity.

In this evaluation we have chosen to treat these three data sets on an equal basis. For a given reaction the preferred value is derived from consideration of the rate data for the reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio (k/k_{ref}) is derived from the absolute values reported in [8a–8f] and [9a–9g]. The preferred value for this ratio is the mean value of these two derived ratios and that given in [10]. The preferred value of k_{ref} is taken as the simple average of the results from [8a–8f] and [9a–9g].

Recently there has appeared a preliminary report [11] giving absolute $O(^1D)$ rate coefficient values obtained by a measurement technique which is different than that used in [8a–8f] or [9a–9g]. When these preliminary results are confirmed and published with enough detail for reanalysis, we may have to reconsider our stated preferred values for these rate coefficients.

3. Atmospheric Chemistry

3.1. Introduction

Recently it has become clear that homogeneous gas-phase reactions are important in determining the behavior of neutral trace-gas species present in the earth's atmosphere below about 70 km altitude. This part of the atmosphere is characterized by two distinct regions. The troposphere lies between the earth's surface and the tropopause at 10–15 km altitude. In this region the temperature falls rapidly with height, and the air is moist and turbulent. Above the tropopause lies the stratosphere which is relatively cool, dry and stable.

The primary initiating force for chemical change in the atmosphere is photochemical, i.e., absorption of solar radiation by stable molecules which emit reactive atomic or free-radical species. The most important effect in the atmosphere is the ozone layer. This layer is the main object when studying the chemistry of the stratosphere. Photochemistry is also important in the troposphere as a scavenging mechanism by which gaseous materials, both natural and man-made, emitted at the earth's surface, are removed from the atmosphere. The growth of emissions in the atmosphere in the industrial twentieth century has increased the possibility of global pollution of the atmosphere and has stimualted intensive study of atmospheric chemistry.

3.2. Stratospheric Chemistry—The Ozone Layer

The basic photochemical-kinetic cycle involved in the production and destruction of ozone in the stratosphere was first suggested by Chapman [12] and consists of the following reactions:

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

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

$$O + O_3 \rightarrow 2O_2 \tag{3}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{4}$$

The rate of destruction of "odd oxygen" $(O + O_3)$ in reaction (3) is, however, insufficient to balance the production rate of O by photodissociation of O_2 in reaction (1) and maintain a steady-state concentration of O_3 which is consistent with observation of the total column density of ozone. Consequently, other "odd oxygen" destruction processes have been suggested, which involve catalytic cycles of the following general type:

$$X + O_3 \rightarrow XO + O_2$$

$$XO + O \rightarrow X + O_2$$

$$\text{net } O + O_3 \rightarrow 2O_2.$$

These cycles can occur when X = H, HO, [13], NO, [14], Cl, [15], and Br, [16], according to current chemical knowledge and available kinetic data. In addition to these pairs of relatively simple reactions, there are a large number of elementary photochemical and chemical reactions which are required to define the concentrations of active HO_x, NO_x, ClO_x and BrO_x species at different altitudes, and thereby to determine their interaction with the ozone budget. Model calculations are concerned with the quantitative treatment of this chemistry, to calculate the ozone column density and any effects on this column of perturbations of the trace gas composition, particularly involving NO_x and ClO_x compounds.

3.3. Tropospheric Chemistry

Many of the trace constituents of the stratosphere are transported from the troposphere and originate initially at the earth's surface. The movement of these constituents through the atmosphere constitutes a cycle, with emission or injection of gaseous constituents, their transport and chemical transformation within the atmosphere, and finally their removal by rain-out or other sink processes. Clearly sink processes operating in the troposphere are important in determining the amount of trace components passing to and from the stratosphere, and hence in potential stratospheric perturbations.

The main photochemical sink processes in the troposphere involve reaction of trace gases with HO radicals, [17] which are produced primarily by the reaction with water vapour of excited atomic oxygen, $O(^1D)$, produced by photolysis of ozone.

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta) \quad \lambda \leq 310 \text{ nm}$$

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

In the sunlit atmosphere, a steady-state concentration of HO is maintained by reactions involving the oxidation of natural methane, via formaldehyde and carbon monoxide to CO_2 and H_2O. Nitrogen oxides are also involved in tropospheric HO_x chemistry through their ability to provide an additional source of odd-oxygen via the reaction

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

$$NO_2 + h\nu \rightarrow NO + O$$

$$\text{net } HO_2 \rightarrow HO + O.$$

Current interest in tropospheric chemistry is directed to the possible global perturbations due to man-made emissions of NO_x and carbon monoxide [18].

The other important chemical sink in the troposphere involves the precipitation elements (cloud droplets and aerosol particles) and a number of the trace gas cycles are closed by rain-out of the water-soluble products of atmospheric oxidation.

3.4. Trace Gas Reactions

In the following paragraphs the cycles of the trace gases involved in stratospheric ozone chemistry are briefly described. Kinetic data have been evaluated in this survey for each of these cycles of reactions.

3.4.a. Reactions of HO_x

The important active species in the HO_x cycle are HO and HO_2. The primary source of these radicals throughout the atmosphere is reaction of $O(^1D)$ atoms with hydrogen-containing compounds, principally H_2O. Stratospheric water vapour results chiefly from oxidation of methane which is transported from the troposphere. Removal of HO_x from the stratosphere is by downward transport of H_2O and H_2O_2 to the troposphere, where they enter the precipitation elements. Photolysis of H_2O_2 can be a minor source of HO:

$$H_2O_2 + h\nu \rightarrow 2HO.$$

3.4.b. Reactions of NO_x

The nitrogen oxides NO and NO_2 are the central species in the NO_x cycle. The chief natural source of stratospheric NO_x comes from the reaction of $O(^1D)$ with nitrous oxide, N_2O, in which one of the channels produces NO:

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

N_2O is emitted from the earth's surface and is long-lived and hence well mixed in the troposphere [19]. The transport rate of N_2O to the stratosphere and the NO_x source can be estimated quite well. Stratospheric NO_x chemistry involves, in addition to NO and NO_2, the higher oxides NO_3 and N_2O_5, peroxynitric acid and nitric acid, the latter being formed by reaction of NO_2 with hydroxyl radicals:

$$HO + NO_2 + M \rightarrow HONO_2 + M.$$

Nitric acid is relatively stable and can be transported down to the troposphere where it is removed either in rain or by absorption at the surface of the earth.

Exhaust emissions from high altitude aeronautic activity are a potential source of stratospheric NO_x. Efforts to estimate the impact of this on stratospheric ozone have extended over a number of years [20].

3.4.c. Reactions of ClO_x

The important active species in the ClO_x cycle are Cl and ClO, which are formed by photochemical or free radical breakdown in the stratosphere of stable chlorine-containing species from the troposphere. The main natural source appears to be methyl chloride, while chlorofluoromethanes are an important man-made source of stratospheric chlorine [21,22].

The principal sink for active ClO_x species is conversion to HCl from which atomic Cl is released only slowly by reaction with HO,

$$HO + HCl \rightarrow H_2O + Cl,$$

allowing transport of HCl to the troposphere where it falls as rain. Conversion of Cl to HCl occurs by reaction with hydrogen-containing compounds, principally methane, with minor routes involving H_2, HO_2 and HCHO. Other compounds which are involved in stratospheric chlorine chemistry are chlorine nitrate ($ClONO_2$) and hypochlorous acid (HOCl) which are formed in the following reactions and are removed primarily by photodissociation.

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

$$ClO + HO_2 \rightarrow HOCl + O_2.$$

These reactions exemplify the close coupling between the chemistry in the NO_x, HO_x and ClO_x cycles.

3.4.d. Reactions of BrO_x

The radicals Br and BrO are potentially involved in ozone chemistry in a manner analogous to Cl and ClO. At the present time at least two potential sources of stratospheric bromine have been identified, namely methyl bromide, used as a soil fumigant and also of natural origin, and also certain fire retardants, e.g., trifluorobromomethane.

Bromine is potentially more active than chlorine in stratospheric chemistry because of the lower stability of HBr compared to HCl, allowing more bromine to remain in the active forms, Br and BrO [23].

3.4.e. Reactions of FO_x

The largest source of fluorine appears to be the chlorofluoromethanes. In contrast to Cl and Br atomic fluorine reacts rapidly with all H-containing species in the atmosphere, even water, to produce HF. HF is very stable toward photochemical and free radical breakdown and acts as a very effective sink for active FO_x species.

3.4.f. Reactions of CH_4

Most of the large amounts of methane produced by biological processes on the earth's surface is oxidized in the troposphere via reaction with HO radicals. A small fraction is transported to the stratosphere where its oxidation provides a source of water vapor.

The oxidation chemistry involves the conversion of the CH_3 radicals to formaldehyde and photolysis of formaldehyde to produce either radical fragments or molecular hydrogen

$$\begin{aligned} HCHO + h\nu &\rightarrow H + HCO \quad \lambda \leq 338\ \text{nm} \\ &\rightarrow H_2 + CO. \end{aligned}$$

The resultant carbon monoxide is oxidized to CO_2 by reaction with HO:

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

3.4.g. The Sulfur Cycle

The thermochemistry of SO_x species, e.g., SO and SO_2, is unfavorable for involvement in the "odd-oxygen" chemistry in the stratosphere. However, sulfur compounds are involved in stratospheric chemistry through their participation in the formation of an aerosol layer in the lower stratosphere. Recent results indicate that the primary source of sulfur in the stratosphere is carbonyl sulfide, OCS, which is photodissociated in the middle stratosphere [24].

In the troposphere SO_2 is an important pollutant from the burning of fossil fuels. Its oxidation can occur homogeneously, e.g., by reaction with HO, or heterogeneously in the precipitation elements. The oxidation products are sulfuric acid and sulfate aerosols.

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4. Data Sheets

4.1. Reactions of O_x

$O + O_2 + M \longrightarrow O_3 + M$

$\Delta H° = -106.5$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.6 \pm 0.6) \times 10^{-35} \exp(510/T)$ [Ar]	200–246	Huie, Herron and Davis, 1972 [1]	(a)
3.6×10^{-34} [Ar]	298		
5.6×10^{-34} [N_2]	298		
11.6×10^{-34} [N_2]	218		
$(5.4 \pm 1.2) \times 10^{-34}$ [N_2]	295	Ball and Larkin, 1973 [2]	(b)
$(5.4 \pm 0.3) \times 10^{-34}$ [O_2]	295	Bevan and Johnson, 1973 [3]	(c)
$(2.7 \pm 0.3) \times 10^{-34}$ [Ar]			
3×10^{-34} [N_2]	300	von Rosenberg and Trainor, 1974 [4]	(d)
$(6.3 \pm 1) \times 10^{-34}$ [O_2]	300	Hogan and Burch, 1976 [5]	(e)
$4.3 \times 10^{-35} (T/900)^{-1.7}$ [Ar]	769–910	Jones and Davidson, 1962 [6]	(f)
$6.0 \times 10^{-35} (T/900)^{-1.7}$ [N_2]	689–863		
$4.3 \times 10^{-35} (T/900)^{-1.7}$ [Ar]	600–1100	Endo, Glänzer and Troe, 1979 [7]	(g)
Reviews and Evaluations			
4.05×10^{-34} [Ar]	300	Baulch et al., 1976 [8]	(h)
5.5×10^{-34} [N_2]	300		
6.07×10^{-34} [O_2]	300		
$7.65 \times 10^{-35} \exp(500/T)$ [Ar]	200–350		
$1.1 \times 10^{-35} \exp(1057/T)$ [Ar]	200–1000		(i)
$6.6 \times 10^{-35} \exp(510/T)$ [Ar]	200–346	Hampson and Garvin, 1977 [9]	

Comments

(a) Flash photolysis-resonance fluorescence at 50-500 Torr; relative efficiencies of M, He: Ar: N_2 = 0.92: 1.0: 1.6 at 298 K, Ar: N_2 = 1.0: 1.7 at 218 K.

(b) Discharge-flow method; relative efficiencies of M, O_2 : N_2 : Ar = 2.1: 2.0: 1.5.

(c) Pulse radiolysis of O_3; relative efficiencies of M, Ar: O_2; N_2O: CO_2 : SF_6 = 2.7: 5.4: 13.0: 31.0.

(d) Flash photolysis with IR and UV detection following vibrationally excited O_3, relative efficiencies of M, O_2 : N_2 = 1:1.

(e) O produced from O_3 pyrolysis, O detection by ESR.

(f) From shock tube experiments on dissociation, relative efficiencies of M, Ar: N_2 = 1.6: 2.4.

(g) From shock tube experiments on dissociation, relative efficiencies of M, He:Ne: Ar: Kr: Xe: N_2: O_2: CO_2 : CF_4 : SF_6 = 4.5: 2.8: 1.6: 2.3: 1.8: 3.5: 3.3: 13.5: 8.5: 22.5.

(h) From recombination data; table of relative efficiencies given; incorrect values reevaluated.

(i) From dissociation data; incorrect values reevaluated.

Preferred Value

$k_0 = 3.6 \times 10^{-34}(T/300)^{-1.96}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 200 – 346 K.

$k_0 = 3.6 \times 10^{-34}(T/300)^{-1.93}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 200 – 1100 K.

$k_0 = 5.6 \times 10^{-34}(T/300)^{-2.36}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 218 – 298 K.

$k_0 = 5.6 \times 10^{-34}(T/300)^{-2.23}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200 – 1100 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 200–350 K.
± 0.2 over range 200–1100 K.

Comments on Preferred Values

The data in the range 200–350 K are in good agreement as are the shock tube data near 1000 K for M= Ar. Relative efficiencies also now agree well near 300 K whereas the efficiencies near 1000 K need to be redetermined by independent measurements.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.8 \pm 1) \times 10^{-12}$	295	Hippler, Schippert and Troe, 1975 [9]	(a)

Comments

(a) Measured $k/k(O + NO_2)$ in photolysis of $NO_2 - O_2$ mixtures in presence of 1–200 atm of N_2; reevaluation of earlier data, accounting for N_2O_5 reactions, with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k_\infty = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 295 K.

Comments on Preferred Values

The data are relatively uncertain because they are derived from the difference of two quantum yields; furthermore the side effects of the reaction $2NO + O_2 \rightarrow 2NO_2$ on the result were uncertain. Absolute rate measurements are required.

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c \simeq 5 \times 10^{21}$ molecules cm^{-3} at 295 K. A broadening factor of $F_c = 0.85 \pm 0.1$ is estimated.

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$O + O_3 \longrightarrow 2O_2$

$\Delta H° = -391.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.1) \times 10^{-14}$	296	Lundell, Ketcheson and Schiff, 1969 [1]	(a)
$(1.3 \pm 0.4) \times 10^{-14}$	300	Husain, Kirsch and Donovan, 1972 [2]	(b)
$(1.1 \pm 0.2) \times 10^{-11} \exp(-2155/T)$	269–409	McCrumb and Kaufman, 1972 [3]	(c)
8.0×10^{-15}	298		
$(2.0 \pm 0.2) \times 10^{-11} \exp(-2280/T)$	220–353	Davis, Wong and Lephardt, 1973 [4]	(d)
9.5×10^{-15}	298		
Reviews and Evaluations			
$1.9 \times 10^{-11} \exp(-2300/T)$	220–1000	Hampson and Garvin, 1978 [5]	(e)
$8.6 \times 10^{-12} \exp(-2090/T)$	200–500	Baulch et al., 1976 [6]	(e)

Comments

(a) Flow system; O atoms produced by N_2O pyrolysis on a heated wire; O_3 detection by UV absorption, O detection by calorimetric probe.

(b) Flash photolysis of O_3, detection of O and O_3 by UV absorption at 121.6 and 130 nm.

(c) Flow system; O atoms produced by O_3 pyrolysis on a Nernst glower.

(d) Laser flash photolysis of O_3 followed by O resonance fluorescence at 130 nm.

(e) Expression based on the 298 K measurements of McCrumb and Kaufman (1972) and Davis, Wong and

Lephardt (1973). High temperature results ($T > 1000$ K) are available but relatively uncertain and not taken into account with much weight.

Preferred Value

$k = 9.5 \times 10^{-15}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

$k = 2.0 \times 10^{-11} \exp(-2280/T)$ cm^{3}molecule^{-1}s^{-1} over range 220–1000 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K, ± 0.3 at 1000 K.

$\Delta (E/R) = \pm 130$ K.

Comments on Preferred Values

The preferred value is that given by Davis, Wong and Lephardt (1973). It overlaps within the larger error limits given with the data of McCrumb and Kaufman (1972). It also agrees with earlier data near 1000 K as reviewed by Baulch et al. (1976).

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

$\Delta H^\circ(1) = -\ 33$ kJ mol^{-1}

$\Delta H^\circ(2) = -\ 190$ kJ mol^{-1}

Rate coefficient data $k = k_1 + k_2$

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.0 \pm 0.5) \times 10^{-11}$	300	Heidner, Husain and Wiesenfeld, 1973 [1]	(a)
$(5.3 \pm 0.6) \times 10^{-11}$	300	Fletcher and Husain, 1976 [2]	(b)
$2.9 \times 10^{-11} \exp((67 \pm 10)/T)$	104–354	Streit et al., 1976 [3]	(c,i)
$(3.7 \pm 0.7) \times 10^{-11}$	300		
$(4.0 \pm 0.6) \times 10^{-11}$	300	Lee and Slanger, 1978 [4]	(d)
Branching Ratios			
$k_1/k = 0.77 \pm 0.2$	300	Lee and Slanger, 1978 [4]	(d)
$k_1/k = 0.8\ (+0.2, -0.3)$	300	Schofield, 1978 [5]	(e)
Reviews and Evaluations			
7.4×10^{-11}	300	Cvetanovic, 1974 [6]	(f)
7.4×10^{-11}	300	Hampson and Garvin, 1975 [7]	(g)
3.7×10^{-11}	298	Schofield, 1978 [5]	(e)
$2.9 \times 10^{-11} \exp(67/T)$	200–300	NASA, 1977 [8]	(h,i)

Comments

(a) Flow system. $[O(^1D)]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm $O(3D_2 \leftarrow 2D_2)$. Analysis of data uses modified Beer-Lambert law: $I_t/I_0 = \exp(-\epsilon(cl)^\gamma)$ with $\gamma = 0.41$.

(b) Same system as described in (a) with modified detection circuitry. Apparently supersedes result reported in [1].

(c) Flow system. $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.

(d) $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. $O_2(^1\Sigma_g^+)$ monitored by time resolved build-up of the $O_2(^1\Sigma_g^+) \rightarrow (^3\Sigma_g^-)$ (1–1) and (0–0) band emissions.

(e) Evaluation. Recommended value of electronic energy transfer efficiency to give $O_2(^1\Sigma_g^+)$ based on all previously reported results. Only newer measurement of this efficiency is that of Lee and Slanger, 1978 [4].

(f) Recommended value based on analysis of complete set of $O(^1D)$ rate data—both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [7].

(g) Accepted recommendation of Cvetanovic, 1974 [6].

(h) Accepted results in Streit et al., 1976 [3].
(i) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k = 4.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-11} \exp(67/T)$ cm^3 molecule^{-1} s^{-1} over range 200–350 K.
$k_1/k = 0.8$.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 100$ K.
$\Delta \log (k_1/k) = \pm 0.1$.

Comments on Preferred Value

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: O(^{1}D) + CO$_2$. The ratio k/k(O(^{1}D) + CO$_2$) is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [6]. These values are the following: 0.37 (NOAA Laboratories [3]); 0.31 (Cambridge Laboratory [2]); 0.35 (Cvetanovic's review [6]); 0.34 (mean value). The preferred value of the rate constant for the reference reaction of O(^{1}D) with CO$_2$ is taken as the simple average of the value reported form NOAA Laboratories (1.0×10^{-10} cm^3 molecule^{-1} s^{-1}, ref. [3] and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^3 molecule^{-1} s^{-1}, ref. [2]). The preferred value for k is then derived from the values k/k(O(^{1}D) + CO$_2$) = 0.34 and k(O(^{1}D) + CO$_2$) = 1.35×10^{-10} cm^3 molecule^{-1} s^{-1}. The temperature dependence in reference [3] is accepted.

The preferred value for k has been derived in this way for consistency with the method used to derive the other O(^{1}D) rate coefficient values recommended in this evaluation. Inclusion of the recent data of Lee and Slanger, 1978 [4] with equal weighting would result in lowering the preferred value of k at 298 K to 4.4×10^{-11} cm^3 molecule^{-1} s^{-1}.

The value recommended in Schofield, 1978 [5] for the efficiency of transfer of the O(^{1}D) electronic energy to give O$_2$ in the $^1\Sigma_g^+$ electronic state has been adopted here. It is based on a number of studies referenced therein and is confirmed by the recent results of Lee and Slanger, 1978 [4].

The predominant fate of the O$_2$($^1\Sigma_g^+$) in the atmosphere would appear to be quenching to the ground state (see reference [9] for values of rate coefficients).

For further comments on O(^{1}D) values see Introduction.

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$O_2 + h\nu \longrightarrow$ 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

Absorption cross section data and evaluations

Wavelength range/nm	Reference	Comments
116–244	Ackerman, 1971 [1]	(a)
135–175	Hudson, 1971 [2]	(a)
175–203	Hudson and Mahle, 1972 [3]	(b)
176–210	Ackerman, Biaumé and Kockarts, 1970 [4]	(c)
176–205	Ackerman and Biaumé, 1970 [5]	(d)
176–205	Frederick and Hudson, 1978 [6]	(e)
176–250	Hudson, 1974 [7]	(f)
177–200	Kockarts, 1971 [8]	(g)
110–240	Laufer, 1973 [9]	(h)
110–240	Krupenie, 1972 [10]	(h)
110–240	Hudson and Kieffer, 1975 [11]	(h)

Quantum yield data and evaluations

Measurement		Wavelength/nm	Reference	Comments
$\phi_1 \cong 1$		175–200	Laufer, 1973 [9]	(i)
$\phi_2 \cong 1$		133–175	Lee et al., 1977 [13]	(j)
ϕ_2 range	0.1–0.9	117–133	Lee et al., 1977 [13]	(j)
$\phi_3 \leq 0.1$		88–120	Lawrence and Mc Ewan, 1973 [14]	(k)
$\phi_3 \leq 0.03$		121.6	Ridley, Atkinson and Welge, 1973 [15]	(l)

Comments

(a) Review and tabulation of absorption cross sections.

(b) Line widths and oscillar strengths of Schumann-Runge bands, cross sections for underlying continua over range 150–300 K.

(c) High resolution cross sections for Schumann-Runge bands.

(d) High resolution study of Schumann-Runge bands.

(c) High resolution study of Schumann-Runge bands, leading to line widths which are, for some lines, smaller than reported by Ackerman and Biaumé [5].

(f) Discussion of cross section data in the range 176–250 nm.

(g) Average cross sections in the Schumann-Runge bands at 160,200 and 300 K.

(h) Discussion of cross section data and photochemical transitions in the range 100–240 nm.

(i) Discussion of quantum yield data from ref. [12].

(j) Measurements of O(^{1}D) yields in the range 117–177 nm.

(k) Absolute quantum yield measurements of O(^{1}S) at 8 wavelengths.

(l) Relative quantum yield measurement of O(^{1}S) at 121.6 nm.

Preferred Values

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

λ/nm	$10^{19}\sigma/cm^2$	ϕ_1	ϕ_2	λ/nm	$10^{19}\sigma/cm^2$	ϕ_1	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)	1*	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 [8]; there is considerable scatter of data at $\lambda \geq 200$ nm with an uncertainty of about ± 20% over the range 200–230 nm. The on-set of the $O(^1D)$ production near 175 nm is given by a smooth, probably temperature dependent function, see refs. [13] and [16]. For $175 < \lambda < 200$ nm we prefer $\phi_1 \cong 1$.

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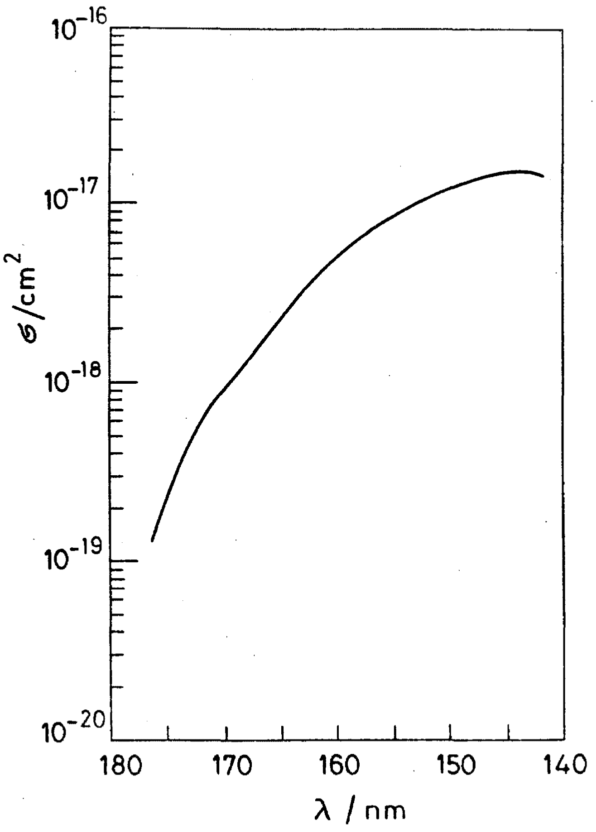

FIGURE 2. Absorption cross section of O_2, 140–175 nm.

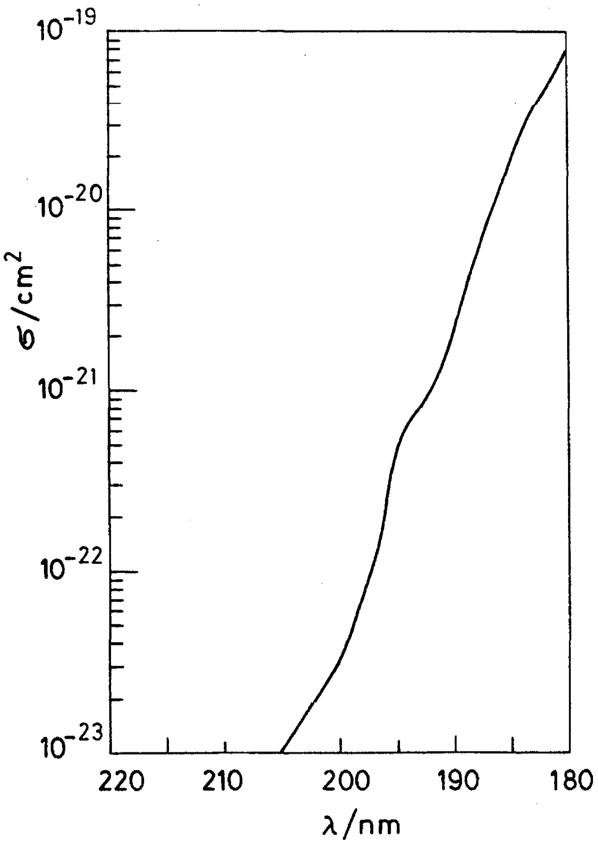

FIGURE 3. Average absorption cross section of O_2 in the Schumann-Runge bands (averages over 2 nm).

$O_3 + h\nu \longrightarrow$ products

Primary photochemical transitions

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

Absorption cross section data and evaluations

Wavelength range/nm	Reference	Comments
117–730	Ackerman, 1971 [1]	(a)
175–850	Hudson, 1974 [2]	(b)
250–340	Vigroux, 1953 [3]	(c)

Quantum yield data and evaluations

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \cong 1$, $\phi_2 \cong 0$	570–630	Castellano and Schumacher, 1962 [4]	(d)
$\phi_5 \cong 1$	250–300	Fairchild and Lee, 1978 [5]	(e)
$0 < \phi_5 < 1$	295–320	Moortgat and Kudszus, 1978 [6]	(f)
$0 < \phi_5 < 1$	295–320	Arnold, Comes and Moortgat, 1977 [7]	(g)
$0 < \phi_5 < 1$	295–320	Moortgat, Kudszus and Warneck, 1977 [8]	(g) (h)
$0 < \phi_5 < 1$	295–320	Philen, Watson and Davis, 1977 [9]	(i)
$0 < \phi_5 < 1$	295–320	Lin and De More, 1973 [10]	(j)
$0 < \phi_5 < 1$	295–320	Moortgat and Warneck, 1975 [11]	(g)
$\phi_6 < 0.05$	240–265	Gauthier and Snelling, 1971 [12]	(k)
$\phi_6 < 0.05$	240–265	Gilpin, Schiff and Welge, 1971 [13]	(k)
$0 < \phi_5 < 1$	303–316	NASA, 1977 [14]	(l)

Comments

(a) Tabulation of cross section data from earlier references.

(b) Discussion and comparison of cross section data from earlier references.

(c) Temperature dependence of cross sections measured over range 181–300 K.

(d) Ozone photolysis with overall quantum yield of 2.

(e) Relative quantum yield measurement indicating no appreciable change of ϕ_5 over range 250–300 nm.

(f) Representation of earlier $\phi_5(\lambda, T)$ measurements in analytical form.

(g) Decrease of $\phi_5(O^1D)$ from 1 to 0 observed over range 307–318 nm.

(h) Measurements at 230–300 K, indicating shift of $\phi_5(\lambda, T)$ toward smaller λ at smaller T.

(i) Decrease of $\phi_5(O^1D)$ observed at wavelengths about 2 nm smaller than in ref. [8] and [9].

(j) Measurements at 235 K in agreement with ref. [8].

(k) Measurements of $O_2(b\,^1\Sigma_g^+)$ indicating minor importance of reaction [6].

(l) Discussion of $\phi_5(O(^1D))$ data from earlier references.

Preferred Values

Absorption cross sections at 298 K

λ/nm	$10^{19}\sigma/\mathrm{cm}^2$	λ/nm	$10^{19}\sigma/\mathrm{cm}^2$	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
138.9–140.8	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	1.05
158.7–161.3	12.0	238.1–241.0	79.7	320	0.291
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	$10^{23}\sigma/\mathrm{cm}^2$
400		580	455
410	2.91	600	489
420	3.99	620	390
440	12.5	640	274
460	35.7	660	207
480	71.1	680	137
500	122	700	91.3
520	178	720	64.0
540	288	730	51.4
560	388		

Temperature coefficient of absorption cross sections

λ/nm	σ(214 K)/σ(300K)	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
250–303	$\phi_5 \cong 1.0$	200–300
304	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
308	0.9	300
310	0.7	300
312	0.3	300
314	0.15	300
316	0.10	300
318	0.003	300
319	0	300
570–630	$\phi_1 = 1.0$	200–300

Comments on Preferred Values

The preferred data for σ at 298 K are taken from Ackerman [1], the temperature coefficient is taken from Vigroux [3]. The quantum yield data for 235 K are from the NASA evaluation, those for 300 K from ref. [7]. The ϕ_5 (λ) curves of refs. [7] and [9] at 300 K are displaced by about 2 nm, this discrepancy can only be resolved by further measurements. ϕ_1 in the Chappuis-band (570–650) is taken from ref. [4].

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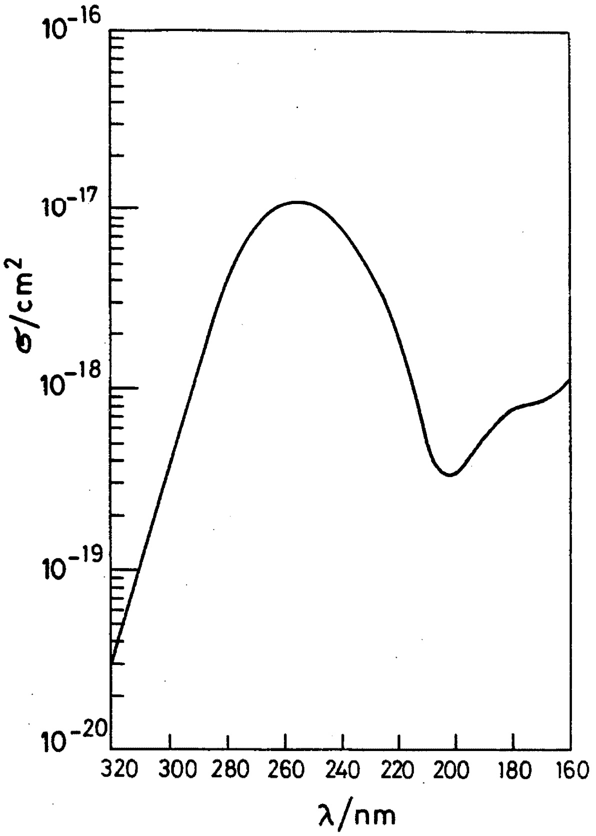

FIGURE 4. Absorption cross section of O_3, 160–320 nm.

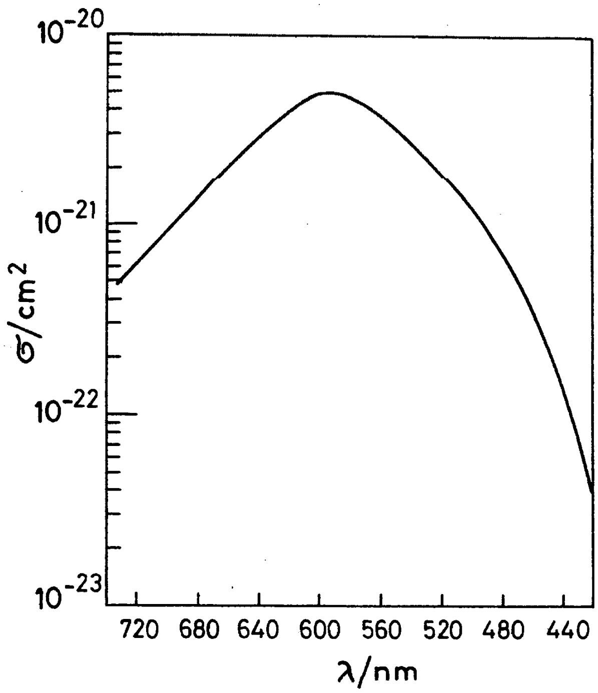

FIGURE 5. Absorption cross section of O_3, 420–730 nm.

4.2. Reactions of HO_x

$$H + HO_2 \rightarrow H_2 + O_2 \quad (1)$$

$$\rightarrow 2HO \quad (2)$$

$$\rightarrow H_2O + O \quad (3)$$

$\Delta H° (1) = -220$ kJ mol^{-1}

$\Delta H° (2) = -142$ kJ mol^{-1}

$\Delta H° (3) = -213$ kJ mol^{-1}

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

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_1 = 8.3 \times 10^{-12}$	297	Moortgat and Allen, 1973 [1]	(a)
$k_2 = 1 \times 10^{-11}$	297		(a)
$k_3 = 6.7 \times 10^{-12}$	297		(a)
$(4.7 \pm 1.0) \times 10^{-11}$	293	Hack et al., 1979 [2]	(b)
Branching Ratios			
$k_1/k = 0.29$	293	Hack, Wagner and Hoyermann, 1978 [3]	(c)
$k_2/k = 0.69$	293		
$k_3/k \leq 0.02$	293		
Reviews and Evaluations			
$k_1 = 4.2 \times 10^{-11} \exp(-350/T)$	290–800	Baulch et al., 1972 [4]	
$k_2 = 4.2 \times 10^{-10} \exp(-950/T)$	290–800		
$k_1 = 4.2 \times 10^{-11} \exp(-350/T)$	300–1000	Lloyd, 1974 [5]	(d)
$k_2 = 4.2 \times 10^{-10} \exp(-950/T)$	300–1000		(d)
$k_3 = 8.3 \times 10^{-11} \exp(-500/T)$	300–1000		(e)

Comments

(a) Secondary reaction in $H + O_2 + M$ system; derived from fit of concentration vs time plots.

(b) Fast flow system, He carrier; radicals generated from $H + O_2 + M$ or $F + H_2O_2$; [HO] and [HO_2] monitored by laser resonance.

(c) Fast-flow system He carrier; radicals generated from $H + O_2 + M$; [H], [O] and [HO] monitored by ESR technique rate coefficient ratios were determined from measurements of concentration profiles at short reaction times.

(d) Recommendation of Baulch et al., 1972 [2].

(e) Temperature coefficient estimated.

Preferred Value

$k = 4.7 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k_1 = 1.4 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k_2 = 3.2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k_3 \leq 9.4 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta \log k_1 = \pm 0.4$ at 298 K.
$\Delta \log k_2 = \pm 0.4$ at 298 K.
$\Delta \log k_3 = {}^{+0.3}_{-?}$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient (k) for the composite reaction (1 + 2 + 3) is that from the recent laser magnetic resonance study of Hack et al., 1979 [2]. The preferred individual rate coefficients, k_1, k_2 and k_3 are from the ratios of Hack, Wagner and Hoyermann, 1978 [3] and the preferred value of k. The earlier data of Moortgat and Allen, 1973 [1] were preliminary results which were not substantiated. There are no data available on the temperature coefficients of reaction (1), (2) or (3) although they would be expected to be small since the reactions involve an atom and a small radical.

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$H + O_2 + M \longrightarrow HO_2 + M$

$\Delta H^\circ = -216$ 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			
2.0×10^{-32} [Ar]	300	Westenberg, Roscoe and de Haas, 1970 [1]	(a)
$(1.6 \pm 0.2) \times 10^{-32}$ [Ar]	298	Hikida, Eyre and Dorfman, 1971 [2]	(b)
$(7.5 \pm 0.3) \times 10^{-33}$ [He]	300	Ahumada, Michael and Osborne, 1972 [3]	(c)
$(6.0 \pm 0.4) \times 10^{-33}$ [Ar]			
$(6.7 \pm 1.1) \times 10^{-33} \exp(238/T)$ [He]	203–404	Kurylo, 1972 [4]	(d)
1.5×10^{-32} [He]	300		
1.9×10^{-32} [Ar]	300	Westenberg and de Haas, 1972 [5]	(e)
$(6.8 \pm 1.1) \times 10^{-33} \exp(345/T)$ [Ar]	220–360	Wong and Davis, 1974 [6]	(f)
2.1×10^{-32} [Ar]	300		
6.1×10^{-33} [Ar]	1260–1910	Getzinger and Blair, 1969 [7]	(g)
5.8×10^{-33} [N_2]			
$(8.3 \pm 3.5) \times 10^{-33}$ [Ar]	1435–1868	Blair and Getzinger, 1970 [8]	(h)
6.9×10^{-33} [O_2]	1900	Peeters and Mahnen, 1973 [9]	(i)
$(6.1 \pm 1.1) \times 10^{-33}$ [Ar]	964–1075	Slack, 1977 [10]	(j)
$(9.1 \pm 1.6) \times 10^{-33}$ [N_2]	980–1176		
$(2.5 \pm 0.3) \times 10^{-32}$ [He]	293	Hack, Hoyermann and Wagner, 1978 [11]	(k)
Reviews and Evaluations			
$4.1 \times 10^{-33} \exp(500/T)$ [Ar]	300–2000	Baulch et al., 1972 [12]	(l)
2.2×10^{-32} [Ar]			
$6.7 \times 10^{-33} \exp(290/T)$ [Ar]	203–404	Hampson and Garvin, 1975 [13]	(m)
$6.6 \times 10^{-33} (T/1000)^{-1.7}$ [N_2]	300–1500	Dixon-Lewis and Williams, 1977 [15]	
$1.0 \times 10^{-32} (T/1000)^{-1.42}$ [N_2]	200–2000	Slack, 1977 [10]	
$5.8 \times 10^{-33} (T/1000)^{-1.0}$ [Ar]	200–2200	Slack, 1977 [10]	
$6.7 \times 10^{-33} \exp(290/T)$ [Ar]	203–404	Hampson and Garvin, 1978 [16]	(l)

Comments

(a) H_2 discharge-flow system at 0.5–2.4 Torr; decay of [H] in presence of O_2 measured by ESR spectroscopy; relative efficiencies of M, Ar : He = 1.0 : 1.0.

(b) Pulse radiolysis study; mixtures of H_2(2 Torr) and O_2(0.98–4.9 Torr) in Ar (500–1130 Torr); decay of [H] followed by Lyman-α spectrophotometry; relative efficiencies of M, H_2 : Ar = 2.9 : 1.0.

(c) Hg-photosensitized decomposition of H_2 with light pulses of 30 ns duration; decay of [H] followed by Lyman-spectrophotometry; relative efficiencies of M, H_2 : Kr : He : Ar : Ne = 2.0 : 1.8 : 1.2 : 1.0 : 0.2.

(d) Flash photolysis-resonance fluorescence technique; pressure range 10–400 Torr for He; relative efficiencies of M, CH_4 : N_2 : He : Ar = 15.7 : 3.4 : 1.0 : 1.0 at 298 K and N_2 : He = 4-5 : 1.0 at 226 K.

(e) Hydrogen discharge-flow system; [H] monitored by ESR spectroscopy; relative efficiencies of M, Ar : He = 1.0 : 1.0.

(f) Flash photolysis-resonance fluorescence technique; pressure range 20–300 Torr for He; relative efficiencies of M, Ar : He : H_2 : N_2 : CH_4 = 1.0 : 0.93 : 3.0 : 2.8 : 22 at 300 K.

(g) Shock tube study with lean H_2–O_2–Ar or H_2–O_2–N_2 mixtures; analysis via HO UV absorption spectroscopy.

(h) Shock tube study with H_2–O_2–Ar mixtures; analysis via H_2O IR emission signals.

(i) Study of CH_4–O_2 flames at 40 Torr; decay of radical pool in the burned gas.

(j) Shock tube study measuring induction times near to the second explosion limit of H_2–O_2 mixtures; computer fit of induction times to yield rate coefficients; Ar values based on experimental data from the literature.

(k) Discharge flow system with ESR detection technique.

(l) Relative efficiencies of M, Ar : He : N_2 : O_2 : H_2O = 1.0 : 1.0 : 1.3 : 1.3 : 21.

(m) Based on Baulch et al., 1972 [12] and subsequent data of Refs. [3–6], [10]; relative efficiencies of M, Ar : He : N_2 : O_2 : H_2O = 1.0 : 1.0 : 3.1 : 3.1 : 25 at 300 K; used also by NASA evaluation, 1977 [14].

Preferred Value

$k_0 = 5.9 \times 10^{-32} (T/300)^{-1.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_0 = 1.8 \times 10^{-32} (T/300)^{-0.8}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 200–2000 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ over range 200–2000 K.

Comments on Preferred Values

The difference in the relative efficiencies of Ar and N_2 is greater than normally observed; the data, therefore, should be reconfirmed.

High Pressure Rate Coefficients

No available experimental data in the intermediate fall-off or high pressure range.

Estimate: $k_\infty \simeq 2.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (300–2000 K, similar to calculations for H + OH and H + NO by Quack and Troe, 1977 [17]). This gives $[Ar]_c \simeq 1.4 \times 10^{22}$ molecule cm^{-3} at 300 K (corresponding to 600 atm).

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$H + O_3 \rightarrow HO + O_2$

$\Delta H° = -321.7$ 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	Phillips and Schiff, 1962 [1]	(a)
$(9.89 \pm 0.26) \times 10^{-11} \exp(-(516 \pm 60)/T)$	298–638	Clyne and Monkhouse, 1977 [2]	(b)
1.75×10^{-11}	298		
$(1.33 \pm 0.32) \times 10^{-10} \exp(-(449 \pm 58)/T)$	219–360	Lee et al., 1978 [3]	(c)
$(2.86 \pm 0.22) \times 10^{-11}$	300		
$(1.50 \pm 0.18) \times 10^{-10} \exp(-(499 \pm 32)/T)$	196–424	Keyser, 1979 [4]	(d)
$(2.79 \pm 0.18) \times 10^{-11}$	298		
Reviews and Evaluations			
$1.2 \times 10^{-10} \exp(-560/T)$	298–638	NASA, 1977 [5]	(e)
$1.0 \times 10^{-10} \exp(-516/T)$	298–638	Hampson and Garvin, 1978 [6]	

Comments

(a) Fast-flow system; [H] and $[O_3]$ monitored by mass spectrometry.

(b) Fast-flow system; [H] monitored by atomic resonance fluorescence.

(c) Flash photolysis, resonance fluorescence detection of H; $[O_3]$ monitored spectrophotometrically.

(d) Fast-flow system; [H] monitored by resonance fluorescence; $[O_3]$ monitored by UV Photometry.

(e) Recommends provisional data of Clyne and Monkhouse [2].

Preferred Value

$k = 2.8 \times 10^{-11}$ 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 recent studies of Lee et al. [3] and Keyser [4] are in excellent agreement. The preferred value is derived from a least-mean-squares treatment of these data (ref [3] and [4]). The rate constant of Phillips and Schiff [1] is also in reasonable agreement with these studies but we are unable to account for the apparent discrepancy involving the data of Clyne and Monkhouse [2].

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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			
$(5 \pm 2) \times 10^{-11}$	265	Clyne, 1963 [1]	(a)
$(5 \pm 2) \times 10^{-11}$	293		
$(1.8 \pm 0.7) \times 10^{-11}$	310	Kaufman and Del Greco, 1963 [2]	(b)
$(5 \pm 2) \times 10^{-11}$	310	Kaufman, 1964 [3]	(c)
5×10^{-12}	300	Westenberg and de Haas, 1965 [4]	(d)
$(4.3 \pm 1.3) \times 10^{-11}$	300	Breen and Glass, 1970 [5]	(e)
$(4.2 \pm 0.3 \times 10^{-11}$	228	Westenberg, de Haas, and Roscoe, 1970 [6]	(f)
$(3.2 \pm 0.3) \times 10^{-11}$	298		
$(3.2 \pm 0.5) \times 10^{-11}$	340		
Relative Rate Coefficients			
3.9×10^{-11}	425	Campbell and Handy, 1977 [7]	(g)
Reviews and Evaluations			
3.8×10^{-11}	300	Baulch et al., 1972 [8]	
4.2×10^{-11}	300–2000	Wilson, 1972 [9]	
3.8×10^{-11}	300	Hampson and Garvin, 1975 [10]	(h)
4.2×10^{-11}	300	NASA, 1977 [11]	(i)
4.2×10^{-11}	300	Hampson and Garvin, 1978 [12]	

Comments

(a) Discharge-flow system; HO from $H + NO_2$; O from $HO + HO \rightarrow H_2O + O$; [H] by emission from $H + NO$; [O] by emission from $O + NO$.

(b) Discharge-flow system; HO from $H + NO_2$; O from $N + NO$; [HO] by ultraviolet absorption spectroscopy.

(c) Hydrogen discharge-flow system; HO from $H + NO_2$; [HO] by ultraviolet absorption spectroscopy; [O] by emission from $O + NO$.

(d) Discharge-flow system; HO from $H + NO_2$; [H] and [HO] by ESR absorption.

(e) Discharge-flow system; HO from $H + NO_2$; [O] and [HO] by ESR absorption.

(f) Discharge-flow; stirred-flow system; homogeneous reactor set inside ESR cavity; HO from $H + NO_2$; [HO] and [O] by ESR absorption.

(g) Discharge-flow system; O from $N + NO \rightarrow N_2 + O$; [O] monitored in $H_2/CO/N_2$ mixtures by $O + CO$ chemiluminescence; k derived from measured ratio, $k/k\,(HO + CO) = 260 \pm 20$ at 425 K and taking $k\,(HO + CO) = 1.5 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} at 425 K (low pressure value).

(h) Recommendation of Baulch et al., 1972 [8].

(i) The NASA Ref. Publ. 1010 lists ref. [10] as its reference source but appears to select the evaluation of Wilson, 1972 [9].

Preferred Value

$k = 3.8 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

We have selected the recommendation of Baulch et al., 1972 [8] which is based on the data of refs. [1–6]; it is also in good agreement with the more recent relative rate coefficient of Campbell and Handy, 1977 [7]. There are no reliable data on the temperature coefficient of this reaction but it is expected to be small. There is a lack of agreement between the forward and reverse rate constants and the equilibrium constant of the system $O + HO \rightleftharpoons O_2 + H$. The preferred value is nearly a factor of two higher than the value calculated from the reverse rate constant and the equilibrium constant.

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$O + HO_2 \rightarrow HO + O_2$

$\Delta H° = -212$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(3.53 \pm 1.0) \times 10^{-11}$	293	Burrows, Harris, and Thrush, 1977 [1]	(a)
$(3.1 \pm 1.0) \times 10^{-11}$	298	Burrows et al., 1978 [2]	(b)
Reviews and Evaluations			
3.5×10^{-11}	293	NASA, 1977 [3]	(c)
3.5×10^{-11}	293	Hampson and Garvin, 1978 [4]	(c)

Comments

(a) Preliminary report of data in ref. [2].

(b) Fast-flow system; O reacted with H_2O_2; [HO] and [HO_2] monitored by laser magnetic resonance spectroscopy; relative rate coefficients (a) $k/k(O + HO) = 0.83$ and (b) $k/k(HO + H_2O_2) = 37$ measured, hence absolute rate coefficients calculated as follows: (a) $k = 3.2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} based on $k(O + HO) = 3.8 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} and (b) $k = 3.1 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} based on $k(HO + H_2O_2) = 8.3 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1}, all at 298 K; result in data table is the average of two determinations.

(c) Recommends data of Burrows, Harris and Thrush, 1977 [1].

Preferred Value

$k = 3.1 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The recent papers of Burrows, Harris and Thrush, 1977 [1] and Burrows et al., 1978 [2] appear to be the first experimental measurement of this rate coefficient. Confirmation and measurement of the temperature coefficient are required. It should be noted that the reliability of the above value of k is dependent upon the realibility of the rate coefficients of the reference reactions ($O + HO$ and $HO + H_2O_2$) as well as any inherent error in the measurement.

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$O + H_2O_2 \rightarrow HO + HO_2$ (1)

$\rightarrow O_2 + H_2O$ (2)

ΔH° (1) = -72 kJ mol^{-1}

ΔH° (2) = -354.66 kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 4 \times 10^{-15}$	300	Foner and Hudson, 1962 [1]	(a)
$4.6 \times 10^{-11} \exp(-3220/T)$	370–800	Albers et al., 1970 [2]	(b)
9.3×10^{-16}	298*		
$(2.75 \pm 0.41) \times 10^{-12} \exp(-(2125 \pm 261)/T)$	283–368	Davis, Wong and Schiff, 1974 [3]	(c)
2.1×10^{-15}	298		
Reviews and Evaluations			
$2.75 \times 10^{-12} \exp(-2125/T)$	283–373	NASA, 1977 [4]	(d)
$2.75 \times 10^{-12} \exp(-2125/T)$	283–373	Hampson and Garvin, 1978 [5]	(d)

Comments

(a) Discharge-flow system; $-d[O]/dt$ measured mass spectrometrically.

(b) Fast-flow system; [O] monitored by ESR absorption.

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

(d) Evaluation based on data of Davis et al. [3].

Preferred Value

$k = 2.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-12} \exp(-2100/T)$ cm^3 molecule^{-1} s^{-1} over range 283–368 K.

Reliability

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

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

Comments on Preferred Values

The preferred value is from the work of Davis, Wong, and Schiff, 1974 [3], although it should be pointed out that in this study a knowledge of the absolute concentration of H_2O_2 is needed, which limits the accuracy of the measurements. Earlier data of Foner and Hudson, 1970 [1] and Albers et al., 1970 [2], from much less direct studies, are not in good agreement with the preferred data at 298 K. Confirmation of this rate coefficient is needed. There are no experimental data regarding the relative rates of reactions (1) and (2).

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$O(^1D) + H_2 \rightarrow HO + H$ (1)
$\rightarrow O(^3P) + H_2$ (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			
$(2.7 \pm 0.3) \times 10^{-10}$	300	Heidner and Husain, 1973 [1]	(a)
$(0.99 \pm 0.3) \times 10^{-10}$	204–352	Davidson et al., 1977 [2]	(b)
Reviews and Evaluations			
2.9×10^{-10}	298	Cvetanović, 1974 [3]	(c)
2.9×10^{-10}	298	Hampson and Garvin, 1975 [4]	(d)
9.9×10^{-11}	200–350	NASA, 1977 [5]	(e)
9.9×10^{-11}	204–352	Hampson and Garvin, 1978 [6]	(f)

Comments

(a) Flash photolysis of O_3 in Hartley band; $O(^1D)$ monitored by time-resolved absorption of atomic resonance radiation at 115.2 nm.

(b) Pulsed laser photolysis of O_3 at 266 nm; $O(^1D)$ monitored by time-resolved emission from $O(^1D) \rightarrow O(^3P)$ transmission at 630 nm.

(c) Review of all rate data up to 1974.

(d) Based on review of Cvetanović [3].

(e) Accepts results in ref. [2].

(f) Recommendation of NASA Ref. Publ. 1010, 1977 [5].

Preferred Value

$k = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} over range 200–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio $k/k(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in ref. [3]. These values are the following: 1.59 (Cambridge Laboratory [1,7]; 0.99 (NOAA Laboratories [2]); 1.86 (Cvetanović's review [3]); 1.48 (mean value).

The preferred value of the rate constant for the reference reaction of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} cm^3 molecule^{-1} s^{-1}, ref. [8]) and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^3 molecule^{-1} s^{-1}, ref. [7]).

The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 1.48$ and $k(O(^1D) + CO_2) = 1.35 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

The temperature dependence in ref. [2] is accepted.

There have been no measurements of the branching ratio (k_1/k_2) for this reaction, but reaction (1) appears to predominate.

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

$\Delta H^\circ (1) = -118.7$ kJ mol^{-1}

$\Delta H^\circ (2) = -196.59$ kJ mol^{-1}

$\Delta H^\circ (3) = -189.2$ 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			
$(3.0 \pm 0.3) \times 10^{-10}$	300	Heidner, Husain and Wiesenfeld, 1973 [1]	(a)
$(2.3 \pm 0.4) \times 10^{-10}$	253–353	Streit et al., 1976 [2]	(b)
Branching ratio			
$k_2/k_1 = 0.01_{-0.01}^{+0.005}$	298	Zellner, Himme, and Wagner, 1979 [3]	(c)
Reviews and Evaluations			
3.5×10^{-10}	298	Cvetanović, 1974 [4]	(d)
3.5×10^{-10}	298	Hampson and Garvin, 1975 [5]	(e)
2.3×10^{-10}	200–350	NASA, 1977 [6]	(f)
2.3×10^{-10}	253–353	Hampson and Garvin, 1978 [7]	(g)

Comments

(a) Flash photolysis of O_3 in Hartley band; $O(^1D)$ monitored by time-resolved absorption of atomic resonance radiation at 115.2 nm.

(b) Pulsed laser photolysis of O_3 at 266 nm; $O(^1D)$ monitored by time-resolved emission from $O(^1D) \rightarrow O(^3P)$ transmission at 630 nm.

(c) Flash photolysis in Hartley continuum above 200 nm of O_3/H_2O mixtures with large excess of H_2O; [HO] monitored by ultraviolet absorption; H_2 determined by gas chromatographic analysis following several consecutive flashes.

(d) Review of all data up to 1974.

(e) Based on Cvetanović review [4].

(f) Accepts results in ref. [2].

(g) Recommendation of NASA Ref. Publ. 1010, 1977 [6].

Preferred Value

$k = 2.8 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} over range 200–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio k/k $(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in ref. [4]. These values are the following: 1.76 (Cambridge Laboratory [1,8]; 2.3 (NOAA Laboratories [2]; 2.21 (Cvetanović's review [4]; 2.09 (mean value).

The preferred value of the rate constant for the reference reaction of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [2]) and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [8]).

The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 2.09$ and $k(O(^1D) + CO_2) = 1.35 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}.

The temperature dependence in ref. [2] is accepted.

The branching ratio recently determined by Zellner et al., [3] requires confirmation.

There appears to be no published data available on k_3.

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$HO + H_2 \rightarrow H_2O + H$

$\Delta H° = -62.8$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.1 \pm 1.1) \times 10^{-15}$	298	Stuhl and Niki, 1972 [1]	(a)
7.6×10^{-15}	298	Westenberg and de Haas, 1973 [2]	(b)
1.8×10^{-14}	352		
3.2×10^{-14}	403		
1.4×10^{-13}	518		
3.6×10^{-13}	628		
6.6×10^{-13}	745		
$(1.8_{-0.6}^{+0.9}) \times 10^{-11} \exp(-2330/T)$	210–460	Smith and Zellner, 1974 [3]	(c)
7.1×10^{-15}	298		
$8.7 \times 10^{-11} \exp(-3250/T)$	1350–1600	Gardiner, Mallard and Owen, 1974 [4]	(d)
$(5.79 \pm 0.26) \times 10^{-15}$	300	Overend, Paraskevopoulos and Cvetanović, 1975 [5]	(e)
$5.9 \times 10^{-12} \exp(-(2008 \pm 150)/T)$	298–425	Atkinson, Hansen and Pitts, 1975 [6]	(f)
7.0×10^{-15}	298		
5.3×10^{-15}	300	Trainor and Von Rosenberg, 1975 [7]	(g)
Reviews and Data Evaluations			
$3.6 \times 10^{-11} \exp(-2590/T)$	300–2500	Baulch et al., 1972 [8]	
$3.8 \times 10^{-11} \exp(-2600/T)$	300–2000	Wilson, 1972 [9]	
$1.94 \times 10^{-15} T^{1.3} \exp(-1825/T)$	250–2500	Dixon-Lewis and Williams, 1977 [10]	
$3.6 \times 10^{-11} \exp(-2590/T)$	300–2500	Hampson and Garvin, 1978 [11]	
$1.66 \times 10^{-16} T^{1.6} \exp(-1660/T)$	240–2500	Zellner, 1979 [12]	(h)

Comments

(a) Pulsed vacuum-ultraviolet photolysis of H_2O; [HO] monitored by resonance fluorescence.

(b) Fast-flow system; HO from $H + NO_2 \rightarrow HO + NO$; [HO] monitored by ESR; results showed non-Arrhenius behaviour.

(c) Flash photolysis of H_2O or $N_2O + H_2$; [HO] monitored by time-resolved resonance absorption; at $T \leq 270$ K the Arrhenius plot showed slight curvature.

(d) Shock-tube study, $H_2:O_2:Ar$; [HO] measured by absorption; k derived from computer stimulation of proposed mechanism.

(e) Flash photolysis of H_2O or $N_2O + H_2$; [HO] monitored by time-resolved resonance absorption.

(f) Flow system; HO from photolysis of H_2O at 105 nm; [HO] monitored by resonance fluorescence.

(g) Flash photolysis of H_2O; [HO] monitored by time-resolved resonance ultraviolet absorption spectroscopy.

(h) Review of data of references [1–4] and earlier data as part of a study of non-Arrhenius behaviour in bimolecular reactions of HO radicals. Reactions with a finite Arrhenius activation energy around room temperature were found to obey temperature dependence of form $AT^n \exp(-E/RT)$.

Preferred Value

$k = 7.1 \times 10^{-15}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

$k = 1.8 \times 10^{-11} \exp(-2330/T)$ cm^{3}molecule s^{-1} over range 210–300 K.

Reliability

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

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

Comments on Preferred Values

There is fairly good agreement among the various recent determinations of the room temperature rate coefficient for this reaction. We have selected the data of Smith and Zellner, 1974 [3] for the preferred data, on the grounds that their study is the most comprehensive within the temperature range of interest (210–460 K). It should be noted, however, that this work revealed that below 270 K the Arrhenius plot for the above reaction displayed some slight upward curvature, for which the authors were unable to account. The above preferred value is in line with previous reviews and evaluations, refs. [8–11]. The recent review of Zellner, 1979 [12] proposed non-Arrhenius behaviour for this and other bimolecular reactions of HO radicals.

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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			
$(1.40 \pm 0.30) \times 10^{-12}$	310	Del Greco and Kaufman, 1962 [1]	(a)
$(2.57 \pm 0.20) \times 10^{-12}$	300	Dixon-Lewis, Wilson and Westenberg, 1966 [2]	(b)
$(2.08 \pm 0.08) \times 10^{-12}$	300	Wilson and O'Donovan, 1967 [3]	(c)
$(8.4 \pm 2.6) \times 10^{-13}$	300	Breen and Glass, 1970 [4]	(d)
$(2.3 \pm 0.3) \times 10^{-12}$	300	Westenberg and de Haas, 1973 [5]	(e)
$(2.1 \pm 0.5) \times 10^{-12}$	298	McKenzie, Mulcahy and Steven, 1973 [6]	(e)
$(1.4 \pm 0.2) \times 10^{-12}$	300	Clyne and Down, 1974 [7]	(f)
$(2.1 \pm 0.1) \times 10^{-12}$	300	Trainor and von Rosenberg, 1974 [8]	(g)
$5.7 \times 10^{-11} \exp(-2500/T)$	1200–1800	Ernst, Wagner and Zellner, 1977 [9]	(h)
$3.0 \times 10^{-12} \exp(-270/T)$	252–353	Wagner, Wagner and Zellner, 1979 [10]	(i)
$(1.3 \pm 0.2) \times 10^{-12}$	298		
Relative Rate Coefficients			
$9.1 \times 10^{-11} \exp(-3500/T)$	1500–2000	Rawlins and Gardiner, 1974 [11]	(j)
Reviews and Data Evaluations			
$1.0 \times 10^{-11} \exp(-550/T)$	300–2000	Baulch et al., 1972 [12]	
2.57×10^{-12}	300	Wilson, 1972 [13]	
1.7×10^{-12}	300	Clyne and Down, 1974 [7]	
$1.0 \times 10^{-11} \exp(-550/T)$	200–300	NASA, 1977 [14]	(k)
$9.3 \times 10^{-12} \exp(-460/T)$	300–2000	Dixon-Lewis and Williams, 1977 [15]	
$1.0 \times 10^{-11} \exp(-550/T)$	300–2000	Hampson and Garvin, 1978 [16]	(k)
$\exp(-27.7 + 1.5 \times 10^{-3}T)$	250–2000	Zellner, 1979 [17]	(l)

Comments

(a) Discharge-flow system; [HO] monitored by ultraviolet absorption spectroscopy; data recalculated on basis of revised absorption coefficients (ref. [18]).

(b) Discharge-flow system; [HO] monitored by movable ESR detection; HO from $H + NO_2$; CO added and final O_2 and CO_2 yields determined by mass spectrometry.

(c) Discharge-flow system; [HO] by ESR detection; HO from $H + NO_2$; excess NO_2 used and CO added; [CO_2] determined by mass spectrometry.

(d) Discharge-flow system; [HO] monitored by ESR spectroscopy.

(e) Discharge-flow system; HO generated from $H + NO_2 \rightarrow HO + NO$; [HO] monitored by ESR spectroscopy.

(f) Fast-flow system; HO from $H + NO_2 \rightarrow HO + NO$; [HO] monitored by resonance fluorescence absorption.

(g) Pulsed photolysis of H_2O; [HO] monitored by time-resolved absorption spectroscopy.

(h) Shock tube study; HNO_3/Ar; [HO] monitored by time-resolved UV resonance absorption.

(i) Flash photolysis-resonance absorption study.

(j) Shock tube study; $[H_2]/[O_2] = 0.1$ in Ar; [HO] measured by ultraviolet absorption; rate coefficient derived from computer simulation of proposed mechanism.

(k) Recommendation of Baulch et al., 1972 [12].

(l) In this review of data of references [1–9] the author presents strong evidence for non-Arrhenius behaviour of HO + HO reaction. The recommended temperature dependence of k is of the form $k = \exp(a + bT)$ but the expression given above does not take account of the more recent data of Wagner, Wagner and Zellner, 1979 [10].

Preferred Value

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

Reliability

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

Comments on Preferred Values

The preferred rate coefficient at 298 K is the mean value of the results of references [1–8] and [10]. In fact, the same average is obtained by taking the mean of the most recent studies references [5–8] and [10].There is more scatter among the room temperature measurements than one might have anticipated and this may be due to the fact that the reaction is very sensitive to wall conditions [4].

The recent review of Zellner, 1979 [17] strongly indicates non-Arrhenius behaviour of the reaction over the entire temperature range of study (250–2000 K). The temperature dependence in the lower temperature range (250–350 K), recently reported by Wagner, Wagner and Zellner, 1979 [10], requires confirmation especially in view of the scatter of measured data at 298 K.

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$HO + HO + M \longrightarrow H_2O_2 + M$

$\Delta H° = 214.3$ 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			
$(2.5 \pm 0.3) \times 10^{-31}$ [N_2]	300	Trainor and von Rosenberg, 1974 [1]	(a)
$(6.5 \pm 2) \times 10^{-31}(T/300)^{-0.7}$ [N_2]	250–350	Wagner and Zellner, 1978 [2]	(b)
$1.9 \times 10^{-32}(T/1000)^{-2.92}$ [Ar]	950–1450	Kijewski and Troe, 1972 [3]	(c)
Reviews and Evaluations			
$2.5 \times 10^{-33} \exp(2550/T)$ [N_2]	700–1500	Baulch et al., 1972 [4]	(d)
$1.25 \times 10^{-32} \exp(900/T)$ [N_2]	200–300	NASA, 1977 [5]	(e)

Comments

(a) Flash photolysis of H_2O; HO concentration monitored by time resolved absorption spectroscopy; no deviations from a third order rate law observed up to pressures of 1 atm.

(b) Flash photolysis of H_2O; HO concentration monitored by time resolved absorption spectroscopy; measurements at 20–400 Torr of N_2; fall-off effects observed and corrected for.

(c) From shock tube study of decomposition of H_2O_2; in agreement with several earlier high temperature studies, see ref. [4]; relative efficiencies of M, Ar: N_2 = 0.67: 1, see ref. [4].

(d) From studies of the reverse decomposition of H_2O_2; no recommendation for recombination at lower temperatures because of widely scattered data.

(e) Based on room temperature value by Trainor and von Rosenberg (1974) and a temperature coefficient similar to that of HO + NO.

Preferred Value

$k_0 = 6.5 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 6.5 \times 10^{-31}(T/300)^{-2.9}$ [Ar] cm^3 molecule^{-1} s^{-1} over range 300–1500 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 300–1500 K.

Comments on Preferred Values

There remains a large uncertainty about the room temperature value, since the discrepancy between the data of Trainor and von Rosenberg (1974) and Wagner and Zellner (1978) is not understood. We prefer Wagner and Zellner's value because it is much more consistent with a theoretical analysis of the rate constant (see Troe, 1977 [6]), and because the expected fall-off behaviour has been observed.

High Pressure Rate Coefficients

First indications of deviation from third order behaviour have been observed in refs. [2] and [3]. If one estimates $k_\infty \simeq 3 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}, one would have $[N_2]_c \simeq 5 \times 10^{19}$ molecules cm^{-3} at 300 K and $[Ar]_c \simeq 1.6 \times 10^{21}$ molecules cm^{-3}. Therefore, fall-off effects can probably not be neglected in studies in the 100 Torr range at 300 K. They can be estimated with $F_c \simeq 0.8$ at 300 K.

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$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H^\circ = -283$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 1.0) \times 10^{-11}$	293	Hack, Preuss and Wagner, 1978 [1]	(a)
Relative Rate Coefficients			
$(2.0 \pm 0.3) \times 10^{-10}$	298	Hochanadel, Ghormley and Ogren, 1972 [2]	(b)
$\sim 1 \times 10^{-10}$	298	DeMore and Tschuikow-Roux, 1974 [3]	(c)
$\sim 3 \times 10^{-11}$	~1200	Glanzer and Troe, 1975 [4]	(d)
$(5.1 \pm 1.6) \times 10^{-11}$	293	Burrows, Harris and Thrush, 1977 [5]	(e)
$(5.1 \pm 1.7) \times 10^{-11}$	298	Burrows et al., 1978 [6]	(f)
$2\text{–}3 \times 10^{-11}$	295	Chang and Kaufman, 1978 [7]	(g)
$\sim 1 \times 10^{-10}$	298	DeMore, 1979 [8]	(h)
Reviews and Evaluations			
$2 \times 10^{-11} - 2 \times 10^{-10}$	300	Hampson and Garvin, 1975 [9]	(i)
3×10^{-11}	200–300	NASA, 1977 [10]	(j)
1.3×10^{-11}	1500	Dixon-Lewis and Williams, 1977 [11]	
3×10^{-11}	200–300	Hampson and Garvin, 1978 [12]	(k)

Comments

(a) Fast flow system; radicals generated from $F + H_2O$ and $F + H_2O_2$; [HO] and $[HO_2]$ monitored by laser magnetic resonance.

(b) Flash photolysis of H_2O in presence of Ar + 2% O_2; $[HO_2]$ monitored by ultraviolet absorption spectroscopy; k determined from computer simulation of data in terms of proposed mechanism.

(c) Steady-state photolysis of $H_2O-O_2-N_2$ mixture at 184.9 nm; $[O_3]$ monitored by spectrophotometry; absolute k at 298 K calculated from experimental ratio $(k \cdot k(HO_2 + O_3))/(k(HO_2 + HO_2) \cdot k(HO + O_3)) = 0.82$ and taking $k(HO_2 + O_3) = 2.0 \times 10^{-15}$; $k(HO_2 + HO_2) \sim 3.5 \times 10^{-12}$ (derived from $1.5 \times 2.3 \times 10^{-12}$, which allows for a $[H_2O]$ corresponding to 4.6 Torr) and $k(HO + O_3) = 6.7 \times 10^{-14}$ cm^{3}molecule^{-1}s^{-1}.

(d) Shock-tube study of the decomposition of $HONO_2$ in the presence of NO_2 and Ar; $[HO_2]$ monitored by ultraviolet absorption spectroscopy; review of earlier high temperature data.

(e) Preliminary report of data in reference [5], based on $k(HO + H_2O_2) = 8.0 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

(f) Fast-flow system; three radical systems studied, (i) $H + NO_2 \rightarrow HO + NO$ followed by $HO + H_2O_2 \rightarrow H_2O + HO_2$, (ii) $H + H_2O_2 \rightarrow H_2 + HO_2$ followed by $H + O_3 \rightarrow HO + O_2$ and (iii) $H + H_2O_2 \rightarrow H_2 + HO_2$ followed by $H + NO_2 \rightarrow HO + NO$; [HO] and $[HO_2]$ monitored by laser magnetic resonance; k derived from $k/k(HO + H_2O_2) = 63.6$ (mean of three systems studied) and taking $k(HO + H_2O_2) = 8.0 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} at 298 K.

(g) Fast-flow system; radicals generated by $H + NO_2 \rightarrow HO + NO$ followed by $HO + O_3 \rightarrow HO_2 + O_2$; [HO] monitored by resonance fluorescence at 309 nm; [HO_2] monitored by titration with NO; k determined from computer simulation of data in terms of proposed mechanism consisting of 12 reactions.

(h) Same experimental system as for ref. [3] (Comment (c)), leading to $(k \cdot k(HO_2 + O_3))/(k(HO_2 + HO_2) \cdot k(HO + O_3)) = 0.79$; absolute k calculated as in Comment (c).

(i) This suggested range of values was not an evaluation.

(j) Based on data of ref. [5] and [7].

(k) Recommendation of NASA, 1977 [9].

Preferred Value

$k = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value was obtained by taking an average of the data from the three most recent studies of Hack and coworkers [1], Thrush and coworkers [5,6] and Chang and Kaufman [7]. The earlier data of Hochanadel, Ghormley and Ogren [2] is not reported in sufficient detail to make a meaningful evaluation. The discrepancy between the preferred data and that derived from the work of DeMore and Tschuikow-Roux [4] and DeMore [8] has been taken [8] to indicate a possible dependence of this rate coefficient on reaction conditions such as pressure and presence of H_2O vapour. (See Comments on Preferred Values for reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$). The large error limits assigned are intended to allow for the possible complications involving the participation of H_2O vapour.

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H^\circ = -143$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.1 \times 10^{-13} T^{1/2} \exp(-600/T)$	300–458	Greiner, 1968 [1]	(a)
9.6×10^{-13}	300		
$(8.0 \pm 1.7) \times 10^{-12} \exp(-670/T)$	298–670	Hack, Hoyermann and Wagner, 1975 [2]	(b)
7.6×10^{-13}	298		
$(6.8 \pm 1.3) \times 10^{-13}$	298	Harris and Pitts, 1979 [3]	(c)
Relative Rate Coefficients			
1.2×10^{-12}	300	Gorse and Volman, 1972 [4]	(d)
6.2×10^{-13}	298	Meagher and Heicklen, 1974 [5]	(e)
Reviews and Evaluations			
$1.7 \times 10^{-11} \exp(-910/T)$	300–800	Baluch et al., 1972 [6]	
$1.7 \times 10^{-11} \exp(-910/T)$	300–800	Hampson and Garvin, 1975 [7]	(f)
$1 \times 10^{-11} \exp(-750/T)$	298–670	NASA, 1977 [8]	(g)
$1.0 \times 10^{-11} \exp(-720/T)$	300–800	Dixon-Lewis and Williams, 1977 [9]	
$1 \times 10^{-11} \exp(-750/T)$	200–300	Hampson and Garvin, 1978 [10]	(h)

Comments

(a) Flash photolysis of H_2O_2; [HO] monitored by ultraviolet absorption spectroscopy.

(b) Fast-flow system; HO from $H + NO_2 \rightarrow HO + NO$; [HO] monitored by ESR.

(c) Flash photolysis, resonance fluorescence detection of HO; $[H_2O_2]$ measured by titration before and after reaction.

(d) Steady-state photolysis of H_2O_2 at 254 nm in presence of CO and O_2; rate coefficient ratio $k/k(HO + CO) = 8.13$ at 298 K derived from kinetic analysis based on measured rate of formation of CO_2; total pressure in system ~10–35 Torr; absolute k calculated taking $k(HO + CO) = 1.5 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} (low pressure value).

(e) Steady-state photolysis of H_2O_2 at 254 nm in the presence of CO and O_2; rate coefficient ratio, $k/k(HO + CO) = 4.1 \pm 0.6$, derived from kinetic analysis based on Φ_{CO_2} measurements; total pressure in system ~50 Torr; absolute k calculated taking $k(HO + CO) = 1.5 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} (low pressure value).

(f) Recommendation of Baulch et al., 1972 [6].

(g) Based on data of refs. [1] and [2].

(h) Recommendation of NASA, 1977 [8].

Preferred Value

$k = 8.0 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

$k = 7.6 \times 10^{-12} \exp(-670/T)$ cm^{3}molecule^{-1}s^{-1} over range 200–700 K.

Reliability

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

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

Comments on Preferred Values

The preferred rate coefficient at 298 K is the mean of the results of refs. [1–3]. The preferred value of (E/R) is that of Hack, Hoyermann and Wagner [3], on the basis of their larger temperature range, and the preferred A-factor was then calculated from the preferred k at 298 K.

At the same time it should be noted that the NASA report [8] questions the validity of the results of both Greiner [1] and Hack et al. [2]. The former involved a large temperature rise from the photolysis flash, and the latter used radical densities of 3×10^{13} cm^{-3} and may have been complicated by the back reaction between the HO_2 product and residual NO from the HO formation step. More work is needed on this reaction.

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$HO + O_3 \rightarrow HO_2 + O_2$

$\Delta H^\circ = -180$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp(-956/T)$	220–450	Anderson and Kaufman, 1973 [1]	(a)
5.3×10^{-14}	298		
$(6.5 \pm 1.0) \times 10^{-14}$	298	Kurylo, 1973 [2]	(b)
$(1.6 \pm 0.5) \times 10^{-12} \exp(-990/T)$	250–300	Wagner, Wagner and Zellner, 1979 [3]	(c)
5.8×10^{-14}	298		
$(1.82^{+0.35}_{-0.29}) \times 10^{-12} \exp((-930 \pm 50)/T)$	238–357	Ravishankara, Wine and Langford, 1979 [4]	(d)
$(7.96 \pm 0.39) \times 10^{-14}$	298		
Relative Rate Coefficients			
$5.0 \times 10^{-12} \exp(-1230/T)$	271–333	DeMore, 1975 [5]	(e)
8.1×10^{-14}	298		
Reviews and Data Evaluations			
$1.6 \times 10^{-12} \exp(-1000/T)$	220–450	Hampson and Garvin, 1975 [6]	
6.5×10^{-14}	300	Baulch et al., 1976 [7]	
$1.5 \times 10^{-12} \exp(-1000/T)$	220–450	NASA, 1977 [8]	(f)
$1.5 \times 10^{-12} \exp(-1000/T)$	200–300	Hampson and Garvin, 1978 [9]	(g)

Comments

(a) Fast-flow system; HO from $H + NO_2 \rightarrow HO + NO$; [HO] monitored by ultraviolet fluorescent scattering at 309 nm.

(b) Flash photolysis-resonance fluorescence study.

(c) Flash photolysis H_2O/O_3 mixtures; [HO] monitored by resonance fluorescence; $[O_3]$ monitored by absorption at 253.7 nm.

(d) Laser flash photolysis study; resonance detection of HO; $[O_3]$ monitored *in situ* before and after each experiment by ultraviolet absorption.

(e) Steady-state photolysis of $O_2-H_2O-CO_2$ mixture at 184.9 nm; $[O_3]$ monitored by spectrophotometry; total pressure of system 730 Torr; absolute k derived from $k/k(HO + CO) = 16.8 \exp(-1230/T)$ and taking $k(HO + CO) = 3.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} independent of temperature (high pressure value); this reference includes preliminary data of W. B. DeMore, [10] ($k/k(HO + CO) = 0.45$ at 300 K).

(f) Adjusted from recommendation of Hampson et al., [11], because of error in derivation of $[O_3]$ from absorption measurement.

(g) Recommendation of NASA, 1977 [8].

Preferred Value

$k = 6.7 \times 10^{-14}$ 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.

$\Delta (E/R) = {}^{+250K}_{-100K}$.

Comments

There is a consensus among the various rate measurements of this reaction, including two recent studies. The preferred rate coefficient at 298 K is the mean of the values of references [1–5]. The preferred value of (E/R) is the rounded-off mean of the values of references [1–5] and the preferred A-factor corresponds to the preferred k at 298 K and the preferred (E/R).

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$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$\Delta H^\circ = -140$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\sim 3 \times 10^{-12}$	298	Foner and Hudson. 1962 [1]	(a)
$(3.6 \pm 0.5) \times 10^{-12}$	300	Paukert and Johnston, 1972 [2]	(b)
6.2×10^{-12}	298	Hochanadel, Ghormley and Ogren, 1972 [3]	(c)
2.5×10^{-12}	298	Hamilton and Lii, 1977 [4]	(d)
$(3.8^{+3.3}_{-1.8}) \times 10_{-14} \exp(+(1245 \pm 180)/T)$	273–338	Cox, 1978 [5]	(e)
2.3×10^{-12}	298		
$<(7.5 \pm 5.0) \times 10^{-13}$	298	Burrows et al., 1978 [6]	(f)
Relative Rate Coefficients			
$(2.5^{+2.5}_{-1.0}) \times 10^{-12}$	1000–1200	Troe, 1969 [7]	(g)
Reviews and Evaluations			
3×10^{-12}	300	Baulch et al., 1972 [8]	
$1.7 \times 10^{-11} \exp(-500/T)$	300–1000	Lloyd, 1974 [9]	
$3 \times 10^{-11} \exp(-500/T)$	300–1000	Hampson and Garvin, 1975 [10]	
2.5×10^{-12}	300	NASA, 1977 [11]	
3.3×10^{-12}	300	Dixon-Lewis and Williams, 1977 [12]	
2.5×10^{-12}	298	Hampson and Garvin, 1978 [13]	

Comments

(a) Discharge-flow system; reaction followed by sampling directly into a mass spectrometer using a molecular beam sampling system; calibration of this system could be in error by as much as a factor of 2; no H_2O present.

(b) HO_2 generated by (i) photolysis of H_2O_2, (ii) photolysis of O_3 in presence of H_2O_2 and (iii) photolysis Cl_2 in presence of H_2O_2; $[HO_2]$ monitored by absorption at 210 nm in molecular modulation technique; no H_2O present; k calculated from $k/\sigma = 8.0 \times 10^5$ cm s^{-1} and taking $\sigma_{210} = 4.5 \times 10^{-18}$ cm^2 molecule^{-1}.

(c) Flash-photolysis of H_2O in presence of H_2 containing 2% O_2; $[HO_2]$ monitored by absorption at 230.5 nm; 21 Torr H_2O present; k calculated from $k/\sigma = 2.9 \times 10^6$ cm s^{-1} and taking $\sigma_{230.5} = 2.17 \times 10^{-18}$ cm^2 molecule^{-1} (ref. [2]).

(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; treatment of data includes previous results of Hochanadel, Ghormley and Ogren, 1974 [3] and accepts the absorption cross-section measurements of HO_2 determined by Paukert and Johnston, 1972 [2]; k refers to measurements with no H_2O present.

(e) HO_2 generated by pulsed photolysis (310–410 nm) of Cl_2 in presence of H_2 and O_2; $[HO_2]$ monitored by molecular modulation ultraviolet absorption spectrometry; data obtained at pressures near 760 Torr with no H_2O present; data yield $k/\sigma(220 \text{ nm}) = (1.1 \pm 0.4) \times 10^4 \exp((1245 \pm 92)/T)$ cm s^{-1}; $\sigma_{220} = 3.5 \times 10^{-18}$ cm^2 molecule^{-1}.

(f) Fast-flow system; $Cl + H_2O_2 \rightarrow HCl + HO_2$ or $F + H_2O_2 \rightarrow HF + HO_2$; $[HO_2]$ monitored by laser magnetic resonance; decay of $[HO_2]$ attributed to either a wall loss or a second-order reaction; the same HO_2 behavior was observed with different wall coatings; no H_2O present; low pressure study, 2 Torr mainly He.

(g) Shock-tube study of decomposition of H_2O_2; $[HO_2]$ and $[H_2O_2]$ monitored by ultraviolet absorption; kinetic analysis of reaction mechanism, $H_2O_2 \rightarrow 2HO$, $HO + H_2O_2 \rightarrow H_2O + HO_2$; $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, $HO + HO_2 \rightarrow H_2O + O_2$; rate coefficient essentially measured relative to $k(HO + H_2O_2)$ (this evaluation).

Preferred Value

$k = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 atmosphere pressure.

Reliability

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

Comments on Preferred Values

We have selected the recent results of Cox, 1978 [5] for the preferred data at 298 K which are in excellent agreement with the data of Hamilton and Lii, 1977 [4]. Cox, 1978 [5] was able to confirm the earlier finding of Hamilton, 1975 [14] that there was a significant increase in the rate coefficient with added H_2O vapor. In addition, the recent low-pressure study of Burrows et al., 1978 [6] strongly suggests that the rate coefficient may be pressure dependent, the value falling off at low pressures. These results together with the negative temperature coefficient observed by Cox, 1978 [5] suggest that the reaction may be complex and that a single expression for k is inadequate. The temperature coefficient reported by Cox, 1978 [5] is recommended only for the limited temperature range quoted, for pressures near 760 Torr and in the absence of H_2O vapor. Until more data become available, values of k for other atmospheric conditions cannot be recommended on a firm basis.

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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H° = -106$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.4) \times 10^{-14} \exp(-(580 \pm 100)/T)$	250–370	Zahniser and Howard, 1978 [1]	(a)
2.0×10^{-15}	298		
Relative Rate Coefficients			
$\sim 7.5 \times 10^{-16}$	300	DeMore, 1973 [2]	(b)
$\leq 1 \times 10^{-16}$	220–450	Anderson and Kaufman, 1973 [3]	(c)
$3.7 \times 10^{-15} \exp(-375/T)$	225–298	Simonaitis and Heicklen, 1973 [4]	(d)
1.1×10^{-15}	298		
$2.1 \times 10^{-14} \exp(-925/T)$	273–332	DeMore, and Tschuikow-Roux, 1974 [5]	(e)
9.4×10^{-16}	298		
$1.2 \times 10^{-14} \exp(-600/T)$	231–334	DeMore, 1979 [6]	(f)
1.6×10^{-15}	298		
Reviews and Evaluations			
$1.7 \times 10^{-13} \exp(-1400/T)$	200–500	Lloyd, 1974 [6]	
$1 \times 10^{-13} \exp(-1250/T)$	225–298	Hampson and Garvin, 1975 [7]	
1.5×10^{-15}	300	Baulch et al., 1976 [8]	
$7.3 \times 10^{-14} \exp(-1275/T)$	200–300	NASA, 1977 [9]	
$7.3 \times 10^{-14} \exp(-1275/T)$	200–300	Hampson and Garvin, 1978 [10]	

Comments

(a) Discharge-flow system; $[HO_2]$ and $[HO]$ monitored by laser magnetic resonance; pressure range 1–4 Torr.

(b) Steady-state photolysis O_2-H_2O-CO mixture at 184.9 nm; $[O_3]$ monitored by spectrophotometry; absolute value of k obtained from measured $k/k(HO_2 + HO_2) \approx 3 \times 10^{-4}$ and value $k(HO_2 + HO_2) = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(c) Fast-slow system; HO generated from $H + NO_2 \rightarrow HO + NO$ and [HO] monitored by ultraviolet fluorescent scattering at 309 nm; absolute value of k obtained from derived $k/k(HO + O_3) \leq 0.1$ over range 220–450 K and value $k(HO + O_3) = 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K; indirect determination.

(d) O_3 photolysis at 253.7 nm in presence of O_2 and H_2; $[O_3]$ monitored by spectrophotometry; absolute value of k obtained from measured $k/k^{1/2}(HO_2 + HO_2) = 1.9 \times 10^{-8} \exp(-1000/T)$ cm$^{3/2}$ molecule$^{-1/2}$ s$^{-1/2}$ and the value $k(HO_2 + HO_2) = 3.8 \times 10^{-14} \exp(+1245/T)$ cm^3 molecule^{-1} s^{-1} ref. [12].

(e) Steady-state photolysis of O_2-H_2O or O_2-H_2O-CO mixtures at 184.9 nm; $[O_3]$ monitored by spectrophotometry; absolute value of k obtained from measured $k/k^{1/2}(HO_2 + HO_2) = 1.1 \times 10^{-7} \exp(-1550/T)$ cm$^{3/2}$ molecule$^{-1/2}$ s$^{-1/2}$ and the value $k(HO_2 + HO_2) = 3.8 \times 10^{-14} \exp(+1245/T)$. cm^3 molecule^{-1} s^{-1}, ref. [12]. (The $[H_2O]$ in these experiments was low enough for this latter expression to be valid.)

(f) Steady-state photolysis of $H_2/O_2/O_3$ mixtures at 253.7 nm; $[O_3]$ monitored by spectrophotometry; k derived from measured ratio $k/k^{1/2}(HO_2 + HO_2) = 6.4 \times 10^{-8} \exp(-1220/T)$ cm$^{3/2}$ molecule$^{-1/2}$ s$^{-1/2}$ and taking $k(HO_2 + HO_2) = 3.8 \times 10^{-14} \exp(+1245/T)$ cm^3 molecule^{-1} s^{-1}, ref. [12]; the addition of H_2O vapor caused a reduction in the value of $k/k^{1/2}(HO_2 + HO_2)$ as expected on the basis of the results for $k(HO_2 + HO_2)$; the $k/k^{1/2}(HO_2 + HO_2)$ value was confirmed by a second experiment involving steady-state photolysis of $H_2O/O_2/N_2$ mixtures at 184.9 nm.

Preferred Value

$k = 2.0 \times 10^{-15}$ 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.

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

Comments on Preferred Values

The preferred data are from the recent direct study of Zahniser and Howard, 1978 [1]. The most recent indirect study of this reaction by DeMore, 1979 [6], involving the measurement of the ratio $k/k^{1/2}(HO_2 + HO_2)$ from steady-state photolysis systems, is in good agreement with the preferred data. Direct confirmation of the rate data is needed, however, in view of the unexpectedly low A-factor.

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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

Absorption cross-section data

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

Quantum yield data

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

Comments

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

Preferred Values

λ/nm	$10^{20}\sigma$/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

Water vapor has a continuous spectrum between 175 and 190 nm; the cross section falls off rapidly towards longer wavelengths. The cross-section data from four studies [1–4] are in reasonable agreement as shown in figure 6. None of these studies report numerical data. The preferred values of the absorption cross section are taken from the review of Hudson, 1974 [6] and were obtained by drawing a smooth curve through the data of Schurgers and Welge, 1968 [4], Watanabe and Zelikoff, 1953 [1] and Thompson, Harteck and Reeves, 1963 [2].

On the basis of the nature of the spectrum and the results of Chou, Lo and Rowland, 1974 [5] on the photolysis of HTO, it is assumed that over the wavelength region 175–190 nm, reaction (2) is the only primary process and that $\phi_2 = 1.0$ [7].

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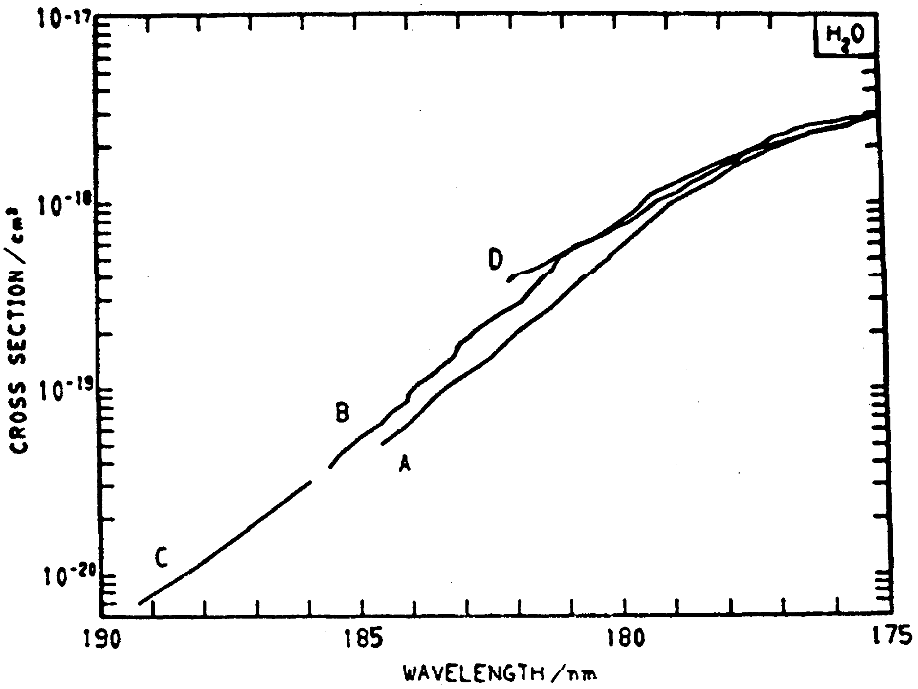

A - Laufer & McNesby[3] B - Watanabe & Zelikoff [1]
C - Thompson, Harteck & Reeves[2]
D - Schurgers & Welge [4]

FIGURE 6. Absorption cross section of H_2O vapor, 175–190 nm.

$H_2O_2 + h\nu \rightarrow$ 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)	351	341
$\rightarrow 2H + O_2$	(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

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190–254	Holt, McLane and Oldenberg, 1948 [1]	(a), (b)
210–350	Molina, Schinke and Molina, 1977 [2]	(a), (b)
195–350	Lin, Rohatgi and DeMore, 1978 [3]	(a), (b)
220–290	Troe, 1972 [4]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1(\text{-}H_2O_2) = 1$	253.7	Volman, 1963 [5]	(d)

Comments

(a) Measured at 298 K.
(b) Data plotted in figure 7.
(c) Measured at 600 and 1100 K.
(d) This result is based on a measured overall quantum yield for the decomposition of H_2O_2 of Φ(-H_2O_2) = 1.7 ± 0.4 and the assumed mechanism, $H_2O_2 + h\nu \rightarrow 2HO$; $HO + H_2O_2 \rightarrow H_2O + HO_2$; $2HO_2 \rightarrow H_2O_2 + O_2$. Greiner [6] has criticized some of the tests in support of this mechanism and suggests that O atoms could be formed in the photolytic step and still give the observed quantum yield for Φ(-H_2O_2). There are no data on this point.

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

As seen from figure 7, there is excellent agreement among the three determinations of the absorption cross section for H_2O_2 vapour at room temperature [1–3]. The preferred values correspond to the line shown in figure 7. The preferred data for σ at 600 and 1100 K are from the work of Troe, 1972 [4]. It is apparent that at $\lambda > 250$ nm there is a significant temperature dependence of σ.

It has been assumed that reaction (1) is the only primary process in the wavelength region 190–350 nm and that for $\lambda > 200$ nm $\phi_1 = 1.0$.

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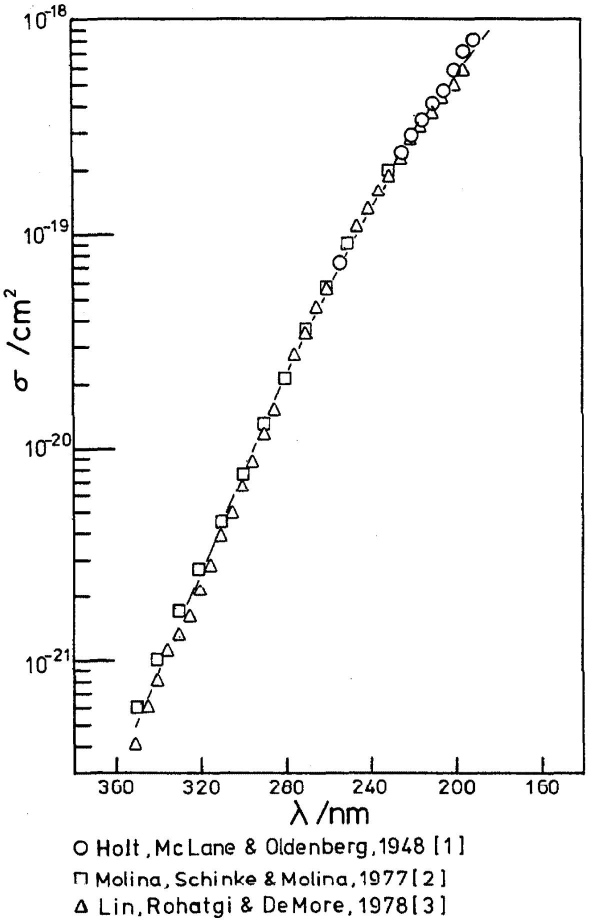

FIGURE 7. Absorption cross section of H_2O_2 vapor, 190–350 nm.

4.3. Reactions of NO_x

$N + O_2 \rightarrow NO + O$

$\Delta H° = -133.3$ kJ mol^{-1}

Rate coefficient data

k /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.38 \times 10^{-11} \exp(-3570/T)$	412–755	Clyne and Thrush, 1961 [1]	(a)
8.6×10^{-17}	298*		
$(2.34 \pm 0.12) \times 10^{-11} \exp(-(3975 \pm 100)/T)$	300–910	Wilson, 1967 [2]	(b)
$(8.0 \pm 1.0) \times 10^{-17}$	300		
$5.5 \times 10^{-12} \exp(-3220/T)$	280–333	Becker, Groth and Kley, 1969 [3]	(c,g)
11.1×10^{-17}	298		
$(10.8 \pm 1.0) \times 10^{-17}$	302	Clark and Wayne, 1970 [4]	(d)
$(7.5 \pm 0.5) \times 10^{-17}$	298	Westenberg, Roscoe and de Haas, 1970 [5]	(b)
Reviews and Evaluations			
$1.1 \times 10^{-14}(T) \exp(-3150/T)$	300–3000	Baulch, et al., 1973 [6]	(e)
$5.5 \times 10^{-12} \exp(-3220/T)$	200–300	NASA, 1977 [7]	(f,g)

Comments

(a) Discharge flow, [N] monitored by titration with NO.

(b) Discharge flow, [N] monitored by ESR.

(c) Static system, [N] monitored by decay of N_2 first positive band intensity.

(d) Discharge flow, [N] monitored by titration with NO.

(e) Evaluation for temperature range 300–3000 K. Considered all studies listed here. Recommended in Hampson and Garvin, 1975 [8].

(f) Accepted results of Becker et al., 1969 [3].

(g) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k = 8.9 \times 10^{-17}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k = 4.4 \times 10^{-12} \exp(-3220/T)$ over range 280–333 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta (E/R) = \pm 350$ K.

Comments on Preferred Value

Preferred value at room temperature given as simple average of 298 K values in references [1–5]. The value of E/R is that of Becker et al., 1969 [3] and is accepted as the most reliable value for use in this low temperature region.

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$N + O_3 \rightarrow NO + O_2$

$\Delta H° = -525$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 1.4) \times 10^{-13}$	300	Phillips and Schiff, 1962 [1]	(a)
$\leq 5 \times 10^{-16}$	300	Stief et al., 1979 [2]	(b)
Reviews and Evaluations			
5.7×10^{-13}	300	Baulch et al., 1973 [3]	(c)
$2 \times 10^{-11} \exp(-1070/T)$	200–300	NASA, 1977 [4]	(d)

Comments

(a) Discharge flow, [N] and [O_3] monitored by mass spectrometric detection, results derived by 2nd order kinetics analysis.

(b) Flash photolysis and discharge flow experiments, [N] monitored by resonance fluorescence. No decay observed, upper limit given based on detection sensitivity.

(c) Accepted results of Phillips and Schiff, 1962 [1] with increased error limits.

(d) Accepted room temperature results of Phillips and Schiff, 1962 [1]. Pre-exponential factor assigned value similar to that for reactions of O_3 with O and with Cl; E/R value derived from fit to room temperature value.

Preferred Value

$k \leq 5 \times 10^{-16}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Comments on Preferred Value

Preferred value is based on results reported by Stief et al., 1979 [2]. It is possible that the value reported by Phillips and Schiff, 1962 [1] is due to the rapid disappearance of O_3 initiated by H atom impurities according to the following catalytic cycle, which is equivalent to the reaction of N with O_3:

$$H + O_3 \rightarrow OH + O_2$$

$$N + OH \rightarrow NO + H.$$

In a study of flame spectra by Garvin and Broida, 1963 [5], visible and ultraviolet emission from possible excited products of reaction of N with O_3 was not observed unless H atoms were in the reaction zone, in which case visible and ultraviolet emission was observed from the species HO, NH, NO, N_2 and NH_2.

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$N + NO \rightarrow N_2 + O$

$\Delta H° = -313.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.2 \pm 1.4) \times 10^{-11} \exp(-(410 \pm 120)/T)$	298–670	Clyne and McDermid, 1975 [1]	(a,g)
$(2.2 \pm 0.2) \times 10^{-11}$	298		
$(2.7 \pm 0.4) \times 10^{-11}$	196–370	Lee et al., 1978 [2]	(b)
$(4.0 \pm 0.2) \times 10^{-11}$	233–400		(c)
$(3.4 \pm 0.9) \times 10^{-11}$	196–400		(d)
Reviews and Evaluations			
2.7×10^{-11}	300–5000	Baulch et al., 1973 [3]	(e)
$8.2 \times 10^{-11} \exp(-410/T)$	200–300	NASA 1977, [4]	(f,g)

Comments

(a) Discharge flow, [N] monitored by mass spectrometry.

(b) Discharge flow, [N] monitored by resonance fluorescence.

(c) Flash photolysis of N_2O, [N] monitored by resonance fluorescence.

(d) Reported value. Derived as mean value of results of two independent methods.

(e) Evaluation, based on all previously reported data. Recommended in Hampson and Garvin, 1975 [5].

(f) Accepted results of Clyne and McDermid, 1975 [1].

(g) Recommended in Hampson and Garvin, 1978 [6].

Preferred Value

$k = 3.4 \times 10^{-11}$ 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

Preferred value is based on results of Lee et al., 1978 [2]. Reliability at room temperature based on consideration of these data and the 298 K results of Clyne and McDermid, 1975 [1]. Based on a critical reexamination of the high temperature data reported in reference [1], the temperature dependence reported is rejected.

References

[1] Clyne, M. A. A. and McDermid, I. S., J. Chem. Soc. Faraday Trans. 1 **71**, 2189 (1975).
[2] Lee, J. H., Michael, J. V., Payne, W. A. and Stief, L. J., J. Chem. Phys. **69**, 3069 (1978).
[3] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System" Butterworths, London (1973).
[4] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).
[5] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.) Tech. Note 866 (1975).
[6] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.) Spec. Publ. 513 (1978).

$$\begin{aligned} N + NO_2 &\rightarrow N_2O + O \quad &(1)\\ &\rightarrow NO + NO \quad &(2)\\ &\rightarrow N_2 + O_2 \quad &(3)\\ &\rightarrow N_2 + 2O \quad &(4)\end{aligned}$$

$\Delta H°(1) = -175$ 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			
$(1.85 \pm 0.22) \times 10^{-11}$	298	Phillips and Schiff, 1965 [1]	(a)
$(1.4 \pm 0.2) \times 10^{-12}$	298	Clyne and McDermid, 1975 [2]	(b)
Reviews and Evaluations			
no recommendation		Baulch et al., 1973 [3]	(c)
1.4×10^{-12}	300	Hampson and Garvin, 1975 [4]	(d)
$2 \times 10^{-11} \exp(-800/T)$	200–300	NASA, 1977 [5]	(e,f)

Comments

(a) Discharge flow system, mass spectrometric detection. Monitored $[NO_2]$ in excess N. From stoichiometric relationships measured under different experimental conditions, the following relative contributions of the primary reaction channels were derived: $k_1/k = 0.43$; $k_2/k = 0.33$; $k_3/k = 0.10$; $k_4/k = 0.13$.

(b) Discharge flow system, mass spectrometric detection. In separate experiments monitored [N] in excess NO_2 and monitored $[NO_2]$ in excess N. Found significant increase in apparent rate constant value as initial stoichiometry was lowered. Measured yield of N_2O. Computer simulation of system used only the reaction channel to yield $N_2O + O$ and the reactions of O with NO_2 and N with NO.

(c) Evaluation in 1973 of all previously published data. No recommendation given.

(d) Accepted results of Clyne and McDermid, 1975 [2]. Accepted both the value of k and the indicated products (i.e., $N_2O + O$).

(e) Accepted 298 K results in reference [2]. "A-factor" selected at 2×10^{-11}; E/R value derived from fit to measured value of k.

(f) Recommended in Hampson and Garvin, 1978 [6].

Preferred Value

$k = 1.4 \times 10^{-12}$ 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 Value

Preferred value is that reported by Clyne and McDermid, 1975 [2]. This recommendation also accepts the mechanism given in that reference, i.e., the only reaction channel is that yielding $N_2O + O$ as products. Confirmation of this mechanism in a separate study is desirable. Temperature dependent data on this rate constant are needed.

References

[1] Phillips, L. F. and Schiff, H. I., J. Chem. Phys. **42**, 3171 (1965).

[2] Clyne, M. A. A. and McDermid, I. S., J. Chem. Soc. Faraday Trans. 1 **71**, 2189 (1975).

[3] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System" Butterworths, London (1973).

[4] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[5] NASA Reference Publication 1010, R. D. Hudson, editor Chapter 1 (1977).

[6] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + NO + M \longrightarrow NO_2 + M$

$\Delta H° = -306.2$ 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			
6.0×10^{-32} [Ar]	296	Slanger, Wood and Black, 1973 [1]	(a)
1.3×10^{-31} [Ar]	241		
$2.6 \times 10^{-32} \exp((450 \pm 100)/T)$ [N_2O]	300–392	Atkinson and Pitts, 1974 [2]	(b)
1.2×10^{-31} [N_2O]	300		
$1.7 \times 10^{-32} \exp(620/T)$ [N_2O]	298–473	Singleton et al., 1975 [3]	(b)
1.3×10^{-31} [N_2O]			
$5.0 \times 10^{-33} \exp(900/T)$ [N_2]	285–425	Campbell and Handy, 1976 [4]	(c)
1.0×10^{-31} [N_2]	300		
$(1.55 \pm 0.2) \times 10^{-32} \exp((584 \pm 35)/T)$ [N_2]	217–250	Whytock, Michael and Payne, 1976 [5]	(d)
$1.18 \times 10^{-31} (T/300^{-1.82}$ [N_2]			
$1.08 \times 10^{-32} \exp(520/T)$ [He]	217–250	Michael, Payne and Whytock, 1976 [6]	(d)
$9.33 \times 10^{-33} \exp(515/T)$ [Ne]			
$9.01 \times 10^{-33} \exp(590/T)$ [Ar]			
6.4×10^{-32} [Ar]	300		
$9.52 \times 10^{-32} \exp(570/T)$ [Kr]			
$1.46 \times 10^{-32} \exp(473 \pm 100/T)$ [Ar]	298–439	Atkinson, Perry and Pitts, 1977 [7]	(a)
$(7.04 \pm 0.7) \times 10^{-32}$ [Ar]	298		
$2.1 \times 10^{-33} (T/2000)^{-1.8}$ [Ar]	1450–2000	Troe, 1969 [8]	(e)
$2.6 \times 10^{-33} (T/2000)^{-1.8}$ [Ar]	1600–2200	Endo, Glänzer and Troe, 1979 [9]	(f)
Relative Rate Coefficients			
$(7.4 \pm 1) \times 10^{-32}$ [N_2]	295	Hippler, Schippert and Troe, 1975 [10]	(g)
8.3×10^{-32} [Ar]			
Reviews and Evaluations			
$3.0 \times 10^{-33} \exp(940/T)$ [Ar]	220–500	Baulch et al., 1973 [11]	(h)
9.6×10^{-32} [N_2]	300		
$1.55 \times 10^{-32} \exp(584/T)$ [N_2]	217–250	NASA, 1977 [12]	(i)

Comments

(a) O production by O_2 photolysis, analysis of NO_2* chemiluminescence decay.

(b) O production by Hg sensitization of N_2O, analysis by modulation phase shift technique monitoring NO_2* emission.

(c) Measurements in a discharge flow stirred reactor.

(d) Flash photolysis of NO with O resonance fluorescence detection.

(e) From dissociation of NO_2 in shock waves.

(f) From shock tube experiments, relative efficiencies of M at 1800 K, He: Ne: Ar: Kr: Xe: N_2 : SO_2 : CF_4 = 5.3: 2.0: 1.5: 1.5: 1.7: 2.5: 5.0: 5.0.

(g) Photolysis of NO_2 in presence of NO; measured $k/k(O + NO_2)$, evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; relative efficiencies of M, He: Ne: Ar: CO: N_2 : CO_2 : CH_4 : C_2H_6 : c-C_3H_6 : C_3F_8 : SF_6 = 2.1: 1.7: 3.0: 3.3: 2.7: 5.0: 5.3: 4.5: 5.3: 6.2: 5.5. k(M) dimethylpropane, dimethylbutane and isopropylbromide also measured.

(h) Relative efficiencies of M, Ar: O_2 : N_2 = 1: 1: 1.4.

(i) Based on ref. [5]; supersedes earlier recommendations such as ref. [11].

Preferred Value

$k_0 = 1.2 \times 10^{-31}(T/300)^{-1.82}$ [N_2] cm^3 molecule^{-1} s^{-1} at 200–300 K.

$k_0 = 6.4 \times 10^{-32}(T/300)^{-1.8}$ [Ar] cm^3 molecule^{-1} s^{-1} at 200–2000 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 200–2000 K.

Comments on Preferred Values

Well established rate data in good agreement with theoretical analysis from ref. [13], preferred values from refs. [5], [6], and [8].

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\geq 4.0 \times 10^{-11}$	1500	Troe, 1969 [8]	(a)
Relative Rate Coefficients			
$(3.0 \pm 0.5) \times 10^{-11}$	295	Hippler, Schippert and Troe, 1975 [9]	(b)

Comments

(a) From shock tube study of dissociation in Ar up to 300 atm; extrapolated from low pressure part of the fall-off curve; reconsideration accounting for weak collision broadening could give an up to 50% higher value.

(b) NO_2 photolysis of NO_2-NO mixtures in N_2 up to 1000 atm; measured $k/k(O + NO_2)$, evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} independent of pressure.

Preferred Value

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

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 300–1500 K.

Comments on Preferred Values

High pressure data analyzed theoretically in ref. [14].

Intermediate Fall-off Range

From the preferred values one derives $[Ar]_c \simeq 4.7 \times 10^{20}$ molecule cm^{-3} and $[N_2]_c \simeq 2.5 \times 10^{20}$ molecule cm^{-3} at 300 K and $[Ar] \simeq 1.3 \times 10^{22}$ molecule cm^{-3} at 1500 K. For M=Ar and N_2 at 300 K, a broadening factor F_c of about 0.85 ± 0.1 is estimated.

References

[1] Slanger, T. G., Wood, B. J. and Black, G., Int. J. Chem. Kinet. **5**, 615 (1973).

[2] Atkinson, R. and Pitts, J. N., Chem. Phys. Lett, **27**, 467 (1974).

[3] Singleton, D. L., Furuyama, S., Cvetanović, R. J. and Irwin, R. S., J. Chem. Phys. **63**, 1003 (1975).

[4] Campbell, I. M. and Handy, B. J., J. Chem. Soc. Faraday Trans. I **71**, 2097 (1975).

[5] Whytock, D. A., Michael, J. V. and Payne, W. A., Chem. Phys. Lett. **42**, 466 (1976).

[6] Michael, J. V., Payne, W. A. and Whytock, D. A., J. Chem. Phys. **65**, 4830 (1976).

[7] Atkinson, R., Perry, R. A. and Pitts, J. N., Chem. Phys. Lett. **47**, 197 (1977).

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[10] Hippler, H., Schippert, C. and Troe, J., Int. J. Chem. Kinet. Symp. **1**, 27 (1975).

[11] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions," Vol. 2, Butterworths, London, 1973.

[12] NASA Reference Publication 1010, "Chlorofluoromethanes and the Stratosphere", R. D. Hudson, Ed., 1977.

[13] Troe, J., J. Phys. Chem. **83**, 114 (1979).

[14] Quack, M. and Troe, J., Ber. Bunsenges. Phys. Chem. **78**, 240 (1974).

$O + NO_2 \rightarrow O_2 + NO$

$\Delta H^\circ = -192.1$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.12 \pm 0.44) \times 10^{-12}$	230–339	Davis, Herron and Huie, 1973 [1]	(a)
9.3×10^{-12}	296	Slanger, Wood and Black, 1973 [2]	(b)
10.5×10^{-12}	240		
$1.85 \times 10^{-10} \times T^{-0.53}$	298–1055	Bemand, Clyne and Watson, 1974 [3]	(c)
$(9.5 \pm 1.1) \times 10^{-12}$	298		
Reviews and Evaluations			
9.1×10^{-12}	220–500	Huie and Herron, 1973 [4]	(d)
$1.7 \times 10^{-11} \exp(-300/T)$	300–550	Baulch et al., 1973 [5]	(e)
9.1×10^{-12}	200–300	NASA, 1977 [6]	(f)

Comments

(a) Flash photolysis, [O] monitored by resonance fluorescence. Recommended in Huie and Herron, 1973 [4]; Hampson and Garvin, 1975 [7]; NASA, 1977 [6]; and in Hampson Garvin, 1978 [8].

(b) Flash photolysis, [O] monitored by chemiluminescent reaction with NO.

(c) Discharge flow system. At 298 K results obtained by two independent techniques: [O] monitored by resonance fluorescence and $[NO_2]$ monitored by mass spectrometry. Results are in good agreement. High temperature results obtained by the resonance fluorescence technique show appreciable scatter.

(d) Evaluation, based on all previously reported data. Only newer results are those in reference [3]. Accepted results reported by Davis et al., 1973 [1] as most extensive data set.

(e) This recommendation is now outdated due to newer results in references [1], [2] and [3].

(f) Accepted results reported in reference [1]. Accompanying note cautioned that there might be a slight negative temperature dependence.

Preferred Value

$k = 9.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} over range 230–340 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta E/R = {}^{+0K}_{-150K}$.

Comments on Preferred Value

Room temperature preferred value is average of values reported in reference [1–3]. There may be a slight negative temperature dependence as indicated by the high temperature results in reference [3], but a temperature-independent value is recommended for temperatures below 340 K.

References

[1] Davis, D. D., Herron, J. T. and Huie, R. E., J. Chem. Phys. **58**, 530 (1973).
[2] Slanger, T. G., Wood, B. J. and Black, G., Int. J. Chem. Kinet. **5**, 615 (1973).
[3] Bemand, P. P., Clyne, M. A. and Watson, R. T., J. Chem. Soc. Faraday Trans. 2 **70**, 564 1974).
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[6] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).
[7] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).
[8] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + NO_2 + M \longrightarrow NO_3 + M$

$\Delta H° = -211$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(9.2 \pm 1) \times 10^{-32}$ $[N_2]$	297	Harker and Johnston, 1973 [1]	(a)
$(8.0 \pm 1) \times 10^{-32}$ $[N_2]$	295	Hippler, Schippert and Troe, 1975 [2]	(b)
Reviews and Evaluations			
6.3×10^{-32} $[N_2]$	295	Baulch et al., 1973 [4]	
1.0×10^{-31} $[N_2]$	298	Hampson and Garvin, 1975 [5]	

Comments

(a) From NO_2 photolysis in the presence of 1 atm of N_2; detection of NO_2 and N_2O_5 concentrations by IR absorption; measured $k/k(O + NO_2)$ evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}. Reevaluated by increasing the measured rate constant by 10% to account for a 10% fall-off below k_0 as measured by Gaedtke et al. (1973) [3].

(b) From NO_2 photolysis at various N_2 pressures; detection of NO_2 by UV absorption; measured $k/k(O + NO_2)$ evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} taking N_2O_5 reactions and fall-off effects into account. Relative efficiencies of M, He: Ne: Ar: CO: N_2: CO_2: CH_4: SF_6 = 3.5: 2.9: 3.5: 5.9: 2.9: 8.5: 10.6: 12; several larger hydrocarbons have also been measured as bath gases.

(c) The evaluations [4] and [5] are based on different reference rate coefficients. There is no difference in the rate coefficient ratios used for the evaluations.

Preferred Value

$k_0 = 9 \times 10^{-32}$ $[N_2]$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

Comments on Preferred Values

Preferred value from Harker and Johnston (1973) and Hippler, Schippert and Troe (1975) accounting for fall-off effects. For a theoretical analysis of k_0 see Troe (1977) [4].

High Pressure Rate Coefficients

Rate coefficient data

$k_\infty/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-11}$	295	Hippler, Schippert and Troe, 1975 [2]	(a)

Comments

(a) From NO_2 photolysis in the presence of 0.1 − 1000 atm of N_2; detection of NO_2 by UV absorption; full fall-off curve obtained. Measured $k/k(O + NO_2)$, assuming pressure independent $k(O + NO_2)$, evaluated with $k(O + NO_2) = 9.3 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$. Full fall-off curve shown in ref. [3].

Preferred Value

$k_\infty = 2.2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ at 295 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 295 K.

Comments on Preferred Values

Only one determination, more experiments desirable.

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c = 2.4 \times 10^{20}$ molecule/cm^3 at 295 K in agreement with the fall-off measurements of ref. [3]. A broadening factor F_c of 0.8 is measured [3] in agreement with theoretical estimates.

References

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[2] Hippler, H., Schippert, C. and Troe, J., Int. J. Chem. Kinet. Symp. 1, 27 (1975).
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[5] Hampson, R. F. and Garvin, D., eds., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1977).

$O + NO_3 \rightarrow O_2 + NO_2$

$\Delta H^\circ = -287$ kJ mol^{-1}

Rate coefficient data

$k/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.0 \pm 0.4) \times 10^{-11}$	298–329	Graham and Johnston, 1978 [1]	(a)
Reviews and Evaluations			
1.0×10^{-11}	300	Hampson and Garvin, 1978 [2]	(b)

Comments

(a) Value derived by computer simulation of complex system (N_2O_5 catalyzed decomposition of O_3 with photolysis of NO_3 and molecular modulation experiments) with 15 step mechanism.

(b) Quoting result reported in reference [1].

Preferred Value

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

Reliability

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

Comments on Preferred Value

Preferred value is the only reported value for this rate constant. Since this value is derived from the analysis of a very complex system and is not confirmed by separate study, it must be used with caution. The temperature dependence is expected to be small.

References

[1] Graham, R. A. and Johnston, H. S., J. Phys. Chem. **82**, 254 (1978).
[2] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + N_2O_5 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3 \times 10^{-16}$	223–300	Kaiser and Japar, 1978 [1]	(a)
Relative Rate Coefficients			
$<2 \times 10^{-14}$	298	Graham and Johnston, 1978 [2]	(b,d)
Reviews and Evaluations			
$<2 \times 10^{-13}$	300	Hampson and Garvin, 1975 [3]	(c,d)

Comments

(a) Discharge flow, $[N_2O_5]$ monitored by mass spectrometry. Upper limit only.

(b) Value derived by computer simulation of complex system. Value depends on identity of products.

(c) Quoting a preliminary value.

(d) Also quoted in Hampson and Garvin, 1978 [4].

Preferred Value

$k \leq 3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} over range 220–300 K.

Comments on Preferred Value

Preferred value is that given by the only published direct study of this reaction. On the basis of the upper limiting value of the rate constant, this reaction can not be of any importance.

References

[1] Kaiser, E. W. and Japar, S. M., Chem. Phys. Lett. **54**, 265 (1978).
[2] Graham, R. A. and Johnston, H. S., J. Phys. Chem. **82**, 254 (1978).
[3] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).
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$O(^1D) + N_2 \rightarrow O(^3P) + N_2$

$\Delta H° = -190$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.9 \pm 0.6) \times 10^{-11}$	300	Heidner, Husain and Wiesenfeld, 1973 [1]	(a)
$2.0 \times 10^{-11} \exp((107 \pm 8)/T)$	104–354	Streit et al., 1976 [2]	(b,g)
$(2.8 \pm 0.6) \times 10^{-11}$	300		
Reviews and Evaluations			
5.4×10^{-11}	300	Cvetanovic, 1974 [3]	(c)
5.4×10^{-11}	300	Hampson and Garvin, 1975 [4]	(d)
2.8×10^{-11}	298	Schofield, 1978 [5]	(e)
$2.0 \times 10^{-11} \exp(107/T)$	200–300	NASA, 1977 [6]	(f,g)

Comments

(a) Flow system. $[O(^1D)]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm $O(3D_2 \leftarrow 2D_2)$. Analysis of data uses modified Beer-Lambert law: $I_t/I_0 = \exp(-\epsilon(cl)^\gamma)$ with $\gamma = 0.41$.

(b) Flow system. $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.

(c) Recommended value based on analysis of complete set of $O(^1D)$ rate data—both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [4].

(d) Accepted recommendation of Cvetanovic, 1974 [3].
(e) Evaluation—details not given.
(f) Accepted results in Streit et al., 1976 [2].
(g) Recommended in Hampson and Garvin, 1978 [7].

Preferred Value

$k = 4.5 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k = 3.2 \times 10^{-11} \exp(107/T)$ cm^{3}molecule^{-1}s^{-1} over range 200–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Value

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio $k/k(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [3]. These values are the following: 0.28 (NOAA Laboratories [2]); 0.40 (Cambridge Laboratory [1], [8]); 0.30 (Cvetanovic's review [3]; 0.33 (mean value). The preferred value of the rate constant for the reference reaction of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [2]) and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [8]). The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 0.33$ and $k(O(^1D) + CO_2) = 1.35 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}. The temperature dependence in reference [2] is accepted. For further comments on $O(^1D)$ values see Introduction.

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

$\Delta H^\circ(1) = -520$ kJ mol^{-1}

$\Delta H^\circ(2) = -340$ kJ mol^{-1}

$\Delta H^\circ(3) = -190$ 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			
$(2.2 \pm 0.2) \times 10^{-10}$	300	Heidner and Husain, 1973 [1]	(a)
$(1.1 \pm 0.2) \times 10^{-10}$	204–359	Davidson et al., 1977 [2]	(b,i)
Branching Ratios			
$k_1/k_2 = 0.92 \pm 0.10$	290	Volltrauer et al., 1979 [3]	(c)
$k_1/k_2 = (0.72 \pm 0.11) + (21.6 \pm 7.0)/T$	170–434	Davidson et al., 1979 [4]	(d)
$k_1/k_2 = 0.80 \pm 0.11$	300		
$k_3/k \leq 0.038$	300		
Reviews and Evaluations			
2.2×10^{-10}	300	Cvetanovic, 1974 [5]	(e)
2.2×10^{-10}	300	Hampson and Garvin, 1975 [6]	(f)
1.2×10^{-10}	298	Schofield, 1978 [7]	(g)
1.1×10^{-10}	200–300	NASA, 1977 [8]	(h,i)

Comments

(a) Flow system. [O(^{1}D)] monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm. O(^{3}D$_2$ ← 2D$_2$). Analysis of data uses modified Beer-Lambert law: $I_t/I_0 = \exp(-\epsilon(cl)^\gamma)$ with $\gamma = 0.41$.

(b) Flow system. [O(^{1}D)] monitored by time resolved decay of the O(^{1}D) → O(^{3}P) emission at 630 nm.

(c) Branching ratio measurements. Product N_2 measured by gas chromatography. NO and its oxidation product NO_2 measured by chemiluminescence analyzer. Value quoted for ratio k_1/k_2 is that measured in excess helium. Lower value (0.73 ± 0.11) measured in absence of helium.

(d) Branching ratio measurements using chemical-ionization mass spectrometry to measure products. Value quoted for ratio k_1/k_2 is that measured in excess helium. Lower value (0.68 ± 0.11) measured in pure N_2O. Reaction channels (1) and (2) are the only significant reaction channels.

(e) Recommended value based on analysis of complete set of O(^{1}D) rate data—both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [6]. Reviewed branching ratio data and recommended value of $k_1/k_2 = 1$.

(f) Accepted recommendation of Cvetanovic, 1974 [5].

(g) Evaluation—details not given.

(h) Accepted results in Davidson et al., 1977 [2] and the branching ratio of unity recommended in Cvetanovic, 1974 [5].

(i) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k_1 = 7.4 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}.
$k_2 = 8.6 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}.
Independent of temperature over range 200–350.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta (E/R)_1 = \Delta (E/R)_2 = \pm 100$ K.

Comments on Preferred Value

Preferred value for k is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: O(^{1}D) + CO_2. The ratio k/k(O(^{1}D) + CO_2) is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [5]. These values are the following: 1.10 (NOAA Laboratories [2], [10]; 1.29 (Cambridge Laboratory [1], [11]; 1.31 (Cvetanovic's review [5]; 1.2 (mean value). The preferred value of the rate constant for the reference reaction of O(^{1}D) with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [10] and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [11]. The preferred value for k is then derived from the values of k/k(O(^{1}D) + CO_2) = 1.2 and k(O(^{1}D) + CO_2) = 1.35×10^{-10} cm^{3}molecule^{-1}s^{-1}. The temperature independence of k reported in reference [2] is accepted.

The conclusion stated in reference [4] that reaction channels (1) and (2) are the only significant reaction channels is accepted. This is equivalent to setting $k = k_1 + k_2$.

The branching ratio $R = k_1/k_2$ reported in reference [4] has only a very slight temperature dependence decreasing from 0.83 at 200 K to 0.78 at 350 K. These results can be approximated by a value of 0.80 independent of temperature. The value of the branching ratio recommended in this review (0.85 ± 0.1) is the simple average of the results in references [3] and [4].

The recommendation given here can be stated in the equivalent form: $k = 1.6 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} and $k_1/k_2 = 0.85 \pm 0.1$. For further comments on O(^{1}D) values see introduction.

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$HO + NO + M \rightarrow HONO + M$

$\Delta H^\circ = -209$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.8 \pm 1.2) \times 10^{-31}(T/295)^{-2.4}$ [N_2]	295–450	Anderson, Margitan and Kaufman, 1974 [1]	(a)
$(7.8 \pm 1.2) \times 10^{-31}$ [N_2]	296	Howard and Evenson, 1974 [2]	(b)
$(15 \pm 5) \times 10^{-31}$ [N_2]	300	Harris and Wayne, 1975 [3]	(c)
$(6.1 \pm 0.5) \times 10^{-31}$ [N_2]	298	Atkinson, Hansen and Pitts, 1975 [4]	(d)
5.6×10^{-31} [N_2]	295	Overend, Paraskevopoulos and Black, 1976 [5]	(e)
$8.2 \times 10^{-31}(T/298)^{-2.5}$ [N_2]	233–505	Anastasi and Smith, 1978 [6]	(f)
Reviews and Evaluations			
$(7 \pm 2) \times 10^{-31}(T/298)^{-2.5}$ [N_2]		Zellner, 1978 [7]	

Comments

(a) Discharge flow system study with resonance fluorescence detection of HO. Pressure range 1–10 Torr; no fall-off correction required in the measured range. Relative efficiencies of M, N_2: Ar: He: = 1.0: 0.58: 0.57.

(b) Discharge flow system study with laser magnetic resonance detection of HO. Pressure range 0.4–5 Torr; no fall-off correction required. Relative efficiencies of M, N_2: Ar: He = 1.0: 0.56: 0.51.

(c) Discharge flow system study. Relative efficiencies of M, N_2: Ar = 1.0: 0.47.

(d) Flash photolysis study with resonance fluorescence detection of HO. Pressure range 25–655 Torr for M=Ar. N_2 value obtained at 25 Torr where about a +10% fall-off correction would be required. Relative efficiencies of M, N_2: Ar = 1.0: 0.7.

(e) Flash photolysis study with resonance absorption detection of HO. Pressure range 25–770 Torr, measurements in the fall-off range extrapolated with the Lindemann-Hinshelwood expression. Relative efficiencies of M, N_2: He: Ar: NO: SF_6: CF_4: H_2O = 1.0: 0.27: 0.4: 8.7: 3.1: 3.3: 8.5.

(f) Flash photolysis study with resonance absorption detection of HO. Range of bath gas concentrations $3.7 \times 10^{17} - 1.6 \times 10^{19}$ molecule cm^{-3}. From measurements over the given temperature range one derives $k_0(296\text{ K}) = 6.6 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k_0 = 6.5 \times 10^{-31}(T/300)^{-2.4}$ [N_2] over the range 220–440 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 220–440 K.

Comments on Preferred Values

Good general agreement consistent with theoretical analysis in ref. [6]; the preferred value was obtained by averaging the data of refs. [1], [2], [4]–[6].

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>0.8 \times 10^{-11}$	298	Atkinson, Hansen and Pitts, 1975 [4]	(a)
1.1×10^{-11}	295	Overend, Paraskevopoulos and Black, 1976 [5]	(b)
0.85×10^{-11}		Anastasi and Smith, 1978 [6]	(c)
Relative Rate Coefficients			
1.0×10^{-11}	298	Sie, Simonaitis and Heicklen, 1976 [8]	(d)
1.2×10^{-11}	298	Cox, Derwent and Holt, 1976 [9]	(e)
Reviews and Evaluations			
$(1.0 \pm 0.2) \times 10^{-11}$	220–300	Zellner, 1978 [7]	

Comments

(a) See comment (d) for k_0; k_∞ from Lindemann-Hinshelwood extrapolations of k in the fall-off range.

(b) See comment (e) for k_0; k_∞ from Lindemann-Hinshelwood extrapolation of k in the fall-off range.

(c) See comment (f) for k_0; k_∞ from reduced Kassel integral extrapolation of k in the fall-off range.

(d) Stationary photolysis of N_2O in the presence of CO, NO and excess H_2 (up to 1 atm). Measured $k/k(OH + CO)$ evaluated with $k(OH + CO) = 2.9 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$. Extrapolation of fall-off curve.

(e) Stationary photolysis of HONO in the presence of added gases and 1 atm of $N_2 + O_2$. Based on $k(OH + H_2) = 7.0 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.

Preferred Value

$k_\infty = 1.0 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ over range 220–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over range 220–400 K.

Comments on Preferred Values

The preferred value is consistent with a theoretical analysis in ref. [6] leading to $k_\infty = 1.5 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c \simeq 1.7 \times 10^{19}$ molecules cm^{-3}. The observed fall-off curves are consistent with an estimated broadening factor $F_c \cong 0.8 \pm 0.1$ at 300 K.

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$HO + NO_2 + M \longrightarrow HONO_2 + M$

$\Delta H^\circ = -207$ 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			
$2.3 \times 10^{-30}(T/295)^{-2.5}$ $[N_2]$	295–450	Anderson, Margitan and Kaufman, 1974 [1]	(a)
2.9×10^{-30} $[N_2]$	296	Howard and Evenson, 1974 [2]	(b)
2.6×10^{-30} $[N_2]$	300	Harris and Wayne, 1975 [3]	(c)
$2.6 \times 10^{-30}(T/296)^{-2.6}$ $[N_2]$	220–550	Anastasi and Smith, 1976 [4]	(d)
$1.0 \times 10^{-30}(T/300)^{-2.9}$ [He]	213–300	Erler, Field and Zellner, 1977 [5]	(e)
$3.1 \times 10^{-32}(T/1000)^{-2.9}$ [Ar]	800–1200	Glänzer and Troe, 1974 [6]	(f)
Reviews and Evaluations			
1.4×10^{-30} [He]	300	Baulch et al., 1973 [7]	
see comment (g)	200–350	NASA, 1977 [8]	(g)
3.1×10^{-30} $[N_2]$	298	Smith and Golden, 1978 [9]	(h)
$2.6 \times 10^{-30}(T/298)^{-2.7}$ $[N_2]$		Zellner, 1978 [10]	

Comments

(a) Discharge flow system study with resonance fluorescence detection of HO; in the pressure range 1–10 Torr $k_0 \propto [N_2]$ was found; relative efficiencies of M, He: Ar: N_2 = 1.0: 1.0: 2.3

(b) Discharge flow system with laser magnetic resonance detection of HO; in the pressure range 0.4–5 Torr a small deviation from $k_0 \propto [N_2]$ was observed but attributed to wall effects.

(c) Discharge flow system study; relative efficiencies of M, Ar: N_2 = 1.0: 1.7

(d) Flash photolysis study with resonance fluorescence detection of HO; with bath gas concentrations in the range $3.2 \times 10^{17} - 1.6 \times 10^{19}$ molecule cm^{-3} a substantial part of the fall-off curve was measured, relative efficiencies of M, N_2 : He: Ar: O_2 : SF_6 = 2.6: 0.9: 1.1: 1.8: 6.7

(e) Discharge flow system study with resonance fluorescence detection of HO; pressure range 2–12 Torr.

(f) Shock wave study of the decomposition of HNO_3; at bath gas concentrations $4.8 \times 10^{18} - 2.0 \times 10^{20}$ a substantial part of the fall-off curve was observed. Given expression includes room temperature data, see however ever also comment (c) to k_∞.

(g) A complex analytical expression as a function of T and log $[N_2]$ is given correlating the data of refs. cited here. Since this expression is only applicable in a limited range of conditions and does not give correct k_0 or k_∞ values, it is omitted here; we recommend instead the use of the more reasonable expressions of this work.

(h) Data evaluation with modified RRKM formalism.

Preferred Value

$k_0 = 2.6 \times 10^{-30}(T/300)^{-2.7}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over range 220–550 K.

$k_0 = 1.0 \times 10^{-30}(T/300)^{-2.9}$ [Ar] cm^3 $molecule^{-1}$ s^{-1} over range 300–1200 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 220–550 K.
$= \pm 0.3$ over range 300–1200 K.

Comments on Preferred Values

The data in the low temperature range appear very reliable and only minor uncertainties because of the fall-off corrections remain; possibly a slight increase of k_0 due to this effect (+10%) could be envisaged. The high temperature data depend on the quality of the fall-off extrapolation and larger uncertainties have to be taken into account. An analysis of k_0 by theory is given in ref. [11].

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.6 \times 10^{-11}(T/296)^{-2.1}$	220–550	Anastasi and Smith, 1976 [4]	(a)
$>8.5 \times 10^{-12}$	298	Atkinson, Perry and Pitts, 1976 [2]	(b)
$\geq 1.9 \times 10^{-12}(T/1000)^{-0.85}$	800–1200	Glänzer and Troe, 1974 [6]	(c)

Comments

(a) Measurements in the lower part of the fall-off range extrapolated to k_∞. Data in the range of 220–360 K are also consistent with a temperature independent k_∞. At $T > 360$ K the extrapolation is very uncertain because of a limited pressure range and the large distance from the high pressure limit. Further remarks, see comments for k_0.

(b) Flash photolysis-resonance fluorescence technique. Measurements in the pressure range 25–648 Torr in Ar. Lindemann–Hinshelwood extrapolation toward k_∞ is responsible for slightly low value of k_∞.

(c) From shock wave study of decomposition of HNO_3 in Ar in the range $6 \times 10^{18} - 1.8 \times 10^{20}$ molecule cm^{-3}. k_∞ obtained by extrapolation of the middle part of the fall-off curve. Larger k_∞ values are possible if weak collision broadening effects are included. Alternative fall-off curves can be constructed with k_0 decreased by about a factor of 1.5 and k_∞ increased by a factor of 10, see ref. [14].

Preferred Value

$k_\infty = 1.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over range 200–360 K (probably also over range 200–1200 K).

Reliability

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

Comments on Preferred Values

The room temperature value of k_∞ appears to be well established. As suggested by a theoretical analysis of k_∞ (Quack and Troe, 1977 [13]), the measured temperature dependence of k_∞ should be used with caution, a temperature independent value of k_∞ being more plausible [13]. Reinspection of the fall-off curves of refs. [4] and [6] indicates that this would also be consistent with the data but require a different construction of the fall-off curves, see ref. [14].

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c \simeq 2.7 \times 10^{18}$ molecule cm^{-3} at 220 K and $[N_2]_c \simeq 6.2 \times 10^{18}$ molecule cm^{-3} at 300 K. The measured fall-off curves can well be represented with $F_c \simeq 0.75 \pm 0.1$ at 300 K and $F_c \simeq 0.8 \pm 0.1$ at 220 K in agreement with theoretical estimates. F_c decreases with temperature; for higher temperatures, calculations of F_c by the methods mentioned in the Introduction should be made. See also [14].

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$HO + HNO_3 \rightarrow H_2O + NO_3$

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

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8 \pm 2) \times 10^{-14}$	240–406	Smith and Zellner, 1975 [1]	(a,f)
$(8.9 \pm 1.3) \times 10^{-14}$	270–470	Margitan, Kaufman and Anderson, 1975 [2]	(b)
$(1.6 \pm 0.3) \times 10^{-13}$	1000–1100	Glanzer and Troe, 1974 [3]	(c)
Reviews and Evaluations			
$6 \times 10^{-13} \exp(-400/T)$	300–650	Tsang, 1973 [4]	(d)
1.3×10^{-13}	300	Baulch et al., 1973 [5]	(d)
1.3×10^{-13}	220–270	Hampson and Garvin, 1975 [6]	(d)
8×10^{-14}	200–300	NASA, 1977 [7]	(e,f)

Comments

(a) Flash photolysis of HNO_3. [OH] monitored by resonance absorption. Experiments with pure HNO_3 ($<$ 0.4% NO_2) over range 240–300 K. Other experiments over range 240–406 K with correction made for effect of 1.4% NO_2 impurity. Value given is that recommended by author for room temperature and below. Within the stated error limits it encompasses all data over entire temperature range. Recommended in NASA, 1977 [7] and in Hampson and Garvin, 1978 [8].

(b) Discharge flow system. Hydroxyl radicals produced by reaction of H atoms with NO_2. [OH] monitored by resonance fluorescence. Value given is mean of values measured at 295, 420 and 465 K. Slightly higher value at 272 K considered by authors to be less reliable.

(c) Thermal decomposition of HNO_3 in shock wave. [NO_3] monitored by absorption.

(d) Evaluation—outdated by newer data in references [1], [2] and [3].

(e) Accepted results of Smith and Zellner, 1975 [1].

(f) Recommended in Hampson and Garvin, 1978 [8].

Preferred Value

$k = 8.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} over range 240–470 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Value

Preferred value is mean of values reported in references [1] and [2]. This is an unusually low A-factor for a simple H atom abstraction and the fact that the indicated products are unconfirmed suggests the need for mechanistic studies. Although the high temperature results in reference [3] have not been used in the derivation of the preferred value, they support the low A-factor. They have been used in calculation of $\Delta E/R$.

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$HO + HO_2NO_2 \rightarrow$ products

Rate coefficient data: no data on this reaction exist

Preferred Value

No preferred value.

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. Presumably the reaction proceeds by H-atom abstraction. The rate coefficient for H-atom abstraction by the HO radical from the related molecule $HONO_2$ is 8.5×10^{-14} $cm^3 molecule^{-1} s^{-1}$, this evaluation. Based on this a value of approximately 1×10^{-13} $cm^3 molecule^{-1} s^{-1}$ is suggested for this rate coefficient. This value must be considered to be very uncertain (to at least an order of magnitude). Clearly studies of this reaction are needed.

$HO_2 + NO \rightarrow HO + NO_2$

$\Delta H° = -20$ kJ mol^{-1}

Rate coefficient data

k/$cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977 [1]	(a,o)
$(3.3 \pm 0.7) \times 10^{-12} \exp((254 \pm 50)/T)$	230–400	Howard, 1979 [2]	(b)
$(8 \pm 2) \times 10^{-12}$	298	Margitan and Anderson, 1978 [3]	(c)
$(7.9 \pm 1.0) \times 10^{-12}$	298	Reimann and Kaufman, 1978 [4]	(d)
$5.7 \times 10^{-12} \exp((130 \pm 270)/T)$	270–425	Leu, 1979 [5]	(e)
$(9.8 \pm 1.6) \times 10^{-12}$	298		
Relative Rate Coefficients			
1.2×10^{-12}	296	Cox and Derwent, 1975 [6]	(f)
$(7.5 \pm 1.7) \times 10^{-12}$	1350–1700	Glanzer and Troe, 1975 [7]	(g)
$(1.9 \pm 0.5) \times 10^{-11} \exp(-(1200 \pm 150)/T)$	298–670	Hack, Hoyermann and Wagner, 1975 [8]	(h)
2.5×10^{-13}	298		
0.8×10^{-12}	296	Simonaitis and Heicklen, 1978 [9]	(i)
$1.0 \times 10^{-11} \exp(-(700 \pm 250)/T)$	245–328	Simonaitis and Heicklen, 1978 [10]	(j)
1.0×10^{-12}	296		
$(8.3 \pm 1.4) \times 10^{-12}$	298	Burrows et al., 1978 [11]	(k)
4.1×10^{-12}	283	Cox and Patrick, 1979 [12]	(l)
Reviews and Evaluations			
2×10^{-13}	300	Hampson and Garvin, 1975 [13]	(m)
8×10^{-12}	200–300	NASA, 1977 [14]	(n,o)

Comments

(a) Discharge flow system. $[HO_2]$ monitored by laser magnetic resonance. From observation of HO_2 decay in steady-state experiments, an upper limit of 4.5×10^{-30} $cm^6 molecule^{-2} s^{-1}$ for the third order rate constant for a potential addition reaction channel was established. If the value of this rate constant is as much as one-tenth of this upper limit, then the addition channel becomes important under atmospheric conditions.

(b) Same system as described in (a).

(c) Discharge flow system. [HO] monitored by resonance fluorescence.

(d) Discharge flow system. [HO] monitored with tunable dye laser.

(e) Discharge flow system. [HO] monitored by resonance fluorescence.

(f) Steady photolysis of HONO in NO_2 and CO at 1 atm $N_2 + O_2$. Observed effect of added NO and NO_2 on rate of formation of nitrogen oxides. Rate constant values derived from computer fit to nine step reaction mechanism. Reaction (2) at a rate of 0.12 times rate of reaction (1) included in mechanism but adduct not observed.

(g) Shock wave pyrolysis of HNO_3. $[HO_2]$ measured by UV absorption. Rate constant values derived from computer fit. Value of k calculated from measured rate of reverse reaction and equilibrium constant.

(h) Discharge flow system. [OH] monitored by ESR technique. Steady-state [HO] and [HO_2] reached in chemical system described by reaction (1) and the reference reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$ $k/k(HO + H_2O_2) = 2.5 \exp(-530/T)$; $k(HO + H_2O_2) = 7.6 \times 10^{-12} \exp(-670/T)$ $cm^3 molecule^{-1} s^{-1}$, this evaluation.

(i) Steady photolysis of N_2-O-H_2-O_2-NO mixtures at 214 nm. Initial quantum yield for NO disappearance monitored by chemiluminescent reaction with O_3. $k/k^{1/2}(HO_2 + HO_2) = 5.1 \times 10^{-7}$; $k(HO_2 + HO_2) = 2.3 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$, this evaluation $k_2/k_1 \leq 2 \times 10^{-3}$ at 1 atm H_2.

(j) Same system as described in (i), $k/k^{1/2}(HO_2 + HO_2) = 6.4 \times 10^{-6} \exp(-700/T)$.

(k) Discharge flow system. [HO] and [HO_2] measured by laser magnetic resonance. Steady-state [HO] and [HO_2] reached in chemical system described by reaction (1) and the reference reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$. $k/k(HO + H_2O_2) = 10.4 \pm 0.5$; $k(HO + H_2O_2) = 8.0 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$, this evaluation.

(l) Periodic photolysis of Cl_2 in excess H_2 and O_2 with NO_2 present. [HO_2] monitored by molecular modulation ultraviolet spectrometry. $k(HO_2 + NO_2 \rightarrow HO_2NO_2) = 9 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$. Study of HONO-CO photolysis system gave $k/k(HO_2 + NO_2) = 4.5 \pm 0.6$. Authors combined these results to derive value of k shown in table.

(m) Evaluation based on indirect studies. Outdated by results of newer, direct studies.

(n) Accepted results of Howard and Evenson, 1977 [1]. Assumed k to be temperature-independent.

(o) Recommended in Hampson and Garvin, 1978 [15].

Preferred Value

$k = 8.4 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.

$k = 4.3 \times 10^{-12} \exp(200/T)$ $cm^3 molecule^{-1} s^{-1}$ over range 230–425 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Value

Preferred value at 298 K is the average of the measured values reported in references [1–5 and 11]. The temperature dependence is derived from a least squares fit to the data of Howard, 1978 [2] and Leu, 1979 [5]. The direct studies have all been made at low pressures, and it is possible that this rate constant may exhibit a pressure dependence. Studies at atmospheric pressures are needed.

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

$\Delta H° = -89$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k/$cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.07) \times 10^{-31}$ [N_2] $(1.0 \pm 0.04) \times 10^{-31}$ [He]	300	Howard, 1977 [1]	(a)
$(2.5 \pm 0.5) \times 10^{-31}$ [N_2]	283	Cox and Patrick, 1979 [2]	(b)
Reviews and Evaluations			
see note (c)		NASA, 1977 [3]	(c)
2.1×10^{-31} [N_2]	300	Zellner, 1978 [4]	(d)

Comments

(a) Discharge flow system study with laser magnetic resonance detection of HO_2. Pressure range 0.5–3 Torr; linear plot of k_0 as a function of [He] with non-zero intercept being interpreted as contribution from the reaction $HO_2 + NO_2 \rightarrow HONO + O_2$. Relative efficiencies of M, He: N_2: O_2: NO_2 = 1.0: 2.1: 1.5: 6.6 ± 3.

(b) Molecular modulation UV spectrometry, HO_2 generation by Cl_2 photolysis in presence of H_2 and O_2; equimolar O_2: N_2 mixtures used in the pressure range 40–600 Torr. Extrapolation to the low pressure limit.

(c) Tentative recommendation to use the same rate constant as for $ClO + NO_2 + M \rightarrow ClONO_2 + M$.

(d) Recommends data of Howard, 1977 [1].

Preferred Value

$k_0 = 2.1 \times 10^{-31}$ [N_2] at 300 K.

Reliability

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

Comments on Preferred Values

Probably reliable data.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>(1.5 \pm 0.5) \times 10^{-12}$	283	Cox and Patrick, 1979 [2]	(a)
$>1.7 \times 10^{-12}$	283	Graham, Winer and Pitts, 1977 [5]	(b)
$(\simeq 5 \times 10^{-12})$			
Reviews and Evaluations			
$(2 \pm 1) \times 10^{-12}$	300	Zellner, 1978 [4]	(c)
6.5×10^{-12}	300	Baldwin and Golden, 1978 [6]	(d)

Comments

(a) See note (b) of k_0. Determination of k_∞ by extrapolating a curved Lindemann-Hinshelwood plot gives an internally consistent fall-off plot; measured value $k = 0.92 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 600 Torr of $N_2 + O_2$ (1:1).

(b) From thermal decomposition of HO_2NO_2 in static reactor, with Fourier transform IR spectroscopy of HO_2NO_2. Measurements at 1 atm of N_2 converted to recombination rate constants with the equilibrium constants given in ref. [7]; comparison of the value $k = 1.75 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 1 atm with the low pressure value k_0 for 1 atm of N_2 of 5×10^{-12} cm^{3}molecule^{-1}s^{-1} leads to $k_\infty \simeq 5 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}.

(c) Based on the data of ref. [5].

(d) Calculation with a restricted rotor RRKM theory fitted to the data of ref. [1] and [5] for HO_2NO_2 decomposition.

Preferred Value

$k_\infty = 5 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is a compromise between the data of ref. [2] and [5].

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c \simeq 2.4 \times 10^{19}$ molecule cm^{-3} at 300 K with an uncertainty of about a factor of 3. The broadening factor at the center is estimated to be about $F_c \simeq 0.7 \pm 0.1$ at 300 K.

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$HO_2NO_2 + M \longrightarrow HO_2 + NO_2 + M$

$\Delta H° = +89$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.2×10^{-20} [N_2]	298	Howard, 1977 [1]	(a) (b)
1.5×10^{-20} [N_2]	298	Cox and Patrick, 1978 [3]	(c) (b)

Comments

(a) Recombination data at 0.5–3 Torr.

(b) Conversion to dissociation data using the equilibrium constant $k(HO_2NO_2) \rightarrow HO_2 + NO_2)/k(HO_2 + NO_2 \rightarrow HO_2NO_2) = 1.68 \times 10^{28} \exp(-11977/T)$ molecule cm^3 from ref. [2]. For experimental details see data sheet on $HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$.

(c) Recombination data over range 40–600 Torr. Extrapolation to k_0 with a curved Lindemann-Hinshelwood plot.

Preferred Value

$k_0 = 1.2 \times 10^{-20}$ [N_2] s^{-1} at 298 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

Comments on Preferred Values

Probably reliable data. Temperature dependence to be estimated with about $k_0(HO_2 + NO_2 \rightarrow HO_2NO_2) \propto T^{-5}$ and the equilibrium constant given in comment (b).

High Pressure Rate Coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.4 \times 10^{14} \exp(-(10420 \pm 250)/T)$	254–283 K	Graham, Winer and Pitts, 1977 [4]	(a)
$>9.2 \times 10^{-2}$	298		
$>2 \times 10^{-4}$	258	Hutton and Kerr, 1979 [5]	(b)
$>4.5 \times 10^{-2}$	298		(c)
$>8.8 \times 10^{-2}$	298	Cox and Patrick, 1978 [3]	(d)

Comments

(a) Heterogeneous reaction of NO_2 and H_2O_2 used to generate HO_2NO_2. Measurements at 1 atm of N_2. HO_2NO_2 detection by Fourier transform IR spectroscopy.

(b) Generation of HO_2NO_2 similar to ref. [4]. Chemiluminescence detection technique. Measurements at 1 atm of N_2.

(c) Extrapolated to 298 K with temperature coefficient of ref. [4].

(d) See comments (b) and (c) for k_0. Extrapolated k_∞ value; the measured value for 1 atm would be a factor of 0.7 lower.

Preferred Value

$k_\infty = 0.09$ s^{-1} at 298 K.

$k_\infty = 1.4 \times 10^{14} \exp(-10420/T)$s^{-1} over range 250–300 K.

Reliability

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

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

Comments on Preferred Values

Low preexponential factor possibly due to measurements over a too limited pressure range. Increase by a factor of 4 is possible as suggested by model calculations for the reverse recombination, see data sheet for $HO_2 + NO_2 \rightarrow HO_2NO_2$. The present preferred values give $[N_2]_c = 7.6 \times 10^{18}$ molecule cm^{-3}.

References

[1] Howard, C. J., J. Chem. Phys. **67**, 5258 (1977).

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

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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			
$(1.73 \pm 0.1) \times 10^{-14}$	298	Stedman and Niki, 1973 [1]	(a)
1.41×10^{-14}	298	Ghormley, Ellsworth and Hochanadel, 1973 [2]	(b)
$(1.81 \pm 0.13) \times 10^{-14}$	298	Bemand, Clyne and Watson, 1974 [3]	(c)
1.70×10^{-14}	290	Becker, Schurath and Seitz, 1974 [4]	(d)
$(2.34 \pm 0.23) \times 10^{-12} \exp(-(1450 \pm 50)/T)$	203–361	Birks et al., 1976 [5]	(e)
$(1.73 \pm 0.09) \times 10^{-14}$	297		
Reviews and Evaluations			
$9 \times 10^{-13} \exp(-1200/T)$	198–330	Herron and Huie, 1973 [6]	(f,h)
$1.5 \times 10^{-12} \exp(-1300/T)$	200–350	Baulch, Drysdale and Horne, 1973 [7]	(f)
$2.1 \times 10^{-12} \exp(-1450/T)$	200–300	NASA, 1977 [8]	(g,i)

Comments

(a) Photolysis of NO_2 in air. In separate experiments monitored $[O_3]$ and [NO] by chemiluminescence detectors.

(b) Flash photolysis system. Monitored $[O_3]$ and $[NO_2]$ by optical absorption.

(c) Flow system. Monitored $[O_3]$ by mass spectrometry.

(d) Large static reactor. Monitored [NO] by monitoring NO_2^* chemiluminescence. No details of measurement given.

(e) Fast flow system. Monitored $[O_3]$ by mass spectrometry.

(f) Evaluation based on all previously reported data. Newer results reported in references [1]–[5].

(g) Evaluation based on results reported in Birks et al., 1976 [5] with lower "A factor" based on reconsideration of primary data.

(h) Recommended in Hampson and Garvin, 1975 [9].

(i) Recommended in Hampson and Garvin, 1978 [10].

Preferred Value

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

$k = 2.3 \times 10^{-12} \exp(-1450/T)$ cm^3 molecule^{-1} s^{-1} over range 200–360 K.

Reliability

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

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

Comments on Preferred Value

Preferred value at room temperature based on results reported in references [1], [3] and [5]. Result in reference [2] is definitely low in comparison with these results. Earlier results are summarized in references [6] and [7]. Temperature dependence reported in reference [5] accepted as being determined in the most complete study covering an extensive temperature range.

References

[1] Stedman, D. H. and Niki, H., J. Phys. Chem. **77**, 2604 (1973).

[2] Ghormley, J. A., Ellsworth, R. L. and Hochanadel, C. J., J. Phys. Chem. **77**, 1341 (1973).

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$NO + NO_3 \rightarrow 2NO_2$

$\Delta H° = -95$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
8.7×10^{-12}	297	Harker and Johnston, 1973 [1]	(a)
$(1.3 \pm 0.7) \times 10^{-11}$	1000–1100	Glanzer and Troe, 1974 [2]	(b)
$(1.9 \pm 0.4) \times 10^{-11}$	297	Graham and Johnston, 1978 [3]	(c)
Reviews and Evaluations			
2×10^{-11} (estimate)	300	Baulch et al., 1973 [5]	(d)
8.7×10^{-12}	300	Hampson and Garvin, 1975 [6]	(e)
1.9×10^{-11}	300	Hampson and Garvin, 1978 [7]	(f)

Comments

(a) Photolysis of NO_2 in long-path infrared cell. $[NO_2]$ and $[N_2O_5]$ monitored as function of time and molecular modulation spectrum of NO_2 obtained in steady flow system. Derived value of $k/K_{eq} = 0.71 \pm 0.05$ s^{-1} where K_{eq} is for system: $NO_2 + NO_3 = N_2O_5$. Authors combined this value with value of $K_{eq} = 1.24 \times 10^{-11}$ cm^3 molecule^{-1} from reference [4] to give value of k listed in table.

(b) Thermal decomposition of HNO_3 in shock wave. Value of k varied to give best fit to observed NO_2 and NO_3 profiles.

(c) Studied kinetics of N_2O_5 catalyzed decomposition of O_3. From analysis of complex system, derived expression for equilibrium constant for system: $NO_2 + NO_3 = N_2O_5$. Authors combined value of K_{eq} at 297 K (2.7×10^{-11} cm^3 molecule^{-1}) with value of k/K_{eq} reported in Harker and Johnston, 1973 [1] to give value of k listed in table.

(d) No recommendation given; only order of magnitude estimate.

(e) Accepted results of Harker and Johnston, 1973 [1].

(f) Accepted results of Graham and Johnston, 1978 [3].

Preferred Value

$k = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Value

Preferred value is that given in reference [3]. This value could be subject to large systematic error because it is derived from analyzing results of two complex systems.

References

[1] Harker, A. B. and Johnston, H. S., J. Phys. Chem. **77**, 1153 (1973).

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

$\Delta H° = -93$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Reviews and Evaluations			
2.6×10^{-32} exp(1480/T) [N_2O_5 + NO]	300-340	Baulch et al., 1973 [1]	(a)

Comments

(a) Converted from dissociation of N_2O_5 with new equilibrium constant from Graham and Johnston, 1978 [2].

Preferred Value

$k_0 = 1.5 \times 10^{-30}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.
$k_0 = 1.5 \times 10^{-30}(T/300)^{-4.6}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 300–340 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 300–340 K.

Comments on Preferred Values

From preferred data for $N_2O_5 + N_2 \longrightarrow NO_2 + NO_3 + N_2$, recalculated using the equilibrium constant from Graham and Johnston, 1978 [2]. For more details, particularly on collision efficiencies for other M, see data sheet $N_2O_5 + M \longrightarrow NO_2 + NO_3 + M$.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$>1.5 \times 10^{-13} \exp(863/T)$	273–300	Graham and Johnston, 1978 [2]	(a,b)
$>2.7 \times 10^{-12}$	298		
<u>Reviews and Evaluations</u>			
$6.8 \times 10^{-13} \exp(580/T)$	273–340	Baulch et al., 1973 [1]	(a)
4.8×10^{-12}	298		

Comments

(a) Recalculated from dissociation of N_2O_5 with equilibrium constant $K = (8.4 \pm 1.8) \times 10^{26} \exp(-(11178 \pm 100)/T)$ molecule cm^{-3}.

(b) Value given for 1 atm.

Preferred Value

$k_\infty = 5 \times 10^{-12}$ 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 Values

Estimated fall-off correction applied. New experiments above 1 atm are needed.

Intermediate Fall-off Range

From the preferred values for k_0 and k_∞ one estimates $[N_2]_c \simeq 3.3 \times 10^{18}$ molecule cm^{-3}.

References

[1] Baulch, D. L., Drysdale, D. D., Horne, D. G. and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions", Vol. 2, Butterworths, London, 1973.

[2] Graham, R. A., and Johnston, H. S., J. Phys. Chem. **82**, 254 (1978).

$N_2O_5 + M \longrightarrow NO_2 + NO_3 + M$

$\Delta H^\circ = +93$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
3.7×10^{-18} [N_2O_5]	324	Johnston, 1953 [1]	(a)
5.0×10^{-19} [Ar]			
8.7×10^{-19} [N_2]			
1.1×10^{-18} [NO]			
6.4×10^{-15} [Ar]	500	Schott and Davidson, 1958 [3]	(b)
<u>Reviews and Evaluations</u>			
$2.2 \times 10^{-5} \exp(-9700/T)$ [N_2O_5 + NO]	300–400	Baulch et al., 1973 [4]	(c)

Comments

(a) Static reactor; decomposition of N_2O_5 in the presence of NO and added inert gases at low pressures (0.2–10 Torr). NO_2 monitored by light absorption.

Relative efficiency of M, N_2O_5 : Ar : N_2 : NO : CO_2 : SF_6 : He : Ne : Kr : Xe : CCl_4 = 1 : 0.135 : 0.234 : 0.30 : 0.396 : 0.32 : 0.124 : 0.09 : 0.159 : 0.147 : 0.551; data by Wilson and Johnston (1953) [2] included.

(b) Shock wave study over range 450–550 K; NO_2 monitored by light absorption.

(c) Review based on data by Mills and Johnston, 1951 [5], and Johnston and Perrine (1951) [6].

Preferred Value

$k_0 = 6.4 \times 10^{-20}\ [N_2]\ s^{-1}$ at 298 K.

$k_0 = 8.8 \times 10^{-6} \exp(-9700/T)\ [N_2]\ s^{-1}$ over range 300–340 K.

$k_0 = 2.2 \times 10^{-7} \exp(-8690/T)\ [Ar]\ s^{-1}$ over range 300–550 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 300–340 K.

Comments on Preferred Values

Following ref. [4] the given values are chosen and the uncertainties estimated. A better representation of the temperature dependence of the measured k_0 would be $k_0 \propto T^{-3.2} \exp(-10729/T)$ for M=N_2 over range 300–340 K and $k_0 \propto T^{-5.3} \exp(-10729/T)$ for M=Ar over range 300–500 K after separating off the term $\exp(-\Delta H^\circ_0/RT)$.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.24 \times 10^{14} \exp(-(10317/T)$	273–300	Mills and Johnston, 1951 [5]	(a)
>0.11	298		
Reviews and Evaluations			
$5.7 \times 10^{14} \exp(-10600/T)$	273–300	Baluch et al., 1973 [4]	(b)

Comments

(a) Static reactor, total pressures up to 7×10^3 Torr. Given values are for 1 atm from Graham and Johnston, 1978 [7].

(b) Based on data from Mills and Johnston, 1951 [5] with extrapolation to k_∞.

Preferred Value

$k_\infty = 0.20\ s^{-1}$ at 298 K.

$k_\infty = 5.7 \times 10^{14} \exp(-10600/T)\ s^{-1}$ over range 273–300 K.

Reliability

$\Delta \log k_\infty = \pm\ 0.3$ over range 273–300 K.

Comments on Preferred Values

Full analysis of fall-off curve required to obtain more accurate extrapolated expression for k_∞.

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$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H° = -105$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.5 \pm 0.8) \times 10^{-17}$	298	Stedman and Niki, 1973 [1]	(a)
$(4.4 \pm 0.6) \times 10^{-17}$	299	Wu, Morris and Niki, 1973 [2]	(b)
$(3.2 \pm 0.5) \times 10^{-17}$	298	Ghormley, Ellsworth and Hochanadel, 1973 [3]	(c)
$(9.76 \pm 0.54) \times 10^{-14} \exp(-(2427 \pm 140)/T)$	260–343	Davis et al., 1974 [4]	(d)
$(3.42 \pm 0.27) \times 10^{-17}$	303		
$(1.34 \pm 0.11) \times 10^{-13} \exp(-(2466 \pm 30)/T)$	231–298	Graham and Johnston, 1974 [5]	(e)
$(3.49 \pm 0.23) \times 10^{-17}$	298		
$(1.57 \pm 0.41) \times 10^{-13} \exp(-(2509 \pm 76)/T)$	259–362	Huie and Herron, 1974 [6]	(f)
$(3.78 \pm 0.07) \times 10^{-17}$	297		
3.24×10^{-17}	289	Becker, Schurath and Seitz, 1974 [7]	(g)
Reviews and Evaluations			
5×10^{-17}	298	Huie and Herron, 1973 [8]	(h)
$9.8 \times 10^{-12} \exp(-3500/T)$	286–302	Baulch, Drysdale and Horne, 1973 [9]	(h)
$1.2 \times 10^{-13} \exp(-2450/T)$	220–340	Hampson and Garvin, 1975 [10]	(i)
$1.2 \times 10^{-13} \exp(-2450/T)$	200–300	NASA 1977 [11]	(j,k)

Comments

(a) Static reactor, reactants at ppm concentration level. [O_3] monitored by chemiluminescence detector.

(b) Same system as in reference [1]. In separate experiments using long-path infrared spectrometry, the stoichiometric ratio ($\Delta NO_2/\Delta O_3$) was measured in O_3 excess (1.88 ± 0.15) and in NO_2 excess (1.68 ± 0.15).

(c) Flash photolysis system. Monitored [O_3] and [NO_2] by optical absorption.

(d) Stop-flow time-of-flight mass spectrometry. [O_3] monitored. "*A* factor" stated in abstract and text is incorrect; correct value given in table (D. D. Davis, private communication).

(e) Long path static cell. [O_3] and [NO_2] monitored in separate experiments by UV absorption spectrometry. Stoichiometric ratio ($\Delta NO_2/\Delta O_3$) measured to be 1.89 ± 0.08.

(f) Stopped-flow system. [O_3] monitored by molecular beam sampling mass spectrometry.

(g) Large static reactor. [O_3] monitored by optical absorption at 253.7 nm. No details of measurement given.

(h) Evaluation—outdated by newer data in references [4–6].

(i) Recommended value derived from a least squares fit of the data points in the three recent temperature dependent studies, references [4–6], to an Arrhenius expression.

(j) Accepted the recommendation in Hampson and Garvin, 1975 [10].

(k) Recommended in Hampson and Garvin, 1978 [12].

Preferred Value

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

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

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Value

Preferred value derived from a least squares fit of the data points in the three recent temperature dependent studies, references [4–6], to an Arrhenius expression.

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NO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H^\circ_0/\mathrm{kJ\ mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$NO + h\nu \rightarrow N(^4S) + O(^3P)$	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	$T_0/\mathrm{cm^{-1}}$	$\lambda(\mathrm{vac})/\mathrm{nm}$	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.

Dissociation of nitric oxide in the atmosphere occurs by absorption from the $v'' = 0$ level of the $X\,^2\pi$ ground state to the $v = 0$ and 1 levels of the $C(^2\pi)$ state in the $\delta(0–0)$ and $\delta(1–0)$ absorption bands followed by predissociation of these states in competition with emission and quenching. This absorption occurs in the same spectral region as the Schumann-Runge absorption bands of O_2. A line by line analysis must be made to determine the overlap between the solar radiation transmitted through the Schumann-Runge bands and the NO absorption lines. This enables one to calculate the effective rate of predissociation of nitric oxide in the atmosphere. Results of such a detailed analysis have been reported by Cieslik and Nicolet, 1973 [2] and by Frederick and Hudson, 1979 [3]. Because of their detail these results are not repeated here. Instead 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, 1979 [3].

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NO_2 + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H^\circ_0/\mathrm{kJ\ mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	398
$\rightarrow NO + O(^1D)$ (2)	490	244

Absorption cross section data

Wavelength range/nm	Reference	Comments
190–420	Johnston and Graham, 1974 [1]	(a)
185–410	Bass, Ledford and Laufer, 1976 [2]	(b)
375–420	Harker, Ho and Ratto, 1977 [3]	(c)
390–420	Davenport, 1978 [4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1	295–445	Jones and Bayes, 1973 [5]	(e)
ϕ_1	313–416	Gaedtke and Troe, 1975 [6]	(f)
ϕ_1	375–420	Harker, Ho and Ratto, 1977 [3]	(g)
ϕ_1	390–420	Davenport, 1978 [4]	(h)
ϕ_2	214–252	Uselman and Lee, 1976 [7]	(i)

Comments

(a) Measured at 294 K with resolution of 1.3 nm. Values tabulated at 5 nm intervals; results of same study tabulated at 1 nm intervals in Graham, 1975 [8].

(b) Measured at 298 K and also at 235 K for 290–410 nm. Resolution < 0.04 nm. Values tabulated at 0.125 nm intervals. Also reports results for N_2O_4.

(c) Measured at 296 K at 0.5 nm intervals with resolution of 0.1 nm.

(d) Measured at 297, 277, 247, 226 and 204 K. Resolution of 0.04 nm at 297 K. Values tabulated at 1 nm intervals.

(e) Relative quantum yields for NO production measured and normalized to literature values at 313 and 366 nm.

(f) Quantum yield for disappearance of NO_2 measured for mixtures containing up to 1000 atm N_2.

(g) Quantum yield for NO_2 photodissociation by pulsed dye laser measured at 1 nm intervals. Values given here are taken from tabulated results provided by the authors.

(h) Quantum yield for NO production measured relative to NO production from NOCl photolysis at six wavelengths for T = 300 and 223 K.

(i) Quantum yield for $O(^1D)$ determined in presence of neopentane from measured yield of neopentanol.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
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

Preferred Values for Quantum Yields

The above table gives values of ϕ_1 at closely spaced wavelength values in the neighborhood 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, 1976 [2]. The absorption spectrum is highly structured; for greater detail the reader should consult reference [2] where values are tabulated every 1/8th nanometer. They agree with the results of reference [4] and agree with results of reference [1] and [3] within a 15 percent range.

The preferred quantum yield values for 375–420 nm are those reported by Harker et al., 1977 [3]. This is the most extensive investigation of quantum yields in this wavelength range. The results of Davenport, 1978 [4] agree well at the six wavelengths studied. Reference [4] gives quantum yield data at 223 K which show that values of ϕ_1 at low temperature are reduced for wavelengths greater than the thermodynamic threshold for photodissociation but are independent of temperature for shorter wavelengths. In agreement with these observations, Pitts, Sharp and Chan, 1964 [9] observed an increase of ϕ_1 with increasing temperature at 405 and 436 nm. The preferred values of ϕ_1 at shorter wavelengths are the values recommended in Jones and Bayes, 1973 [5] which are based on their own relative values normalized to literature values at 313 and 366 nm. The observation by Uselman and Lee, 1976 [7] that $\phi_2 = 0.5 \pm 0.1$, independent of wavelength, for the range 214–242 nm indicates that process (1) is competitive with process (2) at energies above the threshold for process (2).

A recent discussion of the photochemistry of NO_2 is given in Okabe, 1978 [10].

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$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/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
400–704	Graham and Johnston, 1978 [1]	(a)
500–670	Wayne et al., 1978 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1, ϕ_2 $(\phi_1 = \phi_{1a} + \phi_{1b} + \phi_{1c})$	470–700	Graham and Johnston, 1978 [1]	(c)

Comments

(a) Measured at 298 K with resolution of 0.83 nm. Values tabulated at 1 nm intervals, NO_3 was produced in the N_2O_5 catalyzed decomposition of O_3. These results supersede results reported in Johnston and Graham, 1974 [3].

(b) Measured at 298 K with resolution 0.5 to 0.8 nm. NO_3 was produced by addition of NO_2 to a flow of O_3. Relative values reported. Preliminary results.

(c) Measured at 298 and 329 K. Modulation experiments were performed with three broad-band fluorescent lamps with overlapping spectral distributions. Primary quantum yield estimated from product quantum yield, lamp emission spectra and NO_3 absorption spectrum. Only values averaged over specified wavelength ranges are given: λ = 470–610 nm, $\phi_1 = 0.23$, $\phi_2 = 0.77$; λ = 610–700 nm, $\phi_1 = 0.07$, where $\phi_1 = \phi_{1a} + \phi_{1b} + \phi_{1c}$.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
470	51	580	305
475	60	585	277
480	64	590	514
485	69	595	408
490	88	600	283
495	97	605	345
500	99	610	148
505	110	615	196
510	132	620	358
515	140	625	925
520	145	630	566
525	148	635	145
530	194	640	111
535	204	645	62
540	183	650	38
545	181	655	76
550	236	660	736
555	268	665	875
560	307	670	95
565	253	675	37
570	254	680	44
575	274	685	7

Quantum yields
No recommendation

Comments on preferred values

The preferred absorption cross section values come from the tabulated results in Graham and Johnston, 1978 [1] by averaging the values over 5 nm intervals. For greater detail see the original reference. These are the only published final results.

The only published quantum yield data are reported in Graham and Johnston, 1978 [1]. In this study using three *broad band light sources, only values of* ϕ_1 *and* ϕ_2 averaged over specified wavelength ranges are given (see Comment (c) above). Because of the lack of good spectral resolution in the determination of primary quantum yields, no recommendation is given. However calculated photodissociation rates are not very sensitive to the spectral resolution, and it is therefore recommended that modelers use simply the photodissociation rates for NO_3 in the lower atmosphere calculated in reference [1]: $j_1 = 0.04 \pm 0.02\ s^{-1}$ *and* $j_2 = 0.10 \pm 0.02\ s^{-1}$.

Note the extremely low value of $\phi_1 = 0.07$ averaged over the strong 610–700 nm absorption region. This means that absorption in the strong bands centered at 662 and 627 nm does not lead to dissociation under the experimental condition of one atmosphere total pressure.

Also these results indicate a substantial contribution of channel (2) at wavelengths longer than the threshold wavelength (580 nm). Calculations by the authors suggest that only 40 percent of this effect can be accounted for by internal energy.

More experimental work on primary quantum yield values is needed; in particular, studies with good spectral resolution are needed. Also pressure and temperature effects should be investigated.

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$N_2O + h\nu \rightarrow$ 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
210–328	Johnston and Selwyn, 1975 [1]	(a)
173–240	Selwyn, Podolske and Johnston, 1977 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \leq 0.03$	214	Paraskevopoulos and Cvetanovic, 1969 [3]	(c)
$\phi_0 \leq 0.01$	185–230	Preston and Barr, 1971 [4]	(d)

Comments

(a) Measured at 298 K. Results shown in two figures. Good agreement with previous results (Bates and Hayes, 1967 [5] in the range 210 to 235 nm. However, no absorption detected for $\lambda > 260$ nm ($\sigma < 2 \times 10^{-25}$ cm^2), in contrast with results in reference [5].

(b) Measured at five temperatures from 194 to 302 K with resolution of 0.7 nm. Values tabulated at 1 nm intervals. Also, a nine parameter fit expressing σ as a function of λ and T is given.

(c) Photolysis of N_2O at 298 K in presence of neopentane, butene-1 and added gases. Yield of $O(^3P)$ atoms determined from yield of addition products with butene-1.

(d) Photolysis of N_2O containing 1% ^{15}NO at 296 K and λ = 185, 214 and 229 nm. Isotopic composition of product N_2 measured.

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

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

where

$A_1 = 68.21023$ $B_1 = 123.4014$
$A_2 = -4.071805$ $B_2 = -2.116255$
$A_3 = 4.301146 \times 10^{-2}$ $B_3 = 1.111572 \times 10^{-2}$
$A_4 = -1.777846 \times 10^{-4}$ $B_4 = 1.881058 \times 10^{-5}$
$A_5 = 2.520672 \times 10^{-7}$

Quantum yields

$\phi_2 = 1.0$ for λ = 185–230 nm.

Comments on preferred values

The preferred absorption cross section values are from Selwyn, Podolske and Johnston, 1977 [2]. The tabulated values are room temperature values. For values tabulated at 1 nm intervals and five temperatures from 194 to 302 K, consult the original reference. The nine parameter expression for $\ell n\, \sigma(\lambda,T)$ is also from reference [2]. It fits the 310 reported data with a standard deviation of about 4 percent. For a discussion of earlier data see the review by Hudson, 1974 [6].

The preferred value of the quantum yield (ϕ_2 equal to unity) is based on the results reported in Paraskevopoulos and Cvetanovic, 1969 [3], Preston and Barr, 1971 [4], and Greiner, 1967 [7].

A recent discussion of the photochemistry of N_2O is given in Okabe, 1978 [8].

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$N_2O_5 + h\nu \rightarrow$ 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

Absorption cross section data

Wavelength range/nm	Reference	Comments
285–380	Jones and Wulf, 1973 [1]	(a)
205–310	Graham and Johnston, 1978 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(-N_2O_5) = 0.6$	280,265	Holmes and Daniels, 1934 [3]	(c)
$\Phi(-N_2O_5) = 0.62$	280	Murphy, 1969 [4]	(d)

Comments

(a) Spectrograms taken at 298 K.

(b) Measured at 298 K with resolution of 0.83 nm. Corrections were made for absorption by O_3, HNO_3 and NO_2. Values tabulated at 5 nm intervals; results of same study tabulated at 1 nm intervals in Graham, 1975 [5].

(c) Overall quantum yield for disappearance of N_2O_5 measured at 273 K.

(d) Overall quantum yield for disappearance of N_2O_5 measured at 273 K. Measurements also made in presence of 100–600 torr SF_6, CO_2, N_2 and O_2. Overall quantum yield observed to decrease with increasing pressure of added gas.

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, 1978 [2] for 205–310 nm and in Jones and Wulf, 1937 [1] for 320–380 nm. Although over the wavelength range common to both studies, the values reported in reference [2] are higher than those reported in reference [1] because the disagreement decreases steadily towards the long wavelength end of this common range, no adjustment has been made to the values from reference [1] in the statement of preferred values at longer wavelengths.

No recommendation is made for primary quantum yields because the primary photodissociation products have not been identified, and the only quantum yield data reported are for the overall disappearance of N_2O_5. Primary quantum yield values from these data requires the identification of the primary products and knowledge of the extent of their reaction with N_2O_5. Clearly primary quantum yield data are needed.

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HONO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$HONO + h\nu \rightarrow HO + NO$ (1)	202	591
$\rightarrow H + NO_2$ (2)	326	367
$\rightarrow HNO + O$ (3)	423	283

Absorption cross section data

Wavelength range/nm	Reference	Comments
300–400	Johnston and Graham, 1974 [1]	(a)
200–400	Cox and Derwent, 1976 [2]	(b)
310–396	Stockwell and Calvert, 1978 [3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 0.92 \pm 0.16$	365 ± 5	Cox and Derwent, 1976 [2]	(d)

Comments

(a) HONO prepared from mixtures of NO, NO_2 and H_2O. [HONO] calculated assuming equilibrium conditions. Later these same authors found that the actual concentration of HONO was much less than the calculated equilibrium concentration, and therefore the values reported in reference [1] were much too low. (Graham and Johnston, 1977 [4]). Slightly modified values given in Graham, 1975 [5].

(b) HONO prepared from reaction of sulphuric acid with sodium nitrite. Resolution < 0.1 nm. Correction was made for absorption by NO_2. Values are tabulated at 5 nm intervals from 200–310 nm and at 1 nm intervals from 310–400 nm.

(c) HONO prepared from mixtures of NO, NO_2 and H_2O. It was shown that equilibrium conditions were established. Resolution < 1 nm from 325–400 nm. Corrections were made from absorption by NO_2 , N_2O_3 and N_2O_4. Values are tabulated at 1 nm intervals.

(d) Value estimated by comparison of rates of photon absorption by NO_2 and HONO with their measured rates of decomposition in the same photolysis cell. This result supersedes earlier estimate by same method in Cox, 1974 [6] owing to use here of more reliable absorption cross section data.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
310	0	355	26.5
315	0.4	360	7.2
320	4.0	365	18.2
325	3.8	370	20.9
330	8.8	375	3.7
335	5.7	380	8.2
340	17.6	385	14.7
345	11.1	390	1.4
350	10.0	395	0

Quantum yields

$\phi_1 = 1.0$ throughout this wavelength region.

Comments on preferred values

The preferred absorption cross section values are from the tabulated results in Stockwell and Calvert, 1978 [3] by averaging the values over 5 nm intervals. For greater detail see the original reference. These values are preferred over those reported by Cox and Derwent, 1976 [2] because of the use of higher resolution cross section data in correcting for absorption by NO_2. These two studies are in reasonably good agreement. For values at shorter wavelengths, use values tabulated in Cox and Derwent, 1976 [2].

Based on the results of Cox and Derwent, 1976 [2], the preferred value of ϕ_1 is set equal to unity throughout this wavelength range. It should be emphasized that quantum yield data exist for only one wavelength—clearly more data are needed.

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$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_0$/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
190–370	Johnston and Graham, 1973 [1]	(a)
185–325	Biaume, 1973 [2]	(b)
120–170	Beddard, Giachardi and Wayne, 1974 [3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 1.0$	200–315	Johnston, Chang and Whitten, 1974 [4]	(d)

Comments

(a) Continuous absorption spectrum. Values are tabulated at 5 nm intervals from 190–325 nm. Also, it is reported that $\sigma << 10^{-22}$ cm^2 from 330–370 nm.

(b) Measurements made and values tabulated for discrete emission lines of selected lamps. Photodissociation rate for HNO_3 in the stratosphere calculated assuming $\phi_1 = 1.0$.

(c) Results given in figure of molar decadic extinction coefficient as a function of wavelength.

(d) Photolysis of HNO_3 in presence of excess CO and excess O_2 to prevent complications due to secondary reactions. Results are interpreted by a complex reaction scheme.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/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, 1973 [1]. The results of Biaume, 1973, [2] agree. For discussion of earlier results see review by Okabe, 1973 [5].

The preferred value of the quantum yield (ϕ_1 equal to unity) is based on the results of Johnston et al., 1974 [4]. Earlier results of Berces and Forgeteg, 1970 [6] are discussed in review by Okabe, 1973 [5].

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$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	89	1340
$\rightarrow HO + NO_3$ (2)	164	730

Note: $\Delta H°_{298}$ values are given since the heat of formation of HO_2NO_2 at O K is not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
190–330	Graham, Winer and Pitts, 1978 [1]	(a)
195–265	Cox and Patrick, 1979 [2]	(b)

Comments

(a) Measured at 296 K. HO_2NO_2 prepared from NO_2 and H_2O_2. Corrections were made for absorption by H_2O_2, HNO_3 and NO_2.

(b) Measured at 283 K. HO_2NO_2 prepared by photolysis of Cl_2 in excess H_2 with NO_2 present in a mixture of N_2 and O_2 at 1 atmosphere pressure. Correction was made for absorption by O_3, assuming that all the absorption at 265 nm was due to O_3.

Absorption cross sections

λ/nm	$10^{20}\sigma/cm^2$		λ/nm	$10^{20}\sigma/cm^2$
	[1]	[2]		[1]
190	1610		270	28
195	960	404	275	23
200	640	434	280	18
205	430	420	285	14
210	290	378	290	10.9
215	200	298	295	8.4
220	154	220	300	6.2
225	123	163	305	5.0
230	99	120	310	4.2
235	82	93	315	3.6
240	68	76	320	3.0
245	58	65	325	2.6
250	51	54	330	2.0
255	45	44		
260	40	30		
265	35	<10		

Quantum yield data

No data.

Preferred Values

Absorption cross sections

No recommendation—see comments.

Quantum yields

No recommendation can be made for the values of ϕ_1 and ϕ_2, since there are no data to provide a basis for a recommendation.

Comments on preferred values

No recommendation is made for absorption cross section values. The wavelength region of importance for photodissociation in the atmosphere is for $\lambda > 290$ nm. While the two sets of data are in reasonable agreement from 205 to 255 nm, the fall off in values reported in [2] from 255 to 265 nm suggests negligible absorption beyond 270 nm in contrast to the data reported in [1]. This fall off could possibly be accounted for by an overcompensation for absorption by ozone. Alternatively the absorption at long wavelengths reported in [1] could possibly be accounted for by the presence of an absorbing impurity. Additional studies in the important atmospheric photodissociation region ($\lambda > 290$ nm) are needed to resolve the apparent discrepancy between the reported results.

Clearly, data are needed on the identification of primary products and quantum yields.

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4.4. Reactions of CH_4

$$
\begin{aligned}
O(^1D) + CH_4 &\rightarrow HO + CH_3 &(1)\\
&\rightarrow O(^3P) + CH_4 &(2)\\
&\rightarrow H_2O + CH_2 &(3)\\
&\rightarrow CH_2O + H_2 &(4)\\
&\rightarrow CH_3OH &(5)
\end{aligned}
$$

$\Delta H^\circ (1) = -179$ kJ mol^{-1}

$\Delta H^\circ (2) = -189$ kJ mol^{-1}

$\Delta H^\circ (3) = -220$ kJ mol^{-1}

$\Delta H^\circ (4) = -472$ kJ mol^{-1}

$\Delta H^\circ (5) = -564$ 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			
$(3.1 + 0.3) \times 10^{-10}$	300	Heidner and Husain, 1973 [1]	(a)
$(1.3 \pm 0.2) \times 10^{-10}$	298	Davidson et al., 1976 [2]	(b)
$(1.4 + 0.4) \times 10^{-10}$	200–350	Davidson et al., 1977 [3]	(b)
Branching Ratios			
$k_2 = 0$	298	Young, Black and Slanger, 1968 [4]	(c)
$\frac{k_1}{k} = 0.28; \frac{k_4}{k} = 0.05;$ $\frac{k_5}{k} = 0.37; \frac{k_2}{k} = 0.30$	87	DeMore and Raper, 1967 [5]	(d)
$\frac{k_4}{k} = 0.088$	235	Lin and DeMore, 1973 [6]	(e)
$\frac{k_1}{k} = (0.90 \pm 0.02); \frac{k_4}{k} = (0.10 \pm 0.02)$	300	Jayanty, Simonaitis and Heicklen, 1976 [7]	(f)
Reviews and Evaluations			
4.0×10^{-10}	298	Hampson and Garvin, 1975 [8]	(g)
4.0×10^{-10}	298	Cvetanovic, 1974 [9]	(h)
1.4×10^{-10}	198–357	Hampson and Garvin, 1978 [10]	(i)
1.3×10^{-10}	200–300	NASA, 1977 [11]	(j)

Comments

(a) Flash photolysis of O_3 in Hartley Band; $O(^1D)$ monitored by time-resolved absorption of atomic resonance radiation at 115.2 nm.

(b) Pulsed laser photolysis of O_3 at 266 nm; $O(^1D)$ monitored by time-resolved emission from the transition $O(^1D) \rightarrow O(^3P)$ at 630 nm.

(c) $O(^3P)$ production measured using O + NO chemiluminescence in photolysis of O_2 at 147 nm. Conclude $O(^1D) + CH_4$ interaction is entirely by reactive channels.

(d) 254 nm photolysis of $O_3 + CH_4$ in liquid Ar. O_3 by product analysis. Initial insertion product, CH_3OH^*, partially stabilized at 87 K. k_3 assumed to be zero.

(e) Photolysis of $N_2O + CH_4$ at 184.9 nm. Product analysis by gas chromatography.

(f) Photolysis of $N_2O + CH_4 + O_2$ mixtures at 216 nm. Measured N_2 and H_2 products. Channels other than (1) and (4) are negligible.

(g) Accepts the recommendation from [9]; branching ratio $k_4/k = 0.08$ from [6].

(h) Careful review of all relative rate data up to 1974.

(i) Preferred value is based on $O(^1D) \rightarrow O(^3P)$ emission studies from [2] and [3]. Branching ratio $k_4/k = 0.09$.

(j) Accepts [2] and [3] branching ratio $k_4/k = 0.1$.

Preferred Values

$k = 2.4 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} over range 200–300 K.

$k_1/k = 0.9$, $k_4/k = 0.1$ over range 200–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The origin of the discrepancy between the direct measurements using absorption and emission techniques is uncertain at this time. Disagreement centers around the correct value for the correction factor γ to modify Beers Law for $O(^1D)$ absorption in the resonance line. The main complicating feature of the emission studies is the occurrence of secondary chemiluminescence emission from the products of $O(^1D)$–substrate interactions, although steps were taken to minimize this interference in the rate measurements. Measurements of the branching ratios at temperatures above 200 K agree, and they show that channels (1) and (4) are the only important routes over the temperature range of interest for the atmosphere. The recommended values are based on the mean value of $k/k(O(^1D) + CO_2)$ from [1], [3] and [9], ie., 1.81 and the absolute value for $O(^1D)$ reaction with CO_2 taken as the simple average of the values reported in [12] and [3], 1.35×10^{-10} cm^{3}molecule^{-1}s^{-1}. 90 percent of the reaction proceeds by channel (1) and 10 percent via channel (4). The temperature independence found in [3] is accepted. An alternative expression for the preferred values over the range 200–300 K is

$$k_1 = 2.2 \times 10^{-10}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

$$k_4 = 0.24 \times 10^{-10}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

For further discussion of current position on $O(^1D)$ rate constants see introduction.

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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			
$8.1 \times 10^{-11} \exp(-2520/T)$	298–423	Horne and Norrish, 1967 [1]	(a)
1.7×10^{-14}	298		
1.08×10^{-14}	300	Wilson and Westenberg, 1967 [2]	(b)
$5.5 \times 10^{-12} \exp(-1900/T)$	300–500	Greiner, 1970 [3]	(c)
8.8×10^{-15}	300		
$(3.83 \pm 0.20) \times 10^{-12} \exp((-1840 \pm 20)/T)$	290–440	Margitan, Kaufman and Anderson, 1974 [4]	(d)
7.9×10^{-15}	298		
$(2.36 \pm 0.21) \times 10^{-12} \exp((-1710 \pm 88)/T)$	240–373	Davis, Fischer and Schiff, 1974 [5]	(e)
7.43×10^{-15}	298		
$(9.5 \pm 1.4) \times 10^{-15}$	296	Howard and Evenson, 1976 [6]	(f)
$5.75 \times 10^{-21} T^{3.08} \exp(-1010/T)$	300–900	Zellner and Steinert, 1976 [7]	(g)
$(8.8 \pm 0.7) \times 10^{-15}$	300		
$(6.51 \pm 0.26) \times 10^{-15}$	300	Overend and Paraskevopoulos, 1975 [8]	(h)
2.6×10^{-14}	381	Gordon and Mulac, 1975 [9]	(i)
5.5×10^{-14}	416		
Relative Rate Coefficients			
$(7.3 \pm 0.9) \times 10^{-15}$	296	Cox, Derwent and Holt, 1976 [10]	(j)
Reviews and Evaluations			
$4.7 \times 10^{-11} \exp(-2500/T)$	300–2000	Wilson, 1972 [11]	(k)
$1.2 \times 10^{-10} \exp(-2970/T)$	300–1850	Schofield, 1967 [12]	(k)
$2.36 \times 10^{-12} \exp(-1710/T)$	240–373	Hampson and Garvin, 1978 [13]	(l)
$2.35 \times 10^{-12} \exp(-1710/T)$	200–300	NASA, 1977 [14]	(l)

Comments

(a) Flash photolysis of H_2O to produce HO which was followed by time-resolved absorption spectroscopy.

(b) Discharge flow; HO produced by $H + NO_2$ reaction and monitored by ESR.

(c) Flash photolysis; HO monitored by resonance absorption.

(d) Discharge flow; HO monitored by molecular resonance fluorescence in the presence of excess CH_4.

(e) Flash photolysis of CH_4-H_2O-He mixtures; HO monitored by molecular resonance fluorescence. k invariant with pressure up to 200 Torr He.

(f) Discharge flow; HO measured by laser magnetic resonance spectroscopy.

(g) Flash photolysis of CH_4-H_2O-He mixtures; HO by time-resolved resonance absorption. A study over an extended temperature range.

(h) A flash photolysis; resonance absorption study.

(i) Electron Pulse radiolysis of 1 atm H_2O vapour + CH_4; HO by time-resolved absorption.

(j) Rate constant relative to $HO + H_2 \rightarrow H_2O + H$, $k(HO + H_2) = 7.0 \times 10^{-15}$ cm^{3}molecule^{-1}s^{-1}. Photolysis of HONO-CH_4-Air mixtures in a flow system; product analysis; $k/k(HO + H_2) = 1.04 \pm 0.13$.

(k) Emphasizes high temperature data.

(l) Recommend expression from ref. [5].

Preferred Values

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

$k = 2.4 \times 10^{-12} \exp(-1710/T)$ cm^{3}molecule^{-1}s^{-1} 200–300 K.

Reliability

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

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

Comments on Preferred Values

The earlier room temperature values of Horne and Norrish [1] and Wilson and Westenberg [2] are considered too high, the most likely reason being complications due to secondary reactions of HO with reaction products. The high sensitivity of the resonance fluorescence and laser magnetic resonance techniques allowed measurements using very low HO radical densities, virtually eliminating the possibility of interference from secondary reactions. Generally the agreement among all the studies is good.

k seems to be invariant with total pressure, as expected for a simple H-atom abstraction process. The wide range of temperature for which data is available today demonstrates the non-Arrhenius temperature dependence of this reaction. The activation energy increases markedly with temperature, which is expected in any realistic theoretical description of these processes. The only study using temperatures below 296 K is that of Davis et al. [5], and we have given their Arrhenius expression as the preferred value for the temperature range 210–300 K with larger error limits than given in [5]. The expression by Zellner and Steinert [7] based on measurements above room temperature yields essentially identical values to the expression from [5] at 210 and 240 K and gives a value equal to the mean of the data from refs [3]–[8] at 298 K. This expression is recommended for k at temperatures above 300 K.

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$HO + CO \longrightarrow H + CO_2$

$\Delta H^\circ = -104.0$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-13} \exp(-115/T)$	300–500	Greiner, 1969 [1]	(a,b)
1.43×10^{-13}	300		
1.35×10^{-13}	300	Stuhl and Niki, 1972 [2]	(a,c)
$(1.66 \pm 0.50) \times 10^{-13}$	300	Mulcahy and Smith, 1971 [3]	(a,d)
1.33×10^{-13}	298	Westenberg and de Haas, 1973 [4]	(a,e)
2.17×10^{-13}	915		
1.45×10^{-13}	298	Smith and Zellner, 1973 [5]	(a,b,f,)
$(2.15 \pm 0.19) \times 10^{-13} \exp((-80 \pm 40)/T)$	220–373	Davis, Fischer and Schiff, 1974 [6]	(a,c)
1.58×10^{-13}	298		
$(1.56 \pm 0.2) \times 10^{-13}$	296	Howard and Evenson, 1974 [7]	(a,g)
1.25×10^{-13}	298	Trainor and Von Rosenburg, 1974 [8]	(a,b)
$(1.51 \pm 0.08) \times 10^{-13}$	298	Gordon and Mulac, 1975 [9]	(h)
$(1.54 \pm 0.16) \times 10^{-13}$	299	Atkinson, Perry and Pitts, 1976 [10]	(c,i)
1.66×10^{-13} (50 Torr He)	296	Overend and Paraskevopoulos, 1977 [11]	(b,j)
3.16×10^{-13} (350 Torr SF_6)			
$(1.53 \pm 0.15) \times 10^{-13}$ (25 Torr SF_6)	299	Perry, Atkinson and Pitts, 1977 [12]	(c,j)
$(3.43 \pm 0.35) \times 10^{-13}$ (703 Torr SF_6)			
$(1.51 \pm 0.16) \times 10^{-13}$ (25 Torr N_2)	300	Biermann, Zetzsch and Stuhl, 1978 [13]	(b,k)
$(2.83 \pm 0.28) \times 10^{-13}$ (750 Torr N_2)			
Relative Rate Coefficients			
$1.11 \times 10^{-12} \exp(-530/T)$	473–623	Ung and Back, 1964 [14]	(l)
1.87×10^{-13}	298		
$7 \times 10^{-12} \exp(-831/T)$	217–298	Sie, Simonaitis and Heicklen, 1976 [15]	(m)
$(3.45 \pm 0.22) \times 10^{-13}$	298		
$(2.7 \pm 0.2) \times 10^{-13}$	296	Cox, Derwent and Holt, 1976 [16]	(n)
1.38×10^{-13} (100 Torr Air)	300	Chan et al., 1977 [17]	(o)
3.0×10^{-13} (700 Torr Air)			
$(2.69 \pm 0.40) \times 10^{-13}$ ($\geq$ 300 Torr N_2)	305	Butler, Solomon and Snelson, 1978 [18]	(p)
Reviews and Evaluations			
$1.05 \times 10^{-16} T^{1.3} \exp(385/T)$	250–2000	Baulch et al., 1976 [19]	(q)
1.4×10^{-13}	200–300	NASA, 1977 [20]	
$5.1 \times 10^{-13} \exp(-300/T)$	300–2000	Wilson, 1972 [21]	
1.4×10^{-13}	200–400	Hampson and Carvin, 1975 [23]	
3.0×10^{-13}	200–400	Hampson and Garvin, 1978 [22]	(r)

Comments

(a) Experiments conducted at low pressures where no pressure dependence of k was observed.

(b) Flash-photolysis; resonance absorption detection of HO; 100 Torr He.

(c) Flash-photolysis; resonance fluorescence detection of HO.

(d) Discharge flow system with mass spectrometric detection of stable products.

(e) Discharge flow; ESR detection of HO; 1–3 Torr He.

(f) Up to 250 Torr He; slight positive temperature dependence in range 210–460 K.

(g) Discharge flow system; laser magnetic resonance detection of HO.

(h) HO produced by pulsed-radiolysis of 10 Torr H_2O in 10 Torr CO and 710 Torr Ar. HO measured by time-resolved absorption at 308 nm.

(i) No dependence on Ar pressure in the range 25–650 Torr.

(j) Large pressure effect with SF_6; little or no pressure effect with Ar or He.

(k) The pressure effect was demonstrated to depend on the amount of O_2 present in the diluent gas.

(l) Vacuum U.V. photolysis of H_2O with added CO and H_2. Gas chromatographic measurement of CO_2. Unusual pressure effects at low temperature. Total pressure 200–300 Torr. Rate constant relative to $HO + H_2 \rightarrow H_2O + H$; $k(HO + H_2) = 3.5 \times 10^{-11} \exp(-2540/T)$ cm^{3}molecule^{-1}s^{-1}, this evaluation. $k/k(HO + H_2) = (0.032 \pm 0.005) \exp((2013 \pm 150)/T)$.

(m) Relative to $k(HO + H_2) = 3.5 \times 10^{-11} \exp(-2540/T)$ cm^{3}molecule^{-1}s^{-1}, this evaluation. Photolysis of N_2O-H_2-CO mixtures; N_2 and CO_2 formation monitored by gas chromatography. k apparently increased with total pressure and at 700 Torr, mainly H_2, obtained $k/k(HO + H_2) = 0.20 \exp(+1700/T)$. Pressure effect also found for SF_6 but not He.

(n) Relative to HO + $H_2 \rightarrow H_2O$ + H using k(HO + H_2) = 7.0×10^{-15} $cm^3 molecule^{-1} s^{-1}$; Flow system photolysis of HONO-CO-Air mixture at atmospheric pressure. Product analysis. k/k(HO + H_2) = 38.6 ± 2.9 at 298 K.

(o) Static photolysis of HONO-CO-iso C_4H_{10}-Air mixtures with product analysis using long path infra-red spectroscopy. Rate constant relative to HO + $iC_4H_{10} \rightarrow$ products, k(HO + iC_4H_{10}) = 2.4×10^{-12} $cm^3 molecule^{-1} s^{-1}$ [24]. 10^2 k/k(HO + iC_4H_{10}) = 12.7 ± 0.7 and 5.9 ± 0.8 at 700 and 100 Torr, respectively.

(p) Photolysis of H_2O_2-CO-iC_4H_{10}-Air mixtures; analysis of CO_2 product by gas chromatography. Pressure range 100–600 Torr mainly N_2 + O_2; reference reaction HO + CO $\rightarrow$ CO_2 + H at 100 Torr using k(HO + CO) = 1.5×10^{-13} $cm^3 molecule^{-1} s^{-1}$. k(HO + CO) determined relative to k(HO + iC_4H_{10}) at different pressures.

(q) Same expression as obtained by Baulch and Drysdale [26].

(r) Value recommended for 1 atm pressure air.

Preferred Values

For pressures < 100 Torr $k = 1.5 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$, over range. 200–300 K.

For pressures of 760 Torr Air $k = 2.8 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$, 298 K.

Reliability

$\Delta \log k = \pm 0.05$ for low pressure value at 298 K.

$\Delta \log k = \pm 0.1$ for 760 Torr Air value at 298 K.

Comments on Preferred Values

Much of the earlier work on this reaction including the high temperature studies has been reviewed extensively by Baulch and co-workers [19]. Due to the marked non-Arrhenius behavior of the temperature dependence, only the data from lower temperatures (<900 K) has been considered to evaluate k for atmospheric conditions. k apparently exhibits a pressure effect and preferred values for both low and high pressure are given.

The agreement between the various measurements of k, both direct and indirect, at low pressures is remarkably good and the value of k at 298 K can be considered as well-established. The reaction exhibits a small activation energy in the range 200–400 K ($E/R \simeq 100$ K), but for atmospheric modeling the temperature dependence is negligible. The current data strongly indicate a pressure dependence on the overall rate of oxidation of CO to CO_2 at pressures above 100 Torr. Thus the direct measurements [11,12,13] show that HO decay is pressure dependent, and the CO_2 quantum yield measurements [15,17,18] show that CO_2 formation is pressure dependent. The work of Cox et al. [16] indicates that the production of HO_2, presumed to occur via reaction of the H atom with O_2, is pressure dependent.

It has been suggested [25] that the pressure dependence arises from an alternative channel for the HO + CO reaction, involving a stable HOCO entity which can produce CO_2 by reaction with O_2. The recent work of Bierman [13] provides support for this; when O_2 was rigorously excluded from their experimental gas mixtures, k was independent of N_2 pressure up to 760 Torr.

Whatever the origin of the effect, it seems that the high-pressure values should be applied to the low atmosphere. If account is taken of the different diluent gases and reference reactions used, the agreement between the various estimates of the "high pressure" value of k is reasonable. Thus for M = SF_6 (627 Torr) the direct study using resonance fluorescence detection of HO [12] gave a value in close agreement with the value of $k \simeq 3.4 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$ obtained by Sie et al. [15] from their relative rate measurement at 298 K. The relative rate data of Cox et al. [16] and Chan et al. [17], both using 1 atm pressure of Air but with different reference reactions, are in agreement with each other and with the 760 Torr N_2 + O_2 data of Biermann et al. [13]. These form the basis of the preferred value for these conditions. No recommendation is given for intermediate pressures but a linear dependence on pressure between 100 Torr (low pressure value) and 760 Torr (high pressure value) is suggested as the most appropriate form of interpolation for atmospheric chemistry. The temperature dependence in the pressure-dependent region requires investigation.

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$$\begin{aligned} HO + HCHO &\rightarrow H_2O + HCO \quad &(1)\\ &\rightarrow H + HCOOH \quad &(2)\\ &\rightarrow H + CO + H_2O \quad &(3)\end{aligned}$$

$\Delta H^\circ\ (1) = -135\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^\circ\ (2) = -\ 91\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^\circ\ (3) = -\ 64.7\ \mathrm{kJ\ mol^{-1}}$

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

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
0.7×10^{-11}	300	Herron and Penzhorn, 1969 [1]	(a)
$(1.4 \pm 0.35) \times 10^{-11}$	300	Morris and Niki, 1971 [2]	(b)
$1.25 \times 10^{-11} \exp((-90 \pm 150)/T)$	299–426	Atkinson and Pitts, 1978 [3]	(c)
$(9.4 \pm 1.0) \times 10^{-12}$	299		
Relative Rate Coefficients			
$(1.5 \pm 0.1) \times 10^{-11}$	298	Niki et al., 1978 [4]	(d)
6×10^{-12}	268	Smith, 1978 [5]	
$(6.5 \pm 1.5) \times 10^{-12}$	298		(e)
9.6×10^{-12}	334		
Reviews and Evaluations			
8×10^{-11}	300–1600	Wilson, 1972 [6]	
1.4×10^{-11}	300	Hampson and Garvin, 1978 [7]	
$3 \times 10^{-11} \exp(-250/T)$	200–300	NASA, 1977 [8]	

Comments

(a) Discharge flow—mass spectrometric detection of HCHO decay in excess HO; a lower limit estimate of k.

(b) Discharge flow—mass spectrometric measurements of HO, HCHO and products. Formation of products from DHCO and D_2CO indicated (1) was major reaction channel.

(c) Pulsed vacuum U.V. flash photolysis; HO measured by time resolved resonance fluorescence.

(d) Photolysis of HONO-HCHO-C_2D_4 - air mixtures. Product analysis by long-path FTIR spectroscopy giving $k/k(HO + C_2H_4) = 1.8 \pm 0.1$. The value used for the rate constant for the reference reaction $k(HO + C_2H_4) = 8.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} is a mean of recent measurements at pressures near 760 Torr.

(e) Discharge flow-mass spectrometric detection of HCHO and stable products. k was determined by computer fit to complex mechanism, and is relative to $k(HO + HO \rightarrow \text{products}) = 2.2 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 298 K and $E/R = 480$ K for the reference reaction. This differs from the CODATA evaluation for $k(HO + HO)$ which has no temperature dependence. However adjustment cannot be made since a simple relationship for $k/k(HO + HO)$ is not given.

Preferred Values

$k = 1.3 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} over range 200–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The reason for the discrepancy between the two results of Niki and coworkers [2,4] and the flash photolysis study [3] are not apparent since in each study HO + CH_3CHO was also measured (see also Morris, Stedman and Niki [9] and all of the values were insignificantly different from 1.60×10^{-11} cm^{3}molecule^{-1}s^{-1}. The preferred overall value of k is a mean of the values from [2], [3] and [4], with zero activation energy as indicated in [4].

The dominant reaction pathway is widely assumed to be (1), and the studies of Morris and Niki [2] who examined the isotopic distribution of the water product from OH + D_2CO, supports this contention. However formic acid has been observed as a product of formaldehyde photo-oxidation in a number of studies and its origin is not easily ascertained (see data sheet on $HCO + O_2$). The recent suggestion by Horowitz et al. [10] that a substantial proportion of the overall reaction may proceed via channel (2), provides a possible explanation of the observed HCOOH. More evidence is required, however, before a definite value can be recommended for the branching ratio.

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$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$ (1)

$\rightarrow HO + O_2 + CH_3O$ (2)

ΔH° (1) = −140 kJ mol^{-1}

ΔH° (2) = + 44 kJ mol^{-1}

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

$k/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.7^{+18.4}_{-5.4}) \times 10^{-14} \exp[(1296 \pm 364)/T]$	274–338	Cox and Tyndall, 1979 [1]	(a)
$(6.5 \pm 1.0) \times 10^{-12}$	298		
Reviews and Evaluations			
6.8×10^{-14}	298	Demerjian, Kerr and Calvert, 1974 [2]	(b)

Comments

(a) Molecular Modulation Spectrometry; CH_3O_2 and HO_2 generated simultaneously by photolysis of Cl_2 in the presence of CH_4 and H_2 in 1 atm O_2, and monitored by absorption at 250 and 210 nm. Reaction assumed to proceed entirely by channel (1).

(b) Estimate based on application of the geometric mean rule for radical cross combination rate constants, i.e., $k/(k(A + A) \cdot k(B + B))^{1/2} = 2$ where $A = HO_2$ and $B = CH_3O_2$, and using their own evaluations of the recombination rate constants for HO_2 and CH_3O_2.

Preferred Values

$k = 6.5 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.

Reliability

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

Comments on Preferred Values

Since Channel (2) is slightly endothermic, (1) is expected to be the dominant channel at temperatures in the range 200-300 K; this is consistent with the observations in [1] but the occurrence of (2) to a significant extent could lead to an error in the derived value of k. The error from this source is, however, unlikely to exceed the uncertainty limits given with the preferred value, which is based on the only direct measurement of this rate constant. Note that the value of k exceeds both $k(HO_2 + HO_2)$ and $k(CH_3O_2 + CH_3O_2)$ and therefore the geometric mean rule does not apply in this case. The large negative temperature dependence is similar to that observed for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, but this result should be confirmed before a final recommendation can be made.

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$HCO + O_2 \rightarrow HO_2 + CO$ (1)

$HCO + O_2 (+M) \rightarrow HCO_3 (+M)$ (2)

$\Delta H° (1) = -145.9$ kJ mol^{-1}

$\Delta H° (2) \simeq -120$ kJ mol^{-1}

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

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.6 \pm 0.9) \times 10^{-12}$	300	Shibuya et al., 1977 [1]	(a)
$(4.0 \pm 0.8) \times 10^{-12}$	300	Clark, Moore and Reilly, 1978 [2]	(b)
Branching Ratios			
$k_2[M]/k_1 = 5 \pm 1$	265–296	Osif and Heicklen, 1976 [3]	(c)
≥ 9	300	Niki et al., 1977 [4]	(d)
$= 0.4$	300	Demerjian, Kerr and Calvert, 1974 [5]	(e)
$= 0.052 \pm 0.017$	298	Horowitz, Fu Su and Calvert, 1978 [6]	(f)
$= 1.5$	298		
Relative Rate Coefficients			
$(5.7 \pm 1.2) \times 10^{-12}$	298	Washida, Martinez and Bayes, 1974 [7]	(g)
Reviews and Evaluations			
1.7×10^{-13}	298	Demerjian, Kerr and Calvert, 1974 [5]	(h)
5.7×10^{-12}	300	Hampson and Garvin, 1978 [8]	(i)
6×10^{-12}	300	NASA, 1977 [9]	

Comments

(a) Flash photolysis of CH_3CHO-O_2 mixtures; HCO measured by time-resolved absorption at 613.8nm. Up to 513 Torr He had no effect on k giving $k_2 \leq 3 \times 10^{-32}$ cm^6 molecule^{-2}s^{-1}, M = He.

(b) Laser flash photolysis of HCHO; HCO detected by intracavity dye-laser absorption spectroscopy. More details given in [10].

(c) Product analysis in Cl_2 photosensitised oxidation of HCHO. k_2/k_1 based on relative yields of CO and HCOOH, the latter assumed to result from the HCO_3 radical only. Ratio was apparently independent of temperature (265–296 K) and pressure (62–704 Torr, N_2 or He).

(d) Long path i.r. study of HCHO photo-oxidation. Ratio based on HCOOH yield assuming this to be a measure of HCO_3. M = Air at 760 Torr.

(f) Photo-oxidation of HCHO in the presence of low $[O_2]$. 8–12 Torr pressure range. Suggest that HCOOH arises from addition reactions of HO and HO_2 with HCHO. Their ratio $k_2[M]/k_1$ is based on the assumption that $\Phi(CO_2)$ is a measure of HCO_3 formation; 760 torr value estimated assuming third order kinetics for k_2 up to atmospheric pressure. Values given here are for M = HCHO + O_2 at 10 torr and Air at 760 torr, respectively.

(g) Discharge flow; HCO measured by photo-ionisation mass spectrometry. k measured relative to $k(O + HCO \rightarrow \text{products}) = 2.1 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} (measured in the same apparatus) by observing the effect of O_2 on [HCO] in a flowing mixture of O + C_2H_4. $k/k(O + HCO) = (2.74 \pm 0.21) \times 10^{-2}$.

(h) Estimate.

(i) Accepting the value from ref. [7].

Preferred Values

$k_1 = 5.1 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of k_1 is the mean of the three measurements of this rate constant using direct observation of HCO [1], [2], [7]. No recommendation can be made for k_2 but the result based on CO_2 formation in HCHO photo-oxidation [6] is probably the most reasonable, although the value suggested for 1 atm air is almost certainly too high because of high pressure fall-off in k_2. Any conclusions concerning k_2 must remain uncertain until the problem of the mechanism of HCOOH formation in these systems is fully resolved. There are no data for the temperature dependence of k_1, which is, however, expected to be small.

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$CH_3 + O_2 \longrightarrow HO + HCHO$

$\Delta H^\circ = -215$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3.3 \times 10^{-16}$	298	Basco, James and James, 1972 [1]	(a)
Relative Rate Coefficients			
$2.9 \times 10^{-13} \exp(-(940 \pm 250/T))$	259–339	Washida and Bayes, 1976 [2]	(b)
1.1×10^{-14}	298		
Reviews and Evaluations			
$2.1 \times 10^{-12} \exp(-6380/T)$	1200–2600	Walker, 1977 [3]	(c)

Comments

(a) Flash photolysis of azomethane-O_2-N_2; CH_3 decay monitored by absorption at 216 nm with photographic recording; limit of k estimated from the absence of any HO absorption near 308 nm during decay of CH_3.

(b) CH_3 produced by $O + C_2H_4$ in discharge flow system and measured by photo-ionization mass spectrometry. k measured relative to $k(O + CH_3) = 1.0 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} measured in the same apparatus; $k/k(O + CH_3) = (10^{-2.54} \pm 0.35) \exp((-940 \pm 250)/T)$.

(c) Review of high temperature data, mainly from shock-tube experiments, up to 1975. Arrhenius plot of data for temperature range 1200–2580 K reveals large scatter but points from four studies fit a common line giving the expression shown.

Preferred Values

No recommendation.

Comments on Preferred Values

The best defined study of this reaction at low temperatures is that of Washida and Bayes [2] which gave k a factor of 35 greater than that of Basco et al. [1]. However they point out that the conclusions in ref [1] could be in error if the HO produced was consumed in secondary reactions, of which the reaction $CH_3O_2 + HO \longrightarrow$ products seemed likely. In view of the difficulty in reconciling these results, we are unable to give a preferred value.

References

[1] Basco, N., James, D. G. L., and James, F. C., Int. J. Chem. Kinet., **4,** 129 (1972).
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$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$

$\Delta H° = -118$ 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			
2.6×10^{-31} [N_2]	298	Basco, James and James, 1971 [1]	(a)
3.1×10^{-31} [N_2]	298	Parkes, 1977 [2]	(b)
Relative Rate Coefficients			
6.1×10^{-33} exp(1000/T) [N_2]	259–339	Washida and Bayes, 1976 [3]	(c)
1.8×10^{-31} [N_2]	298		

Comments

(a) Flash photolysis of azomethane-O_2-N_2 mixtures, pressure range 30–380 Torr; CH_3 monitored by UV absorption at 216 nm, Lindemann-Hinshelwood plot for extrapolation to k_0 and k_∞.

(b) Molecular modulation spectroscopy. Photolysis of azomethane-O_2-N_2 mixtures; pressure range 20–760 Torr; CH_3 and CH_3O_2 measured by UV absorptions at 216 and 240 nm, respectively. Lindemann-Hinshelwood extrapolation toward k_0 and k_∞.

(c) $k(CH_3 + O_2 + M \longrightarrow CH_3O_2 + M) + k(CH_3 + O_2 \longrightarrow HO + HCHO)$ measured relative to $k(O + CH_3 \longrightarrow$ products); evaluated with $k(O + CH_3) = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Extrapolation to low pressure limit.

Preferred Value

$k_0 = 2.6 \times 10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 2.6 \times 10^{-31}$ $(T/300)^{-3}$ [N_2] cm^3 molecule^{-1} s^{-1} over range 260–340 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 260–340 K.

Comments on Preferred Values

The preferred value is a compromise between the three values available. The fall-off extrapolation procedures should be improved.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.8×10^{-12}	298	Van den Bergh and Callear, 1971 [4]	(a)
0.5×10^{-12}	298	Basco, James and James, 1971 [1]	(b)
1.2×10^{-12}	298	Parkes, 1977 [2]	(c)
2.2×10^{-12}	295	Hochanadel et al., 1977 [5]	(d)
Relative Rate Coefficients			
1.7×10^{-12}	298	Laufer and Bass, 1975 [6]	(e)

Comments

(a) Flash photolysis of $(CH_3)_2Hg$ in the presence of O_2 in C_3H_8; pressure range 30–300 Torr of C_3H_8. CH_3 monitored by UV absorption at 216 nm. RRKM extrapolation toward k_∞.

(b) See comment (a) for k_0; k_∞ value derived probably too low because of the use of the Lindemann-Hinshelwood extrapolation. The experiments of ref. [4] were closer to k_∞ since the more efficient bath gas C_3H_8 was used.

(c) See comment (b) for k_0.

(d) Flash photolysis of azomethane-O_2-N_2 mixtures at 745 Torr of N_2. CH_3 and CH_3O_2 measured in absorption. 12 percent fall-off correction applied using the results of ref. [1].

(e) Flash photolysis of azomethane-O_2-N_2(He, Ar) mixtures. Product analysis by gas chromatography. Pressure range 50–700 Torr. RRKM extrapolation to k_∞. Rate measured relative to $CH_3 + CH_3 \longrightarrow C_2H_6$; evaluated with their own value of $k(CH_3 + CH_3 \longrightarrow C_2H_6) = 9.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, i.e., 2 × the generally accepted value. Reducing $k(CH_3 + CH_3)$ by a factor of 2 gives $k_\infty = 0.85 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}.

Preferred Value

$k_\infty = 2 \times 10^{-12}$ 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 Values

The value of k_∞ appears to be low such that experiments at pressures above 1 atm are needed. With the preferred values one calculates $[N_2]_c = 7.7 \times 10^{18}$ molecule cm^{-3}.

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$CH_3O + O_2 \rightarrow HO_2 + HCHO$

$\Delta H^\circ = -121.2$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.0 \pm 1.3) \times 10^{-15}$	373	Hoare and Whytock, 1967 [1]	(a)
2.0×10^{-15}	373	Alcock and Mile, 1975 [2]	(b)
2.5×10^{-17}	300	Weaver et al., 1975 [3]	(c)
9×10^{-16}	300	Wiebe et al., 1975 [5]	(d)
$5 \times 10^{-13} \exp(-(2000 \pm 1400)/T)$	396–442	Barker, Benson and Golden, 1977 [6]	(e)
6×10^{-16}	298*		
2.0×10^{-15}	300	Kirsch and Parkes, 1977 [7]	(f)
5.8×10^{-15}	423		
3×10^{-15}	410	Selby and Waddington, 1977 [8]	(g)
Reviews and Evaluations			
$1.6 \times 10^{-13} \exp(-3300/T)$	not stated	Heicklen, 1973 [12]	
$1.6 \times 10^{-13} \exp(-3300/T)$	200–300	NASA, 1977 [13]	(h)
$1.6 \times 10^{-13} \exp(-3300/T)$		Hampson and Garvin, 1978 [14]	(h)

Comments

(a) Photo-oxidation of acetone; Alcock and Mile [2] derived k from these data by analysis of a complex mechanism. Reference reaction undefined.

(b) Photolysis of $(CH_3)_2N_2$-O_2-2,3 dimethylbutane mixtures at 100 °C. Product analysis with computer optimation of rate constants in complex mechanism. Reference reaction: $CH_3O + (CH_3)_3CH \rightarrow CH_3OH + (CH_3)_3C$; $k = 3.2 \times 10^{-13} \exp(-2060/T)$ cm^{3}molecule^{-1}s^{-1} [9].

(c) Photo-oxidation of $(CD_3)_2N_2$. Product analysis by mass-spectrometry. Also derived similar result from previous work of Shortridge and Heicklen [4]. Reference reaction: $CH_3O + CH_3O \rightarrow CH_3OH + HCHO$; $k = 4 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} [10]; $k/k'^{1/2}(CH_3O + CH_3O) = 4 \times 10^{-12}$ cm$^{3/2}$molecule$^{-1/2}$s$^{-1/2}$.

(d) Photolysis of CH_3ONO in the presence of NO,NO_2 and O_2. $\phi(CH_3ONO_2)$ measured by mass-spectrometry. Reference Reaction: $CH_3O + NO \rightarrow CH_3ONO$; $k = 2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} [11]; $k/k(CH_3O + NO) = 4.7 \times 10^{-5}$.

(e) Thermal decomposition of dimethylperoxide in the presence of NO_2 and O_2. Measured $[NO_2]$ and total pressure as a function of time. Reference reaction: $CH_3O + NO_2 \rightarrow CH_3ONO_2$; $k = 1.0 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} based on relative rates of reaction of NO_2 and NO with CH_3O [6] and $k(CH_3O + NO)$ given in [11]; $k/k(CH_3O + NO_2) = 10^{-1.33 \pm 1.46} \exp(-(2000 \pm 1400)/T)$.

(f) Photo-oxidation of Azoisobutane. Molecular Modulation Spectrometry and product analysis. Reference reaction: $CH_3O + (CH_3)_3CH \rightarrow CH_3OH + (CH_3)_3C$, $k(CH_3O + (CH_3)_3CH) = 3.2 \times 10^{-13} \exp(-2060/T)$ cm^{3}molecule^{-1}s^{-1}, [9]. $k/k_{ref} = 6.0$ at 300 K and 2.3 ± 1.0 at 423 K.

(g) Pyrolysis of ditert-butyl peroxide-O_2-N_2 at 410 K. Product analysis by G. C. Reference reaction: $CH_3O + CH_3O \rightarrow$ products, but complex mechanism.

(h) Accepts evaluation in [12].

Preferred Values

$k = 6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5 \times 10^{-13} \exp(-2000/T)$ cm^3 molecule^{-1} s^{-1} over range 300–450 K.

Reliability

$\Delta \log k = \pm 0.6$ at 298 K.

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

Comments on Preferred Values

The large disparities in the different estimates of k_1 arise from the complexity of the chemical systems used to evaluate this rate constant, and also are partly due to experimental difficulties in the analysis of complex products. The recommended expression is based on the work of Barker et al. [6] and it gives a reasonable prediction of the k_1 values at 300 K from the photolysis of CH_3ONO, and the higher temperature oxidation studies. The earlier work at room temperature [3,4] based on $2CH_3O \rightarrow$ products as a reference reaction gives a value that is evidently much too low, probably due to some problem in interpretation of the chemistry.

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$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$ (1)

$$\begin{aligned} CH_3O_2 + CH_3O_2 &\rightarrow CH_3OH + HCHO + O_2 && (1)\\ &\rightarrow 2CH_3O + O_2 && (2)\\ &\rightarrow CH_3OOCH_3 + O_2 && (3) \end{aligned}$$

$\Delta H^\circ (1) = -323.9$ kJ mol^{-1}

$\Delta H^\circ (2) = +\ 14.6$ kJ mol^{-1}

$\Delta H^\circ (3) = -178.9$ 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			
4.4×10^{-13}	300	Parkes et al., 1973 [1]	(a)
$(5.5 \pm 1.0) \times 10^{-13}$	300	Parkes, 1977 [2]	(b)
$(3.8 \pm 0.7) \times 10^{-13}$	300	Hochanadel et al., 1977 [3]	(c)
$(4.4 \pm 1.0) \times 10^{-13}$	300	Anastasi, Smith and Parkes, 1978 [4]	(d)
Branching Ratios			
$(k_1 + k_3)/k_2 = 2.0 \pm 0.4$	298	Parkes, 1974 [5]	(e)
$(k_1 + k_3)/k_2 = 1.0$	373	Alcock and Mile, 1975 [6]	(f)
$(k_1 + k_3)/k_2 = 1.3$	298	Weaver et al., 1975 [7]	(g)
$k_3/k = 0.07$			
Reviews and Evaluations			
$\sim 10^{-11}$	300	Heicklen, 1968 [9]	(h)
7×10^{-14}	300	Demerjian, Kerr and Calvert, 1974 [10]	(i)

Comments

(a) Preliminary upper limit value; Molecular Modulation Spectrometry (MMS), CH_3O_2 observed in absorption at 240 nm. Upper limit value since overall decay constant may be a factor of between 1.1 and 1.33 larger than k due to secondary chemistry in the system, see [2] for discussion. $k/\sigma(240) = 10 \times 10^4$ cm s^{-1}; $\sigma = 4.4 \times 10^{-18}$ cm^2 at 240 nm.

(b) MMS; upper limit k value supersedes that from [1] due to systematic error in latter. Rate constants for individual channels based on branching ratio from [5] and model chemistry: $k_1 + k_3 = (3.0 \pm 0.8) \times 10^{-13}$ and $k_2 = 1.6 \pm 0.4 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1}. No temperature dependence on k over range 288–298 K; $k/\sigma(240) = 10 \pm 2 \times 10^4$ cms^{-1}; $\sigma = 5.5 \times 10^{-18}$ cm^2 at 240 nm.

(c) Flash photolysis of azomethane-O_2; CH_3O_2 by time resolved absorption at 248 nm. Overall decay constant given, which is an upper limit for k due to possible secondary chemistry; $k/\sigma(248) = 13 \pm 2 \times 10^4$ cm s^{-1}; $\sigma = 2.9 \times 10^{-18}$ cm^2 at 248 nm.

(d) Flash photolysis of azomethane-O_2; CH_3O_2 by absorption at 240 nm. Overall decay constant given, which is an upper limit for k; $k/\sigma = (8 \pm 2) \times 10^4$ cms^{-1}; $\sigma = 5.5 \times 10^{-18}$ cm^2 at 240 nm.

(e) MMS and product analysis in photolysis of azomethane-O_2-i C_4H_{10} mixtures.

(f) Product analysis of photolysis of azomethane-O_2-dimethylbutane mixtures. Computer optimisation of rate constants in complex system.

(g) Photo-oxidation of $CD_3N_2CD_3$ with analysis by mass spectrometry gave, for CD_3O_2, $(k_1 + k_3)/k_2 = 3.55$ and $k_3/k = 0.18$. CH_3O_2 rate constants from their analysis of results of Shortridge and Heicklen [8].

(h) Estimate.

(i) Estimate based on liquid phase results.

Preferred Values

$k = 4.6 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1} at 298 K.
$k_2/k = 0.33$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta \log k_2/k = \pm 0.15$ at 298 K.

Comments

The recent direct determinations of k, refs. [1]–[4] supersede all previous estimates which were either too high [9] or too low [10]. The preferred value is taken from the direct measurements of Parkes [2] because this is the only analysis which considers in detail the (small) difference between the overall chemical removal of CH_3O_2 and the actual rate constant k.

The branching ratio is not so well defined although all of the data indicate that more than 50 percent of the reaction leads to non-radical products at 298 K. Insufficient data are available for recommendation of a temperature dependence either for k or the branching ratio. The preferred values at 298 K may also be expressed as: $k_1 + k_3 = 3.1 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1}; $\Delta \log (k_1 + k_3) = \pm 0.2$. $k_2 = 1.5 \times 10^{-13}$ cm^{3}molecule^{-1}s^{-1}; $\Delta \log k_2 = \pm 0.3$.

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$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (1)$$

$$\rightarrow CH_2O + HONO \quad (2)$$

$$CH_3O_2 + NO + M \rightarrow CH_3O_2NO + M \quad (3)$$

$\Delta H^\circ\ (1) = -\ 49.8\ kJ\ mol^{-1}$

$\Delta H^\circ\ (2) = -285.7\ kJ\ mol^{-1}$

$\Delta H^\circ\ (3) = > -80\ kJ\ mol^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$> 1 \times 10^{-12}$	298	Anastasi, Parkes and Smith, 1978 [1]	(a)
$(8 \pm 2) \times 10^{-12}$	295	Plumb et al., 1979 [2]	(b)
$(6.5 \pm 2.0) \times 10^{-12}$	298	Cox and Tyndall, 1979 [3]	(c)
Branching Ratios			
$k_1/k = 0.80 \pm 0.15$	298	Simonaitis and Heicklen, 1974 [4]	(d)
$k_1/k = 1$	296	Pate, Finlayson and Pitts, 1974 [5]	(e)
Relative Rate Coefficients			
1.2×10^{-12}	298	Cox et al., 1976 [6]	(f)
Reviews and Evaluations			
6.2×10^{-13}	298	Demerjian, Kerr and Calvert, 1974 [7]	
$3.3 \times 10^{-12} \exp(-500/T)$	200–300	NASA, 1977 [8]	

Comments

(a) Flash photolysis of $(CH_3)_2N_2$-O_2-NO mixtures. CH_3O_2 followed by time-resolved absorption; lower limit value based on absence of observed CH_3O_2 signal in the presence of NO.

(b) Discharge flow; mass spectrometric detection of CH_3O_2 and decay followed in the presence of excess NO; small correction to first order decay due to interfering ion at mass 47. CH_3O_2 produced by $O + C_2H_4 + O_2$. Error limits reflect overall experimental error.

(c) Molecular Modulation Spectrometry; CH_3O_2 followed by absorption at 250 nm in photolysis of Cl_2-CH_4-O_2-NO mixtures. k determined by computer simulation of results taking into account the reaction of CH_3O_2 with NO_2 product from channel (1). Error limits reflect overall experimental error.

(d) Photolysis of N_2O-CH_4-O_2-NO at 214 nm. $\Phi(NO_2)$ and $\Phi(CH_3ONO_2)$ measured; supersedes previous work from the same group which was apparently erroneous.

(e) Photolysis of $(CH_3)_2N_2$-O_2-NO in 1 atm N_2. NO_2 and CH_3ONO_2 by long path infrared spectroscopy.

(f) Photolysis of HONO-CH_4-NO-Air mixtures at 1 atm pressure Φ(NO) by chemiluminescence. k_1 relative to $k(CH_3O_2 + CH_3O_2 \rightarrow \text{products}) = 4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [9]. Lower limit value. Branching ratio $k_1/k \geq 0.92$ also given.

Preferred Values

$k_1 = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

Although pathway (2) is the most exothermic, considerable rearrangement of the reactant molecules is required, so that the simple O-atom transfer step (1) or association (3) will be more favored kinetically at ambient temperatures. The product of (3), methylperoxynitrite, is unknown and is almost certainly unstable: the net forward rate of (3) is predicted to be zero, at least at ambient temperatures, due to redissociation of CH_3O_2NO to CH_3O_2 + NO. Thus reaction (1) is expected to be the dominant path, in agreement with the observations. The preferred value is a weighted mean of the two recent direct measurements of k_1 which are entirely in accord with the lower limits reported previously. As expected, the value of k_1 is similar to the rate constant for the analogous reaction of HO_2 with NO, i.e., 8.4×10^{-12} cm^3 molecule^{-1} s^{-1} (this evaluation).

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$$CH_3O_2 + NO_2 \rightarrow CH_3O + NO_3 \quad (1)$$

$$\rightarrow HCHO + HONO_2 \quad (2)$$

$$\rightarrow CH_3ONO + O_2 \quad (3)$$

$$CH_3O_2 + NO_2\ (+\ M) \rightarrow CH_3O_2NO_2\ (+\ M) \quad (4)$$

$\Delta H^\circ\ (1) = +\ 45.1\ \text{kJ mol}^{-1}$

$\Delta H^\circ\ (2) = -284.2\ \text{kJ mol}^{-1}$

$\Delta H^\circ\ (3) = -105.8\ \text{kJ mol}^{-1}$

$\Delta H^\circ\ (4) = -\ 80\ \text{kJ mol}^{-1}$

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

$k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.3) \times 10^{-12}$ (540 Torr N_2)	276	Cox and Tyndall, 1979 [1]	(a)
$(1.2 \pm 0.2) \times 10^{-12}$ (50 Torr Ar + CH_4)	276		
Relative Rate Coefficients			
3.4×10^{-12} (760 Torr, mainly CH_4)	298	Simonaitis and Heicklen, 1974 [2]	(b)
3.8×10^{-13} (760 Torr Air)	298	Cox et al., 1976 [3]	(c)
Reviews and Evaluations			
$k_4/k = 0.75 \pm 0.05$	298	Hampson and Garvin, 1978 [4]	
$k_2/k = 0.25 \pm 0.10$	300	Heicklen, 1973 [5]	
$k_1/k < 0.1$			

Comments

(a) Molecular Modulation Spectrometry; CH_3O_2 detected by absorption at 250 nm in photolysis of Cl_2-CH_4-O_2-NO_2 mixtures in a flow system. Decay lifetime of CH_3O_2 measured in the presence of excess NO_2.

(b) Photolysis of N_2O-CH_4-O_2 in presence of NO and NO_2. $\Phi(NO_2)$ and $\Phi((CH_3)_2N_2)$ measured. Rate constant relative to $k(CH_3O_2 + NO \rightarrow \text{products})$ for which a value of $7.5 \times 10^{-12}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ (CODATA value) has been used here. Also found $k_1/k = 0$.

(c) Photolysis of HONO-CH_4-NO_2-Air mixtures at 1 atm pressure. NO_2 apparently did not inhibit the oxidation of NO to NO_2 via CH_3O_2 + NO which determines the upper limit rate constant given, relative to a value of $7.5 \times 10^{-12}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ for $k(CH_3O_2 + NO \rightarrow \text{products})$. The technique does not distinguish reaction (1) from CH_3O_2 + NO, and therefore the value given is for $k_2 + k_3 + k_4$.

Preferred Values

$k_4 = 1.6 \times 10^{-12}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ over range 200–300 K in air at 500–760 Torr.

$k_1 = k_2 = k_3 = 0.$

Reliability

$\log k_4 = \pm 0.5$ at 298 K.

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

Comments on Preferred Values

The exothermic pathways (2) and (3) require considerable rearrangement of the reactants and will not therefore be kinetically favorable at ambient temperatures. Similarly the endothermicity of reaction (1) together with the observations from ref [2] suggest that this channel is unimportant. Reaction (4) has now been identified as a major channel, forming methylperoxy-nitrate as product

[6]. At room temperature it most likely dissociates via the reverse of (4), by analogy with peroxyacetylnitrate [7] and peroxynitric acid [8,9]. This interpretation is consistent with the observations in [3] and also in [10], since there would be no net removal of CH_3O_2 by reaction with NO_2 in these systems.

The preferred values are based on the direct measurements [1] obtained at 276 K, and assuming that the reaction proceeds only via channel (4). The results in [1] indicate a slight pressure dependence, but k_4 is almost certainly pressure dependent at lower pressures. It is recommended, however, that the reaction $CH_3O_2 + NO_2$ be neglected in modeling atmospheric chemistry, until more information is available on the stability of the $CH_3O_2NO_2$ product.

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$HCHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_0$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HCHO + h\nu \rightarrow H + HCO$ (1)	358.4	334
$\rightarrow H_2 + CO$ (1)	−9.1	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–380	McQuigg and Calvert, 1969 [1]	(a)
290–360	Calvert et al., 1972 [2]	(b)
303.0–352.5	Glasgow, and Bass, 1978 [3]	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength/nm	Reference	Comments
$\phi \simeq 1$	250–380 nm	McQuigg and Calvert, 1969 [1]	(d)
$\phi_1/\phi_2 = 0$	355		
$\phi_1/\phi_2 = 5$	280		
$\phi_1 = 0.15$	330	Lewis, Tang and Lee, 1976 [4]	(e)
$\phi_1 = 0.37$ (maximum)	314		
$\phi_1 = 0.1$	330	Marling, 1977 [5]	(f)
$\phi_1 = 0.76$ (maximum)	304		
$\phi_1 \leq 0.01$	333.2	Clarke, Moore and Nogar, 1978 [6]	(g)
$\phi_1 = 0.70$	299.1		
$\phi = 0.68$	353.5		
$\phi > 0.9$	< 338		
$\phi_1 = 0.68 \pm 0.1$	275.4	Lewis and Lee, 1978 [7]	(h)
$\phi_1 = 0.64 \pm 0.1$	288.2		
$\phi_1 = 0.68 \pm 0.05$	303.5		
$\phi_1/\phi = 0.15 \pm 0.10$	355	Moortgat et al., 1978 [8]	(i)
$\phi_1/\phi = 0.80 \pm 0.05$	305		
$\phi_1 = 0$	337	Horowitz and Calvert, 1978 [9]	(j)
$\phi_1 = 0.7$	317.5		
$\phi = 0.75$	337		
$\phi = 1.0$	< 335		
$\phi = 1.0 \pm 0.2$	< 330		
$\phi = 0.75$	342	Moortgat and Warneck, 1979 [10]	(k)
$\phi = 0.35$	355		
$\phi_1 \leq 0.1$	> 340		
$\phi_1 = 0.833$	303.9		
Evaluation			
Table showing ϕ_1 and ϕ as function of wavelength. Also σ as function of λ, 290–360 nm.		Hampson and Garvin, 1978 [11]	(l)

Comments

(a) At 353 K, low resolution (~ 1 nm estimated); molar decadic extinction coefficients given in $1\ mol^{-1} cm^{-1}$.

(b) Based on measurements from ref [1]; extinction coefficients given in $1\ mol^{-1} cm^{-1}$ and averaged over 10 nm intervals.

(c) Data at 296 and 223 K; σ about 30% lower at 223 K for $\lambda \geq 330$ nm; cross sections given in cm^2 $molecule^{-1}$.

(d) Flash photolysis of HCHO, DCHO and DCDO: Product analysis by mass spectrometry; ϕ_1/ϕ_2 from H_2, HD and D_2 distribution in products.

(e) Laser photolysis of HCHO using selected vibrational levels. H atom detected by HNO chemiluminescence. Some large variations in ϕ_1 at short λ, depending on level excited.

(f) Ion-laser photolysis of DCHO using both selected vibrational levels and wide band (3.0 nm) irradiation H_2, D_2 and HD measured by mass-spectrometry. Only relative quantum yields measured. Data have been normalized to give $\phi_1 = 0.76$ at 304 nm.

(g) Laser photolysis of HCHO and DCDO with and without added NO to scavenge H and CHO. Analysis of H_2, CO and D_2 by gas chromatography. Values given are those obtained using high [NO], see ref [9]. Absolute quantum yields measured.

(h) Photolysis of HCHO-Butene mixtures at low pressures. Product analysis by gas chromatography. Absolute quantum yields measured.

(i) Photolysis of HCHO (~ 30 ppm) in synthetic air at 1 atm. Also in 1 atm N_2 with added C_3H_6 (to scavenge H and HCO). $\Phi(H_2)$ and $\Phi(CO)$ measured by gas chromatography. Relative quantum yields measured. ϕ_1/ϕ decreased again at $\lambda \lesssim 280$ nm.

(j) Photolysis of pure HCHO and HCHO + i = C_4H_8 mixtures. $\Phi(H_2)$ measured; in pure HCHO gives $\phi_1 + \phi_2$; in i-C_4H_8 mixture gave ϕ_2. At $\lambda > 330$ nm addition of CO_2 quenched ϕ_2 but ϕ_1 was unaffected.

(k) Experimental technique as ref [8] but wider range of conditions including variation of pressure. ϕ independent of pressure for ≤ 330 nm. Pressure dependence of ϕ_2 at > 330 nm demonstrated and quenching parameters for Air as diluent determined. Absolute quantum yields measured.

(l) Based on recent data also presented in this survey

Preferred Values

Absorption cross sections and quantum yields[a] for HCHO photolysis in air at 760 Torr and 300 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	ϕ_1	ϕ_2
280	2.4	0.63	0.37
290	3.2	0.73	0.27
300	3.3	0.77	0.23
310	3.1	0.76	0.24
320	2.4	0.63	0.37
330	2.4	0.31	0.64
340	2.0	0	0.67
350	0.8	0	0.40
360	0.2	0	0.14

[a] Values averaged for 10 nm wavelength range centered on indicated wavelength.

Pressure dependences of quantum yields for HCHO photolysis in air

ϕ_1, independent of pressure; ϕ_2, independent of pressure at $\lambda < 330$ nm

	ϕ_2				
λ/nm \ Pressure/torr	760	500	250	100	0
340	0.66	0.75	0.86	0.94	1.0
355	0.26	0.35	0.52	0.73	1.0

Comments on preferred values

Although the primary processes in the photolysis of HCHO has been the subject of study for nearly 40 yrs, large disparities have existed regarding both the relative importance of ϕ_1 and ϕ_2 and the energy requirements of process (1). Until very recently the most definitive data seemed to be that of McQuigg and Calvert [1] published in 1969, and these have been widely used to calculate photo-dissociation constants for HCHO in the atmosphere. Only the data from 1969 on are reviewed here.

The results for ϕ_1 and ϕ_2 are plotted on figure 8. It should be noted that the published data of Lewis et al. [4] have been normalized to $\phi_1 = 0.76$ at 305 nm as also is the data of Marling [5]. The $\phi_1 + \phi_2$ and ϕ_1 values of Moortgat and Warneck [10], Clarke et al. [6] and Horowitz and Calvert [9] are, however, totally independent measurements. The plot illustrates the good agreement between the recent data on formaldehyde photolysis. Particularly gratifying is the agreement in detail on the threshold wavelength for process (1) the fall-off in $\phi_1 + \phi_2$ at longer wavelengths and the absolute values of ϕ_1.

The preferred values for ϕ_1 and ϕ_2 for pressures near 1 atm (760 Torr) and 300 K are taken from the smooth line drawn through all the experimental data shown in figure 8. The absorption cross sections were recalculated from the figures given in [1].

Two recent studies [9,10] have demonstrated a pressure dependence in ϕ at $\lambda \geq 330$ nm, which is shown to be an effect on ϕ_2 only. This must be taken into account for calculating J values for H_2 production from HCHO in the stratosphere. We have given pressure dependencies of ϕ_2 at 340 and 355 nm calculated using quenching constants C of 0.00068 and 0.00366 Torr^{-1}, respectively, in the equation $\phi_2^{-1} = 1 + CP$ where P is pressure in torr. The values of C are taken from [10].

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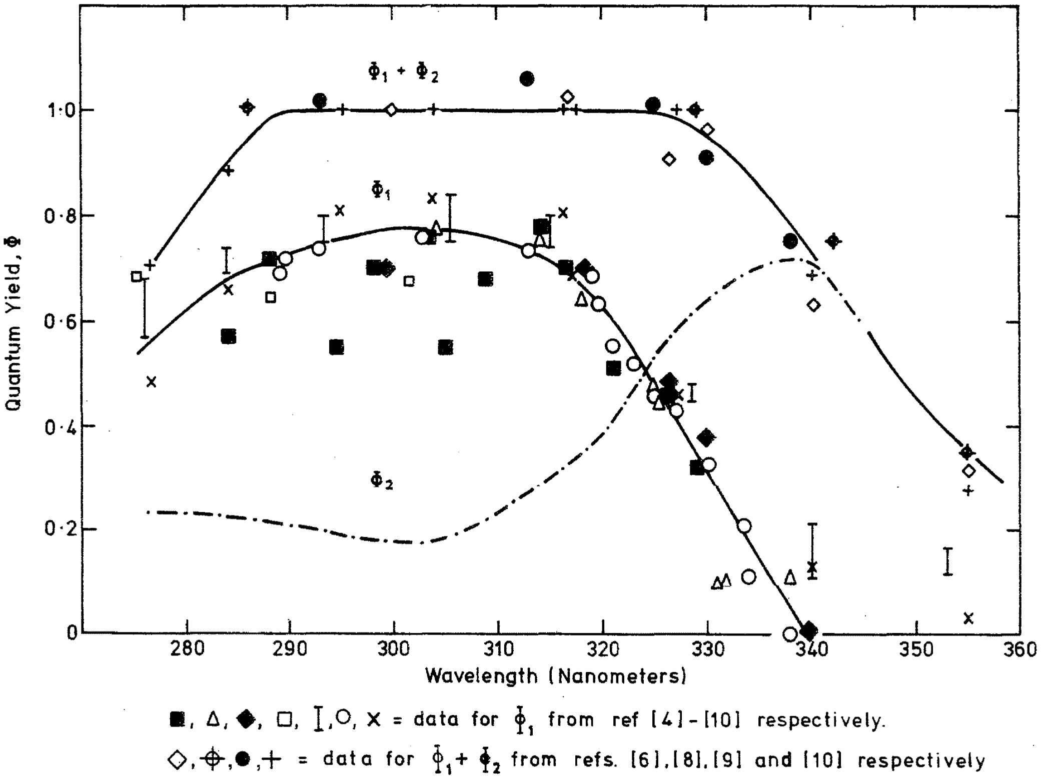

FIGURE 8. Wavelength dependence of HCHO photolysis quantum yields.

$CH_3OOH + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ mol^{-1a}	$\lambda_{threshold}$/nm
$CH_3OOH + h\nu \rightarrow CH_3O + HO$ (1)	184.6	647
$\rightarrow CH_3 + HO_2$ (2)	278.6	429
$\rightarrow CH_3O_2 + H$ (3)	356.3	335

[a] Calculated assuming $\Delta H°_0 = \Delta H°_{298}$: $C_p°$ data not available for CH_3OOH.

No experimental data are available for either the absorption cross-sections or quantum yields for photodissociation of methyl hydroperoxide.

Preferred Values

In the absence of data on CH_3OOH, it is recommended that modelers utilize for CH_3O_2H the absorption cross sections recommended for H_2O_2. By analogy with other peroxide species, it is probable that $\Phi_1 = 1$, $\Phi_2 = \Phi_3 = 0$ for all wavelengths $\geq$ 200 nm [1].

Reference

[1] Hampson, R. F., J. Phys. Chem. Ref. Data 2, 290 (1973).

4.5. Reactions of SO_x

$O + H_2S \rightarrow HO + HS$

$\Delta H^\circ = -44$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4 \pm 2) \times 10^{-12}$	300	Liuti, Dondes and Harteck, 1966 [1]	(a)
$(4.8 \pm 0.4) \times 10^{-14}$	300	Niki and Weinstock, 1967 [2]	(b)
$(1.4 \pm 0.2) \times 10^{-14}$	295	Cupitt and Glass, 1970 [3]	(c)
$(2.9 \pm 0.7) \times 10^{-13} \exp(-(750 \pm 50)/T)$	205–300	Hollinden, Kurylo and Timmons, 1970 [4]	(d)
$(9.8 \pm 0.17) \times 10^{-14}$	300		
3.5×10^{-14}	300	Takahashi, 1970 [5]	(e)
$(7.2 \pm 1.1) \times 10^{-12} \exp(-(1660 \pm 50)/T)$	263–495	Whytock et al., 1976 [6]	(f)
$(2.97 \pm 0.23) \times 10^{-14}$	298		
Reviews and Evaluations			
$6.3 \times 10^{-13} \exp(-920/T)$	200–350	Schofield, 1973 [7]	(g)
$7.2 \times 10^{-12} \exp(-1660/T)$	203–493	Hampson and Garvin, 1978 [8]	(h)

Comments

(a) Discharge flow; $[O]_0/[H_2S]_0$ in range 0.7–2.0. Rate constant based on stoichiometry of 5 obtained from assumed mechanism. Experimental stoichiometry in range 4–7. Wall reactions evident.

(b) Discharge flow; $[H_2S]$, [H], [SO] followed by mass spectrometry. Few details given.

(c) Discharge flow; [O], [H], [SO] followed by e.s.r. [O], [H], [SO] profiles generated by numerical integration of rate equations derived from assumed mechanism. k varied to give best match with experiment. Good fit for $[O]_0 > [H_2S]_0$ but not for H_2S in excess. $[H_2S]$ excess leads to sulfur deposits on walls.

(d) Discharge flow; e.s.r. detection of [O]. H_2S in excess. Stoichiometry assumed to be 3.5 on basis of assumed mechanism and some experimental observations.

(e) Discharge flow; O atoms from discharge in N_2O/Ar mixtures. Chemiluminescence from excited SO, SO_2, O_2 observed. Decay of intensity with time when gas flow terminated was followed and from it, an assumed stoichiometry of 5, rate constant calculated.

(f) Flash photolysis; resonance fluorescence detection of O. Large excess of H_2S giving first order decay of [O].

(g) Based on the results from [1] and [4].

(h) Accepts the work of [6].

Preferred Values

$k = 2.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.2 \times 10^{-12} \exp(-1660/T)$ cm^3 molecule^{-1} s^{-1} over range 250–500 K.

Reliability

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

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

Comments on Preferred Values

Until very recently all measurements of the rate of this reaction had been by discharge flow methods [1–5]. Under the conditions used in these studies (concentration of O comparable with that of H_2S) it is necessary to know the stoichiometry of the reaction to determine the rate constant. In most studies a stoichiometry based on the expected reaction mechanism has been used. This approximation is the most likely source of the discrepancies between the values of k using this technique. The preferred value is from a flash photolysis study in which care was taken to achieve first order conditions for the O atom decay and independence of k over a range of H_2S concentrations [6].

Measurements of E/R at temperatures close to 298 K have yielded values ranging from 750 to 1700. The preferred value is taken from [6].

The alternative path for the reaction, $O + H_2S \rightarrow SO + H_2$ has been shown to be unimportant at 298 K [1].

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$O + CS \rightarrow CO + S$

$\Delta H^\circ = -355$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.06 \pm 0.14) \times 10^{-11}$	305	Slagle, Graham, Gilbert and Gutman, 1975 [1]	(a)
$(2.24 \pm 0.36) \times 10^{-11}$	300	Bida, Breckenridge and Kolln, 1976 [2]	(b)
$(2.6 \pm 0.4) \times 10^{-10} \exp(-(760 \pm 140)/T)$	156–215	Lilenfeld and Richardson, 1977 [3]	(c)
2.0×10^{-11}	298*		
Relative Rate Coefficients			
2.2×10^{-11}	298	Hancock and Smith, 1971 [4]	(d)
Reviews and Evaluations			
$3.8 \times 10^{-10} \exp(-970/T)$	300–1100	Kondratiev, 1972 [6]	(e)
$\sim 10^{-11} - 10^{-12}$	200–900	Schofield, 1973 [7]	(f)
2.2×10^{-11}	300	Baulch et al., 1976; Hampson and Garvin, 1978 [8]	(g)

Comments

(a) Discharge flow; [CS] by mass spectrometry. $[O]/[CS]_0 \geq 20$. Rate coefficient unaffected by threefold variation of $[O]/[CS]_0$.

(b) Discharge flow; [CS] by absorbance at 257.6 nm, [O] by NO afterglow. $[CS]/[O] \geq 10$. [O] maintained constant by presence of O_2 which regenerates O atoms, consumed in the main reaction, by $S + O_2 \rightarrow SO + O$.

(c) Discharge flow; e.s.r. and mass spectrometric detection. Rate determined from (i) CO formation in excess of CS, (ii) CS disappearance in excess of O. At low temperature presence of O_2 produces an interfering chain reaction. To avoid this problem, at low temperature, a discharge through NO rather than O_2 was used as a source of O atoms.

(d) Discharge flow; O added to CS_2, infrared chemiluminescence from O + CS reaction monitored. NO_2 added to compete for O atoms. $k/k(O + NO_2) = 2.3$ found. Rate coefficient quoted in table based on $k(O + NO_2) = 9.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) Based on [4] and the order of magnitude value of $\geq 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1100 K obtained by Homann, Krome and Wagner [5].

(f) Based on [4], [5] and unpublished work of Callear and Dickson.

(g) Based on [4].

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-10} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over range 150–300 K.

Reliability

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

$\Delta (E/R) = \pm 250$ K.

Comments on preferred values

Because of its significance in the CO chemical laser this reaction has been the subject of several recent studies [1–4]. The values of k at 298 K fall within a range of about 20%. The preferred value is the mean of these measurements, all of which seem reliable. The preferred value of E/R is taken from [3].

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$$O + OCS \rightarrow SO + CO \quad (1)$$

$$\rightarrow CO_2 + S \quad (2)$$

$\Delta H^\circ (1) = -213$ kJ mol^{-1}

$\Delta H^\circ (2) = -224$ kJ mol^{-1}

Rate coefficient data, $k = k_1$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
(1) Absolute Rate Coefficients			
$\sim 10^{-14}$	298	Rolfes, Reeves and Harteck, 1965 [1]	(a)
$(9.0 \pm 1.3) \times 10^{-15}$	298	Sullivan and Warneck, 1965 [2]	(b)
$2.0 \times 10^{-10} \exp(-2950/T)$	290–465	Hoyermann, Wagner and Wolfrum, 1967 [3]	(c)
1.5×10^{-14}	300		
$1.08 \times 10^{-10} \exp(-2770/T)$	300–1150	Homann, Krome and Wagner, 1968 [4]	(d)
9.8×10^{-15}	300*		
$3.2 \times 10^{-11} \exp(-2280/T)$	273–808	Westenberg and de Haas, 1969 [5]	(e)
$(1.4 \pm 0.1) \times 10^{-14}$	297		
$(1.19 \pm 0.06) \times 10^{-14}$	297	Breckenridge and Miller, 1972 [6]	(f)
$(1.65 \pm 0.13) \times 10^{-11} \exp(-(2165 \pm 30)/T)$	263–502	Klemm and Stief, 1974 [7]	(g)
$(1.2 \pm 0.1) \times 10^{-14}$	298		
$(2.0 \pm 0.3) \times 10^{-11} \exp(-(2140 \pm 40)/T)$	239–404	Wei and Timmons, 1975 [8]	(h)
$(1.35 \pm 0.13) \times 10^{-14}$	295		
$(1.39 \pm 0.14) \times 10^{-14}$	296	Manning, Braun and Kurylo, 1976 [9]	(i)
$(1.17 \pm 0.12) \times 10^{-14}$	298	Yoshida and Saito, 1978 [10]	(j)
Relative Rate Coefficients			
$1.51 \times 10^{-14} \exp(-1100/T)$	298–523	Krezenski, Simonaitis and Heicklen, 1971 [11]	(k)
Reviews and Evaluations			
1.1×10^{-14}	298	Heiklen, et al., 1969 [12]	(l)
$7.3 \times 10^{-11} \exp(-2610/T)$	unspecified	Kondratiev, 1972 [13]	(m)
$6.8 \times 10^{-11} \exp(-2550/T)$	270–1500	Schofield, 1972 [14]	(n)
$2.6 \times 10^{-11} \exp(-2250/T)$	190–600	Baulch et al., 1976 [15]	(o)

Comments

(a) Discharge flow; [O] > [OCS]; SO + O emission monitored, [CO] determined by mass spectrometry. Authors quote unpublished result of Dondes and Safrany to the effect that $k_1/k_2 > 10^3$. No CO_2 found in products.

(b) Discharge flow; [CO], [SO] monitored by mass spectrometry.

(c) Discharge flow; excess OCS over O; [O], [SO], [SO_2] followed by e.s.r. spectroscopy. Reaction 2 assumed to be unimportant.

(d) Discharge flow; [O] > [OCS]; [OCS], [SO] followed by mass spectrometry. Arrhenius expression is based on authors' results in range 764–1123 K and those in ref. [3]. Only small amounts of CO_2 found in products and therefore channel 2 considered unimportant.

(e) Discharge flow; OCS in large excess; [O], [SO] by e.s.r. spectrometry; [CO] by mass spectrometry. No CO_2 detected in products.

(f) Method similar to that in ref. [4]. No details of measurement of k_1 given since main aim of the work was investigation of reaction of O_2 ($^1\Delta g$) with SO($^3\Sigma^-$).

(g) Flash photolysis of OCS/O_2/Ar mixtures; [O] monitored by resonance fluorescence. Rate constant value independent of wide range of reagent mixtures and total pressures of approx. 40–200 Torr.

(h) Discharge flow; [O] followed by e.s.r. [OCS]/[O] varied in range 20–150.

(i) Flash photolysis of OCS/O_2Ar/CH_3F (or CH_2F_2) mixtures; resonance fluorescence detection of [O]. Main purpose of study to investigate the effects of enhanced vibrational energy of OCS on k. Little effect found.

(j) Flow discharge; [SO] determined by microwave spectroscopy [OCS] >> [O].

(k) Mercury photosensitized photolysis of N_2O in presence of OCS and 2-trifluoromethylpropene. [CO], [N_2], [olefinaldehyde], [olefin oxide] determined by mass spectrometry. Rate constant for O reaction with the olefin taken from [12].

(l) Based on data from [1–5].

(m) No details given.

(n) Based on [2–5]. Also quotes relative rate measurements of ref. [11] but rejects them because of uncertainty in the rate constant of the reference reaction.

(o) Uses data from [2–8]. Less weight given to data at higher temperatures (>600 K).

Preferred Values

$k = 1.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6 \times 10^{-11} \exp(-2250/T)$ cm^3 molecule^{-1} s^{-1} over range 220–600 K.

Reliability

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

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

Comments on Preferred Values

The values obtained for k are in excellent agreement over a wide range of temperatures, and of pressures ($\leq$200 torr). The studies at higher temperatures (>600 K) give values of k which are significantly higher than our preferred Arrhenius expression which is based on all the results below 600 K. The available evidence suggests that channel (2) only becomes significant at temperatures above 600 K. Approximate values of k_2/k_1 measured are: 10^{-3} at 298 K [16], 10^{-2} at 500 K [4] and 1 at 1100 K [17].

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$$\mathbf{O + CS_2 \rightarrow CS + SO \quad (1)}$$

$$\mathbf{\rightarrow CO + S_2 \quad (2)}$$

$$\mathbf{\rightarrow OCS + S \quad (3)}$$

ΔH° (1) = $-$ 89 kJ mol^{-1}

ΔH° (2) = -348 kJ mol^{-1}

ΔH° (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			
$(1.0 \pm 0.5) \times 10^{-11} \exp(-(300 \pm 150)/T)$	305–410	Smith, 1967 [1]	(a)
4.2×10^{-12}	305		
$8.3 \times 10^{-12} \exp(-950/T)$	300–920	Homann, Krome and Wagner, 1968 [3]	(b)
3.5×10^{-13}	300*		
$(2.08 \pm 0.08) \times 10^{-12}$	227	Westenberg and de Haas, 1969 [4]	(c)
$(3.0 \pm 0.3) \times 10^{-12}$	297		
$(7.8 \pm 0.3) \times 10^{-12}$	538		
$(3.7 \pm 0.3) \times 10^{-12}$	298	Callear and Hedges, 1970 [5]	(d)
$(4.0 \pm 0.3) \times 10^{-12}$	302	Slagle, Gilbert and Gutman, 1974 [6]	(e)
$(2.8 \pm 0.4) \times 10^{-11} \exp(-(650 \pm 35)/T)$	218–293	Wei and Timmons, 1975 [7]	(f)
$(3.1 \pm 0.2) \times 10^{-12}$	293		
$(4.8 \pm 0.3) \times 10^{-12}$	249	Graham and Gutman, 1977 [9]	(g)
$(5.9 \pm 0.5) \times 10^{-12}$	273		
$(6.8 \pm 0.3) \times 10^{-12}$	295		
$(8.5 \pm 1.0) \times 10^{-12}$	335		
$(11.1 \pm 0.5) \times 10^{-12}$	376		
$(14.1 \pm 1.0) \times 10^{-12}$	431		
$(18.6 \pm 1.3) \times 10^{-12}$	500		
Branching Ratios			
$k_3/k = (9.8 \pm 0.4) \times 10^{-2}$	249	Graham and Gutman, 1977 [9]	(g)
$(9.8 \pm 0.5) \times 10^{-2}$	273		
$(9.6 \pm 0.6) \times 10^{-2}$	295		
$(9.4 \pm 0.5) \times 10^{-2}$	335		
$(8.7 \pm 0.5) \times 10^{-2}$	376		
$(8.2 \pm 0.1) \times 10^{-2}$	431		
$(8.1 \pm 0.7) \times 10^{-2}$	500		
Relative Rate Coefficients			
$k_3 \sim 2 \times 10^{-12}$	1100	Homann, Krome and Wagner, 1968 [3]	(b)
Reviews and Evaluations			
4.2×10^{-12}	298	Wood and Heicklen, 1971 [10]	(h)
$(6.3 \pm 1.5) \times 10^{-11} \exp(-(880 \pm 80)/T)$	200–1100	Kondratiev, 1972 [11]	(j)
3.5×10^{-12}	298	Morley, Ridley and Smith, 1972 [12]	(k)
3.5×10^{-12}	298	Stuart, Dawson and Kimbell, 1972 [13]	(l)
$8.3 \times 10^{-11} \exp(-960/T)$	Unspecified	Howgate and Barr, 1978 [14]	(m)
$1.7 \times 10^{-11} \exp(-570/T)$	200–1000	Schofield, 1973 [15]	(n)
$3.7 \times 10^{-11} \exp(-700/T)$	200–1000	Baulch, Drysdale, Duxbury and Grant, 1976; Hampson and Garvin, 1978 [16]	(o)

Comments

(a) Flash photolysis of $NO_2/CS_2/Ar$ mixtures. [CS], [CS_2] monitored as a function of time yielding the absolute value of k quoted. Value of k relative to (k(O + NO_2) + (k(O + NO_2 + M)) also obtained. In other experiments iso-butene and but-1-ene added yield k/k(O + isobutene) and k/k(O + but-1-ene). In later work Smith claims that there is no evidence of OCS or S_2 in products [2].

(b) Discharge flow; [O] > [CS_2], [CS_2], [SO] followed by mass spectrometry and final products, SO_2, CO, CO_2 determined. No evidence found for channel (2) but k_3/k estimated to be ~0.05 at 1100 K. Own value of k used to obtain k_3.

(c) Discharge flow; $[CS_2] > [O]$. [SO] monitored by e.s.r. $[CS_2]$, [CO] by mass spectrometry. CO found attributed to $O + CS \rightarrow CO + S$. Stoichiometry of 2 determined and used in obtaining rate constant. This value of the stoichiometry is suspect (see comment f).

(d) Flash photolysis of $CS_2/Hg/N_2O$ mixtures. [CS], [O] followed by kinetic absorption spectroscopy. No evidence of $O + CS \rightarrow CO + S$, all O atoms react with CS_2.

(e) Crossed molecular beams of O, CS_2. [S], $[S_2]$, [OCS], [CS], [SO] monitored by mass spectrometry. $k_3/k = 0.09$. k_1/k could not be determined because of rapid removal of CS by $O + CS \rightarrow CO + S$ but the results suggest that it is in the range 0.7–0.85. Evidence found for channel 2 but subsequent reactions of S_2 prevent accurate determination of k_2/k; approximate value of 0.05–0.20 suggested.

(f) Discharge flow; $[CS_2]/[O] > 5$. Stoichiometry factor of 2 (as measured in [4]) used to obtain rate constant. However this system has recently been modeled [8] and it has been shown that under the conditions used in ref. [4] and [7] a steady state is not reached and an effective stoichiometry of 1.2–1.5 would have been appropriate.

(g) Discharge flow; $[CS_2]$, [OCS] monitored by mass spectrometry. Rate constant determined with O in "great excess". k_3/k deduced from $\Delta[OCS]/\Delta CS_2$ with O and CS_2 at comparable initial concentrations. Arrhenius plot for k shows evidence of curvature particularly if the results of [3] at high temperatures are accepted. Authors therefore do not derive an Arrhenius expression from their results. k_3/k shows only slight temperature dependence dropping by approx. 15% in going from 249 K to 500 K.

(h) Evaluation, based on [1,4].

(j) Evaluation, based on [1,3,4,10].

(k) Evaluation, based on [1,3,4].

(l) Evaluation, based on [1,3,4].

(m) Evaluation, based on [3,5].

(n) Evaluation, based on [3,5].

(o) Evaluation, based on [1,4,7]. Questions accuracy of results of [3].

Preferred Values

$k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.8 \times 10^{-11} \exp(-700/T)$ cm^3 molecule^{-1} s^{-1} over the range 200–500 K.

Reliability

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

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

Comments on Preferred Values

Reaction (1) is accepted to be the predominant path at ambient temperatures [1,6,9,17]. The reaction products are formed with a substantial degree of vibration which in some conditions may affect the rate of any subsequent reactions in which they participate. The measurements using flow discharge methods agree on the temperature coefficient of the reaction over the temperature range 200–500 K. However the absolute values of k at 298 K differ by approximately a factor of 2. This is probably due in some part to the incorrect stoichiometry being used in some of the studies [4], [7] but, after correcting for this, the resulting rate constants at 298 K are still approximately 50 percent lower than the most recent values [9] using different conditions. The flash photolysis results tend to favor the lower values. The preferred value at 298 K is a compromise between the results in [4], [5], [6], [7], [9].

Despite evidence that the Arrhenius plot is not linear over a wide temperature range [1], the Arrhenius expression recommended is a good approximation for the small temperature range which we have considered.

The only quantitative measurement of the relative importance of the alternative reaction channels are those of Gutman et al. [6], [9]. Their measurements of k_3/k, when combined with our preferred values of k, yield $k_3 = 3.2 \times 10^{-12} \exp(-520/T)$, with $\Delta \log k = \pm 0.3$ and $\Delta(E/R) = \pm 150$ K over the range 200–500 K.

There are no data for k_2, but there is evidence that it occurs, possibly with about the same probability as reaction (3), [6], [17].

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$O + SO_2 + M \longrightarrow SO_3 + M$

$\Delta H^\circ = -348.0$ 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			
$9.2 \times 10^{-32} \exp(-1000/T)$ [N_2O]	299–392	Atkinson and Pitts, 1974 [1]	(a)
3.2×10^{-33} [N_2O]	298		
$1.07 \times 10^{-31} \exp(-1400/T)$ [He]	248–415	Westenberg and de Haas, 1975 [2]	(b)
9.8×10^{-34} [He]	298		
2.3×10^{-33} [N_2]	298		
$3.4 \times 10^{-32} \exp(-1130/T)$ [N_2]	220–353	Davis, 1976 [3]	(c)
7.7×10^{-34} [N_2]	298		
$3.1 \times 10^{-32} \exp(-1009/T)$ [Ar]	299–400	Atkinson and Pitts, 1978 [5]	(d)
1.05×10^{-33} [Ar]	298		
1.37×10^{-33} [N_2]	298		
$1.7 \times 10^{-33} (T/200)^{-4.3}$ [Ar]	1700–2500	Astholz, Glänzer and Troe, 1979 [6]	(e)
Reviews and Evaluations			
$1.1 \times 10^{-31} (T/1000)^{-4} \exp(-2646/T)$ [Ar]	250–2500	Troe, 1978 [7]	(f)
1.9×10^{-33} [Ar]	298		
1.8×10^{-33} [Ar]	2000		

Comments

(a) Modulation technique with Hg-sensitized decomposition of N_2O, pressure range 54–135 Torr.

(b) Discharge flow system study with ESR detection of O atoms. Relative efficiencies of M, $N_2 : He : SO_2 = 1.0 : 0.42 : 4.0$. Pressure range 0.7–6.7 Torr.

(c) Flash photolysis-resonance fluorescence technique; relative efficiencies of M, $N_2 : He : Ar : SO_2 = 1.0 : 0.45 : 0.87 : 56$.

(d) Flash photolysis-NO_2 chemiluminescence technique; relative efficiencies of M, $N_2 : Ar : SO_2 = 1.0 : 0.71 : 6.9$.

(e) From thermal dissociation of SO_3 in shock waves, SO_2 detection by UV absorption spectroscopy.

(f) Evaluation by use of theory assuming a barrier of about 22 kJ mol^{-1} for the spin-forbidden reaction $O(^3P) + SO_2(^1A_1) \longrightarrow SO_3(^1A_1)$.

Preferred Value

$k_0 = 1.4 \times 10^{-33}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 4.0 \times 10^{-32} \exp(-1000/T)$ [N_2] cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_0 = 8.3 \times 10^{-31} (T/1000)^{-3.75} \exp(-2650/T)$ [Ar] cm^3 molecule^{-1} s^{-1} over range 200–2500 K.

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 300 K.}$$
$$= \pm 0.5 \text{ over range 200–2500 K.}$$
$$\Delta(E/R) = {}^{+200\text{ K}}_{-100\text{ K}} \text{ over range 200–400 K.}$$

Comments on Preferred Values

This is a spin-forbidden reaction with an energy barrier E_0. The rate coefficient should be represented by an expression of the type $k_0 \propto T^{-n} \exp(-E_0/RT)$. The unambiguous separation of the rate constant into the preexponential and exponential term has not been possible.

High Pressure Rate Coefficients

No experimental data. However, near room temperature the transition from third order to second order behavior should be observed just above 1 atm, since the reaction is forbidden, see estimates in ref. [7].

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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
Absolute Rate Coefficients			
7.8×10^{-12}	300	Niki, Morris and Breitenbach, 1972 [1]	(a)
$2.3 \times 10^{-11} \exp(-450/T)$	298–885	Westenberg and de Haas, 1973 [2]	(b)
$(5.5 \pm 0.3) \times 10^{-12}$	298		
$(3.1 \pm 0.5) \times 10^{-12}$	298	Stuhl, 1974 [3]	(c)
$(5.2 \pm 0.5) \times 10^{-12}$	297–424	Perry, Atkinson and Pitts, 1976 [4]	(d)
Reviews and Evaluations			
4.8×10^{-12}	300	Cox, 1975 [5]	(e)
Reviews and Evaluations			
$1.1 \times 10^{-11} \exp(-200/T)$	300–500	Baulch et al., 1976 [6]	(f)

Comments

(a) Discharge flow; HO generated from $H + NO_2$; H_2O, H_2S, SO_2 analyzed by mass spectrometry. Few details available. From the nature of the products, e.g., SO_2 successive oxidation steps of H_2S by HO must take place.

(b) Discharge flow; HO generated from $H + NO_2$; [H], [HO], [HS] followed by e.s.r. Walls boric acid coated; loss of HO to walls negligible. $[H_2S]/[HO] > 8$. Sulphur deposits form eventually on walls demonstrating the presence of secondary reactions, but under the conditions used computer modeling of the system suggests that in the measurement zone the overall stoichiometry is unity.

(c) Flash photolysis of $He/H_2O/H_2S$ mixture. [HO] followed by resonance fluorescence.

(d) Flash photolysis of $Ar/H_2O/H_2S$ mixture. [HO] followed by resonance fluorescence.

(e) Flowing mixtures of $HNO_2/NO/NO_2$/air photolysed (330–380 nm) to produce HO radicals. [HONO], [NO], $[NO_2]$ measured by chemiluminescence. Effects of additions of H_2S on $d[NO]/dt$ and $d[NO_2]/dt$ could be related to rate constant ratio k/k(HO + HONO). k_x determined from similar experiments giving its value relative to rate constants for reactions of HO with CO, CH_4 and H_2 [6]. Value used for k(HO + HONO)—6.6×10^{-12} cm^3 molecule^{-1}s^{-1}. Uncertainty in k/k(HO + HONO) is ±12%; uncertainty in k(HO +HONO) is ±50%; hence uncertainty in k must be at least ±50 percent.

(f) Based on [2], [4].

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 the range 250–400 K.

Reliability

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

$\Delta (E/R) = \pm 225$ K.

Comments on Preferred Values

There is excellent agreement at 298 K between two recent measurements of k by different methods [2], [4]. The value of Niki et al. [1] appears to be a preliminary value which has not been reported in detail. The remaining value [3] is some 40 percent lower although the technique is similar to that in [4]. The preferred value at 298 K is based on [2], [4]. However the temperature dependence of k found in these two studies is significantly different. The preferred value of E/R is an average of the two.

References

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HO + OCS → Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<7 \times 10^{-15}$	299	Atkinson, Perry and Pitts, 1978 [1]	(a)
$<2 \times 10^{-14}$	430		
$(5.7 \pm 1.2) \times 10^{-14}$	296	Kurylo, 1978 [2]	(b)
Relative Rate Coefficients			
3.9×10^{-13}	298	Cox, 1975 [3]	(c)

Comments

(a) Flash photolysis of flowing gas mixtures of H_2O/OCS/Ar; wavelengths down to LiF cut-off (105 nm) used; [HO] followed by resonance fluorescence. The HO decay rates vary in a non-linear manner with OCS concentration and depend on the energy of the flash. This is due to secondary reactions of OH with photolysis products. Because of this, only an upper limit for k is obtained.

(b) Flash photolysis of flowing gas mixtures. Some variation of rate of HO decay with OCS concentration and flash energy observed. It is suggested that this is due to photolysis of the OCS as well as reactions of radicals with products. By restricting the photolysis wavelength to >165 nm (suprasil window) both effects are reduced to negligible proportion, but decreased in precision.

(c) Flowing mixtures of $HNO_2/NO/NO_2$/air, photolysed (330–380 nm) to produce HO radicals. [HONO], [NO], [NO_2] measured by chemiluminescence. Effects of addition of H_2S on $d[NO]/dt$ and $d[NO_2]/dt$ could be related to rate constant ratio k/k(HO + HONO). k(HO + HONO) determined from similar experiments giving its value relative to the rate constants for reactions of HO with CO, CH_4 and H_2. Value used for k(HO + HONO)—6.6 × 10^{-12} cm^3 molecule^{-1} s^{-1}. Uncertainty in k/k(HO + HONO) is ±18%; uncertainty in k(HO + HONO) is ±50%; hence uncertainty in k must be ≃ ±60 percent. In private, the author has indicated that the value of k may be too high by at least a factor of 10 because of quantities of H_2S in the OCS used.

Preferred Values

$k \leq 6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = ^{+0.7}_{-?}$.

Comments on Preferred Values

The two available values for k [2] [3] differ by more than an order of magnitude. Because of the doubtful purity of the OCS used in the relative rate measurements the result from the fast flow measurements is preferred, but we suggest that it be treated as an upper limit. The reaction products have not been identified but on the basis of the thermochemistry it is likely that the first step is addition. Further work on this reaction is required.

References

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HO + CS_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<7 \times 10^{-14}$	300	Atkinson, Perry and Pitts, 1978 [1]	(a)
$<1 \times 10^{-13}$	425		
$(1.9 \pm 0.3) \times 10^{-13}$	296	Kurylo, 1978 [2]	(b)

Comments

(a) Flash photolysis of flowing gas mixture of H_2O/CS_2/Ar; wavelengths down to LiF cut-off (105 nm) used; [HO] followed by resonance fluorescence. The HO decay rates vary in a non-linear manner with CS_2 concentration and vary with the energy of the flash. Chemiluminescence is also observed. Because of these complications only an upper limit for k is obtained.

(b) Technique similar to [1] (comment (a)), photolysis wavelength restricted to >165 nm (suprasil cut-off). No chemiluminescence observed and good linearity between [HO] decay rate and CS_2 concentration found.

Preferred Values

$k \leq 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = ^{+0.7}_{-?}$.

Comments on Preferred Values

The preferred value is the only value available at present. The technique appears sound but we suggest that it be treated as an upper limit until more work is done on this reaction. The reaction products have not been identified; it is likely that the first step in the reaction is one of addition.

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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
Absolute Rate Coefficients			
$(7.2 \pm 2.6) \times 10^{-31}$ [N_2]	300	Harris and Wayne, 1975 [1]	(a)
$7.0 \times 10^{-31} (T/300)^{-2.9}$ [N_2]		Erler, Field and Zellner, 1975 [2]	(b)
4.9×10^{-31} [N_2]	300	Davis, 1976 [4]	(c)
2.9×10^{-31} [N_2]	300	Atkinson, Perry and Pitts, 1976 [6]	
3.6×10^{-31} [N_2]	300	Erler and Zellner, 1978 [7]	(e)
Relative Rate Coefficients			
1.6×10^{-31} [N_2]	300	Castleman and Tang, 1976 [8]	(f)
Reviews and Evaluations			
$(3 \pm 1.5) \times 10^{-31}$ [N_2]	300	Zellner, 1978 [3]	

Comments

(a) Discharge flow system study. Relative efficiencies of M, N_2 : Ar = 1 : 0.63.

(b) Discharge flow system study.

(c) Measurements cited in ref. [5] for M−He, Ar and N_2 in the pressure range 5–500 Torr; extrapolated to k_0 and k_∞.

(d) Flash photolysis study; converted from M=Ar with an assumed relative efficiency N_2:Ar=1.8:1. Pressure range 25–650 Torr extrapolated with Lindemann-Hinshelwood plot to k_0 and k_∞.

(e) Flash photolysis study.

(f) Steady state photolysis. Measured k/k(OH + CO) evaluated with the low pressure value k(OH + CO)=1.5 $\times 10^{-13}$cm^3 molecule^{-1}s^{-1}. Pressure range 20–1000 Torr; extrapolation to k_0 and k_∞ with a nearly linear Lindemann-Hinshelwood plot.

Preferred Value

$k_0 = 3 \times 10^{-31} (T/300)^{-2.9}$ [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 Values

Preferred value as in the evaluation by Zellner [1978]. Results are scattered, new measurements are needed.

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
8.3×10^{-13}	300	Atkinson, Perry and Pitts, 1976 [6]	(a)
9.0×10^{-13}	300	Davis, 1976 [4]	(b)
18×10^{-13}	435	Gordon and Mulac, 1975 [9]	(c)
Relative Rate Coefficients			
11×10^{-13}	294	Cox, 1975 [10]	(d)
13×10^{-13}	297	Castleman and Tang, 1976 [8]	(e)
Reviews and Evaluations			
$(1.2 \pm 0.4) \times 10^{-12}$	300	Zellner, 1978 [3]	

Comments

(a) See comment (d) of k_0.

(b) See comment (c) of k_0.

(c) Pulse radiolysis in H_2O vapour at 1 atm.

(d) Steady-state photolysis in the presence of 1 atm $N_2 + O_2$. Measured $k/k(OH + CO)$. Evaluated with the effective value of $k(OH + CO) = 2.85 \times 10^{-13}$ at 1 atm.

(e) See comment (f) of k_0, but evaluated with the effective value of $k(OH + CO) = 2.85 \times 10^{-13}$ at 1 atm.

Preferred Value

$k_\infty = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ over range 200–400 K.

Comments on Preferred Values

See comment for k_0.

Intermediate Fall-off Range

From the preferred values one calculates $[N_2]_c \simeq 4 \times 10^{18}$ molecules cm^{-3} at 300 K. The broadening factor F_c is estimated to be 0.7 ± 0.1 at 300 K.

References

[1] Harris, G. W. and Wayne, R. P., J. Chem. Soc. Faraday Trans.I, **71**, 610 (1975).
[2] Erler, K., Field, D. and Zellner, R.cited in ref. [3].
[3] Zellner, R., Ber. Bunsenges. Phys. Chem. **82**, 1172 (1978).
[4] Davis, D. D., University of Maryland Rept (1976), data cited in ref. [5].
[5] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).
[6] Atkinson, R., Perry, R. A. and Pitts, J. N., J. Chem. Phys. **65**, 306 (1976).
[7] Erler, K. and Zellner, R., cited in ref. [3].
[8] Castleman, A. W. and Tang, I. N., J. Photochem. **6**, 349 (1976).
[9] Gordon, S. and Mulac, W. A., Int. J. Chem. Kinet., Symp. **1**, 289 (1975).
[10] Cox, R. A., Int. J. Chem. Kinet., Symp. **1**, 379 (1975).

$HO_2 + SO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(7.3 \pm 1.2) \times 10^{-16}$	300	Payne, Stief and Davis, 1973 [1]	(a)
$<1 \times 10^{-18}$	300	Graham et al., 1979 [2]	(b)
Reviews and Evaluations			
9×10^{-16}	300	Hampson and Garvin, 1978 [3]	(c)

Comments

(a) Photolysis of $H_2O/CO/^{18}O_2/N_2$ mixtures; formation of $C^{16}O_2$ and $C^{16,18}O_2$ monitored by mass spectrometry. Presence of SO_2 affects ratio of isotopic forms of CO_2 postulated to be due to reaction of HO_2 with SO_2. Rate constant ratio $k/k^{1/2}(HO_2 + HO_2)$ found. Authors used $k(HO_2 + HO_2) = 3.3 \times 10^{-12}$cm^3 molecule^{-1} s^{-1}; value tabulated here calculated using $k(HO_2 + HO_2) = 2.3 \times 10^{-12}$cm^3 molecule^{-1} s^{-1}, as recommended in this review. Error limits on $k(HO_2 + HO_2)$ are not included in the error quoted.

(b) Decomposition of HO_2NO_2 in presence of SO_2. $[HO_2NO_2]$ monitored by infra-red absorption spectrometry. SO_2 has no detectable influence on rate of disappearance of HO_2NO_2. Hence only an upper limit to k can be estimated.

(c) Based on [1], recalculated using their own recommended value for $k(HO_2 + HO_2)$.

Preferred Values

No recommendation—see Comments on Preferred Values.

Comments on Preferred Values

The discrepancy between the two reported measurements of k is large. Both methods are indirect but have been applied with apparent success to other reactions, although, in this respect, the work of [2] appears the more reliable. Until confirmatory studies are forthcoming we prefer to make no recommendation. The products of the reaction have not been identified; the mechanism may be addition.

References

[1] Payne, W. A., Stief, L. J., and Davis, D. D., J. Am. Chem. Soc. **95**, 7614 (1973).

[2] Graham, R. A., Winer, A. M., Atkinson, R. and Pitts Jr., J. N., J. Phys. Chem. **83**, 1563 (1979).

[3] Hampson Jr., R. F., and Garvin, D., ed., Nat. Bur. Stand. (U.S.), Spec. Publ., 513 (1978).

$S + O_2 \rightarrow SO + O$

$\Delta H^\circ = -22.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.7 \times 10^{-11} \exp(-2820/T)$	675–1090	Homann, Krome and Wagner, 1968 [1]	(a)
1.3×10^{-15}	298*		
$(2.0 \pm 0.5) \times 10^{-12}$	298	Fair and Thrush, 1969 [2]	(b)
$(2.8 \pm 0.3) \times 10^{-12}$	298	Fair, Van Roodselaar and Strausz, 1971 [3]	(c)
$(1.5 \pm 0.3) \times 10^{-12}$	298	Clyne and Townsend, 1975 [4]	(d)
$(2.2 \pm 0.3) \times 10^{-12} \exp(-(0 \pm 50)/T)$	252–423	Davis, Klemm and Pilling, 1972 [5]	(e)
$(1.7 \pm 0.3) \times 10^{-12}$	298	Donovan and Little, 1972 [6]	(f)
Reviews and Evaluations			
2.2×10^{-12}	250–450	Schofield, 1973 [7]	(g)
2.2×10^{-12}	250–450	Baulch et al., 1976 [8]	(h)

Comments

(a) Flow system; S atoms produced by (i) reaction of O atoms with S_2, (ii) discharge in S_2/Ar mixtures. Results from the two sources are in agreement but the rate expression derived, when extrapolated to 298 K, gives a value of k three orders of magnitude lower than values obtained in other studies. The reasons for the discrepancy are not clear.

(b) Flow system; S atoms generated by reaction of H atoms with H_2S. [O] determined by NO titration, [SO] by SO_2 chemiluminescence.

(c) Flash photolysis $OCS/O_2/CO_2$ (or Ar/CO_2) mixtures. Disappearance of both $S(^3P_2)$ and $S(^3P_1)$ followed by light absorption. $[O_2]$ in large excess, decay of S first order in both [S] and $[O_2]$.

(d) Flow discharge; S atoms generated by discharge in Ar/SO_2 mixtures [S], [O] followed by resonance fluorescence.

(e) Flash photolysis of (i) $OCS/O_2/He$, (ii) $OCS/O_2/CO_2$ mixtures. [S] and [O] followed by resonance fluorescence. Delay of 200 μs before monitoring fluorescence ensures that $S(^1D, ^1S)$ are quenched before data collection commences. Data from CO_2 mixtures preferred because of greater likelihood that complications from $S(^1D, ^1S)$ are avoided.

(f) Flash photolysis of $OCS/O_2/Ar$ or N_2 mixtures; $[O_2] >> [S]$; $[S(^3P_1)]$ monitored by light absorption.

(g) Based on [2–5]. Results of [1] not used.

(h) Based on [2–6]. Results of [1] not used.

Preferred Values

$k = 2.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 230–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta (E/R) = \pm 100$ K.

Comments of Preferred Values

There is good agreement among the values of k obtained at 298 K with discharge flow [2,4] and flash photolysis [3,5,6] using both absorption and fluorescence to follow the course of the reaction. The preferred value is based on these studies. The temperature dependence of

k is less well characterized. Measurements over the range 252–423 K reveal no significant temperature dependence [5] but a significant energy of activation is found at higher temperatures [1]. For the lower temperatures the results of [5] are preferred but with wider error limits because of the lack of confirmatory studies.

References

[1] Homann, K. H., Krome, G., and Wagner, H. Gg., Ber. Bunsenges. Phys. Chem., **72**, 998 (1968).

[2] Fair, R. W., and Thrush, B. A., Trans. Faraday Soc., **65**, 1557 (1969).

[3] Fair, R. W., Van Roodselaar, A., and Strausz, O. P., Can. J. Chem., **49**, 1659 (1971).

[4] Clyne, M. A. A., and Townsend, L. W., Int. J. Chem. Kinet., Symp. 1, 73 (1975).

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[6] Donovan, R. J. and Little, D. J., Chem. Phys. Lett., **13**, 488 (1972).

[7] Schofield, K., J. Phys. Chem. Ref. Data, **2**, 25 (1973).

[8] Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S., "Evaluated Kinetic Data for High Temperature Reactions Vol. 3", Butterworths, London (1976).

$S + O_3 \rightarrow SO + O_2$

$\Delta H^\circ = -415$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.3) \times 10^{-11}$	298	Clyne and Townsend, 1975 [1]	(a)

Comments

(a) Discharge flow, S atoms produced by discharge in Ar/SO_2 mixture; O_3/O_2 mixture in large excess; $[O_3]$ by absorption spectrophotometry. [S] by resonance fluorescence.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The preferred value accepts the only available experimental determination. The method was direct, and in the same study a number of other rate coefficients for S atom reactions were measured giving results in good agreement with other techniques.

References

[1] Clyne, M. A. A., and Townsend, L. W., Int. J. Chem. Kinet., Symp. 1, 73 (1975).

$HS + O_2 \rightarrow HO + SO$

$\Delta H^\circ = -101$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<10^{-13}$	298	Cupitt and Glass, 1975 [1]	(a)
$\cong 2 \times 10^{-13}$	1250	Matsuda and Bauer, 1975 [2]	(b)

Comments

(a) Discharge flow studies on reactions of H and O atoms with HS radicals. In presence of O_2 no evidence was found for the reaction with HS indicating that it was much slower than other competing reaction (H + HS) in the system.

(b) Shock tube study of the oxidation of methyl mercaptan. SO_2 and H_2O products were assumed to be formed via the reaction of HS with O_2. The reaction $CH_3SH + HS \rightarrow H_2S + CH_3S$ is in competition with it. The yields of SO_2, H_2O and H_2S indicate that the rate constants for the two competing reactions are approximately equal at 1250 K.

Preferred Values

See Comments on Preferred Values.

Comments on Preferred Values

There are insufficient data to give a preferred value but limit [1] is probably reliable.

References

[1] Cupitt, L. T., and Glass, G. P., Int. J. Chem. Kinet., Symp. 1, 39 (1975).
[2] Matsuda, S., and Bauer, S. H., Int. J. Chem. Kinet., Symp. 1, 462 (1975).

$CS + O_2 \rightarrow CO + SO$ (1)

$\rightarrow OCS + O$ (2)

ΔH° (1) = -378 kJ mol^{-1}

ΔH° (2) = -165 kJ mol^{-1}

Rate coefficient data $k = k_1 + k_2$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k < 3 \times 10^{-18}$	298	Callear and Dickson, 1971 [1]	(a)
$k < 8 \times 10^{-18}$	300–670	Breckenridge, Kolln and Moore, 1975 [2]	(b)
$k_2 = (4.5 \pm 1.7) \times 10^{-19}$	293	Richardson, 1975 [3]	(c)
$k_2 = (5.9 \pm 1.3) \times 10^{-18}$	495		
Branching Ratios			
$k_2/k_1 = 1.2$	298	Wood and Heicklen, 1971 [4], 1973/74 [5]	(d)
$k_2/k_1 = 1.2$	341–415	Wood and Heicklen, 1971 [6]	(e)

Comments

(a) Flash photolysis of CS_2/O_2 mixtures; [CS] monitored by light absorption.

(b) Discharge flow; CS produced by discharge through Ar/CS_2 mixture; [CS] followed by light absorption.

(c) Discharge flow; CS produced by a discharge through CS_2; [CS], [SO_2], [CO], [OCS], measured by mass spectrometry. Very slow linear flow rate ($\cong$ 100 cm s^{-1}) necessary to observe reaction. SO_2, a product formed via reaction (1), is at least one order of magnitude lower in concentration than CO and OCS.

(d) Photolysis of CS_2/O_2 mixtures; analysis of products (CO, OCS, SO_2, S_2O) by gas chromatography. Light of wavelength 313 nm used in [4], which has insufficient energy to dissociate the CS_2, but CS postulated to be formed by reaction of electronically excited CS_2 with O_2. In later study [5], λ = 213.9 nm which can photodissociate CS_2.

(e) Explosion limits of CS_2/O_2 mixtures determined by gas chromatography. [CO]/[OCS] relatively unaffected by pressure and temperature changes, and the value of 0.84 found for the ratio is the same as that found from the photochemical studies [4], [5]. Explosion limits modelled on basis of assumed mechanism of 8 reaction; computer fit to data yielded value for k_2/k_1.

Preferred Values

See Comments on Preferred Values.

Comments on Preferred Values

The reactions of CS with O_2 are slow at 298 K and, despite a number of studies, it is only recently that a direct measurement of k_2 has been made [3]. The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies [4–6] indicate comparable importance but in the more direct flow system study [3] k_1 was found to be at least an order of magnitude less than k_2. More work is required on these reactions.

References

[1] Reported in Hancock, G., and Smith, I. W. M., Trans. Faraday Soc., **67**, 2586 (1971).
[2] Breckenridge, W. H., Kolln, W. S., and Moore, D. S., Chem. Phys. Lett., **32**, 290 (1975).
[3] Richardson, R. J., J. Phys. Chem., **79**, 1153 (1975).
[4] Wood, W. P., and Heicklen, J., J. Phys. Chem., **75**, 854 (1971).
[5] Wood, W. P., and Heicklen, J., J. Photochem., **2**, 173 (1973/74).
[6] Wood, W. P., and Heicklen, J., J. Phys. Chem., **75**, 861 (1971).

$SO + O_2 \rightarrow SO_2 + O$

$\Delta H^\circ = -52.6$ kJ mol^{-1}

Rate coefficient data

$k/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<3.3 \times 10^{-16}$	300	Halstead and Thrush, 1966 [2]	(a)
$8.7 \times 10^{-10} \exp(-9710/T)$	750–1100	Merryman and Levy, 1967 [3]	(b)
6.1×10^{-24}	298*		
$5.8 \times 10^{-13} \exp(-3270/T)$	580–1145	Homann, Krome and Wagner, 1968 [4]	(c)
1.0×10^{-17}	298*		
$(3 \pm 3) \times 10^{-11} \exp(-(5000 \pm 2000)/T)$	440–530	Williams, 1968 [5]	(d)
1.5×10^{-18}	298*		
$(1.60 \pm 0.04) \times 10^{-10} \exp(-14600/T)$	1600–2100	Sheen, 1970 [6]	(e)
8.4×10^{-32}	298*		
$<8 \times 10^{-17}$	297	Breckenridge and Miller, 1972 [7]	(f)
Reviews and Evaluations			
$2.21 \times 10^{-12} \exp(-3900/T)$	440–1145	Cupitt and Glass, 1970 [8]	(g)
$(7.5 \pm 5.0) \times 10^{-13} \exp(-3250 \pm 590/T)$	440–3100	Kondratiev, 1972 [9]	(h)
$3.0 \times 10^{-13} \exp(-2820/T)$	400–2500	Schofield, 1973 [10]	(i)
$7.5 \times 10^{-13} \exp(-3250/T)$	440–2100	Baulch et al., 1976; Hampson and Garvin, 1978 [11]	(j)

Comments

(a) Discharge flow; SO produced by discharge in SO_2/Ar mixtures, O_2 added downstream of SO_2 afterglow extinction point. No renewal of SO_2 afterglow observed, allowing upper limit for k_1 to be calculated.

(b) $H_2S/O_2/N_2$ flames at 0.1 and 0.05 atmosphere; $[O_2]$, $[SO_2]$ by mass spectrometric probe, $[SO + SO_2]$ by probe sampling and wet analysis. Difficulty experienced in obtaining reliable values for $[SO_2]$ and [SO]. Their work [3] supersedes earlier, similar work at high pressures and temperature [1]. Large scatter on results, and value found for temperature coefficient must be rejected.

(c) Discharge flow; O atoms added to OCS/O_2/Ar mixtures; [SO], $[SO_2]$, [CO], [OCS], [O], O_2 by mass spectrometry. [SO] calibrated by titration with NO_2. k determined from the variation of $d[SO_2]/dt$ with O_2 at constant [SO].

(d) Discharge flow; SO produced by (i) discharge in SO_2, (ii) O + OCS reaction. Method otherwise as in [2].

(e) Shock tube study on CS_2/O_2/Ar mixtures; incident and reflected shocks; chemiluminescence from SO + O and SO absorption followed. The value for the temperature coefficient seems unacceptably high. The same work has yielded a similarly high value for the $CS + O_2$ reaction.

(f) Discharge flow; SO produced by discharge in SO_2/He mixture added to O_2/He mixture. [SO] monitored by e.s.r. Little [SO] decay observed.

(g) Based on [3–5].

(h) Least mean squares fit to data of [3–6].

(i) Results of [3] largely ignored, recommended value based on [4–6].

(j) Based mainly on [4], [5]. Slightly higher energy of activation than that recommended by Schofield accepted; unpublished work reported by Wagner [12] supports a value of E/R of >3500 K.

Preferred Values

$k = 9 \times 10^{-18}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.

$k = 6 \times 10^{-13} \exp(-3300/T)$ $cm^3 molecule^{-1} s^{-1}$ over temperature range 300–1000 K.

Reliability

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

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

Comments on Preferred Values

The reaction is sufficiently slow at room temperature to make its study difficult and the preferred values must be based on measurements made at higher temperatures. The results of Homann et al. [4] appear to be the most reliable, all other studies giving either very scattered results or very large temperature coefficients for the reaction. The preferred values are therefore basically those from reference [4] but the uncertainty limits have been widened to reflect the dearth of reliable data.

References

[1] Levy, A., Merryman, E. L., Comb. and Flame, **9**, 229 (1965).

[2] Halstead, C. J., and Thrush, B. A., Proc. R. Soc. London, Ser. A, **295**, 363 (1966).

[3] Merryman, E. L., and Levy, A., J. Air. Poll. Control Ass., **17**, 800 (1967).

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[5] Williams, D. J., Comb. and Flame, **12**, 165 (1968).

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[10] Schofield, K., J. Phys. Chem. Ref. Data, **2**, 25 (1973).
[11] Baulch, D. L., Drysdale, D. D., Duxbury, J. and Grant, S., "Evaluated Kinetic Data for High Temperature Reactions", Vol. 3, Butterworths, London (1976); Hampson Jr., R. F. and Garvin, D., Ed., Nat. Bur. Stand. (U.S.), Spec. Publ., 513 (1978).
[12] Wagner, H. Gg., 14th Comb. Symp., 27 (1973).

$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H^\circ = -445$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.3) \times 10^{-12} \exp(-(1060 \pm 200)/T)$	223–303	Halstead and Thrush, 1966 [1]	(a)
7×10^{-14}	298		
Reviews and Evaluations			
$(2.5 \pm 0.3) \times 10^{-12} \exp(-(1060 \pm 200)/T)$	223–303	Schofield, 1973 [2]	(b)

Comments

(a) Discharge flow; SO produced by discharge in (i) O_2/Ar mixtures followed by addition of OCS, (ii) SO_2/Ar mixtures; O_3 added after O atoms had decayed. [SO] determined by titration with NO_2. SO_2 chemiluminescence monitored. Emission observed from electronically excited states $SO_2(^1B)$ and $SO_2(^3B)$.

(b) Accepts value from [1].

Preferred Values

$k = 6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.5 \times 10^{-12} \exp(-1100/T)$ cm^3 molecule^{-1} s^{-1} over the range 220–300 K.

Reliability

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

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

Comments on Preferred Values

This highly exothermic reaction yields electronically excited SO_2 as well as ground state products. States formed in the initial reaction are $SO_2(X\,^1A)$ $SO_2(^1B)$, and possibly $SO_2(^3B)$, the last two giving rise to chemiluminescence [1], [3]. However at 298 K the rate constants for formation of the ^1B and ^3B states are approximately 10^{-3} and 10^{-4} times the value for $X\,^1A$ formation. Thus the overall rate constant is effectively that for formation of ground state SO_2 over the temperature range quoted. There is only one measurement of the rate constant [1], which we accept as reliable, but with wider error limits than suggested in the original measurements.

References

[1] Halstead, C. J., and Thrush, B. A., Proc. R. Soc. London, Ser. A., **295**, 380 (1966).
[2] Schofield, K., J. Phys. Chem. Ref. Data, **2**, 25 (1973).
[3] Kaldor, A., Braun, W., and Kurylo, M. J., J. Chem. Phys., **61**, 2496 (1974).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H^\circ = -245$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(1.4 \pm 0.1) \times 10^{-11}$	298	Clyne, Halstead and Thrush, 1966 [1]	(a)

Comments

(a) Discharge flow; SO produced by discharge through SO_2/Ar mixtures. NO_2 added reacts with both SO and O; competition yields $k(O + NO_2)/k(SO + NO_2) = 0.67 \pm 0.07$, $k(O + NO_2)$ taken from this survey to give quoted value of $k(SO + NO_2)$.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value is the sole available measurement. Further work on this reaction is required.

Reference

[1] Clyne, M. A. A., Halstead, C. J., and Thrush, B. A., Proc. R. Soc. London, **295**, 355 (1966).

$SO_3 + H_2O \rightarrow$ Products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
9×10^{-13}	300	Castleman et al., 1974 [1]	(a)

Comments

(a) Fast flow system. Reactant concentrations monitored by mass spectrometry. Excess H_2O used.

Preferred Values

See comments on Preferred Values.

Comments on Preferred Values

In the only reported investigation of this reaction it was not possible to identify the initially formed products (possibly H_2SO_4 or $SO_3 \cdot H_2O$). The reaction appeared to be second rather than third order despite the low pressure used, but the pressure range covered was small (1–1.3 Torr). The rate constant is surprisingly high and until there are confirmatory studies we prefer to make no recommendation.

Reference

[1] Castleman Jr., A. W., Davis, R. E., Munkelwitz, H. R., Tang, I. N., and Wood, W. P., Int. J. Chem. Kinet., Symp. 1., 629 (1975).

$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ (1)

$\rightarrow CH_3O_2SO_2$ (2)

$\Delta H^\circ (1) = -92$ kJ mol^{-1}

Rate coefficient data $k = k_1 + k_2$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(5.3 \pm 1.1) \times 10^{-15}$	Room	Kan et al., 1979 [1]	(a)

Comments

(a) Flash photolysis of azo methane/O_2/SO_2 mixtures. Temperature not specified, presumably ≅ 300 K. Decay of [CH_3 O_2] followed by absorption at 265 nm. Products of reaction not identified. Rate coefficient is measured relative to k for $2CH_3O_2 \rightarrow$ products.

Preferred Values

See Comments on Preferred Values.

Comments on Preferred Values

Alkyl peroxy radicals react relatively slowly with SO_2 and this one measurement of the rate constant for CH_3O_2 is probably best considered to be an upper limit as indicated in [1]. Until it is confirmed we make no recommendations.

Reference

[1] Kan, C. S., McQuigg, R. D., Whitbeck, M. R., and Calvert, J. G., Int. J. Chem. Kinet. **11**, 921 (1979).

$OCS + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$OCS + h\nu \rightarrow CO + S$ (1)	303	394
$\rightarrow CO + S(^1D)$ (2)	414	288

Absorption cross section data

Wavelength range/nm	Reference	Comments
200–260	Sidhu et al., 1966 [1]	(a)
200–260	Breckenridge and Taube, 1970 [2]	(b)
125–250	Rabalais et al., 1971 [3]	(c)

Quantum yield data $\phi = \phi(1) + \phi(2)$

Measurements	Wavelength/nm	Reference	Comments
$\phi(1) < 0.24$ $\phi(2) > 0.66$ $\phi = 0.90$	229 and 254	Sidhu et al., 1966 [1]	(d)
$\phi(2)/\phi = 0.74 \pm 0.04$	229 and 254	Breckenridge and Taube, 1970 [2]	(e)

Comments

(a) Temperature, 299 K. No banded structure observed contrary to [3] and [2].

(b) Temperature, 298 K.

(c) Temperature not specified, presumably room temperature.

(d) Photolysis of well purified OCS with Hg lamp (254 nm) and Cd lamp (229 nm). Actinometry by photolysis of HBr and Hg/propane. From yield of CO, primary quantum yields for OCS removal $\phi(-OCS) = 0.90$. Paths (1) and (2) distinguished by insertion reaction of $S(^1D)$ with paraffins to give mercaptans; $S(^3P)$ does not insert. Hg photosensitized decomposition of OCS also gives $\phi = 0.90$. No evidence for decomposition paths other than (1) and (2).

(e) Photolysis of OCS/CS_2 and OCS/N_2O mixtures. Hg (254 nm) and Cd (229 nm) lamp used with filters. Products analysed by v.p.c. and mass spectrometry.

Comments on Preferred Values

The absorption spectrum at wavelengths >190 nm consists of a continuum with banded structure superimposed, covering the range 190–260 nm. The bands are diffuse and have not been analysed in detail. The data of [1–3] are in good agreement but the spectrum of [2] seems to be slightly better resolved and is preferred. Values of the absorption cross section have been taken from the original results kindly supplied by the authors rather than the spectrum in [2]. Only paths (1) and (2) are possible at the wavelengths used in the quantum yield measurements. The value of $\phi = 0.90$ [1] is based upon the measured quantum yield of CO production of 1.8 and the well verified fact that S atoms react rapidly with OCS to give CO and S_2. The values for $\phi(1)/\phi(2)$ from the two studies are in excellent agreement.

Preferred Values

Absorption cross sections[a] and quantum yields for OCS photolysis at 298 K

λ/nm	$10^{20}\sigma/cm^2$	$\phi(1)$	$\phi(2)$
205	7.4		
210	14.0		
215	24.4		
220	29.2		
225	31.8		
230	24.6	0.24	0.66
235	15.9		
240	8.8		
245	4.1		
250	1.84		
255	0.78	0.24	0.66

[a] Values averaged for 5 nm range centered on tabulated wavelength.

References

[1] Sidhu, K. S., Csizmadia, I. C., Strausz, O. P., and Gunning, H. E., J.A.C.S., **88**, 2412 (1966).

[2] Breckenridge, W. H., and Taube, H., J. Chem. Phys., **53**, 1750 (1970).

[3] Rabalais, J. W., McDonald, J. M., Scherr, V. and McGlynn, S. P., Chem. Rev., **71**, 73 (1971).

$CS_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$CS_2 + h\nu \rightarrow CS + S$	426	281
$\rightarrow CS + S(^1D)$	537	223

Absorption cross section data

Wavelength range/nm	Reference	Comments
125–350	Rabalais et al., 1971 [1]	(a)

Quantum yield data

See Comments on Preferred Values.

Comments

(a) Temperature not specified, presumably room temperature.

Preferred Values

Absorption cross sections[a] for CS_2 photolysis at 298 K

λ/nm	$10^{21}\sigma$/cm^2
295	9.6
305	46.1
315	71.7
325	48.2
335	5.3
345	2.6
355	0.51

[a] Values averaged for 10 nm range centered on tabulated wavelength.

Comments on Preferred Values

The absorption spectrum of CS_2 at wavelengths greater than 200 nm consists of two strongly structural bands (190–220 nm and 290–350 nm), the former having an absorption cross section approximately 5–10 times the latter. The only detailed determination of the absorption cross sections appears to be that of [1]. However the results are given in the form of a small diagram from which it would be extremely difficult to obtain accurate values in view of the strongly banded nature of the spectrum. The values tabulated above were supplied by Dr. R. A. Cox, A.E.R.E., Harwell, U. K. To the extent to which comparison is possible they agree with the value in [1].

Photolysis at wavelengths >230 nm appears only to produce electronically excited CS_2 molecules. At $\lambda < 220$ nm formation of $S(^3P)$ is observed [2] but not $S(^1D)$. No quantum yield measurements have been made.

References

[1] Rabalais, J. W., McDonald, J. M., Scherr, V., and McGlynn, S. P., Chem. Rev., **71**, 73 (1971).

[2] Callear, A. B., Proc. R. Soc. London, Ser. A., **276**, 401 (1963).

4.6. Reactions of FO_x

$O + FO \rightarrow O_2 + F$

$\Delta H^\circ = -279$ kJ mol^{-1}

Rate Coefficient Data: No available experimental data.

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 FO is similar to that of ClO and BrO. The experimentally determined rate constants for ClO and BrO at ~298 K are $(5.2 \pm 0.5) \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} [1] and $(2.5_{-1.0}^{+2.5}) \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} [2], respectively. The temperature dependence of the rate constant is expected to be small. The temperature dependence of the analogous ClO reaction has been studied twice with somewhat different results. The values reported for E/R are -76 K [3] and $+224$ K [4].

References

[1] Watson, R. T., J. Phys. Chem. Ref. Data, **6**, 871 (1977).

[2] Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., Int. J. Chem. Kinet. **8**, 425 (1976).

[3] Zahniser, M. S., and Kaufman, F., J. Chem. Phys. **66**, 3673 (1977).

[4] Clyne, M. A. A., and Nip, W. J., J. Chem. Soc. Faraday Trans. I. **72**, 2211 (1976).

$O + FO_2 \rightarrow O_2 + FO$

$\Delta H^\circ = -153$ kJ mol^{-1}

Rate Coefficient Data: no available experimental data.

Preferred Value

$k = 5 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence.

$O(^1D) + HF \rightarrow HO + F \quad (1)$
$\rightarrow O(^3P) + HF \quad (2)$

ΔH° (1) = -46.9 kJ mol^{-1}
ΔH° (2) = -189.4 kJ mol^{-1}

Rate Coefficient Data: no available experimental data.

Preferred Value

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

Reliability

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

Comments on Preferred Value

k is assumed to be comparable to most other O^1D rate constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence.

$F + H_2 \rightarrow HF + H$

$\Delta H^\circ = -134.8$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.66 \times 10^{-10} \exp(-805/T)$	298–400	Homann, Solomon, Warnatz, Wagner and Zetzsch, 1970 [1]	(a)
1.84×10^{-11}	298		
$(3.0 \pm 0.7) \times 10^{-11}$	293	Dodonov, Lavrovskaya, Morozov, and Tal'roze, 1971 [2]	(b)
6.3×10^{-11}	298	Kompa and Wanner, 1972 [3]	(c)
$(6.6 \pm 1.7) \times 10^{-12}$	293	Rabideau, Hecht and Lewis, 1972 [4]	(d)
$(2.5 \pm 1.2) \times 10^{-11}$	298	Clyne, McKenney and Walker, 1973 [5]	(e)
$(2.5 \pm 0.7) \times 10^{-11}$	297	Bozzelli, 1973 [6]	(f)
$1.55 \times 10^{-10} \exp(-544/T)$	195–296	Igoshin, Kulakov, and Nikitin, 1974 [7]	(g)
2.47×10^{-11}	296		
2.3×10^{-12}	300	Lam Thanh My, Peyron, and Puget, 1974 [8]	(h)
Reviews and Evaluations			
2.5×10^{-11}	298	Foon and Kaufman, 1975 [9]	

Comments

(a) Discharge flow: mass spectrometric detection of F in the presence of an excess concentration of H_2. Atomic fluorine was generated from the N + NF_2 reaction and measured quantitatively by titration with ClNO.

(b) Discharge flow: mass spectrometric detection of H_2 and H in the presence of an excess concentration of F (F atom determination somewhat suspect—mass balance among F, F_2 and SiF_4). Diffusion effects taken into account—technique referred to as the "Diffusional cloud in flux" method.

(c) Flash photolysis of WF_6. Rate of removal of F, in the presence of an excess concentration of H_2, related to the intensity of the HF laser emission.

(d) Discharge flow: EPR detection of F and H. Atomic F produced from the reaction of atomic H with F_2.

(e) Discharge flow: mass spectrometric detection of H_2 in the presence of an excess concentration of F. Atomic fluorine concentrations determined using the ClNO titration reaction.

(f) Discharge flow: mass spectrometric detection of F (magnetic deflection mode).

(g) Discharge laser: pulse times as a function of $[H_2]$ and initiating energy.

(h) Laser cavity-pulse length as a function of $[NF_3]$ and $[H_2]$.

Preferred Value

$k = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.0 \times 10^{-10} \exp(-620/T)$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

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

$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

The value of k at 298 K seems to be fairly well established with the results reported in references [1,2,5–7] being in excellent agreement considering the diverse nature of the experimental techniques used. The value reported in reference [3] appears to be too high by a factor of ~2.5, whereas the values reported in references [4] and [8] are too low by factors of 4 and 10 respectively. The preferred value at 298 K is taken to be the mean of the values reported in references [1,2,5–7]. However, the magnitude of the temperature dependence cannot be considered to be well established with values of E/R of 805 K [1] and 544 K [7] being reported. The preferred Arrhenius parameters were derived by estimating A to be 2×10^{-10} cm^3 molecule^{-1} s^{-1}, and calculating an E/R value to yield the preferred value at 298 K of 2.5×10^{-11} cm^3 molecule^{-1} s^{-1}. For detailed comments refer to the reviews of Foon and Kaufman [9] and Jones and Skolnik [10].

References

[1] Homann, K. H., Solomon, W. E., Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Ber Bunsenges, Phys. Chem., **74**, 585 (1970).

[2] Dodonov, A. F., Lavrovskaya, G. K., Morozov, I. I., and Tal'roze, V. L., Dokl. Akad. Nauk USSR, 198, 622 (1971); Dokl. Phys. Chem. (Engl Trans.), **198**, 440 (1971).

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[10] Jones, W. E., and Skolnik, E. G., Chem. Rev., **76**, 563 (1976).

$F + O_2 + M \rightarrow FO_2 + M$

$\Delta H^\circ = -29$ 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			
$5.2 \times 10^{-34} \exp(656/T)$ [He]	272–362	Zetzsch, 1973 [1]	(a)
4.7×10^{-33} [He]			
$(7 \pm 2) \times 10^{-33}$ [He]	293	Arutyunov, Popov and Chaikin, 1976 [2]	(b)
$(1.7 \pm 0.4) \times 10^{-32}$ $[N_2]$	293		
$(6 \pm 2) \times 10^{-33}$ [Ar]	293		
$(5.4 \pm 0.6) \times 10^{-33}$ [He]	298	Chen et al., 1977 [3]	(c)
$(1.5 \pm 0.3) \times 10^{-32}$ $[O_2]$	298		
$(5.0 \pm 0.6) \times 10^{-33}$ $[F_2]$	298		
$(8.4 \pm 0.9) \times 10^{-33}$ [Ar]	298		

Comments

(a) Discharge flow system, mass spectrometric detection of F and FO_2.

(b) Discharge flow system, ESR detection of F.

(c) Flash photolysis, infrared-chemiluminescence detection of vibrationally excited HF.

Preferred Value

$k_0 = 1.1 \times 10^{-32}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 1.1 \times 10^{-32} (T/300)^{-2}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over range 270–360 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ over range 270–360 K.

Comments on Preferred Values

The preferred value is based upon three factors: (a) the average of the three determinations of k_0 (M=He) at 300 K, (b) the relative efficiency of N_2:He from ref. [2], and (c) the temperature coefficient for M = He from ref. [1].

High Pressure Rate Coefficients

No experimental data available. A value of $k_\infty \cong 3 \times 10^{-11} \mathrm{cm^3 molecule^{-1} s^{-1}}$ is estimated as calculated for F + NO + M ⟶ FNO + M [4]. This gives $[N_2]_c \cong 2.7 \times 10^{21}$ molecules $\mathrm{cm^{-3}}$ at 300 K.

Preferred Value

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

Reliability

$\Delta \log k_\infty = \pm 0.5$ over range 200–400 K.

Comments on Preferred Values

Rough estimate indicating fall-off effects only to occur in the 10–100 atm range.

References

[1] Zetzsch, C., First Europ. Symp. on Combust. (ed. Weinberg, F. S., Academic Press, London) p. 35 (1973)

[2] Arutyunov, V. S., Popov, L. S. and Chaikin, A. M., Kinet. Katal. **17**, 286 (1976) (Russ.); p. 251 (1976) (Engl.).

[3] Chen, H. L., Trainor, D. W., Center, R. E., and Fyfe, W. I., J. Chem. Phys. **66**, 5513 (1977).

[4] Quack, M. and Troe, J., Ber. Bunsenges. Phys. Chem. **81**, 329 (1977).

$F + O_3 \rightarrow FO + O_2$

$\Delta H^\circ = -114 \mathrm{\ kJ\ mol^{-1}}$

Rate coefficient data

$k/\mathrm{cm^3 molecule^{-1} s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-11} \exp(-(226 \pm 200)/T)$	253–365	Wagner, Zetzsch and Warnatz, 1972 [1]	(a)
1.3×10^{-11}	298		

Comments

(a) Discharge flow: mass spectrometric detection of O_3.

Preferred Value

$k = 1.3 \times 10^{-11} \mathrm{\ cm^3 molecule^{-1} s^{-1}}$ at 298 K.
$k = 2.8 \times 10^{-11} \exp(-226/T) \mathrm{\ cm^3 molecule^{-1} s^{-1}}$ over range 250–365 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Value

Value appears to be quite reasonable in view of the well known reactivity of atomic chlorine with O_3.

Reference

[1] Wagner, H. Gg., Zetzsch, C., Warnatz, J., Ber. Bunsenges, Phys. Chem. **76**, 526 (1972).

$F + H_2O \rightarrow HF + HO$

$\Delta H^\circ = -72.0 \mathrm{\ kJ\ mol^{-1}}$

Rate coefficient data

$k/\mathrm{cm^3 molecule^{-1} s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.2 \times 10^{-11} \exp(-201/T)$	243–365	Zetzsch, 1971 [1]	(a)
1.1×10^{-11}	298		

Comments

(a) Discharge flow: mass spectrometric technique.

Preferred Value

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.2 \times 10^{-11} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1} over range 240–360 K.

Reliability

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

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

Comments on Preferred Values

This value was reported in the review of Jones and Skolnik [2]. The reactivity appears to be somewhat lower than might be expected for such a hydrogen abstraction reaction (see table in reference [3]).

References

[1] Zetzsch, C., Ph.D. dissertation, Georg-August University, Göttingen (1971).

[2] Jones, W. E., and Skolnik, E. G., Chem. Rev. **76**, 563 (1976).

[3] Foon, R., and Kaufman, M., Progress Reaction Kinetics **8**, 81 (1975).

$F + CH_4 \rightarrow HF + CH_3$

$\Delta H° = -139.0$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.5 \times 10^{-10} \exp(-579/T)$	298–450	Wagner, Warnatz, and Zetzsch, 1971 [1]	(a)
7.9×10^{-11}	298		
$(6.0_{-3}^{+6}) \times 10^{-11}$	300	Clyne, McKenney and Walker, 1973 [2]	(b)
7.2×10^{-11}	298	Kompa and Wanner, 1972 [3]	(c)
Relative Rate Coefficients			
$1.6 \times 10^{-10} \exp(-307/T)$	253–348	Foon and Reid, 1971 [4]	(d)
6×10^{-11}	298		
$>1 \times 10^{-10}$	298	Pollock and Jones, 1973 [5]	(e)
Reviews and Evaluations			
8.0×10^{-11}	298	Foon and Kaufman, 1975 [6]	

Comments

(a) Discharge flow: mass spectrometric detection of F in the presence of excess CH_4. Atomic fluorine produced from the $N + NF_2 \rightarrow N_2 + 2F$ reaction. A ratio of $2.06 \exp(226/T)$ can be obtained for $k/k(F + H_2)$ by combining this value of k with the $k(F + H_2)$ value reported by Homann et al. [8] in the same experimental apparatus. This yields a value of 4.35 for $k/k(F + H_2)$ at 298 K.

(b) Discharge flow: mass spectrometric detection of CH_4 in the presence of excess F (produced from a He/F_2 discharge). The F atom concentrations were determined using the ClNO titration reaction. Combining this value of k with their value of $k(F + H_2)$ yields a value of 2.4 for $k/k(F + H_2)$ at 298 K.

(c) Flash photolysis of WF_6. Rate of removal of F, in the presence of an excess concentration of CH_4, related to the intensity of the HF laser emission. Combining this value with their value for $k(F + H_2)$ yields a value of 1.14 for $k/k(F + H_2)$ at 298 K.

(d) Competitive fluorination-consumption technique. $k/k(F + H_2) = 0.82 \exp(+313/T)$. $k(F + H_2) = 2.0 \times 10^{-10} \exp(-620/T)$ cm^3 molecule^{-1} s^{-1}. $k/k(F + H_2) = 2.4$ at 298 K.

(e) A lower limit was determined for k relative to $k(F + NO \rightarrow FNO)$.

Preferred Value

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

$k = 3.0 \times 10^{-10} \exp(-400/T)$ cm^3 molecule^{-1} s^{-1} over range 250–450 K.

Reliability

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

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

Comments on Preferred Values

The three absolute rate coeffcients determined at 298 K are in good agreement, however, this may be somewhat fortuitous as the ratios of $k/k(F + H_2)$ determined by these same groups can only be considered to be in fair agreement, 4.35 [1], 2.4 [2] and 1.14 [3]. The values determined for k at 298 K from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 2.4 reported for $k/k(F + H_2)$ in reference [4] is in good agreement with that reported in reference [2]. The preferred value for k at 298 K of 8.0×10^{-11} cm^3 molecule^{-1} s^{-1} is a weighted (according to their reliability) mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported in references [1] and [4], and the preferred Arrhenius parameters of the F + H_2 reaction. This reaction has recently been reviewed by both Foon and Kaufman [6], and Jones and Skolnik [7].

References

[1] Wagner, H. Gg., Warnatz, J., and Zetzsch, C., Analos Assoc. Quim. Argentina, **59**, 169 (1971).

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[8] Homann, K. H., Solomon, W. C., Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Ber. Bunsenges. Phys. Chem., **74**, 815 (1970).

$FO + O_3 \rightarrow F + 2O_2$ (1)
$\rightarrow FO_2 + O_2$ (2)

$\Delta H^\circ (1) = -172$ kJ mol^{-1}

$\Delta H^\circ (2) = -239$ kJ mol^{-1}

Rate Coefficient Data: no direct experimental data available.

Preferred Value

None.

Comments

The FO + O_3 reaction has two possible pathways which are exothermic, resulting in the production of F + $2O_2$ or FO_2 + O_2. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have provided some relevant kinetic information. Starrico et al. [1] measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2F + O_2$ (the latter reaction has been studied twice (Wagner et al., 1972 [2], Clyne and Watson, 1974 [3]) but although the value of $[F]_{\text{produced}}/[FO]_{\text{consumed}}$ is known to be close to unity it has not been accurately determined). Consequently it is impossible to ascertain from the experimental results of Starrico et al. whether or not the high quantum yields for ozone destruction should be attributed to the FO + O_3 reaction producing either F + $2O_2$ or FO_2 + O_2 (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al. utilized a low pressure discharge flow: mass spectrometric system to study the F + O_3 and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the FO + O_3 reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} cm^{3}molecule^{-1}s^{-1} is about a factor of 4 greater than that reported by Clyne and Watson (1974), which may possibly be attributed to either reactive impurities being present in their system, e.g., O(^{3}P), or that the FO + O_3 reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the FO + O_3 reaction rate constant from existing experimental data. It is worth noting that the analogous ClO + O_3 reactions are extremely slow (~10^{-18} cm^{3}molecule^{-1}s^{-1}) [4], and upper limits of 8×10^{-14} cm^{3}molecule^{-1}s^{-1} [5] and 5×10^{-15} cm^{3}molecule^{-1}s^{-1} [6] have been reported for k(BrO + O_3).

References

[1] Starrico, E. H., Sicre, S. E., and Schumacher, H. J., Z. Physik Chem. N.F. **31**, 385 (1962).

[2] Wagner, H. Gg., Zetzsch, C., and Warnatz, J., Ber Bunsenges. Phys. Chem. **76**, 526 (1972).

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[6] Sander, S. P., and Watson, R. T., manuscript in preparation (1978).

$FO + NO \rightarrow F + NO_2$

$\Delta H^\circ = -239$ kJ mol^{-1}

Rate Coefficient Data: no available experimental data.

Preferred Value

$k = 2 \times 10^{-11}$cm^{3}molecule^{-1}s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

Although there have been no experimental studies of this reaction, it has been used as a rapid titration reaction by Clyne and Watson [1]. The estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of ClO and BrO. The experimentally determined rate constants for ClO and BrO at ~298 K are $1.8 \times 10^{-11} \mathrm{cm}^3$ $\mathrm{molecule}^{-1} \mathrm{s}^{-1}$ and $2.1 \times 10^{-11} \mathrm{cm}^3 \mathrm{molecule}^{-1} \mathrm{s}^{-1}$, respectively, (this evaluation). 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 -200 K [2] and -296 K [3] for ClO, and -296 K [4] and -181 K [5] for BrO.

References

[1] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I. **70**, 1109 (1974).

[2] Zahniser, M. S., and Kaufman, F., J. Chem. Phys. **66**, 3673 (1977).

[3] Leu, M. T., and DeMore, W. B., J. Phys. Chem. **82**, 2049 (1978).

[4] Leu, M. T., Chem. Phys. Lett. **61**, 275 (1979).

[5] Watson, R. T., and Sander, S. P., Manuscript in preparation (1978).

$FO + NO_2 + M \rightarrow FO\,NO_2 + M$

$\Delta H^\circ = -132$ kJ mol^{-1}

Rate coefficient data: no experimental data available.

Preferred Value

$k_0 = 1.7 \times 10^{-31} (T/300)^{-3} [N_2]$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$k_\infty = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

$F_c = 0.7$

Reliability

$\Delta \log k = \pm 0.7$ over range 200–400 K.

Comments on Preferred Values

Values preferred are those derived for $ClO + NO_2 + M \rightarrow ClONO_2 + M$; no large difference to that system is expected.

$FO + FO \rightarrow 2F + O_2$ (1)

$\rightarrow FO_2 + F$ (2)

$\rightarrow F_2 + O_2$ (3)

$\Delta H^\circ (1) = -59$ kJ mol^{-1}

$\Delta H^\circ (2) = -126$ kJ mol^{-1}

$\Delta H^\circ (3) = -218$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5 \pm 2.8) \times 10^{-12}$	298	Clyne and Watson, 1974 [1]	(a)
Relative Rate Coefficients			
3.3×10^{-11}	298	Wagner, Zetzsch and Warnatz, 1972 [2]	(b)

Comments

(a) Discharge flow: mass spectrometric detection of FO and NO_2 (unreacted FO was converted to NO_2 via the rapid $NO + FO \rightarrow NO_2 + F$ reaction).

(b) Discharge flow: mass spectrometric detection of F, FO, F_2 and O_3. From the time behavior of these species a value was derived for k, and information concerning the relative importance of the three channels obtained. This value of k is sensitive to the value of $k(F + O_3)$, and the assumed reaction mechanism.

Preferred Value

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

Reliability

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

Comments on Preferred Value

Although the value of k reported by Clyne and Watson was obtained in a more direct manner than that of Wagner et al., and as such is less susceptible to error due to the presence of complicating secondary reactions and thus would normally be preferred, the value to be preferred in this assessment is a weighted average of the two studies. From the data of Wagner et al. [2] it can be seen that the dominant reaction channel is that producing 2F + O_2. However, their data base is not adequate to conclude that it is the only process.

References

[1] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I, **70**, 1109 (1974).

[2] Wagner, H. Gg., Zetzsch, C., and Warnatz, J., Ber. Bunsenges. Phys. Chem., **76**, 526 (1972).

HF + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_0$/kJ mol^{-1}	$\lambda_{threshold}$/nm
HF + $h\nu \rightarrow$ H + F	566.57	211

HF is optically transparent within the wavelength region of interest in this review, i.e., $\lambda > 165$nm. Safary et al. [1] observed the onset of a weak absorption continuum at 161.3nm where the absorption cross section had a value of ~1.5×10^{-22} cm^2 molecule^{-1}.

Reference

[1] Safary, E., Romand, J., and Vodar, B., J. Chem. Phys., **19**, 379 (1951).

COF_2 + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_0$/kJ mol^{-1}	$\lambda_{threshold}$/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(^{3}P)	(4)	697	172

Absorption cross section data

Wavelength range/nm	Reference	Comments
184.9–226	Chou et al., 1977 [1]	(a)

Quantum Yield Data: No available experimental data.

Comments

(a) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals. The spectrum shows considerable structure.

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	4.0	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].

By analogy with $COCl_2$ photolysis process (2) would be expected to be the primary photolytic process within the wavelength region of interest, 185nm $\leq \lambda \leq$ 226nm. The uncertainties in the values of $\Delta H°_f$ for COF are ± 60 kJ mol^{-1} which results in an uncertainty of ±25nm in $\lambda_{threshold}$ for process (2). Therefore, the true value of $\lambda_{threshold}$ for process (2) lies between 200nm and 250nm. Considering the uncertainties associated with $\lambda_{threshold}$ for process (2), the observation of a highly structured spectrum, and the lack of any experimental quantum yield data, there is an urgent need for quantitative quantum yield data, and for absorption cross section data at low temperatures.

Reference

[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.

$FONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
$FONO_2 + h\nu \rightarrow FO + NO_2$ (1)	132	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 any experimental data. In all probability, the absorption cross sections will be significantly lower than those of $ClONO_2$, resulting in low atmospheric J values.

4.7. Reactions of ClO_x

O + HCl → HO + Cl

$\Delta H° = +3.4$ kJ mol^{-1}

Rate coefficient data

k/$cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.75 \pm 0.6) \times 10^{-12} \exp(-2260/T)$	295–371	Balakhnin, Egorov and Interzarova, 1971 [1]	(a)
9.36×10^{-16}	300		
$(1.9 \pm 0.27) \times 10^{-11} \exp(-(3584 \pm 70)/T)$	356–628	Wong and Belles, 1972 [2]	(b)
1.14×10^{-16}	298*		
$2.5 \times 10^{-12} \exp(-2970/T)$	293–440	Brown and Smith, 1975 [3]	(c)
1.3×10^{-16}	300		
$(5.2 \pm 0.9) \times 10^{-11} \exp(-(3755 \pm 400)/T)$	350–454	Ravishankara, et al. 1977 [4]	(d)
1.75×10^{-16}	298*		
$(8.5 \pm 1.7) \times 10^{-12} \exp(-(3220 \pm 150)/T)$	293–718	Hack, Mex, and Wagner, 1977 [5]	(a)
$(1.55 \pm 0.33) \times 10^{-16}$	293		
Reviews and Evaluations			
$1.14 \times 10^{-11} \exp(-3370/T)$	293–718	Watson, 1977 [6]	
$1.14 \times 10^{-11} \exp(-3370/T)$	293–718	NASA, 1977 [7]	

Comments

(a) Discharge flow, [O] monitored by EPR.

(b) Stirred reactor, [O] monitored mass spectrometrically.

(c) Discharge flow, [O] monitored in presence of NO via NO_2* chemiluminescence.

(d) Flash photolysis: resonance fluorescence detection of [O].

Preferred Value

$k = 1.4 \times 10^{-16}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

$k = 1.1 \times 10^{-11} \exp(-3370/T)$ cm^{3}molecule^{-1}s^{-1} over range 293–718 K.

Reliability

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

$\Delta (E/R) = \pm 350$ K.

Comments on Preferred Values

Fair agreement exists between the results of Brown and Smith [3], Wong and Belles [2], Ravishankara et al. [4] and Hack et al. [5] at 300 K (some of the values quoted for k at 298 K were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~7 lower than that of Balakhnin et al. [1]. Unfortunately the values reported for E/R are in complete disagreement ranging from 2260–3755 K. The preferred value was based on the results reported in references [2–5], but not those reported in reference [1].

References

[1] Balakhnin, V. P., Egorov, V. I., and Interzarova, E. I., Kinet. Catal. **12**, 299 (1971).

[2] Wong, E. L., and Belles, F. R., NASA Tech Note. 1971. NASA TN D-6495. Chem. Abs. **76**, 1832g (1972).

[3] Brown, R. D. H., and Smith, I. W. M., Int. J. Chem. Kinet. **7**, 301 (1975).

[4] Ravishankara, A. R., Smith, G., Watson, R. T., and Davis, D. D., J. Phys. Chem. **81**, 2220 (1977).

[5] Hack, W., Mex, G., and Wagner, H. G., Ber. Bunsenges. Phys. Chem. **81**, 677 (1977).

[6] Watson, R. T., J. Phys. Chem. Ref. Data **6**, 871 (1977).

[7] NASA Ref. Pub. #1010. Chlorofluoromethanes and the Stratosphere, Chapter 1, R. D. Hudson, editor (1977).

$O + ClO \rightarrow O_2 + Cl$

$\Delta H° = -230.3$ kJ mol^{-1}

Rate coefficient data

k/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.0 \times 10^{-11}$	300	Clyne and Coxon, 1966 [1]	
$>1.3 \times 10^{-11}$	300	Freeman and Phillips, 1968 [2]	
1.2×10^{-11}	300	Basco and Dogra, 1971 [3]	(a)
$(5.3 \pm 0.8) \times 10^{-11}$	298	Bemand, Clyne and Watson, 1973 [4]	(b)
$(5.7 \pm 2.3) \times 10^{-11}$	298	Bemand, Clyne and Watson, 1973 [4]	(c)
$(1.07 \pm 0.15) \times 10^{-10} \exp(-(224 \pm 38)/T)$	220–425	Clyne and Nip, 1976 [5]	(b)
5.2×10^{-11}	298		
Relative Rate Coefficients			
$(7 \pm 1.5) \times 10^{-11}$	1250	Park, 1976 [6]	(d)
$4.19 \times 10^{-11} \exp(-(11 \pm 130)/T)$	218–295	Zahniser and Kaufman, 1977 [7]	(e)
$(4.25 \pm 0.85) \times 10^{-11}$	295		
Reviews and Evaluations			
$1.07 \times 10^{-10} \exp(-224/T)$	220–425	Watson, 1977 [8]	(f)
$7.7 \times 10^{-11} \exp(-130/T)$	220–298	NASA, 1977 [9]	(g)

Comments

(a) Data incorrectly analyzed (see reference [4]).

(b) Discharge flow: resonance fluorescence detection of O(^{3}P) in the presence of an excess concentration of ClO.

(c) Discharge flow: mass spectrometric detection of ClO in the presence of an excess concentration of O(^{3}P). Although this value is in good agreement with the preferred value, the precision of the mass spectrometric technique for this reaction was lower than that of the resonance fluorescence studies [4,5].

(d) This value was derived from an experimental determination of $k/k(O + Cl_2)$ at 1250 K. Unfortunately there appears to be great potential for error in this study: (a) the value of $k(O + Cl_2)$ is not well established at 1250 K (± factor of ~2), and (b) the values reported for σ_{Cl_2} and σ_{ClO} (k is quadratically dependent upon σ_{ClO}) are questionable. Therefore, the reliability of this determination is no better than a factor of ~2–3, and it must be considered fortuitous that the value reported is within 25% of the value derived from the preferred Arrhenius expression at 1250 K.

(e) k was measured relative to $k(Cl + O_3)$ using the discharge flow technique in conjunction with resonance fluorescence detection of [Cl] and resonance absorption detection of [O, ^{3}P], in a system where O(^{3}P), Cl, ClO and O_3 had reached a steady state condition. The tabulated Arrhenius expression was obtained by combining the experimentally determined ratio of $1.55 \exp(+(246 \pm 30)/T)$ for $k/k(Cl + O_3)$ with the preferred Arrhenius expression for $k(Cl + O_3)$ from this evaluation: $k(Cl + O_3)$ taken to be $2.7 \times 10^{-11} \exp(-257/T)$ cm^3

molecule^{-1} s^{-1}. The uncertainty limits reflect the uncertainties in both $k/k(Cl + O_3)$ and $k(Cl + O_3)$. An alternate Arrhenius expression can be derived (that shown in the original publication) by using the value of $k(Cl + O_3)$ determined by Zahniser et al. [10] in the same experimental apparatus: $k(Cl + O_3) = 2.17 \times 10^{-11} \exp(-171/T)$ cm^3 molecule^{-1} s^{-1} yielding a value of $3.38 \times 10^{-11} \exp(+(75 \pm 40)/T)$ cm^3 molecule^{-1} s^{-1} for k. Although both $k/k(Cl + O_3)$ and $k(Cl + O_3)$ were determined in the same experimental apparatus the evaluated Arrhenius expression was used for $k(Cl + O_3)$ because the measurement of a rate constant ratio should be less susceptible to systematic errors than an individual absolute determination of a rate constant, assuming that the chemistry of the reacting system is fully understood. The value tabulated for k at 295 K was derived by combining the experimental value of $k/k(Cl + O_3)$ of 3.45 ± 0.16 and a value of 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} for $k(Cl + O_3)$. The value of $k(Cl + O_3)$ determined by Zahniser et al. [10] at 298 K is in excellent agreement with the value preferred in this evaluation, and would result in the same value of k.

(f) Value reported by Clyne and Nip [5].

(g) This expression is based on values of 5.0×10^{-11} cm^3 molecule^{-1} s^{-1} and 4.4×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 and 230 K, respectively. These values were deduced from the experimental data reported in the original references [4,5,7].

Preferred Value

$k = 5.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.5 \times 10^{-11} \exp(-120/T)$ cm^3 molecule^{-1} s^{-1} over range 220–425 K.

Reliability

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

$\Delta (E/R) = \pm 120$ K.

Comments on Preferred Values

The preferred value at 298 K is a weighted mean, according to precision, of the data reported in references [4,5,7]. The Arrhenius parameters were derived by taking a mean of the two tabulated values of E/R [5,7], and adjusting the A-factor to yield the preferred value for k at 298 K.

References

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[2] Freeman, G. C., and Phillips, L. F., J. Phys. Chem. **72**, 3025 (1968).

[3] Basco, N., and Dogra, S. K., Proc. R. Soc. London Ser. A. **323**, 29 (1971).

[4] Bemand, P. P., Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I. **69**, 1356 (1973).

[5] Clyne, M. A. A., and Nip, W., J. Chem. Soc. Faraday Trans I. **72**, 2211 (1976).

[6] Park, C., J. Phys. Chem. **80**, 565 (1976).

[7] Zahniser, M. S., and Kaufman, F., J. Chem. Phys. **66**, 3673 (1977).

[8] Watson, R. T., J. Phys. Chem. Ref. Data **6**, 871 (1977).

[9] NASA Ref. Pub. #1010. "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

[10] Zahniser, M. S., Kaufman, F., and Anderson, J. G., Chem. Phys. Lett. **37**, 226 (1976).

$O + ClONO_2 \rightarrow ClO + NO_3$ (1)

$\rightarrow OClO + NO_2$ (2)

$\rightarrow O_2 + ClONO$ (3)

$\Delta H^\circ(1) = -102$ kJ mol^{-1}

$\Delta H^\circ(2) = -140$ kJ mol^{-1}

$\Delta H^\circ(3) = \sim -234$ 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			
$(2.0 \pm 0.2) \times 10^{-13}$	245	Ravishankara, et al. 1977 [1]	(a)
$(3.4 \pm 0.6) \times 10^{-12} \exp(-(840 \pm 60)/T)$	213–295	Molina, Spencer and Molina 1977 [2]	(b)
$(2.0 \pm 0.4) \times 10^{-13}$	295		
$(1.87 \pm 1.29) \times 10^{-12} \exp(-(692 \pm 167)/T)$	225–273	Kurylo, 1977 [3]	(c)
1.8×10^{-13}	298*		
Reviews and Evaluations			
$3.0 \times 10^{-12} \exp(-808/T)$	213–295	NASA, 1977 [4]	(d)

Comments

(a) Static system flash photolysis: resonance fluorescence detection of $O(^3P)$. Handling $ClONO_2$ was reported to be more difficult than usual owing to its instability on metal or wet surfaces.

(b) Discharge flow: chemiluminescence detection of atomic oxygen ($O + NO \rightarrow NO_2^*$).

(c) Flowing system flash photolysis: resonance fluorescence detection of $O(^3P)$.

(d) This is a composite expression derived by Kurylo (1977) based on his data combined with that reported by Molina et al. (1977).

Preferred Value

$k = 1.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.0 \times 10^{-12} \exp(-808/T)$ cm^3 molecule^{-1} s^{-1} over range 213–295 K.

Reliability

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

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

Comments on Preferred Values

The results reported by Molina et al. [2] and Kurylo [3] are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara et al. [1] at 245 K is a factor of 2 greater than those from the other studies [2,3] and this may possibly be attributed to either, (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in their $ClONO_2$, or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products.

References

[1] Ravishankara, A. R., Davis, D. D., Smith, G., Tesi, G. and Spencer, J., Geophys. Res. Lett. 4, 7 (1977).

[2] Molina, L. T., Spencer, J. E., and Molina, J. J., Chem. Phys. Lett. 45, 158 (1977).

[3] Kurylo, M. J., Chem. Phys. Lett. 49, 467 (1977).

[4] NASA Ref. Pub. No. 1010, "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

$$
\begin{aligned}
O(^1D) + CF_2Cl_2 &\rightarrow ClO + CF_2Cl \quad (1)\\
&\rightarrow O(^3P) + CF_2Cl_2 \quad (2)
\end{aligned}
$$

$\Delta H^\circ(1) = -112.2$ kJ mol^{-1}

$\Delta H^\circ(2) = -189.4$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.8 \pm 0.5) \times 10^{-10}$	298	Fletcher and Husain, 1976 [1]	(a)
$(1.45 \pm 0.5) \times 10^{-10}$	298	Davidson et al., 1978 [2]	(b)
Relative Rate Coefficients			
2.0×10^{-10}	298	Jayanty, Simonaitis and Heicklen, 1975 [3]	(c)
3.9×10^{-10}	298	Atkinson et al., 1976 [4]	(d)
2.3×10^{-10}	298	Green and Wayne, 1977 [5]	(e)
Reviews and Evaluations			
2.1×10^{-10}	298	Watson, 1977 [6]	(f)
2.0×10^{-10}	298	NASA, 1977 [7]	(g)

Comments

(a) Flash photolysis. $[O^1D]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm, $O(3D_2 \leftarrow 2D_2)$. Data analysis used a modified Beer-Lambert law: $I_t/I_0 = \exp(-\sigma(cl)^\gamma)$ with $\gamma = 0.41$. A value of 2.2 was obtained for $k/k(O^1D + N_2O)$.

(b) Flash photolysis, $[O^1D]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. A value of 1.3 was obtained for $k/k(O^1D + N_2O)$.

(c) By monitoring the production of N_2 as a function of $[CF_2Cl_2]/[N_2O]$ a value of 1.2 was obtained for $k/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) By monitoring $\Delta[CF_2Cl_2]/\Delta[N_2O]$ as a function of $[CF_2Cl_2]/[N_2O]$ using IR spectroscopy, a value of 2.4 was obtained for $k_1/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) By monitoring $\Delta[CF_2Cl_2]/\Delta[N_2O]$ as a function of $[CF_2Cl_2]/[N_2O]$ using IR spectroscopy, a value of 1.4 was obtained for $k_1/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(f) This value was based on combining the mean of the ratios reported for $k/k(O^1D + N_2O)$ in references [3] and [4], with the value of $k(O^1D + N_2O)$ reported by Davidson et al. [8]. $k/k(O^1D + N_2O) = 1.8$, $k(O^1D + N_2O)$ was erroneously taken to be $1.17 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ rather than $1.10 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$.

(g) The value reported from the resonance absorption study [1] was multiplied by 0.41 (the γ-factor). This was equivalent to assuming that the correct value of γ was 1.0—based upon the observation that most absolute rate constants obtained using the resonance absorption technique are a factor of ~2.2 greater than those obtained using the $O(^1D) \rightarrow O(^3P)$ emission technique.

Preferred Value

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

Reliability

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

Comments on Preferred Values

The preferred value was obtained by taking the mean value of $k/k(O^1D + N_2O)$ reported in references [1–5], and combining it with the preferred value of $1.63 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ for $k(O^1D + N_2O)$ from this evaluation. $k/k(O^1D + N_2O) = 1.7$. The absolute rate coefficient studies, [1] and [2], monitored the total rate of removal of O^1D in the presence of an excess concentration of CF_2Cl_2. Consequently, these studies measured $k_1 + k_2$ and could not provide any information concerning the relative importance of the two channels ((1) and (2)). The relative rate coefficient study of Jayanty et al. [3] measured $(k_1 + k_2)/k(O^1D + N_2O)$, whereas the relative rate coefficient studies of Atkinson et al. [4] and Green and Wayne [5] only measured the reactive channel, i.e., $k_1/k(O^1D + N_2O)$. Consequently, the values of $(k_1 + k_2)/k(O^1D + N_2O)$ reported in references [1–3] should be greater than the values of $k_1/k(O^1D + N_2O)$ reported in references [4] and [5] if the quenching channel (2) is an important process. Inspection of the data shows that it is scattered and that from these studies a value cannot be deduced for k_1/k_2. Values of 2.2 [1], 1.3 [2] and 1.2 [3] were reported for $(k_1 + k_2)/k(O^1D + N_2O)$ in contrast to values of 2.4 [4] and 1.4 [5] for $k_1/k(O^1D + N_2O)$. The flash photolysis: plate photometric technique has been utilized [9] to verify that ClO is a primary product of the $O^1D + CF_2Cl_2$ reaction. By monitoring $\Delta[ClO]_{produced}/\Delta[O_3]_{removed}$ a value of ≥ 0.47 was reported for $k_1/(k_1 + k_2)$. This value is a lower limit as $\Delta[ClO]$ may have been underestimated due to removal by any $O(^3P)$ formed in reaction (2).

References

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$$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2 \quad (1)$$

$$\rightarrow O(^3P) + CFCl_3 \quad (2)$$

$\Delta H^\circ(1) = -148 kJ mol^{-1}$

$\Delta H^\circ(2) = -189.4 kJ mol^{-1}$

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

$k/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.7) \times 10^{-10}$	298	Fletcher and Husain, 1976 [1]	(a)
$(2.2 \pm 0.7) \times 10^{-10}$	298	Davidson et al., 1978 [2]	(b)
Relative Rate Coefficients			
2.4×10^{-10}	298	Jayanty, Simonaitis, and Heicklen, 1975 [3]	(c)
4.3×10^{-10}	298	Atkinson et al., 1976 [4]	(d)
Reviews and Evaluations			
2.44×10^{-10}	298	Watson, 1977 [5]	(d)
2.3×10^{-10}	298	NASA, 1977 [6]	(f)

Comments

(a) Flash photolysis. [O^1D] monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm, $O(3D_2 \leftarrow 2D_2)$. Data analysis used a modified Beer-Lambert law: $I_t/I_0 = \exp(-\sigma(cl)^\gamma)$ with $\gamma = 0.41$. A value of 2.5 was obtained for $k/k(O^1D + N_2O)$.

(b) Flash photolysis. [O^1D] monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. A value of 2.0 was obtained for $k/k(O^1D + N_2O)$.

(c) By monitoring the production of N_2 as a function of $[CFCl_3]/[N_2O]$ a value of 1.5 was obtained for $k/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) By monitoring $\Delta[CFCl_3]/\Delta[N_2O]$ as a function of $[CFCl_3]/[N_2O]$ using IR spectroscopy, a value of 2.65 was obtained for $k_1/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) This value was based on combining the mean of the ratios reported for $k/k(O^1D + N_2O)$ in references [3] and [4], with the value of $k(O^1D + N_2O)$ reported by Davidson et al. [7]. $k/k(O^1D + N_2O) = 2.07$; $k(O^1D + N_2O)$ was erroneously taken to be 1.17×10^{-10} cm^3 molecule^{-1} s^{-1} rather than 1.10×10^{-10} cm^3 molecule^{-1} s^{-1}.

(f) The value reported from the resonance absorption study [1] was multiplied by 0.41 (the γ-factor). This was equivalent to assuming that the correct value of γ was 1.0—based upon the observation that most absolute rate constants obtained using the resonance absorption technique are a factor of ~2.2 greater than those obtained using the $O(^1D) \rightarrow O(^3P)$ emission technique.

Preferred Value

$k = 3.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value was obtained by taking the mean value of $k/k(O^1D + N_2O)$ and combining it with the preferred value of 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} for $k(O^1D + N_2O)$ from this evaluation. $k/k(O^1D + N_2O) = 2.15$. The absolute rate coefficient studies [1] and [2] monitored the total rate of removal of O^1D in the presence of an excess concentration of $CFCl_3$. Consequently these studies measured $k_1 + k_2$ and could not provide any information concerning the relative importance of the two channels ((1) and (2)). The relative rate coefficient study of Jayanty et al. [3] measured $(k_1 + k_2)/k(O^1D + N_2O)$, whereas the relative rate coefficient study of Atkinson et al. [4] only measured the reactive channel, i.e., $k_1/k(O^1D + N_2O)$. Consequently the values of $(k_1 + k_2)/k(O^1D + N_2O)$ reported in references [1–3] should be greater than the value of $k_1/k(O^1D + N_2O)$ reported in reference [4] if the quenching channel (2) is an important process. Values of 2.5 [1], 2.0 [2] and 1.5 [3] were reported for $(k_1 + k_2)/k(O^1D + N_2O)$ in contrast to a value of 2.65 [4] for $k_1/k(O^1D + N_2O)$. Obviously as this data base makes no sense, a value of k_1/k_2 cannot be deduced. The flash photolysis-plate photometric technique has been utilized [8] to verify that ClO is a primary product of the $O^1D + CFCl_3$ reaction. By monitoring $\Delta[ClO]_{produced}/\Delta[O_3]_{removed}$ a value of ≥ 0.39 was reported for $k_1/(k_1 + k_2)$. This value is a lower limit as $\Delta[ClO]$ may have been underestimated due to removal by any $O(^3P)$ formed in reaction (2).

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$$\begin{aligned} O(^1D) + CCl_4 &\rightarrow ClO + CCl_3 \quad (1) \\ &\rightarrow O(^3P) + CCl_4 \quad (2) \end{aligned}$$

$\Delta H^\circ(1) = -161$ kJ mol^{-1}

$\Delta H^\circ(2) = -189$ 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			
$(8.5 \pm 1.1) \times 10^{-10}$	298	Fletcher and Husain, 1976 [1]	(a)
$(3.1 \pm 0.9) \times 10^{-10}$	298	Davidson et al., 1978 [2]	(b)
Relative Rate Coefficients			
3.4×10^{-10}	298	Jayanty, Simonaitis and Heicklen, 1975 [3]	(c)
$\geq 4.9 \times 10^{-10}$	298	Atkinson et al., 1976 [4]	(d)
Reviews and Evaluations			
3.54×10^{-10}	298	Watson, 1977 [5]	(e)

Comments

(a) Flash photolysis. [O^{1}D] monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm, $O(3D_2 \leftarrow 2D_2)$. Data analysis used a modified Beer-Lambert law: $I_t/I_0 = \exp(-\sigma(cl)^\gamma)$ with $\gamma = 0.41$. A value of 3.9 was obtained for $k/k(O^1D + N_2O)$.

(b) Flash photolysis. [O^{1}D] monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. A value of 2.8 was obtained for $k/k(O^1D + N_2O)$.

(c) By monitoring the production of N_2 as a function of $[CCl_4]/[N_2O]$ a value of 2.1 was obtained for $k/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) By monitoring $\Delta[CCl_4]/\Delta[N_2O]$ as a function of $[CCl_4]/[N_2O]$ using IR spectroscopy a value of ≥ 3.0 was obtained for $k_1/k(O^1D + N_2O)$. $k(O^1D + N_2O)$ taken to be 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} (this evaluation).

(e) This value was based upon multiplying the ratio, $k/k(O^1D + N_2O)$ reported by Jayanty et al. [1] by 1.45, and combining this with the value of $k(O^1D + N_2O)$ reported by Davidson et al. [6] which was erroneously taken to be 1.17×10^{-10} cm^3 molecule^{-1} s^{-1} rather than 1.10×10^{-10} cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k = 4.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value was obtained by combining the mean value of $k/k(O^1D + N_2O)$ reported in references [1–3] with the preferred value of 1.63×10^{-10} cm^3 molecule^{-1} s^{-1} for $k(O^1D + N_2O)$ from this evaluation. $k/k(O^1D + N_2O) = 2.93$. The lower limit reported in reference [4] was not used in the derivation of the preferred value. The absolute rate coefficient studies [1] and [2], monitored the total rate of removal of O^{1}D in the presence of an excess concentration of CCl_4. Consequently, these studies measured $k_1 + k_2$ and could not provide any information concerning the relative importance of the two channels ((1) and (2)). The relative rate coefficient study of Jayanty et al. [3] measured $(k_1 + k_2)/k(O^1D + N_2O)$, whereas the relative rate coefficient study of Atkinson et al. [4] only measured the reactive channel, i.e., $k_1/k(O^1D + N_2O)$. Consequently the values of $(k_1 + k_2)/k(O^1D + N_2O)$ reported in references [1–3] should be greater than the value of $k_1/k(O^1D + N_2O)$ reported in reference [4] if the quenching channel (2) is an important process. Unfortunately the values reported for $(k_1 + k_2)/k(O^1D + N_2O)$ are somewhat scattered, 3.9 [1], 2.8 [2] and 2.1 [3] and only a lower limit of ≥ 3.0 [4] has been reported for $k_1/k(O^1D + N_2O)$. Therefore, from this data base it is not possible to determine the relative importance of the two channels.

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$Cl + H_2 \rightarrow HCl + H$

$\Delta H^\circ = +4.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.1×10^{-14}	298	Rodebush and Klingelhoefer, 1933 [1]	(a,b)
4.1×10^{-15}	273		
8.0×10^{-13}	523	Ashmore and Chanmugan, 1953 [2]	(a,b)
$(2.0 \pm 0.5) \times 10^{-11} \exp(-(2164 \pm 101)/T)$	251–456	Westenberg and de Haas, 1968 [3]	(a,c,g)
$(1.35 \pm 0.07) \times 10^{-14}$	297		
$(8.0 \pm 2.0) \times 10^{-11} \exp(-(2655 \pm 200)/T)$	479–610	Benson, Cruickshank and Shaw, 1969 [4]	(a,d,h)
$(1.1 \pm 0.2) \times 10^{-14}$	298*		
$(1.25 \pm 0.1) \times 10^{-14}$	298	Davis, Bass and Braun, 1970 [5]	(a,e,i)
$(5.5 \pm 0.5) \times 10^{-11} \exp(-(2391 \pm 50)/T)$	213–350	Watson et al., 1975 [6]	(a,e)
$(1.80 \pm 0.2) \times 10^{-14}$	298		
$(2.66 \pm 0.42) \times 10^{-11} \exp(-(2230 \pm 60)/T)$	200–500	Lee et al., 1978 [7]	(a,e)
$(1.70 \pm 0.13) \times 10^{-14}$	301		
Absolute Rate Coefficients Derived from Reverse Reaction			
5.90×10^{-12}	1071	Steiner and Rideal, 1939 [8]	(a,j,k)
4.57×10^{-12}	1031		
4.07×10^{-12}	960		
3.27×10^{-12}	901		
$3.2 \times 10^{-11} \exp(-(2099 \pm 98)/T)$	195–373	Clyne and Stedman, 1966 [9]	(a,g,k,l,m)
2.12×10^{-14}	294		
$7.2 \times 10^{-11} \exp(-(2285 \pm 48)/T)$	195–497	Westenberg and de Haas, 1968 [3]	(a,c,k,l)
3.75×10^{-14}	297		
$\sim 1.7 \times 10^{-14}$	295	Spencer and Glass, 1975 [10]	(a,c,k,n)
$(1.55 \pm 0.04) \times 10^{-11} \exp(-(2123 \pm 100)/T)$	298–521	Ambidge, Bradley, and Whytock, 1976 [11]	(a,c,k,o)
1.25×10^{-14}	298		
Relative Rate Coefficients			
See $Cl + CH_4$ data sheets.			
Reviews and Evaluations			
$1.38 \times 10^{-10} \exp(-2750/T)$	273–1071	Fettis and Knox, 1964 [12]	(a,p)
$3.7 \times 10^{-11} \exp(-2146/T)$	195–610	Clyne and Walker, 1973 [13]	(a,q)
$5.6 \times 10^{-11} \exp(-2254/T)$	195–496	Clyne and Walker, 1973 [13]	(a,r)
$3.5 \times 10^{-11} \exp(-2290/T)$	200–300	Watson, 1977 [14]	(a,s)
$3.5 \times 10^{-11} \exp(-2290/T)$	200–300	NASA, 1977 [15]	(a,s)

Comments

(a) See the review of Watson, 1977 [14] for detailed comments.

(b) Data not used to determine the preferred value.

(c) Discharge flow: ESR detection of atomic species.

(d) Static cell: thermal decomposition of ICl as a source of atomic chlorine in the presence of H_2.

(e) Flash photolysis: resonance fluorescence detection of Cl.

(f) Discharge flow: chemiluminescence detection of atomic species.

(g) Although the value of k at 298 K is in excellent agreement with that reported in reference [5], it could be significantly underestimated due to the regeneration of Cl via the rapid $H + Cl_2$ reaction. This hypothesis would explain why their value is lower than the preferred one of Watson et al., 1975 at 298 K. Therefore, although the Arrhenius expression obtained in this study is in good agreement with that reported by Whytock et al., this could still be fortuitous as it is in disagreement with the results of Watson et al., and Benson et al.

(h) A rather limited temperature range was used in this study to determine the Arrhenius parameters of this reaction. Consequently, it is quite likely that these parameters are rather inaccurate even though the individual data points are reliable. Therefore, extrapolation of their expression outside the temperature range of their study is not advisable.

(i) The value reported may have been overestimated by ~10% (it was assumed that $I_F \propto [Cl]^{0.9}$ rather than $I_F \propto [Cl]$), and a revised value has been entered in these tables.

(j) These results should have low weighting due to the uncertainty regarding the effect of the presence of molecular O_2 [16].

(k) Calculated by using the reported values of k in conjunction with the thermodynamic values of K_{eq}.

(l) These results are at variance with the direct determination of k. Experimental data obtained in reference [10] strongly indicated that the values reported for k(H + HCl) are overestimated due to a secondary removal process for atomic hydrogen.

(m) The values reported for k predict that the activation energy increases with temperature. This was not observed over the same temperature range in references [3,11]. The data can be approximated by the Arrhenius expression shown.

(n) The stoichiometry of the reaction, $([\mathrm{Cl}]_{\mathrm{formed}}/[\mathrm{H}]_{\mathrm{reacted}})$ and the rate of removal of atomic hydrogen were dependent upon the treatment of the reactor surfaces. It was concluded that the results reported in references [3] and [9] for k(H + HCl) are too high due to secondary removal of H atoms via the following mechanism: $\mathrm{H} + \mathrm{HCl} \rightarrow \mathrm{H_2} + \mathrm{Cl}$; $\mathrm{Cl} + \mathrm{HCl} \overset{\text{wall}}{\rightleftarrows} \mathrm{HCl_2}$; $\mathrm{H} + \mathrm{HCl_2} \rightarrow 2\,\mathrm{HCl}$: By extrapolating the stoichiometry to unity (at which point secondary reactions should be negligible), a value of $\sim 4.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} was obtained for k(H + HCl). However, a more accurate extrapolation would yield a value of $\sim 5.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for k(H + HCl)—the value of k entered in the table was based on the re-evaluated value for k(H + HCl).

(o) The stoichiometry of the reaction, n, was deduced to have a value of exactly 2 at high $[\mathrm{HCl}]_0/[\mathrm{H}]_0$ ratios. However, this conclusion may not be completely correct, nor might the postulated mechanism.

(p) A review of references [1,2,8]. Their interpretation of the published data is shown in the table.

(q) This rate constant expression includes data from references [9,3(k(H + HCl)), 4 and 5], but rejects the determination of k from reference [3].

(r) This rate constant expression is based on data from references [9,3(k(H + HCl)), and 5].

(s) This value is based on the results obtained below 300 K in the recent studies reported by Watson et al., [6] and Whytock et al. [7]. However, if the data of Benson et al. [4] and Westenberg and de Haas [3] are included with all the data from references [6] and [7], the overall expression is almost identical.

Preferred Value

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

$k = 4.7 \times 10^{-11} \exp(-2340/T)$ cm^3 molecule^{-1} s^{-1} over range 210–1070 K.

Reliability

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

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

Comments on Preferred Values

This Arrhenius expression for k was obtained by combining the results of Watson et al. [6], Benson et al. [4], and Steiner and Rideal [8] (as modified by Benson). This expression is almost identical to the expression obtained from the results of Watson et al. [6] alone. Although the results of Watson et al. [6] and Whytock et al. [7] agree below 300 K, the data at and above 300 K are in poor agreement. Whytock et al. argue that their results are correct due to their agreement with Westenberg and de Haas [3], and with the H + HCl study of Ambidge et al. [11]. However, the values of k at 298 K reported in these three studies are not in particularly good agreement, the data of Westenberg and de Haas is not beyond question, and all of the H + HCl studies appear to be subject to surface problems in the flow reactors, thus restricting the precision and accuracy of the results (to date the H + HCl reaction has not been studied in a flash photolysis: resonance fluorescence system where heterogeneous processes are minimized). Also, the following reasons suggest that the results of Watson et al. are correct, (a) good agreement with Benson et al. at ~600 K, (b) agreement with the corrected values of Steiner and Rideal at ~1000 K, (c) better agreement for $k(\mathrm{Cl} + \mathrm{CH_4})$ when these results are combined with the competitive chlorination results for $k/k(\mathrm{Cl} + \mathrm{CH_4})$.

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$Cl + HO_2 \rightarrow HCl + O_2$ (1)

$\rightarrow ClO + HO$ (2)

$\Delta H^\circ(1) = -216$ kJ mol^{-1}

$\Delta H^\circ(2) = +18$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$(2.1_{-1.3}^{+3.2}) \times 10^{-11}$	295	Leu and DeMore, 1976 [1]	(a,b)
$(2.5 \pm 1.0) \times 10^{-11}$	306	Cox and Derwent, 1977 [2]	(c)
$(7.3 \pm 1.9) \times 10^{-11}$	298	Poulet, Le Bras and Combourieu, 1978 [3]	(a,d)
$(4.5 \pm 0.5) \times 10^{-11}$	293	Burrows et al., 1978 [4]	(e)
Reviews and Evaluations			
3×10^{-11}	298	Watson, 1977 [5]	(f)
3×10^{-11}	298	NASA, 1977 [6]	(f)

Comments

(a) Discharge flow: mass spectrometric detection of HO_2 and H_2O_2. k determined relative to $k(Cl + H_2O_2)$. Absolute HO_2 concentrations are required—obtained by estimating the relative mass-spectrometric sensitivities of HO_2 and H_2O_2.

(b) $k/k(Cl + H_2O_2) = 48$; $k(Cl + H_2O_2)$ taken to be 4.3×10^{-13} cm^3 molecule^{-1} s^{-1}. $S[HO_2^+]/S[H_2O_2^+] = 0.72$ at 15 electron volts, where S = mass spectrometric calibration factor.

(c) Stopped-flow uv absorption system. Rate of H_2O_2 formation monitored as a function of $[H_2]$ in a $Cl_2/O_2/H_2$ mixture. Value of k sensitive to values of $k(Cl + H_2)$, $k(HO_2 + HO_2)$, and $k(Cl + ClOO)$.

(d) $k/k(Cl + H_2O_2) = 170 \pm 45$; $k(Cl + H_2O_2)$ taken to be 4.3×10^{-13} cm^3 molecule^{-1} s^{-1}. $S[HO_2^+]$ assumed to be equal to $S[H_2O_2^+]$, where S = mass spectrometric sensitivity.

(e) Discharge flow: laser magnetic resonance detection of HO_2—calibrated on absolute basis. k determined relative to $k(Cl + H_2O_2)$. $k/k(Cl + H_2O_2) = 104 \pm 12$; $k(Cl + H_2O_2)$ taken to be 4.3×10^{-13} cm^3 molecule^{-1} s^{-1}. An upper limit of 4.4×10^{-13} cm^3 molecule^{-1} s^{-1} was determined for k_2 by observing the direct production of HO.

(f) Based on the data of Leu and DeMore [1].

Preferred Value

$k_1 = 4.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 4.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The values of $k/k(Cl + H_2O_2)$ reported in references [1], [3] and [4] are in poor agreement. The discrepancy between the two mass-spectrometric results may be attributed to inaccurate estimations of the mass-spectrometric sensitivity for HO_2. The preferred value was obtained by averaging these three values with the value reported in reference [2].

Based upon the data reported in reference [4] an upper limit of 4.1×10^{-13} has been placed on k_2 (1% total rate constant).

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$Cl + H_2O_2 \rightarrow HCl + HO_2$ (1)
$\rightarrow HOCl + HO$ (2)
$\rightarrow ClO + H_2O$ (3)

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

$\Delta H^\circ(2) = -24$ kJ mol^{-1}

$\Delta H^\circ(3) = -124.5$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.2_{-2.6}^{+5.2}) \times 10^{-13}$	298	Watson et al., 1976 [1]	(a)
$(6.2 \pm 1.5) \times 10^{-13}$	295	Leu and DeMore, 1976 [2]	(b)
$(1.24 \pm 0.74) \times 10^{-12} \exp(-(384 \pm 168)/T)$	265–400	Michael et al., 1977 [3]	(c)
$(3.64 \pm 0.52) \times 10^{-13}$	299		
$(4.0 \pm 0.4) \times 10^{-13}$	298	Poulet, Le Bras and Combourieu, 1978 [4]	(b)
$(1.05 \pm 0.31) \times 10^{-11} \exp(-(982 \pm 102)/T)$	298–424	Keyser, 1979 [5]	(d)
$(4.14 \pm 0.2) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(3.4 \pm 0.8) \times 10^{-13}$	298	Poulet, Le Bras and Combourieu, 1978 [4]	(e)
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(-384/T)$	265–400	Watson, 1977 [6]	(f)
$1.7 \times 10^{-12} \exp(-384/T)$	265–400	NASA, 1977 [7]	(f)

Comments

(a) Flash photolysis: resonance fluorescence detection of Cl. The factor of 2 uncertainty in the reported rate constant was due to heterogeneous decomposition of H_2O_2 on the reactor surfaces which limited the precision of H_2O_2 concentration measurements. The value entered in the data sheet is different from that reported in the original paper which was in error as pointed out by Michael et al. [3].

(b) Discharge flow: mass spectrometric detection of H_2O_2. An advantage of this technique is that accurate values of $[H_2O_2]$ are not required.

(c) Flash photolysis: resonance fluorescence detection of Cl. A flowing reactor cell was used to minimize heterogeneous decomposition of H_2O_2. However, two expressions were reported for k between 265 and 400 K due to some uncertainty as to whether H_2O_2 decomposed within the reaction or not. The A-factor is significantly lower than expected on theoretical grounds.

(d) Discharge flow: resonance fluorescence detection of atomic chlorine. H_2O_2 concentrations were measured both before and after the reaction zone with no evidence for heterogeneous decomposition.

(e) Discharge flow: mass spectrometric detection of H_2O_2 and CH_4. $k/k(Cl + CH_4) = 3.25 \pm 0.8$. $k(Cl + CH_4)$ taken to be 1.04×10^{-13} cm^3 molecule^{-1} s^{-1}.

(f) This expression is based on the activation energy reported by Michael et al. (1977) and an A-factor that has been modified to yield the mean of the values reported for k at 298 K by Michael et al. (1977) and Leu and DeMore (1976). This value is in good agreement with that reported by Watson et al. (1976).

Preferred Value

$k = 4.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1 \times 10^{-11} \exp(-980/T)$ cm^3 molecule^{-1} s^{-1} over range 265–424 K.

Reliability

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

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

Comments on Preferred Values

The preferred value at 298 K was obtained by taking a weighted (by precision) mean of all reported values. The preferred value for the Arrhenius expression is taken to be that reported by Keyser [5]. The A-factor reported by Michael et al. [3] is considerably lower than that expected from theoretical consideration, and may be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data reported in references [3] and [5] are in excellent agreement at, and below 300 K. More data is required before the Arrhenius parameters can be considered to be well established. At present there are no experimental data quantitatively indicating the relative importance of the three routes, although several studies have shown that reaction (1) is a major channel [2,4,8].

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$Cl + O_3 \rightarrow ClO + O_2$

$\Delta H^\circ = -161.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>6.7 \times 10^{-13}$	300	Clyne and Coxon, 1968 [1]	
$(1.85 \pm 0.36) \times 10^{-11}$	298	Clyne and Watson, 1974 [2]	(a)
$(3.08 \pm 0.30) \times 10^{-11} \exp(-(290 \pm 25)/T)$	220–350	Watson, et al., 1976 [3]	(b)
$(1.20 \pm 0.10) \times 10^{-11}$	298		
$(2.17 \pm 0.43) \times 10^{-11} \exp(-(170 \pm 30)/T)$	205–366	Zahniser, Kaufman and Anderson, 1976 [4]	(c,d)
$(1.23 \pm 0.25) \times 10^{-11}$	295		
$(2.72 \pm 0.45) \times 10^{-11} \exp(-(298 \pm 39)/T)$	213–298	Kurylo and Braun, 1976 [5]	(b,d)
$(1.02 \pm 0.15) \times 10^{-11}$	298		
$(5.18 \pm 0.5) \times 10^{-11} \exp(-(418 \pm 28)/T)$	221–629	Clyne and Nip, 1976 [6]	(c)
$(1.33 \pm 0.26) \times 10^{-11}$	298		
$(1.3 \pm 0.3) \times 10^{-11}$	295	Leu and DeMore, 1976 [7]	(a)
Reviews and Evaluations			
$2.7 \times 10^{-11} \exp(-257/T)$	205–298	Watson, 1977 [8]	(e)
$3.34 \times 10^{-11} \exp(-310/T)$	205–464		
$2.7 \times 10^{-11} \exp(-257/T)$	205–298	NASA, 1977 [9]	(e)

Comments

(a) Discharge flow: mass spectrometric detection of O_3.

(b) Flash photolysis: resonance fluorescence detection of Cl.

(c) Discharge flow: resonance fluorescence detection of Cl.

(d) The A factors shown above are ~8% lower than those reported in the original papers due to a revision in the value used for the ozone absorption cross section.

(e) This evaluation was based on data obtained from Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976), and Clyne and Nip (1976).

Preferred Value

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

$k = 2.7 \times 10^{-11} \exp(-257/T)$ cm^3 molecule^{-1} s^{-1} over range 205–298 K.

Reliability

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

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

Comments on Preferred Values

The results reported for k at 298 K in references [3–6] are in good agreement, and have been used to determine the preferred value at this temperature. The values reported in references [7] (owing to the wide error limits) and [2] (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205–300 K. In this temperature range, the rate constants at any particular temperature agree to within (30–40%). Although the values of the activation energy obtained by Watson et al., and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently (~17%) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the value of the other four studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for E/R (170–418 K). However, there is no reason to prefer any one set of data to any other, therefore the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature ($\leq$466 K) experimental data would yield the following Arrhenius expression: $k = 3.34 \times 10^{-11} \exp(-310/T)$ cm^3 molecule^{-1} s^{-1}.

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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			
$(1.35 \pm 0.1) \times 10^{-13}$	298	Davis, Braun and Bass, 1970 [1]	(a,b,c)
$5.1 \times 10^{-11} \exp(-(1790 \pm 37)/T)$	300–686	Clyne and Walker, 1973 [2]	(d)
$(1.31 \pm 0.1) \times 10^{-13}$	300		
$(1.84 \pm 0.14) \times 10^{-11} \exp(-(1409 \pm 101)/T)$	295–490	Poulet, Le Bras and Combourieu, 1974 [3]	(d,e)
$(1.36 \pm 0.1) \times 10^{-13}$	295		
$(1.20 \pm 0.3) \times 10^{-13}$	295	Leu and DeMore, 1976 [4]	(d)
$(7.94 \pm 0.7) \times 10^{-12} \exp(-(1260 \pm 35)/T)$	218–401	Watson et al., 1976 [5]	(a,b)
$(1.13 \pm 0.1) \times 10^{-13}$	298		
$(6.51 \pm 0.79) \times 10^{-12} \exp(-(1229 \pm 27)/T)$	200–299	Whytock et al., 1977 [6]	(a,b,f)
$(1.13 \pm 0.07) \times 10^{-13}$	299		
$(1.84 \pm 0.28) \times 10^{-11} \exp(-(1545 \pm 52)/T)$	299–500		
$(1.08 \pm 0.07) \times 10^{-13}$	298	Michael and Lee, 1977 [7]	(b,g)
$(7.93 \pm 1.53) \times 10^{-12} \exp(-(1272 \pm 51)/T)$	218–322	Manning and Kurylo, 1977 [8]	(a,b)
$(1.04 \pm 0.1) \times 10^{-13}$	296		
$(8.2 \pm 0.6) \times 10^{-12} \exp(-(1320 \pm 20)/T)$	200–300	Zahniser, Berquist and Kaufman, 1978 [9]	(b,f,g)
$(0.99 \pm 0.15) \times 10^{-13}$	298		
$2.25 \times 10^{-11} \exp(-1623/T)$	300–500		
$(1.26 \pm 0.13) \times 10^{-13}$	298	Poulet, Le Bras and Combourieu, 1978 [10]	(d)
$(1.06 \pm 0.7) \times 10^{-11} \exp(-(1415 \pm 200)/T)$	268–423	Lin, Leu and DeMore, 1978 [11]	(d)
$(0.96 \pm 0.09) \times 10^{-13}$	296		
$(7.4 \pm 2.0) \times 10^{-12} \exp(-(1291 \pm 68)/T)$	220–298	Keyser, 1978 [12]	(b,f,g)
$(1.01 \pm 0.02) \times 10^{-13}$	298		
$(1.65 \pm 0.32) \times 10^{-11} \exp(-(1530 \pm 68)/T)$	298–423		
Relative Rate Coefficients			
(a) Relative to $Cl + H_2$:			
$1.50 \times 10^{-11} \exp(-1510/T)$	293–484	Pritchard, Pyke and Trotman-Dickenson, 1954 [13]	(h,j)
0.95×10^{-13}	298		
$1.41 \times 10^{-11} \exp(-1510/T)$	193–593	Knox and Nelson, 1959 [14]	(i,j)
0.89×10^{-13}	298		
(b) Relative to $Cl + C_2H_6$:			
$1.77 \times 10^{-11} \exp(-(1504 \pm 23)/T)$	232–633	Knox, 1955 [15]	(k,n)
1.13×10^{-13}	298		
$1.62 \times 10^{-11} \exp(-(1524 \pm 186)/T)$	349–563	Pritchard, Pyke and Trotman-Dickenson, 1955 [16]	(l,n)
0.97×10^{-13}	298		
$(3.1 \pm 0.6) \times 10^{-14}$	243	Lee and Rowland, 1977 [17]	(m)
$(1.6 \pm 0.2) \times 10^{-13}$	298		
$(4.0 \pm 0.5) \times 10^{-13}$	361		
$(1.85 \pm 0.18) \times 10^{-11} \exp(-(1528 \pm 21)/T)$	220–296	Lin, Leu and DeMore, 1978 [11]	(n,o)
$(1.09 \pm 0.05) \times 10^{-13}$	296		
(c) Relative to $Cl + CH_3Cl$:			
$1.53 \times 10^{-11} \exp(-(1503 \pm 75)/T)$	298–484	Pritchard, Pyke and Trotman-Dickenson, 1955 [16]	(p)
0.99×10^{-13}	298		
Reviews and Evaluations			
$7.29 \times 10^{-12} \exp(-1260/T)$	200–299	Watson, 1977 [18]	(q)
$7.3 \times 10^{-12} \exp(-1260/T)$	200–299	NASA, 1977 [19]	(q)

Comments

(a) Flash photolysis: resonance fluorescence detection of Cl.

(b) It is essential to use methane which is not contaminated with the higher alkanes (i.e., C_2H_6 and C_3H_8), even in the part per million (ppm) range owing to their enhanced reactivity toward atomic chlorine: $k/(Cl + C_2H_6) \sim 2 \times 10^{-3}$ at 298 K. Each of the studies [5–9, 12], except [1], reported the impurity levels to be low in the methane used in their studies ($C_2H_6 \leq 20-30$ ppm, and C_3H_8 non detectable).

(c) The value reported in the paper was probably overestimated by 10% by taking the relationship between I_f and [Cl] to be: $I_f \propto [Cl]^{0.9}$ (based on theoretical considerations, not experimental). If $I_f \propto [Cl]$, as found in other studies (for $[Cl] \leq 10^{12}$ cm^{-3}), then the value calculated for k would be 1.35×10^{-13} cm^3 molecule^{-1} s^{-1} (corrected value entered in the table). In addition, the methane used in this study was reported to contain ~100 ppm of C_2H_6, resulting in a further overestimate of k by ~5% (as the accuracy of the analysis is uncertain it is not possible to correct the data adequately).

(d) Discharge flow: mass spectrometric detection of CH_4 in excess of Cl. Consequently, the purity of CH_4 is not particularly critical. The accuracy of the results may be limited if γ(Cl), the heterogeneous wall removal coefficient of atomic chlorine varies upon addition of CH_4 to the flow system—this effect was reported in reference [2].

(e) Limited data which appear to be of low precision.

(f) In each of these studies non-linear Arrhenius behavior was observed.

(g) Discharge flow: resonance fluorescence detection of Cl.

(h) Competitive chlorination, reagent consumption. $k/k(Cl + H_2) = 0.32 \exp(+(830 \pm 75)/T)$; $k(Cl + H_2) = 4.7 \times 10^{-11} \exp(-2340/T)$ cm^3 molecule^{-1} s^{-1}.

(i) Competitive chlorination, product analysis. $k/k(Cl + H_2) = 0.30 \exp(+(830 \pm 30)/T)$; $k(Cl + H_2) = 4.7 \times 10^{-11} \exp(-2340/T)$ cm^3 molecule^{-1} s^{-1}.

(j) Combining the average value of $k/k(Cl + H_2) = (0.31 \exp(+830/T))$ with a measured range of values for $k(Cl + H_2)$ yields a set of absolute rate expressions for k.

The competitive chlorination studies were performed over a wide temperature range (193–593 K) and the difference in the activation energies was reported to remain constant (Whytock et al. [22] measured $k(Cl + H_2)$ from 200–500 K and reported linear Arrhenius behavior). Consequently combining a linear Arrhenius expression for $k(Cl + H_2)$ with the competitive chlorination results yields a linear Arrhenius expression for k between 193 and 593 K. This result conflicts with the findings of the direct studies of Cl + CH_4 [6,7,12] which reported non-linear Arrhenius behavior over the same temperature range. The preferred value for $k(Cl + H_2)$ is shown as entry (b) above—see the Cl + H_2 data sheet.

(k) Competitive chlorination, product analysis. $k/k(Cl + C_2H_6) = 0.23 \exp(-(1414 \pm 186)/T)$; $k(Cl + C_2H_6) = 7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1}. The expression shown has been modified by Lin et al. [11] from that shown in the original publication.

(l) Competitive chlorination, reagent consumption. $k/k(Cl + C_2H_6) = 0.21 \exp(-(1434 \pm 186)/T)$; $k(Cl + C_2H_6) = 7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1}.

(m) Competitive chlorination, product analysis. $k/k(Cl + C_2H_6) = (5.88 \pm 1.05) \times 10^{-4}$ at 243 K, $(2.78 \pm 0.31) \times 10^{-3}$ at 298 K, and $(6.67 \pm 0.89) \times 10^{-3}$ at 361 K. $k(Cl + C_2H_6) = 7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1}.

(n) These three expressions for $k/k(Cl + C_2H_6)$ can be seen to be in excellent agreement. A mean value of 0.23 $\exp(-1429/T)$ can be derived for $k/k(Cl + C_2H_6)$. Combining this value of $k/k(Cl + C_2H_6)$ with the preferred value for $k(Cl + C_2H_6)$ ($7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1}) yields: $k = 1.77 \times 10^{-11} \exp(-1519/T)$ cm^3 molecule^{-1} s^{-1}. The competitive chlorination studies were performed between 220 and 633 K, and within this temperature range the activation energy difference was reported to be constant. This, combined with the knowledge that the Cl + C_2H_6 reaction exhibits linear Arrhenius behavior between 220 and 604 K, means that these competitive chlorination experiments predict linear Arrhenius behavior for Cl + CH_4 between 220 and 600 K, which contradicts the findings of the direct studies [6,7,12].

(o) Competitive chlorination, product analysis. $k/k(Cl + C_2H_6) = (0.24 \pm 0.2) \exp(-(1438 \pm 21)/T)$; $k/k(Cl + C_2H_6)$ at 296 K $= (1.89 \pm 0.08) \times 10^{-3}$; $k(Cl + C_2H_6) = 7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1}.

(p) Competitive chlorination, reagent consumption. $k/k(Cl + CH_3Cl) = 0.45 \exp(-(247 \pm 75)/T)$; $k(Cl + CH_3Cl) = 3.4 \times 10^{-11} \exp(-1256/T)$ cm^3 molecule^{-1} s^{-1}.

(q) This value was based on the results of the four direct studies which measured k at stratospheric temperatures [5–7,9]. It did not consider the discharge flow: mass spectrometric results that determined k at and above 300 K [2–4] or any of the competitive chlorination results.

Preferred Value

$k = 1.04 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.9 \times 10^{-12} \exp(-1360/T)$ cm^3 molecule^{-1} s^{-1} over range 200–300 K.

$k(Cl + H_2)$/cm^3 molecule^{-1} s^{-1}	Reference	$k(Cl + CH_4)$/cm^3 molecule^{-1} s^{-1}	k_{CH_4} (298 K)/cm^3 molecule^{-1} s^{-1}
(a) $5.5 \times 10^{-11} \exp(-2375/T)$	[20]	$1.7 \times 10^{-11} \exp(-1545/T)$	0.95×10^{-13}
(b) $4.7 \times 10^{-11} \exp(-2340/T)$	[21]	$1.45 \times 10^{-11} \exp(-1510/T)$	0.91×10^{-13}
(c) $3.5 \times 10^{-11} \exp(-2290/T)$	[22]	$1.09 \times 10^{-11} \exp(-1460/T)$	0.81×10^{-13}
(d) $2.66 \times 10^{-11} \exp(-2230/T)$	[23]	$8.25 \times 10^{-12} \exp(-1400/T)$	0.75×10^{-13}
(e) $2.0 \times 10^{-11} \exp(-2164/T)$	[24]	$6.2 \times 10^{-12} \exp(-1334/T)$	0.71×10^{-13}

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta (E/R) = \pm 150$ K.

Comments on Preferred Values

The values reported from the absolute rate coefficient studies for k at 298 K range from 0.99 to 1.48×10^{-13} cm^3 molecule^{-1} s^{-1} with a mean value of 1.16×10^{-13} cm^3 molecule^{-1} s^{-1}. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.05×10^{-13} cm^3 molecule^{-1} s^{-1} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weighting to the values reported in references [5–9,11,12]. The values derived for k at 298 K from the competitive chlorination studies [11,12–16] range from $0.95-1.13 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, with an average value of 1.02×10^{-13} cm^3 molecule^{-1} s^{-1}. The preferred value was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been eight absolute studies of the activation energy. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported values it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three studies have been performed between ~200 and 500 K [6,9,12] and in each case a strong non-linear Arrhenius behavior was observed. This behavior tends to partially explain the large variance in the values of E/R reported between those other investigators who studied this reaction primarily below 300 K [5,8] and those who studied it primarily above 300 K [2,3,11]. The agreement below 300 K is very good, with values of (a) E/R ranging from 1229–1320 K, and (b) k at 230 K ranging from $(2.64-3.32) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The mean of the two discharge flow [9,12] results is 2.67×10^{-14} cm^3 molecule^{-1} s^{-1}, whilst the mean of the three flash photolysis [5,6,8] results is 3.19×10^{-14} cm^3 molecule^{-1} s^{-1}. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Above 300 K the three resonance fluorescence studies [6,9,12] reported (a) "averaged" values of E/R ranging from 1530–1623 K, and (b) values for k at 500 K ranging from $(7.74-8.76) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Three mass spectrometric studies [2,3,11] have been performed above 300 K with E/R values ranging from 1409–1790 K. The data of Poulet et al. [3] is sparse and scattered, that of Clyne and Walker [2] shows too strong of a temperature dependence (compared to all other absolute and competitive studies) and k at 298 K is ~20% higher than the preferred value at 298 K, whilst that of Lin et al. [11] is in fair agreement with the resonance fluorescence results. In conclusion, it should be stated that the best value of k from the absolute studies, both above and below 300 K, is obtained from the resonance fluorescence studies.

As stated in the earlier notes (j,n), the competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k at 230 K from $(2.11-2.54) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} with a mean value of 2.27×10^{-14} cm^3 molecule^{-1} s^{-1}. The preferred value is an expression which attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04×10^{-13} cm^3 molecule^{-1} s^{-1}, and at 230 K is 2.70×10^{-14} cm^3 molecule^{-1} s^{-1} (these averages include results from the three competitive chlorination systems). The preferred Arrhenius expression essentially yields values similar to those obtained in the discharge flow: resonance fluorescence studies.

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[23] Value reported by: Whytock, D. A., Lee, J. H., Michael, J. V. Payne, W. A., and Stief, L. J., J. Chem. Soc. Faraday Trans. I. **73,** 1530 (1977).

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$Cl + C_2H_6 \rightarrow HCl + C_2H_5$

$\Delta H^\circ = -22.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.0 \pm 1.5) \times 10^{-11}$	298	Davis, Braun, and Bass, 1970 [1]	(a,b)
$(7.29 \pm 1.23) \times 10^{-11} \exp(-(61 \pm 44)/T)$	222–322	Manning and Kurylo, 1977 [2]	(a)
$(5.93 \pm 0.44) \times 10^{-11}$	296		
$(5.5 \pm 0.5) \times 10^{-11}$	298	Watson et al., 1979 [3]	(a)
$8.3 \times 10^{-11} \exp(-(130 \pm 18)/T)$	220–604	Lewis et al., 1979 [4]	(c)
$(5.2 \pm 0.3) \times 10^{-11}$	298		
$(5.75 \pm 0.5) \times 10^{-11}$	298	Watson and Ray, 1979 [5]	(d)
Relative Rate Coefficients			
See the $Cl + CH_4$ data sheets			
Reviews and Evaluations			
$7.3 \times 10^{-11} \exp(-61/T)$	222–322	Watson, 1977 [6]	(e)

Comments

(a) Flash photolysis: resonance fluorescence detection of Cl.

(b) The value reported in reference [1] was probably overestimated by 10% (the authors assumed that $I_F \propto [Cl]^{0.9}$, whereas a linear relationship between I_F and [Cl] probably held under their experimental conditions), and therefore the corrected value has been entered in the data sheet.

(c) Discharge flow: resonance fluorescence detection of Cl.

(d) Discharge flow: mass spectrometric detection of C_2H_6.

(e) The preferred value was that reported by Manning and Kurylo [2].

Preferred Value

$k = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.7 \times 10^{-11} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1} over range 220–350 K.

Reliability

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

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

Comments on Preferred Values

These five studies are in excellent agreement at ~298 K. The two values reported ror E/R are in good agreement, considering the numerous experimental difficulties associated with determining small temperature dependences of rate constants. A simple least squares fit to all the available data would unfairly weight the data of Lewis et al. due to the larger temperature range covered. Therefore, the preferred value is an expression which best fits the data of references [2] and [4] between 220 and 350 K.

References

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$Cl + H_2CO \rightarrow HCl + HCO$

$\Delta H° = -67.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.48 \pm 0.5) \times 10^{-11}$	200–500	Michael et al., 1979 [1]	(a)
$(7.46 \pm 0.43) \times 10^{-11}$	298		
$(1.09 \pm 0.4) \times 10^{-10} \exp(-(131 \pm 98)/T)$	223–323	Anderson and Kurylo, 1979 [2]	(a)
$(7.18 \pm 0.61) \times 10^{-11}$	293		
Relative Rate Coefficients			
$(7.4 \pm 0.6) \times 10^{-11}$	298	Niki et al., 1978 [3]	(b)

Comments

(a) Flash photolysis: resonance fluorescence detection of Cl.

(b) Static cell: competitive photochlorination between H_2CO and C_2H_6 utilizing Fourier Transform Infrared Spectroscopy. $k/k(Cl + C_2H_6) = 1.3 \pm 0.1$ at 298 K. $k(Cl + C_2H_6)$ taken to be 5.7×10^{-11} cm^3 molecule^{-1} s^{-1}.

Preferred Value

$k = 7.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.9 \times 10^{-11} \exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over range 200–500 K.

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

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

Comments on Preferred Values

The preferred value at 298 K is taken to be an average of the three reported values which are in excellent agreement. The preferred values for the Arrhenius parameters were obtained from a least squares fit to all the data reported in references [1] and [2]. All data should be considered to be in good agreement.

References

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$Cl + HNO_3 \rightarrow HCl + NO_3$

$\Delta H° = -8.2$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.8 \pm 3.4) \times 10^{-15}$	295	Leu and DeMore, 1976 [1]	(a)
$1.5 \times 10^{-11} \exp(-(4378 \pm 856)/T)$	439–633	Poulet, LeBras, and Combourieu, 1978 [2]	(b)
$< 2 \times 10^{-17}$	298		
Reviews and Evaluations			
6.8×10^{-15}	295	Watson, 1977 [3]	(c)
$1 \times 10^{-11} \exp(-2170/T)$	200–300	NASA, 1977 [4]	(d)

Comments

(a) Discharge flow: mass spectrometric detection of HNO_3. The authors reported that the HNO_3 only decayed between 10 and 20% in the course of a typical experiment.

(b) Discharge flow: mass spectrometric detection of NO_2^+ (HNO_3 was monitored at m/e 46). Allowance was made for the contribution to the NO_2^+ signal by NO_2).

(c) Value reported by Leu and DeMore [1].

(d) This Arrhenius expression has an estimated A-factor, and a value of E/R which yields the value of k at 298 K reported by Leu and DeMore [1].

Preferred Value

$k \leq 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = {}^{+0.3}_{-2.5}$ at 298 K.

Comments on Preferred Values

Neither study can be considered to be definitive. Poulet et al. [2] postulated that Leu and DeMore [1] were observing removal of HNO_3 via a heterogeneous process. While this hypothesis is certainly tenable, the value of E/R reported by Poulet et al. [2] is much higher than would be expected (resulting in a surprisingly low value for k at 298 K). Although this reaction is not important in atmospheric chemistry, additional studies are required to provide accurate Arrhenius parameters. Until further data becomes available the preferred value is based on assuming that the data of Leu and DeMore [1] represents an upper limit. The uncertainties in k at 298 K allow for the data of Poulet et al. [2] to be correct. There is no preferred value for E/R.

References

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$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$

$\Delta H° = -6.6$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.1 \pm 0.4) \times 10^{-10} \exp(-(1787 \pm 70)/T)$	300–604	Clyne and Walker, 1973 [1]	(a)
$(4.5 \pm 0.45) \times 10^{-13}$	300		
$(3.36 \pm 0.71) \times 10^{-11} \exp(-(1250 \pm 57)/T)$	233–322	Manning and Kurylo, 1977 [2]	(b)
$(5.1 \pm 0.14) \times 10^{-13}$	296		
$(3.7 \pm 0.4) \times 10^{-11} \exp(-(1287 \pm 150)/T)$	245–350	Watson et al., 1978 [3]	(b)
$(4.87 \pm 0.5) \times 10^{-13}$	298		
Relative Rate Coefficients			
See Cl + CH_4 data sheets.			
Reviews and Evaluations			
$3.4 \times 10^{-11} \exp(-1256/T)$	233–350	Watson, 1977 [4]	(c)

Comments

(a) Discharge flow: mass spectrometric detection of CH_3Cl.

(b) Flash photolysis: resonance fluorescence detection of Cl.

(c) A least squares fit of the individual data points of Manning and Kurylo [2] and Watson et al. [3] has been used to derive the preferred Arrhenius expression for k. This expression should be used with caution outside the stated temperature range. A preferred value of $(4.9 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} was derived for k at 298 K from the data of the three direct studies.

Preferred Value

$k = 4.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.4 \times 10^{-11} \exp(-1260/T)$ cm^3 molecule^{-1} s^{-1} over range 233–350 K.

Reliability

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

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

Comments on Preferred Values

The results are in good agreement at 298 K. However, the value of the activation energy measured by Watson et al. and Manning and Kurylo is significantly lower than that measured by Clyne and Walker, as was also the case when these groups measured the rate constant for the Cl + CH_4 reaction. The discharge flow: mass spectrometric technique may be subject to a systematic error, and it is therefore recommended that the flash photolysis results be used for stratospheric calculations in the 200–300 K temperature range (see discussion of the Cl + CH_4 studies). In the discussion of the Cl + CH_4 reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the A factor (as measured in the flash photolysis studies) is already $\sim 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and the significant curvature which would be required in the Arrhenius plot to make the data compatible would result in an unreasonably high value for A ($>2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

References

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$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$ (1)

$\rightarrow ClONO + ClO$ (2)

$\Delta H^\circ(1) = -77$ kJ mol^{-1}

$\Delta H^\circ(2) = +4$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8_{-6}^{+8}) \times 10^{-14}$	245	Ravishankara et al., 1976 [1]	(a)
$(1.68_{-1.33}^{+6.44}) \times 10^{-12} \exp(-(607 \pm 388)/T)$	224–273	Kurylo and Manning, 1977 [2]	(a)
2.2×10^{-13}	298*		
Reviews and Evaluations			
$1.68 \times 10^{-12} \exp(-607/T)$	224–273	NASA, 1977 [3]	(b)

Comments

(a) Flash photolysis: resonance fluorescence detection of Cl.

(b) This value is based on the data reported by Kurylo and Manning [2].

Preferred Value

$k = 2.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.7 \times 10^{-12} \exp(-610/T)$ cm^3 molecule^{-1} s^{-1} over range 224–273 K.

Reliability

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

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

Comments on Preferred Values

Considering the experimental difficulties associated with handling $ClONO_2$, and the low precision of the data of Ravishankara et al. [1], the results are in fair agreement at 245 K. Therefore, the preferred value is taken to be that reported by Kurylo and Manning [2]. Neither study reported any information which could be used to assess the relative importance of the two channels. The A-factor is lower than would be expected from theoretical considerations. However, this may be an artifact of the restricted temperature range over which the reaction was studied.

References

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$HO + HCl \rightarrow H_2O + Cl$

$\Delta H^\circ = -67.4$ kJ mol^{-1}

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.3×10^{-11}	1920–1940	Wilson, O'Donovan, and Fristrom, 1969 [1]	(a)
$(6.4 \pm 1.5) \times 10^{-13}$	295	Takacs and Glass, 1973 [2]	(b)
$(2.0 \pm 0.1) \times 10^{-12} \exp(-(312 \pm 10)/T)$	225–460	Anderson, Zahniser and Kaufman, 1974 [3]	(c)
$(6.7 \pm 0.4) \times 10^{-13}$	297		
$(4.1_{-1.4}^{+2.0}) \times 10^{-12} \exp(-(528 \pm 25)/T)$	210–460	Smith and Zellner, 1974 [4]	(d)
$(6.9 \pm 1.0) \times 10^{-13}$	298		
$(3.25 \pm 0.3) \times 10^{-12} \exp(-(473 \pm 39)/T)$	250–402	Ravishankara et al., 1977 [5]	(e)
$(6.65 \pm 0.39) \times 10^{-13}$	298		
$(6.6 \pm 1.7) \times 10^{-13}$	293	Hack, Mex, and Wagner, 1977 [6]	(b,f)
Reviews and Evaluations			
$2.96 \times 10^{-12} \exp(-425/T)$	220–300	Watson, 1977 [7]	(g)
$3.0 \times 10^{-12} \exp(-425/T)$	220–300	NASA, 1977 [8]	(g)

Comments

(a) Flame inhibition study.

(b) Discharge flow: EPR detection of HO.

(c) Discharge flow: resonance fluorescence detection of HO.

(d) Flash photolysis: resonance absorption detection of HO.

(e) Flash photolysis: resonance fluorescence detection of HO.

(f) Hack et al., report that E/R is small between 293 and 567 K, but the lack of an adequate data base precluded a quantitative assessment of its value.

(g) This evaluation was based on the data of Anderson et al. (1974), Smith and Zellner (1974), and Ravishankara et al. (1977).

Preferred Value

$k = 6.6 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 3.0 \times 10^{-12} \exp(-425/T)$ cm^3 $molecule^{-1}$ s^{-1} over range 210–460 K.

Reliability

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

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

Comments on Preferred Values

There is good agreement between these five groups of workers at ~298 K, and the preferred value at this temperature is the average of the five. The Arrhenius expression was derived by giving an equal weighting to data reported in references [3–5].

References

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$HO + ClO \rightarrow HO_2 + Cl$ (1)

$\rightarrow HCl + O_2$ (2)

ΔH° (1) = −18 kJ mol^{-1}

ΔH° (2) = −234 kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.1 \pm 1.3) \times 10^{-12}$	298	Leu and Lin, 1979 [1]	(a)

Comments

(a) Discharge flow: resonance fluorescence detection of HO in the presence of excess ClO. A lower limit of 0.65 was determined for k_1/k by measuring $[HO_2]_{produced}/[HO]_{removed}$. As HO_2 could be removed by secondary kinetic processes, the true value of k_1/k may even be unity.

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 Values

To date there has only been one determination of k. No preferred value is given for the branching ratio. Data are urgently required for the temperature dependence of not only k, but individually for k_1 and k_2.

References

[1] Leu, M. T., and Lin, C. L., Geophys. Res. Lett., **6**, 425 (1979).

$HO + ClONO_2 \rightarrow HOCl + NO_3$ (1)

$\rightarrow HO_2 + ClONO$ (2)

$\rightarrow HNO_3 + ClO$ (3)

ΔH° (1) = −72 kJ mol^{-1}

ΔH° (2) = −20 kJ mol^{-1}

ΔH° (3) = −98 kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.7 \pm 0.4) \times 10^{-13}$	245	Ravishankara et al., 1977 [1]	(a)
$(1.19 \pm 0.1) \times 10^{-12} \exp(-(333 \pm 22)/T)$	246–387	Zahniser, Chang and Kaufman, 1977 [2]	(b)
$(3.93 \pm 0.11) \times 10^{-13}$	295		
Reviews and Evaluations			
$1.2 \times 10^{-12} \exp(-333/T)$	246–387	NASA, 1977 [3]	(c)

Comments

(a) Static system flash photolysis: resonance fluorescence detection of HO. Handling $ClONO_2$ was reported to be more difficult than usual owing to its instability on metal or wet surfaces.

(b) Discharge flow: resonance fluorescence detection of HO.

(c) This evaluation is based on the data of Zahniser et al. [2].

Preferred Value

$k = 3.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.2 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over range 246–387 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The results are in good good agreement at ~245 K (within 25%) considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser et al. [2]. Neither study reported any data on the reaction products.

References

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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			
$(3.6 \pm 0.8) \times 10^{-14}$	298	Howard and Evenson, 1976 [1]	(a)
$(1.84 \pm 0.18) \times 10^{-12} \exp(-(1097 \pm 35)/T)$	240–400	Davis et al., 1976 [2]	(b)
$(4.3 \pm 0.2) \times 10^{-14}$	298		
$4.1 \times 10^{-12} \exp(-(1359 \pm 150)/T)$	298–422	Perry, Atkinson, and Pitts, 1976 [3]	(b)
$(4.4 \pm 0.5) \times 10^{-14}$	298		
Relative Rate Coefficients			
$(4.5 \pm 0.9) \times 10^{-14}$	298	Davis, Hogan, and Oh, 1975 [4]	(c)
9.1×10^{-14}	298	Cox et al., 1976 [5]	(d)
$(2.7 \pm 0.6) \times 10^{-14}$	305	Butler, Solomon, and Snelson, 1978 [6]	(e)
Reviews and Evaluations			
$2.18 \times 10^{-12} \exp(-1142/T)$	240–422	Watson, 1977 [7]	(f)
$2.2 \times 10^{-12} \exp(-1142/T)$	240–422	NASA, 1977 [8]	(f)

Comments

(a) Discharge flow: laser magnetic resonance detection of HO.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) Davis et al. [4] photolyzed H_2O in a static cell in the presence of CO and CH_3Cl, producing steady-state concentrations of HO (the exact steady state concentration of HO was governed by the concentrations of CO and CH_3Cl which were added to the cell). Thus relative rate constants, $k/k(HO + CO)$ were obtained by monitoring relative [HO] using laser induced fluorescence. $k/k(HO + CO) = 0.3 \pm 0.06$; $k(HO + CO) = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (diluent gas = He).

(d) $k/k(HO + CH_4) = 12.2$. $k(HO + CH_4) = 7.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

(e) Relative to HO + CO at 400 torr of $N_2 + O_2$. $k/k(HO + CO) = 0.11 \pm 0.03$; $k(HO + CO) = 2.37 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 400 torr of $N_2 + O_2$.

(f) These evaluated expressions are based on all the absolute rate coefficient data (references [1–3], and the data of reference [4]).

Preferred Value

$k = 4.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.2 \times 10^{-12} \exp(-1140/T)$ cm^3 molecule^{-1} s^{-1} over range 240–422 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 only absolute rate coefficient data. The studies which determined $k/k(HO + CO)$ are excluded until the kinetic behavior between HO + CO is better understood, and the accuracy of the $HO + CH_3Cl$: $HO + CH_4$ study (reference [5]) was probably no better than a factor of 2. Within the temperature range covered by studies [2] and [3] (298–400 K) the results agree to within 20%. However, the value of k obtained by using the Arrhenius expression of reference [3] at 240 K would be ~40% lower than the value obtained directly at that temperature by reference [2]. The preferred value was obtained from a least squares fit to the data in references [2] and [3]. Equal weighting was given to each of the bimolecular rate constants (3 from [3], and 5 from [2]).

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$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$

$\Delta H^\circ = -66$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.21 \times 10^{-12} \exp(-(1636 \pm 151)/T)$	297–434	Atkinson, Hansen and Pitts, 1975 [1]	(a)
4.7×10^{-15}	297		
$(3.4 \pm 0.7) \times 10^{-15}$	298	Howard and Evenson, 1976 [2]	(b)
$(9.25 \pm 1.0) \times 10^{-13} \exp(-(1575 \pm 71)/T)$	250–350	Watson et al., 1977 [3]	(a)
$(4.8 \pm 0.2) \times 10^{-15}$	298		
$(1.2 \pm 0.16) \times 10^{-12} \exp(-(1657 \pm 39)/T)$	253–427	Chang and Kaufman, 1977 [4]	(c)
$(4.25 \pm 0.28) \times 10^{-15}$	296		
$(2.1 \pm 0.6) \times 10^{-12} \exp(-(1780 \pm 150)/T)$	263–373	Handwerk and Zellner, 1978 [5]	(d)
$(4.6 \pm 0.8) \times 10^{-15}$	293		
$(9.6 \pm 1.6) \times 10^{-12} \exp(-(2311 \pm 200)/T)$	294–426	Clyne and Holt, 1979 [6]	(c)
$(3.3 \pm 0.7) \times 10^{-15}$	294		
Reviews and Evaluations			
$1.21 \times 10^{-12} \exp(-1648/T)$	250–434	Watson, 1977 [7]	(e)
$1.20 \times 10^{-12} \exp(-1660/T)$	250–434	NASA, 1977 [8]	(f)

Comments

(a) Flash photolysis: resonance fluorescence detection of HO.

(b) Discharge flow: laser magnetic resonance detection of HO.

(c) Discharge flow: resonance fluorescence detection of HO.

(d) Flash photolysis: resonance absorption detection of HO.

(e) Based on the data reported in references [1–3].

(f) Based on the data reported in references [1–4].

Preferred Value

$k = 4.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-1670/T)$ cm^3 molecule^{-1} s^{-1} over range 240–400 K.

Reliability

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

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

Comments on Preferred Values

The values reported for k at ~298 K are in fair agreement. Consequently the preferred value for k at 298 K is a simple mean of all the results (corrected to 298 K). However, the Arrhenius expression reported by Clyne and Holt is in poor agreement with those reported in references [1,3–5], and as such the data reported by Clyne and Holt is not considered when deriving the preferred Arrhenius expression. The preferred Arrhenius expression was derived to best fit the data reported in references [1,3–5].

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$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$

$\Delta H° = -92$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.4) \times 10^{-14}$	298	Howard and Evenson, 1976 [1]	(a)
$1.75 \times 10^{-12} \exp(-(1253 \pm 150)/T)$	298–423	Perry, Atkinson, and Pitts, 1976 [2]	(b)
$(2.7 \pm 0.3) \times 10^{-14}$	298		
$(1.87 \pm 0.2) \times 10^{-12} \exp(-(1245 \pm 26)/T)$	245–375	Watson et al., 1977 [3]	(b)
$(2.88 \pm 0.3) \times 10^{-14}$	298		
$(1.16 \pm 0.17) \times 10^{-12} \exp(-(1070 \pm 40)/T)$	241–396	Chang and Kaufman, 1977 [4]	(c)
$(3.04 \pm 0.11) \times 10^{-14}$	296		
$(4.75 \pm 0.9) \times 10^{-12} \exp(-(1430 \pm 100)/T)$	293–413	Clyne and Holt, 1979 [5]	(c)
$(3.54 \pm 0.26) \times 10^{-14}$	293		
Reviews and Evaluations			
$1.59 \times 10^{-12} \exp(-1204/T)$	245–423	Watson, 1977 [6]	(d)
$1.3 \times 10^{-12} \exp(-1127/T)$	241–423	NASA, 1977 [7]	(e)

Comments

(a) Discharge flow: laser magnetic resonance detection of HO.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) Discharge flow: resonance fluorescence detection of HO.

(d) Based on the data of references [1–3].

(e) Based on the data of references [1–4].

Preferred Value

$k = 2.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5 \times 10^{-12} \exp(-1180/T)$ cm^3 molecule^{-1} s^{-1} over range 240–400 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 derived using the data reported in references [1–4]. The data of Clyne and Holt [5] were not considered as they are in poor agreement with the other data within the temperature range studied, e.g. there is a difference of ~65% at 400 K.

References

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$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$

$\Delta H^\circ = -94\ \mathrm{kJ\ mol^{-1}}$

Rate coefficient data

$k/\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.3) \times 10^{-14}$	298	Howard and Evenson, 1976 [1]	(a)
$(3.72 \pm 0.4) \times 10^{-12} \exp(-(1627 \pm 50)/T)$	260–375	Watson et al., 1977 [2]	(b)
$(1.59 \pm 0.2) \times 10^{-14}$	298		
$(1.9 \pm 0.24) \times 10^{-12} \exp(-(1331 \pm 37)/T)$	275–405	Chang and Kaufman, 1977 [3]	(c)
$(2.2 \pm 0.3) \times 10^{-14}$	298		
$(2.4 \pm 0.8) \times 10^{-12} \exp(-(1394 \pm 113)/T)$	293–430	Clyne and Holt, 1979 [4]	(c)
$(1.81 \pm 0.16) \times 10^{-14}$	293		
$(5.4 \pm 1.8) \times 10^{-12} \exp(-(1810 \pm 100)/T)$	253–363	Kurylo et al., 1979 [5]	(b)
$(1.08 \pm 0.20) \times 10^{-14}$	296		
$(5.03 \pm 1.27) \times 10^{-12} \exp(-(1798 \pm 91)/T)$	278–457	Jeong and Kaufman, 1979 [6]	(c,g)
$(1.06 \pm 0.09) \times 10^{-14}$	293		
Relative Rate Coefficients			
3.0×10^{-14}	298	Cox et al., 1976 [7]	(d)
Reviews and Evaluations			
$3.72 \times 10^{-12} \exp(-1627/T)$	260–375	Watson, 1977 [8]	(e)
$3.5 \times 10^{-12} \exp(-1562/T)$	260–405	NASA, 1977 [9]	(f)

Comments

(a) Discharge flow: laser magnetic resonance detection of HO.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) Discharge flow: resonance fluorescence detection of HO.

(d) $k/k(HO + CH_4) = 4.0$; $k(HO + CH_4) = 7.5 \times 10^{-15}\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

(e) Based on the results of Watson et al. [2].

(f) Evaluation based on the data reported in references [1–3].

(g) This is not the expression given in the abstract of [6]. It is given in the body of the paper and results from a data analysis which includes reasonable estimates of systematic errors.

Preferred Value

$k = 1.2 \times 10^{-14}\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ at 298 K.

$k = 5.1 \times 10^{-12} \exp(-1800/T)\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ over range 250–460 K.

Reliability

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

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

Comments on Preferred Values

This evaluation is based on the recent data of Kurylo et al. [5] and Jeong and Kaufman [6] whose results are in excellent agreement. The earlier results [1–4,7] are rejected in favor of the recent results. The CH_3CCl_3 used in the early studies may have been contaminated with olefinic impurities. The *A*-factors reported in references [5] and [6] appear to be more reasonable than those reported in references [3] and [4] which are somewhat lower than might be expected for H abstraction from a molecule containing a methyl group. This evaluation is different from that reported in CODATA Bulletin #33 [10] which was based on the data reported in references [1–4].

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$ClO + HO_2 \rightarrow HOCl + O_2$ (1)
$\rightarrow HCl + O_3$ (2)
$\rightarrow HOOClO$ (3)

$\Delta H^\circ(1) = -182$ kJ mol^{-1}

$\Delta H^\circ(2) = -53$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 1.5) \times 10^{-12}$	298	Birks and Leck, 1979 [1]	(a)
$(3.8 \pm 0.7) \times 10^{-12}$	298	Reimann and Kaufman, 1978 [2]	(b)
$(8.5 \pm 1.9) \times 10^{-13}$	298	Poulet, Le Bras, and Combourieu, 1978 [3]	(c)
$(6.0 \pm 1.2) \times 10^{-12}$	298	Stimpfle, Perry and Howard, 1979 [4]	(d)
Reviews and Evaluations			
2×10^{-13}	298	NASA, 1977 [5]	(e)

Comments

(a) Discharge flow: mass spectrometric detection of HOCl.

(b) Discharge flow: resonance fluorescence detection of HO (unreacted HO_2 is converted to HO via the rapid $NO + HO_2 \rightarrow NO_2 + HO$ reaction).

(c) Discharge flow: mass spectrometric detection of HO_2. HOCl was observed as a reaction product.

(d) Discharge flow: laser magnetic resonance detection of HO_2.

(e) There were no experimental data. k was assumed to be intermediate between $k(HO_2 + HO_2)$ and $k(ClO + ClO)$.

Preferred Value

$k = 5.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value was obtained by taking a simple mean of the results reported in studies [1,2,4]. This procedure was adopted, because the value reported in reference [3] is significantly lower than those reported in references [1,2,4]. Because not all of the studies have yet been published some of the values may change prior to publication. As for any radical-radical reaction the magnitude of the temperature dependence is expected to be small ($E/R = 0^{+200\text{ K}}_{-500\text{ K}}$). Although process (1) is expected to be the dominant reaction channel, and HOCl has been observed to be a reaction product [1,3], there is no data concerning process (2) (of stratospheric importance when $k_2 \geq 0.01\, k_1$).

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$ClO + NO \rightarrow Cl + NO_2$

$\Delta H^\circ = -38.1$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>3 \times 10^{-13}$	300	Coxon, 1968 [1]	
$(1.7 \pm 0.2) \times 10^{-11}$	298	Clyne and Watson, 1974 [2]	(a)
$(5.72 \pm 0.18) \times 10^{-12} \exp(+(296 \pm 20)/T)$	227–415	Leu and DeMore, 1978 [3]	(a)
$(1.53 \pm 0.11) \times 10^{-11}$	299		
$(1.75 \pm 0.2) \times 10^{-11}$	298	Watson and Ray, 1979 [4]	(a)
Relative Rate Coefficients			
$1.4 \times 10^{-11} \exp(+(116 \pm 200)/T)$	230–295	Zahniser and Kaufman, 1977 [5]	(b)
$(2.2 \pm 0.4) \times 10^{-11}$	295		
Reviews and Evaluations			
$8.0 \times 10^{-12} \exp(+250/T)$	220–298	Watson, 1977 [6]	(c)
$1.0 \times 10^{-11} \exp(+200/T)$	230–295	NASA, 1977 [7]	(d)

Comments

(a) Discharge flow: mass spectrometric detection of ClO.

(b) The value of k was measured relative to $k(Cl + O_3)$ by utilizing the discharge flow: resonance fluorescence technique to monitor steady state concentrations of Cl atoms in the presence of NO and O_3. The tabulated values of k were derived by combining the experimentally determined values of $k/k(Cl + O_3)$ of $0.52 \exp(+(373 \pm 75)/T)$, and 1.85 ± 0.2 at 298 K, with the preferred value of $2.7 \times 10^{-11} \exp(-257/T)$ cm^3 molecule^{-1} s^{-1} for $k(Cl + O_3)$ taken from this evaluation. An alternate expression of $1.13 \times 10^{-11} \exp(+(200 \pm 100)/T)$ cm^3 molecule^{-1} s^{-1} was reported in the original publication by using a value for $k(Cl + O_3)$ of $2.2 \times 10^{-11} \exp(-170/T)$ cm^3 molecule^{-1} s^{-1} which was determined by Zahniser et al. [8] in the same experimental apparatus. See the O + ClO reaction, comment (e), for further pertinent discussion.

(c) The preferred value at 298 K was obtained by taking the mean of the three reported values [2,3,5]. The Arrhenius expression was derived by taking an average of the two values of E/R (the values shown in the original publications), and the A-factor was adjusted so that the expression yielded the preferred value of 1.85×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.

(d) The recommended rate constant was based on a value of k at 298 K equal to the average of two available experimental measurements (Clyne and Watson, 1974; and Zahniser and Kaufman, 1977), and the temperature dependence reported by Zahniser and Kaufman (1977).

Preferred Value

$k = 1.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 8.9 \times 10^{-12} \exp(+210/T)$ cm^3 molecule^{-1} s^{-1} over range 227–415 K.

Reliability

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

Comments on Preferred Values

The results of the three mass spectrometric studies [2–4] are in excellent agreement at 298 K. However, until it can be shown that the value reported in reference [5] is in error, the preferred value at 298 K is taken to be the mean of the results reported in references [2–5]. The temperature dependences reported in references [3] and [5] are in fair agreement. The Arrhenius expression was derived by taking the average of the two values of E/R, and the A-factor was adjusted so that the expression yielded the preferred values of 1.8×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.

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$ClO + NO_2 + M \longrightarrow ClONO_2 + M$

$\Delta H^\circ = -109$ kJ mol^{-1}

Low Pressure Rate Coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.2) \times 10^{-31}$ [N_2]	297	Zahniser, Chang and Kaufman, 1977 [1]	(a)
$(8.3 \pm 0.1) \times 10^{-32}$ $(T/300)^{-3.15}$ [He]	251–365		
$(4.4 \pm 0.66) \times 10^{-33}$ exp$(1087/T)$ [N_2]	250–356	Birks et al., 1977 [2]	(b)
1.8×10^{-31} [N_2]	298		
$(9.3 \pm 0.28) \times 10^{-32}$ [He]	297		
$(3.69 \pm 0.24) \times 10^{-33}$ exp$(1150/T)$ [N_2]	298–417	Leu, Lin and DeMore, 1977 [3]	(c)
1.8×10^{-31} [N_2]	298		
$(2.66 \pm 0.35) \times 10^{-33}$ exp$(1140/T)$ [He]	248–417		
1.2×10^{-31} [He]	298		
1.4×10^{-31} [N_2]	298	Handwerk and Zellner, 1978 [4]	(d)
0.6×10^{-31} $(T/298)^{-2.4}$ [N_2]	333–363	Knauth, 1978 [6]	(e)
$(1.0 \pm 0.3) \times 10^{-31}$ [He]	298	Stimpfle, Perry and Howard, 1978 [7]	(f)
$(2.1 \pm 0.6) \times 10^{-31}$ [N_2]	298		
$(1.5 \pm 0.5) \times 10^{-31}$ [O_2]	298		
4.7×10^{-33} exp$(1056/T)$ [N_2]	274–339	Cox and Lewis, 1979 [8]	(g)
1.6×10^{-31} [N_2]	298		
Reviews and Evaluations			
1.8×10^{-31} $(T/298)^{-3.34}$ [N_2]	200–300	NASA, 1977 [9]	(h)
$(1.6 \pm 0.2) \times 10^{-31}$ $(T/298)^{-3.0}$ [N_2]		Zellner, 1978 [5]	

Comments

(a) Discharge flow system study with ClO detection by Cl resonance fluorescence after conversion by added NO. Pressure range 1.5–6.5 Torr; practically no fall-off corrections are required.

(b) Discharge flow system study with mass spectrometric detection. Pressure range 1–5 Torr; practically no fall-off corrections required.

(c) Discharge flow system study with mass spectrometric detection. Pressure range 1–9 Torr. Relative efficiencies of M, N_2:He:Ar = 1.0: 0.68: 0.65.

(d) Flash photolysis study.

(e) From thermal decomposition of $ClONO_2$ in flow system converted with equilibrium constant. Pressure range 20–375 Torr; assumed that the reaction was in the low pressure range.

(f) Discharge flow system; laser magnetic resonance detection of ClO.

(f) Modulated photolysis; UV absorption detection of ClO. Pressure range studied 25–612 Torr, small deviations from third order observed near 1 atm.

(h) Based on the data of ref. [1]. The expression for the [M]-dependence of k, given as proposed by ref. [1], should not be used since it diverges outside the indicated pressure range.

Preferred Value

$k_0 = 1.7 \times 10^{-31} (T/300)^{-3.0}$ [N_2] over range 250–400 K.
$k_0 = 1.0 \times 10^{-31} (T/300)^{-3.0}$ [He] over range 250–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ over range 250–400 K.

Comments on Preferred Values

Good agreement between various measurements consistent with theoretical analysis in ref. [5].

High Pressure Rate Coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$> (3 \pm 1) \times 10^{-12}$	298	Handwerk and Zellner, 1978 [4]	(a)
Reviews and Evaluations			
1.45×10^{-11}	298	Smith and Golden, 1978 [10]	(b)
0.62×10^{-11}	298	Zellner, 1977 [11]	(c)
$(1.2 \pm 0.4) \times 10^{-11}$	298	Zellner, 1978 [5]	(d)

Comments

(a) Flash photolysis at 625 Torr of N_2 to be extrapolated to k_∞.

(b) Modified RRKM calculation.

(c) Transition state theory with maximum free energy calculation.

(d) Based on ref. [4] with extrapolation to k_∞.

Preferred Value

$k_\infty = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ over range 200–400 K.

Comments on Preferred Values

Value not well defined and new measurements at pressures above 1 atm are needed.

Intermediate Fall-off Range

From the preferred values one derives $[N_2]_c \simeq 7 \times 10^{19}$ molecule cm^{-3} at 300 K and $[N_2]_c \simeq 2 \times 10^{19}$ molecule cm^{-3} at 200 K. One estimates $F_c \simeq 0.8 \pm 0.1$ at 200 K and $F_c \simeq 0.7 \pm 0.1$ at 300 K.

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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
230–390	Ferguson, Slotin, and Style, 1936 [1]	(a)
290–450	Jaffe and DeMore, 1977 [2]	(b,c)
200–450	Molina and Molina, 1978 [3]	(b,d)
200–420	Knauth, Alberti, and Clausen, 1979 [4]	(b,e)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_2 \simeq 1$	~310	Molina, Ishiwata and Molina, 1979 [5]	(f)

Comments

(a) Plate photometry. Optical pathlength = 1000 cm. $T = 318$ K. HOCl produced in the gas phase by distillation of a 0.2 M solution of HOCl.

(b) The ultraviolet absorption spectrum of HOCl was determined from the vapor phase equilibrium $Cl_2O + H_2O \rightleftharpoons 2\ HOCl$.

(c) K_{eq} was estimated to be 0.07 ± 0.01 at 298 K. Optical pathlength = 10 cm.

(d) K_{eq} was estimated to be 0.25 at 298 K. Optical pathlengths of 10 and 180 cm were used. Although Molina and Molina reported that K_{eq} should not be less than 0.2, or greater than 0.35, they demonstrated the effect of assuming different values of K_{eq} on their calculated values of σ. Whereas calculated values of σ between 320 nm and 380 nm are insensitive to the assumed value of K_{eq}, below 320 nm the calculated values of σ are quite sensitive to the value of K_{eq}.

(e) K_{eq} was determined to be 0.132 ± 0.008 at 333 K. From this value of K_{eq} a value of 0.082 was derived for K_{eq} at 298 K. Optical pathlengths of 10.57 and 100 cm were used. Four isobestic points were observed for HOCl and Cl_2O at 214, 233, 335 and 380 nm. Spectral resolution ranged between 0.3 and 1.0 nm.

(f) A Cl_2O:H_2O:HOCl equilibrium mixture was photolyzed using a narrow line laser at four wavelengths close to 310 nm which were coincident with transitions in the $A^2\Sigma$–$X^2\Pi(0-0)$ absorption system of OH. Absolute OH concentrations were monitored using the calibrated laser induced resonance fluorescence technique. Using the HOCl absorption cross sections reported by Knauth et al. [4] and the measured absolute OH concentrations, it was deduced that Φ_2 has a value close to unity.

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. The studies of Jaffe and DeMore [2], Molina and Molina [3], and Knauth et al. [4] 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 constant determined by Knauth et al. is assumed to be most accurate due to their use of higher cell temperatures. Their derived value of 0.08 at 298 K is in good agreement with that reported by Jaffe and DeMore. 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. (see fig. 2 reference [3]). Consequently, assuming that the correct value of K_{eq} at 298 K is ~0.08 there is good agreement between the results of Molina and Molina, and Knauth et al. The early results of Ferguson et al. [1] are rejected, as are the results of Jaffe and DeMore whose values for σ at $\lambda > 290$ nm are now thought to be too large. In contrast to these experimental studies which show a quite strong absorption band extending to ~400 nm, the theoretical predictions of Jaffe and Langhoff [6] and Hirsch et al. [7] indicate negligible absorption at all wavelengths greater than 300 nm. Unpublished data of Timmons, and Hisatsune, quoted in Jaffe and Langhoff, also show negligible absorption beyond 300 nm. However, the results of these theoretical calculations, and the data of Timmons, and Hisatsune, are at present rejected in favor of the results of Knauth et al. [4]. A study of the absorption cross sections at stratospheric temperatures, and in an anhydrous environment, are required before the spectrum of HOCl can be considered to be well known. The preferred value of unity for Φ_2 is based on the experimental data of Molina et al. [5] at ~310 nm, and the theoretical calculations of Jaffe and Langhoff [6], and Hirsch et al. [7] which show that all low-lying excited states of HOCl are unstable relative to dissociation into, and correlate with, $HO(^2\Pi)$ and Cl.

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COFCl + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/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(^{3}P)	(5)	706	169

Note: ΔH°_{298} values are given since the heat of formation of COFCl at 0 K is not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
186–226	Chou et al., 1977 [1]	(a)

Quantum Yield Data: No experimental data available.

Comments

(a) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals. The spectrum shows some structure.

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.

References

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$ClONO_2$ + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ mol^{-1}	$\lambda_{\text{threshold}}$/nm
$ClONO_2$ + $h\nu \rightarrow$ ClO + NO_2	(1)	109	1100
$\rightarrow$ Cl + NO_3	(2)	166	721
$\rightarrow$ ClONO + O(^{3}P)	(3)	306	391
$\rightarrow$ ClONO + O(^{1}D)	(4)	496	241

Note: ΔH°_{298} values are given since the heats of formation of $ClONO_2$ and ClONO at 0 K are not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
215–300	Martin and Gareis, 1956 [1]	(a)
186–460	Rowland, Spencer and Molina, 1976 [2]	(b)
185–460	Jesson, Glasgow and Meakin, 1976 [3]	(c)
190–450	Molina and Molina, 1979 [4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_3 = 1$	302.5	Smith, Chou, and Rowland, 1977 [5]	(e)
$\Phi_2 \sim 1$	260–380	Chang et al., 1979 [6]	(f)

Comments

(a) Graphical representation of data.

(b) Absorption cross sections measured at 296 K using an optical path length of 10 cm. Values tabulated and shown graphically at 5 nm intervals.

(c) Absorption cross sections measured using an optical pathlength of 10 cm. Graphical representation of data.

(d) Absorption cross sections determined at 227 K, 243 K and 296 K with a spectral resolution of 0.2 nm using optical pathlengths of 10 and 180 cm. Values tabulated and shown graphically at 5 nm intervals.

(e) Photolysis of pure $ClONO_2$ (10–100 Torr) at 302.5 nm and 295 K using gas chromatography and infra-red spectroscopy for a quantitative product analysis. From the following measurements; $\Phi(-ClONO_2) = 4.0 \pm 0.6$; $\Phi(O_2) = 1.0 \pm 0.15$; $\Phi(Cl_2) = 2.0 \pm 0.3$ and $\Phi(N_2O_5) = 2_{-1}^{+2}$; and an assumed reaction mechanism, it was concluded that the dominant primary photolytic products are ClONO and $O(^3P)$. This conclusion was supported by the observation that neither HCl nor HNO_3 were produced upon photolysis of $ClONO_2/C_2H_6$ mixtures. Similar results were reported for photolysis at 334.1 nm.

(f) The Very Low-Pressure Photolysis (VLPΦ) technique, equipped with a modulated molecular-beam mass spectrometer, was used to monitor $ClONO_2$ and its photolysis products. Broad band photolysis, 260 nm–380 nm. $\Phi(NO_3) \geq 0.5 \pm 0.3$; $\Phi(Cl) = 1.0 \pm 0.2$; $\Phi(ClO) \leq 0.03$; $\Phi(O,^3P) \sim 0.1 \pm 0.02$. Upon addition of C_2H_6, the appearance of HCl confirmed the presence of atomic chlorine (in the absence of C_2H_6 atomic chlorine recombines on the reactor walls to produce Cl_2). It was concluded that the predominant or, perhaps, exclusive photolysis pathway is (2).

Preferred Values

Absorption cross sections for $ClONO_2$ photolysis at 296 K, 243 K and 277 K

λ/nm	$10^{20}\sigma/cm^2$		
	296 K	243 K	227 K
190	589		555
195	381		358
200	307		293
205	299		293
210	329		330
215	360		362
220	344		348
225	286		282
230	210		206
235	149		141
240	106		98.5
245	77.0		70.6
250	57.7	50.9	52.6
255	44.7	39.1	39.8
260	34.6	30.1	30.7
265	26.9	23.1	23.3
270	21.5	18.0	18.3
275	16.1	13.5	13.9
280	11.9	9.98	10.4
285	8.80	7.73	7.50
290	6.36	5.36	5.45
295	4.56	3.83	3.74
300	3.30	2.61	2.51
305	2.38	1.89	1.80
310	1.69	1.35	1.28
315	1.23	0.954	0.892
320	0.895	0.681	0.630
325	0.655	0.502	0.463
330	0.514	0.381	0.353
335	0.397	0.307	0.283
340	0.323	0.255	0.246
345	0.285	0.223	0.214
350	0.246	0.205	0.198
355	0.218	0.183	0.182
360	0.208	0.173	0.170
365	0.179	0.159	0.155
370	0.162	0.140	0.142
375	0.139	0.130	0.128
380	0.122	0.114	0.113
385	0.108	0.100	0.098
390	0.090	0.083	0.082
395	0.077	0.070	0.069
400	0.064	0.058	0.056
405	0.055		
410	0.044		
415	0.035		
420	0.027		
425	0.020		
430	0.016		
435	0.013		
440	0.009		
445	0.007		
450	0.005		

Quantum yields for $ClONO_2$ photolysis at 298 K.

$\Phi_2 = 1.0$ for λ >260 nm.

Comments on Preferred Values

The preferred values of the absorption cross sections are those of Molina and Molina [4]. The earlier measurements of Rowland et al. [2] and Jesson et al. [3] are typically 15–20% larger over most of the wavelength range, increasing to ~40% near 400 nm. Preference is given to the data of Molina and Molina due to the utilization of a longer absorption cell, and more carefully purified samples of $ClONO_2$. The data of Molina and Molina shows that the maximum temperature effect occurs around 330 nm, and decreases at longer wavelengths. This observation was interpreted to mean that the shoulder from 320–450 nm is not due to the same electronic transition that is responsible for the maximum around 220 nm, and that the absorption cross sections of the weak band centered around 375 nm are not particularly temperature dependent.

In view of the more direct nature of the photolysis study of Chang et al. [6] the results of this study are, for the present time, preferred over those of Smith et al. [5]. However, a more complete study of the photolysis products over the entire wavelength range are required, especially in view of the results of Molina and Molina [4] which indicate two distinct electronic transitions.

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$COCl_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/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: $\Delta H°_{298}$ values are given since the heat of formation of COCl at 0 K is not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
253.7	Heicklen, 1965 [1]	(a)
200–290	Moule and Foo, 1971 [2]	(b)
240–280	Okabe, 1977 [3]	(c)
184.9–226	Chou et al., 1977 [4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
	>220	Wijnen, 1961 [5]	(e)
	253.7	Heicklen, 1965 [1]	(f)

Comments

(a) A value of (0.91 ± 0.01) × 10^{-3} mm^{-1} cm^{-1} (base 10) was reported for the extinction coefficient at 253.7 nm. T = 298 K. This is equivalent to a value of (6.47 ± 0.07) × 10^{-20} cm^2 $molecule^{-1}$.

(b) A graph of optical density (OD) as a function of wavelength is shown. Approximate experimental conditions reported, i.e., 40 torr $COCl_2$, l = 10 cm, T = 298 K. All bands at wavelengths greater than 285 nm observed to exhibit a strong temperature dependence.

(c) Values tabulated for the extinction coefficient at 10 nm intervals, and at 253.7 nm. T = 296 K.

(d) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals. Continuum with little structure.

(e) Photolysis of $COCl_2/C_2H_4$ mixtures with broad band illumination, λ >220 nm, from 291–403 K. Process (2) assumed to dominate. Yield of CO shown to be proportional to I_0 and $[COCl_2]$. No evidence for COCl being stable—assumed to thermally dissociate into CO and Cl.

(f) $\Phi(CO)$ shown to be constant as a function of I_0 (253.7 nm) at 296 K.

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	213.9	11.7
187.8	137	216.2	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 λ >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 $\leq \lambda \leq 226$ nm, and Okabe [3] for 240 nm $\leq \lambda \leq 280$ 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 $COCl_2$.

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$CF_2Cl_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/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: $\Delta H°_{298}$ values are given since the heats of formation of $CFCl_2$ and CF_2Cl at 0 K are not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
~210–225	Larcher et al., 1950 [1]	(a)
~205–220	Gordus, and Bernstein, 1954 [2]	(b)
120–200	Doucet, Sauvageau and Sandorfy, 1973 [3]	(c)
186–216.2	Rowland and Molina, 1975 [4]	(d)
174–216	Robbins, Rose and Boykin, 1975 [5]	(e)
213.9	Rebbert and Ausloos, 1975 [6]	(f)
185–230	Bass and Ledford, 1976 [7]	(g)
186–226	Chou et al., 1977 [8]	(d,h)
159–240	Hubrich, Zetzsch and Stuhl, 1977 [9]	(i)
190–220	Vanlaethem–Meuree, Wisemberg and Simon, 1978 [10]	(j)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(-CF_2Cl_2) = 1.12 \pm 0.09$	184.9	Milstein and Rowland, 1975 [11]	(k)
$\Phi_2 = 0.91$, $\Phi_5 = 0.09$	213.9	Rebbert and Ausloos, 1975 [6]	(l)
$\Phi_2 = 0.64$, $\Phi_5 = 0.36$	184.9		
$\Phi_2 = 0.56$, $\Phi_5 = 0.40$	163.3		
Φ_2 ~1.0	213.9	Jayanty, Simonaitis, and Heicklen, 1976 [12]	(m)

Comments

(a) Extinction coefficients plotted as a function of frequency.

(b) The extinction coefficients are plotted logarithmically as a function of frequency. The value of σ was stated to be 9.5×10^{-21} cm^{3}molecule^{-1} at 209.6 nm.

(c) Results given in a figure of molar extinction coefficient as a function of wavelength. The spectral region of stratospheric importance was not of prime interest in this study.

(d) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals.

(e) Absorption cross sections tabulated at 2 nm intervals. Resolution = 0.07 nm.

(f) Absorption cross sections determined at 213.9 nm using a Zn arc from 234–442 K. Using the formulae of Chou et al. [8], the data below 295 K can be fit if a value of 5.4×10^{-5} is used for constant B.

(g) Absorption cross sections determined at 0.2 nm intervals, with a spectral resolution of 0.05 nm at 296 K and 223 K. Values tabulated at 5 nm intervals in reference [7], and at 2 nm intervals in Watson [13]. Using the formulae of Chou et al. [8], the data at 223 K fits if a value of 3.5×10^{-5} is used for the constant B.

(h) Absorption cross sections determined at six temperatures in the range 212–257 K. Results tabulated and shown graphically in the form σ_T/σ_{296}. The data can be fit with reasonable accuracy by the following three parameter equation: $\sigma_T = \sigma_{296} \exp(B(\lambda-1849)\,(T-296))$ for wavelength, λ(in Ångstrom units) and absolute temperature, T. The value of B is 3.6×10^{-5}. Absorption cross sections have been tabulated for 230 K and 252 K in reference [14].

(i) Absorption cross sections shown graphically, and also tabulated for 208 K and 298 K at <3 nm intervals. Using the formula of Chou et al. [8], the data at 208 K can be fit if a value of 4.25×10^{-5} is used for the constant B.

(j) Absorption cross sections shown graphically, and also tabulated for 259 K, 279 K and 296 K at 2 nm and 500 cm^{-1} intervals. Using the formulae of Chou et al. [8], the data at 255 K and 279 K can be fit if values of 5.35×10^{-5} and 4.4×10^{-5} are used for the constant B. Therefore, the best overall fit occurs if a value of 4.9×10^{-5} is used for the constant B.

(k) Photolysis of CF_2Cl_2/O_2 mixtures at 184.9 nm. $\Phi(-CF_2Cl_2)$ and $\Phi(CO_2)$ determined gas chromatographically. $\Phi(CO_2) = 1.11 \pm 0.05$. The primary process was assumed to produce $CF_2Cl + Cl$ (2). The CF_2Cl was assumed to react with O_2 to produce COF_2 through the CF_2ClOO intermediate. The COF_2 was converted to CO_2 on the silica-gel column.

(l) Photolysis of CF_2Cl_2/C_2H_6 mixtures. C_2H_6 used as a Cl atom scavenger. Gas chromatography, and mass spectrometry used to determine the product distribution. Based on an assumed reaction mechanism, and the product distribution, quantum yields are derived for C_2H_5, CF_2Cl and CF_2. Although it was not possible to obtain an unambiguous answer as to whether the CF_2 was produced via process (1) or (5), the data (especially at 184.9 nm and 163.3 nm) strongly suggested that process (5) is more important than process (1). However, a value of Φ_1 of ≤0.04 cannot be excluded. No evidence for breakage of C-F bonds was obtained, i.e., $\Phi_3 \cong \Phi_4 \cong \Phi_6 \cong \Phi_7 = 0$.

(m) Photolysis of CF_2Cl_2/O_2 mixtures at 298 K and 213.9 nm. COF_2 inferred to be a reaction product with a quantum yield, $\Phi(COF_2)$, $= 1.0 \pm 0.2$ by monitoring CO_2 by gas chromatography. COF_2 was quantitatively converted to CO_2 on the silica gel column. The quantum yield for Cl_2 production, $\Phi(Cl_2)$, was determined to be 0.52–0.66 using ultraviolet absorption detection. No explanation can be given for $\Phi(Cl_2)$ being less than $\Phi(COF_2)$. These results were taken to indicate that process (2) is the dominant photochemical process with a quantum yield near unity.

Preferred Values

Absorption cross sections for CF_2Cl_2 photolysis at 298 K

λ(nm)	$10^{20}\sigma/cm^2$	λ(nm)	$10^{20}\sigma/cm^2$
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 Ångstrom 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 [4], Robbins et al. [5], Bass and Ledford [7], Chou et al. [8], Hubrich et al. [9] and Vanlaethem–Meuree et al. [10]. The values reported in these studies are in excellent agreement, better than 10%, over the complete wavelength range. The temperature dependence of the absorption cross sections can be adequately described by the expression shown. The values of B that best fit the reported data range from 3.5×10^{-5} to 5.4×10^{-5}. Therefore, the preferred value of 4.1×10^{-5} for B is a weighted average of all the derived values from references [6–10]. This expression is valid for wavelengths greater than 184.9 nm. At wavelengths shorter than 184.9 nm the absorption cross sections are not expected to exhibit any significant temperature dependence, indeed, Hubrich et al. [9] show slightly higher values for σ 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 [6] at 163.3 nm ($\Phi_2 = 0.56$), 184.9 nm ($\Phi_2 = 0.64$), 213.9 nm ($\Phi_2 = 0.91$), and ≥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, equal $1-\Phi_2$. Processes (1) and (5) are equivalent in the atmosphere due to the rapid photolysis of Cl_2. Therefore, even if process (1) had contributed to the production of CCl_2 radicals in the quantum yield studies it is of little consequence for photochemical modelling of the stratosphere.

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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

Wavelength range/nm	Reference	Comments
~220–245	Larcher et al., 1950 [1]	(a)
~215–235	Gordus and Bernstein, 1954 [2]	(b)
120–214	Doucet, Sauvageau and Sandorfy, 1973 [3]	(c)
186–226	Rowland and Molina, 1975 [4]	(d)
174–238	Robbins, Rose and Boykin, 1975 [5]	(e)
148–225	Huebner et al., 1975 [6]	(f)
185–210	Green and Wayne, 1975 [7]	(g)
185–230	Bass and Ledford, 1976 [8]	(h)
186–226	Chou et al., 1977 [9]	(i,d)
158–275	Hubrich, Zetzsch, and Stuhl, 1977 [10]	(j)
190–220	Vanlaethem–Meuree, Wisemberg and Simon, 1978 [11]	(k)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 \sim 1.0$	213.9	Marsh and Heicklen, 1965 [12]	(l)
$\Phi_1 = 0.98$, $\Phi_5 \sim 0.05$	213.9	Rebbert and Ausloos, 1975 [13]	(m)
$\Phi_1 = 0.70$, $\Phi_5 \sim 0.30$	184.9		
$\Phi_1 = 0.50$, $\Phi_5 \sim 0.45$	163.3		
$\Phi_1 \sim 1.0$	213.9	Jayanty, Simonaitis and Heicklen, 1975 [14]	(n)

Comments

(a) Extinction coefficients plotted as a function of frequency.

(b) The extinction coefficients are plotted logarithmically as a function of frequency. The value of σ was stated to be 9.5×10^{-21} cm^{2}molecule^{-1} at 225 nm.

(c) Results given in a figure of molar extinction coefficient as a function of wavelength. The spectral region of atmospheric importance was not of prime interest in this study.

(d) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals.

(e) Absorption cross sections tabulated at 2 nm intervals. Resolution = 0.07 nm.

(f) Apparent absorption cross sections tabulated at <5 nm intervals. Derived from electron energy-loss measurements.

(g) Absorption cross sections measured at ~300 K shown graphically. Spectral bandwidth ≤0.5 nm. Precision reported to vary between 10 and 30%.

(h) Absorption cross sections determined at 0.2 nm intervals, with a spectral resolution of 0.05 nm at 296 K and 223 K. Values tabulated at 5 nm intervals in reference [8], and at 2 nm intervals in Watson [15].

(i) Absorption cross sections determined at 213 K, 232 K and 252 K. Results given in a figure of σ_T/σ_{296}. The data have been tabulated for each temperature in reference [16].

(j) Absorption cross sections shown graphically, and also tabulated for 208 K and 298 K at <5 nm intervals.

(k) Absorption cross sections shown graphically, and also tabulated for 255 K, 279 K and 296 K at 2 nm and 500 cm^{-1} intervals.

(l) Photolysis of $CFCl_3/NO$ and $CFCl_3/O_2$ mixtures at 213.9 nm. Observation of $CFCl_2NO$ as a reaction product was taken to indicate that Φ_1 was the dominant primary process.

(m) Photolysis of $CFCl_3/C_2H_6$ mixtures. C_2H_6 used as a Cl atom scavenger. Gas chromatography and mass spectrometry used to determine the product distribution. Based on an assumed reaction mechanism, and the product distribution, quantum yields are derived for C_2H_5, $CFCl_2$ and CFCl. The data strongly suggest that at both 213.9 nm and 184.9 nm the quantum yield for removal of $CFCl_3$ is unity, that elimination of Cl_2 (process 2) is unimportant, and that C–F bonds are not broken even at shorter wavelengths (163.3 nm and 147 nm).

(n) Photolysis of $CFCl_3/O_2$ and $CFCl_3/O_3$ mixtures at 298 K and 213.9 nm. COFCl inferred to be a reaction product with a quantum yield, Φ(COFCl), = 0.9 ± 0.15 by monitoring CO_2 by gas chromatography. COFCl was quantitatively converted to CO_2 on the silica gel column. The quantum yield for Cl_2 production, $\Phi(Cl_2)$, was determined to be 0.50–0.63 using ultraviolet absorption detection. No explanation can be given for $\Phi(Cl_2)$ being lower than Φ(COFCl). These results were taken to indicate that process (1) is the dominant photochemical process with a quantum yield near unity.

Preferred Values

Absorption cross sections for $CFCl_3$ photolysis at 298 K

λ(nm)	$10^{20}\sigma$/cm^2	λ(nm)	$10^{20}\sigma$/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	0.0184
198	80.1	250	0.00978
200	64.7	255	0.00586
202	50.8	260	0.00285
204	38.8	265	0.00176
206	29.3	270	0.00124
208	21.2	275	0.00093

Absorption cross sections for $CFCl_3$ photolysis at temperatures below 298 K

λ(nm)	$10^{20}\sigma$/cm^2			
	210 K	225 K	240 K	255 K
190	178	178	178	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 [4], Robbins et al. [5], Bass and Ledford [8], Chou et al. [9], Hubrich et al. [10] and Vanlaethem-Meuree et al. The values reported in these studies are in excellent agreement, better than 10% over the wavelength range ~180 nm ≤ λ ≤230 nm. The values shown for λ >230 nm are those reported by Hubrich et al. [10]. The temperature dependence of the absorption cross sections cannot be fit 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 [8], Chou et al. [9] and Hubrich et al. [10] are in good agreement. However, the low temperature data of Vanlaethem-Meurre et al. [11] is in less satisfactory agreement. Vanlaethem-Meuree et al. [11] reported a temperature dependence for σ even at short wavelengths, i.e., $\lambda \leq 200$ nm. This is inconsistent with the data reported in the other studies [8–10], especially considering the limited temperature range of their study. The preferred absorption cross sections at temperatures below 298 K were derived from the data reported in references [8–10]. Values were estimated for $\sigma(T)/\sigma(298\ \mathrm{K})$ at 5 nm intervals from 190–230 nm for 210 K, 225 K, 240 K and 255 K (temperature range relevant to photochemical models of the stratosphere). These estimated values of $\sigma(T)/\sigma(298\ \mathrm{K})$ were then combined with the preferred values of the absorption cross sections at 298 K.

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 [13] 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, equal $1-\Phi_1$. Processes (2) and (5) are equivalent in the atmosphere due to the rapid photolysis of Cl_2. Therefore, even if process (2) had contributed to the production of CFCl radicals in the quantum yield studies, it is of little consequence for photochemical modeling of the stratosphere.

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$CCl_4 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_0/kJ mol^{-1}	$\lambda_{\mathrm{threshold}}$/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
~230–260	Larcher et al., 1950 [1]	(a)
205–250	Gordus and Bernstein, 1954 [2]	(b)
110–200	Russell, Edwards and Raymonda, 1973 [3]	(c)
250	Curie, Sidebottom and Tedder, 1974 [4]	(d)
184.9; 253.7	Davis et al., 1975 [5]	(e)
186–226	Rowland and Molina, 1975 [6]	(f)
174–238	Robbins, Rose and Boykin, 1975 [7]	(g)
313	Rebbert and Ausloos, 1976 [8]	(h)
190–252	Vanlaethem-Meuree, Wisemberg and Simon, 1978 [9]	(i)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi_1 \sim 1$, $\Phi_2 > 0$	250	Curie, Sidebottom, and Tedder, 1974 [4]	(j)
$\Phi_1 \sim 1$	253.7	Davis et al., 1975 [5]	(k)
$\Phi_1 \sim 0.4$, $\Phi_2 + \Phi_3 \sim 0.6$	184.9		
$\Phi_2 \sim 1$ (low pressure)	213.9	Jayanty, Simonaitis, and Heicklen, 1975 [10]	(l)
$\Phi_1 \sim 1$ (high pressure)			
$\Phi_1 = 0.9$. $\Phi_2 + \Phi_3 = 0.05$	213.9	Rebbert and Ausloos. 1976 [8]	(m)
$\Phi_1 = 0.25$, $\Phi_2 + \Phi_3 = 0.76$	163.3		

Comments

(a) Extinction coefficients reported in graphical form.

(b) Extinction coefficients shown graphically, and also tabulated at ≤ 5 nm intervals.

(c) Absorption cross sections reported graphically from 110–200 nm. The region of stratospheric interest, $\lambda > 185$ nm, was not of prime interest in their study.

(d) The temperature dependence of the extinction coefficient at 250 nm was shown graphically for the temperature range 297–477 K. Within this range, the value of ϵ was shown to increase by a factor of ~15.

(e) Absorption cross sections were explicitly reported at four wavelengths including: 6.85×10^{-21} cm^{2}molecule^{-1} (253.7 nm), and 3.94×10^{-18} cm^{2}molecule^{-1} (184.9 nm) (this assumes the reported values of ϵ(cm^{-1}atm^{-1}) were to the base 10). In addition to the tabulated data, Davis et al. reported the absorption spectrum in graphical form from 120–200 nm. However, this figure is cosmetic and data derived from it should not be used (the drifting baseline was not shown).

(f) Absorption cross sections measured at 296 K. Tabulated values averaged over 500 cm^{-1} intervals.

(g) Absorption cross sections tabulated at 2 nm intervals. Spectral resolution = 0.07 nm.

(h) Values of $\leq (3.7 \pm 0.4) \times 10^{-26}$ and 2.3×10^{-25} cm^{2}molecule^{-1} were reported for σ(313 nm) at 300 K and 376 K, respectively. These values were determined by photolyzing CCl_4/Cl atom scavenger mixtures at 313 nm and using gas chromatography for product analysis. The absorption cross sections were derived assuming that each photon absorbed produced a Cl atom which was then scavenged by C_2H_6.

(i) Absorption cross sections shown graphically, and also tabulated for 279 K and 298 K at 2 nm and 500 cm^{-1} intervals.

(j) From the photolysis of CCl_4/cyclohexane mixtures at 250 nm, and between 308 K and 558 K, it was deduced from the gas chromatographic analysis of the product distribution that although process (1) was the major route, process (2) was also significant. However, no quantitative information on the relative magnitudes of Φ_1, and Φ_2 was reported.

(k) CCl_4 and CCl_4/Br_2 mixtures were photolyzed at several wavelengths (253.7, 184.9, 147.0 and 106.7 nm) at 298 K. From a gas chromatographic analysis of the reaction products, Davis et al. determined values for $\Phi(-Br_2)$, $\Phi(CCl_xBr_y)$, etc., and deduced that $\Phi_1 \sim$ unity at 253.7 nm, and $\Phi_1 \sim 0.4$, and $\Phi_2 + \Phi_3 \sim 0.6$ at 184.9 nm. From the experimental data it was deduced that CCl_2 radicals rapidly insert into CCl_4 to form $C_2Cl_6^*$, which can either be quenched to form C_2Cl_6 or can decompose to form $2CCl_3$ radicals.

(l) CCl_4/O_2 and CCl_4/O_3 mixtures were photolyzed at 298 K. Quantitative analysis of the reaction products, $COCl_2$ and Cl_2, was performed using gas chromatography and infra-red and ultraviolet absorption spectroscopy. The results were interpreted in terms of an excited CCl_4^* mechanism. Jayanty et al. postulated that at low pressures the CCl_4^* complex entirely decomposes into CCl_2 (singlet) and Cl_2, whereas at higher pressures CCl_4^* is quenched to CCl_4^{**} which then decomposes into CCl_3 and Cl. These authors, like Davis et al. [5], assume that CCl_2 radicals insert into CCl_4 to produce $2CCl_3$ radicals which then react with O_2 or O_3 to produce $COCl_2$. At low total pressures $\Phi(COCl_2)$ was determined to be ~2.

(m) CCl_4 was photolyzed in the presence of HCl, HBr and C_2H_6 at several wavelengths (213.9, 163.3 and 147.0 nm). From the gas chromatographic detection of the reaction products it was concluded that $\Phi_1 = 0.9$, $\Phi_2 + \Phi_3 = 0.05$ at 213.9 nm; $\Phi_1 = 0.25$, $\Phi_2 + \Phi_3 = 0.76$ at 163.3 nm. In contrast to Davis et al. [5] and Jayanty et al. [10], Rebbert and Ausloos concluded that CCl_2 radicals do not insert into CCl_4 to produce two CCl_3 radicals.

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	214	33.3
176	1007	216	27.2
178	976	218	21.8
180	772	220	17.0
182	589	222	13.0
184	450	224	9.61
186	318	226	7.19
188	218	228	5.49
190	144	230	4.07
192	98.9	232	3.01
194	74.4	234	2.16
196	68.2	236	1.51
198	66.0	238	1.13
200	64.8	240	0.784
202	62.2	242	0.579
204	60.4	244	0.414
206	56.5	246	0.314
208	52.0	248	0.240
210	46.6	250	0.189
212	39.7	252	0.150

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 Yields 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 [2], Rowland and Molina [6], Robbins et al. [7] and Vanlaethem-Meuree et al. [9]. The agreement between the values reported in these studies is excellent, better than 10%, over the entire wavelength range. The preferred values of the absorption cross sections at 279 K are those reported by Vanlaethen-Meuree 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 Vanlaethen-Meuree et al. [9], Curie et al. [4] and Rebbert and Ausloos [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. [5] 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, equal $1-\Phi_1$. Processes (2) and (3) are equivalent in the atmosphere due to the rapid photolysis of Cl_2. Therefore, even if process (2) had contributed to the production of CCl_2 radicals in the quantum yield studies, it is of little consequence for photochemical modelling of the stratosphere.

References

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[9] Vanlaethem-Meuree, N., Wisemberg, J., and Simon, P. C., Bull. Acad. R. Belgique, Cl. Sci., **64,** 23 (1978).

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$O + HBr \rightarrow HO + Br$

$\Delta H^\circ = -61.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.4 \pm 1.0) \times 10^{-14}$	298	Takacs and Glass, 1973 [1]	(a)
$(4.0 \pm 0.7) \times 10^{-12} \exp(-(1359 \pm 50)/T)$	267–430	Brown and Smith, 1975 [2]	(b)
$(4.45 \pm 0.2) \times 10^{-14}$	303		
$(1.34 \pm 0.14) \times 10^{-11} \exp(-(1807 \pm 40)/T)$	298–554	Singleton and Cvetanovic, 1978 [3]	(c)
3.1×10^{-14}	298		
Reviews and Evaluations			
$7.6 \times 10^{-12} \exp(-1571/T)$	267–430	NASA, 1977 [4]	(d)

Comments

(a) Discharge flow: EPR detection of O, Br and HO.

(b) Discharge flow: chemiluminescence detection of O via the $O + NO \rightarrow NO_2^*$ afterglow.

(c) Slow flow: molecule modulation technique. Atomic oxygen produced from the Hg photosensitized decomposition of N_2O, and detected via the $O + NO \rightarrow NO_2^*$ afterglow.

(d) This evaluation was based on the data reported in references [1–3], misquoted in NASA 1010 notes.

Preferred Value

$k = 3.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.0 \times 10^{-12} \exp(-1560//T)$ cm^3 molecule^{-1} s^{-1} over range 250–400 K.

Reliability

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

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

Comments on Preferred Values

As the values reported for k at 298 K [1–3] are in fair agreement, the mean is taken to be the preferred value. The agreement between the values deduced from the Arrhenius expressions reported at stratospheric temperatures is rather poor, e.g. the values differ by ~70% at 250 K. The preferred value has been derived to best fit both sets of data between 250 and 400 K. The A-factor derived for the preferred expression and that reported in reference [2] appear to be lower than would be expected. This, combined with the absence of data at stratospheric temperatures leads to considerable uncertainty in the values of k between 200 and 260 K.

References

[1] Takacs, G. A., and Glass, G. P., J. Phys. Chem. **77**, 1182 (1973).

[2] Brown, R. D., and Smith, I. W. M., Int. J. Chem. Kinet., **7**, 301 (1975).

[3] Singleton, D. L., and Cvetanovic, R. J., Canad. J. Chem. **56**, 2934 (1978).

[4] NASA Ref. Pub. #1010. "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

$O + BrO \rightarrow O_2 + Br$

$\Delta H^\circ = -263.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5_{-1.5}^{+2.5}) \times 10^{-11}$	298	Clyne, Monkhouse and Townsend, 1976 [1]	(a)
Relative Rate Coefficients			
$\geq 6.6 \times 10^{-11}$	293	Clyne and Cruse, 1970 [2]	(b)
Reviews and Evaluations			
3×10^{-11}	298	NASA, 1977 [3]	(c)

Comments

(a) Discharge flow: resonance fluorescence detection of Br and O. The value shown was derived from two independent methods of determining the rate constant: (a) monitoring Br atom formation in the absence of NO yielded a value of $(1.0_{-0.7}^{+2.0}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, (b) monitoring O atom decay in the absence of NO yielded a value of $(7_{-6}^{+4}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The authors reported that the Br atom formation rate data are rather more sensitive to the magnitude of k than are the O atom decay data. Therefore, the value shown in the table reflects the results obtained from both sets of data.

(b) Discharge flow: UV absorption detection of BrO. Atomic oxygen was added to a known [Br_2], and from the observed BrO concentration a value of ≥ 40 was deduced for $k/k(O + Br_2)$. The authors obtained their lower limit of k by assuming that $k(O + Br_2)$ was $\geq 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Based on the recent [1] value of $k(O + Br_2)$ of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}, it is clear that the ratio reported must be wrong and thus rejected.

(c) Based on the data shown in reference [1].

Preferred Value

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

Reliability

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

Comments on Preferred Value

This value appears to be reasonable in the light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for such an atom-radical process, e.g., O + ClO.

References

[1] Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., Int. J. Chem. Kinet. **8,** 425 (1976).

[2] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66,** 2214 (1970).

[3] NASA Ref. Pub. #1010. "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

$Br + HO_2 \rightarrow HBr + O_2$

$\Delta H^\circ = -151$ kJ mol^{-1}

Rate Coefficient Data: no experimental data available.

Preferred Value

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

Reliability

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

Comments on Preferred Value

The rate constant for such an atom-radical process is expected to be rapid and relatively insensitive to temperature.

$Br + H_2O_2 \rightarrow HBr + HO_2$

$\Delta H^\circ = -9.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 2 \times 10^{-14}$	298	Leu and DeMore, 1978 [1]	(a)
Reviews and Evaluations			
$5 \times 10^{-12} \exp(-1570/T)$	200–300	NASA, 1977 [2]	(b)

Comments

(a) Unpublished data. Discharge flow: mass spectrometric detection of H_2O_2.

(b) An estimate based on the provisional value reported for k at 298 K by Leu and DeMore [1].

Preferred Value

$k \leq 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = {}^{+0.3}_{-1.7}$ at 298 K.

Comments on Preferred Values

No temperature dependent data available. An estimate for the Arrhenius expression would be: $k < 5 \times 10^{-12} \exp(-1570/T)$ cm^3 molecule^{-1} s^{-1}. The A-factor was chosen to be consistent with that determined for the Cl + H_2O_2 reaction.

References

[1] Leu, M. T., and DeMore, W. B., unpublished data, Jet Propulsion Laboratory, 1978.

[2] NASA Ref. Pub. #1010, "Chlorofluoromethanes and the Stratosphere," Chapter 1, R. D. Hudson, editor (1977).

$Br + O_3 \rightarrow BrO + O_2$

$\Delta H° = -129$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$>1.6 \times 10^{-12}$	~300	Clyne and Coxon, 1968 [1]	(a,e)
$(3.4 \pm 1.0) \times 10^{-13}$	300	Clyne and Cruse, 1970 [2]	(a)
$(7_{-4}^{+7}) \times 10^{-13}$	300	Cruse, 1971 [3]	(a)
$(1.19 \pm 0.2) \times 10^{-12}$	298	Clyne and Watson, 1975 [4]	(b)
$(3.34 \pm 0.4) \times 10^{-11} \exp(-(978 \pm 36)/T)$	224–425	Leu and DeMore, 1977 [5]	(b)
$(1.16 \pm 0.16) \times 10^{-12}$	298		
$(7.74 \pm 0.5) \times 10^{-12} \exp(-(603 \pm 16)/T)$	200–360	Michael et al.. 1978 [6]	(c)
$(1.01 \pm 0.18) \times 10^{-12}$	298		
$(9.45 \pm 2.48) \times 10^{-12} \exp(-(659 \pm 64)/T)$	234–360	Michael and Payne, 1979 [7]	(d)
$(1.12 \pm 0.07) \times 10^{-12}$	298		
Reviews and Evaluations			
$3.0 \times 10^{-11} \exp(-937/T)$	224–425	NASA, 1977 [8]	(f)

Comments

(a) Discharge flow: UV absorption detection of O_3.

(b) Discharge flow: mass spectrometric detection of O_3.

(c) Flash photolysis: resonance fluorescence detection of Br.

(d) Discharge flow: resonance fluorescence detection of Br.

(e) Second order conditions.

(f) Value based on unpublished data of Leu and DeMore.

Preferred Value

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.4 \times 10^{-11} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over range 220–360 K.

Reliability

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

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

Comments on Preferred Values

The results reported for k at 298 K in references [4–7] are in excellent agreement, and the preferred value is derived by taking a simple mean of these four values. The temperature dependences reported for k in references [5–7] are only in fair agreement. There is a spread of 25% in k at 220 K and 50% at 360 K. Although the results reported in references [6] and [7] are in good agreement, there is no reason at present to discard the results of reference [5]. Therefore, until further results are reported, the preferred value has been derived to fit the data reported in references [4–7].

References

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[2] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66**, 2214 (1970).

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[8] NASA Ref. Pub. #1010. "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

$HO + HBr \rightarrow H_2O + Br$

$\Delta H^\circ = -132.6$ kJ mol$^-$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.1 \pm 1.0) \times 10^{-12}$	295	Takacs and Glass, 1973 [1]	(a)
$(1.19 \pm 0.12) \times 10^{-11}$	249–416	Ravishankara, Wine and Langford, 1979 [2]	(b)
$(1.17 \pm 0.10) \times 10^{-11}$	298		
Relative Rate Coefficients			
$\sim 2.65 \times 10^{-11}$	1875–1975	Wilson, O'Donovan and Fristrom, 1969 [3]	(c)
Reviews and Evaluations			
5.1×10^{-12}	298	NASA, 1977 [4]	(d)

Comments

(a) Discharge flow: EPR detection of HO. Secondary reactions involving HO were only of minor importance.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) k estimated from flame inhibition study.

(d) Value reported in reference [1].

Preferred Value

$k = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over range 249–416 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 250$ K.

Comments on Preferred Values

Takacs and Glass combined the results of studies, [1] and [3], and obtained the following Arrhenius expression, $(3.7 \pm 0.7) \times 10^{-11} \exp(-(579 \pm 70)/T)$ cm^3 molecule^{-1} s^{-1}. However, this expression is not recommended as the extrapolation is over too wide a temperature range. The two values reported for k at 298 K differ by a factor of 2, therefore until another study is performed, the preferred value is taken to be a simple mean of these values [1,2]. The data reported by Ravishankara et al. [2] shows that the rate constant exhibits no temperature dependence between 249–416 K. This observation is compatible with the estimated A-factor being comparable to the value of k at 298 K.

References

[1] Takacs, G. A., and Glass, G. P., J. Phys. Chem. **77**, 1060 (1973).
[2] Ravishankara, A. R., Wine, P. H., and Langford, A. O., Chem. Phys. Lett., **63**, 479 (1979).
[3] Wilson, W. E., O'Donovan, J. T., and Fristrom, R. M., Symp. Combust. 12th, 929 (1969).
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$HO + CH_3Br \rightarrow H_2O + CH_2Br$

$\Delta H^\circ = -80$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.8) \times 10^{-14}$	298	Howard and Evenson, 1976 [1]	(a)
$(7.93 \pm 0.79) \times 10^{-13} \exp(-(889 \pm 53)/T)$	244–350	Davis et al., 1976 [2]	(b)
$(4.14 \pm 0.43) \times 10^{-14}$	298		
Reviews and Evaluations			
$7.93 \times 10^{-13} \exp(-889/T)$	244–350	NASA, 1977 [3]	(c)

Comments

(a) Discharge flow: laser magnetic resonance detection of HO.

(b) Flash photolysis: resonance fluorescence detection of HO.

(c) Expression reported in reference [2].

Preferred Value

$k = 3.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 7.6 \times 10^{-13} \exp(-890/T)$ cm^3 molecule^{-1} s^{-1} over range 244–350 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 the mean of the two results which are in excellent agreement. The *A*-factor reported by Davis et al. [2] has been modified so that the Arrhenius expression yields the preferred value of *k* at 298 K. The *A*-factor of the Arrhenius expression appears low for H abstraction from a methyl group.

References

[1] Howard, C. J., and Evenson, K. M., J. Chem. Phys. **64**, 197 (1976).

[2] Davis, D. D., Machado, G., Conaway, B. C., Oh, Y., and Watson, R. T., J. Chem. Phys. **65**, 1268 (1976).

[3] NASA Ref. Pub. #1010, "Chlorofluoromethanes and the Stratosphere," Chapter 1, R. D. Hudson, editor (1977).

$BrO + HO_2 \rightarrow HOBr + O_2$ (1)

$\rightarrow HBr + O_3$ (2)

$\Delta H^\circ(1) = -207$ kJ mol^{-1}

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

Rate Coefficient Data: no available experimental data

Preferred Value

$k = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

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

Comments on Preferred Value

This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of BrO is similar to that of ClO. The temperature dependence for such a radical-radical process is expected to be small, i.e., $E/R < \pm 500$ K. Reaction (1) would be expected to be the dominant reaction pathway.

$BrO + NO \rightarrow Br + NO_2$

$\Delta H^\circ = -71$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.8) \times 10^{-12}$	293	Clyne and Cruse, 1970 [1]	(a)
$\sim 5 \times 10^{-12}$	293	Cruse, 1971 [2]	(a,b)
$(2.2 \pm 0.4) \times 10^{-11}$	298	Clyne and Watson, 1975 [3]	(c)
$(2.3 \pm 0.3) \times 10^{-11}$	298	Ray and Watson, 1979 [4]	(c)
$1.28 \times 10^{-11} \exp((181 \pm 46)/T)$	224–396	Watson, Sander, and Yung, 1979 [5]	(d)
$(2.15 \pm 0.25) \times 10^{-11}$	298		
$(7.11 \pm 0.23) \times 10^{-12} \exp((296 \pm 10)/T)$	230–425	Leu, 1979 [6]	(c)
$(1.89 \pm 0.16) \times 10^{-11}$	298		
Reviews and Evaluations			
2.1×10^{-11}	298	NASA, 1977 [7]	(e)

Comments

(a) Discharge flow: UV absorption detection of BrO. Value somewhat dependent upon the rate constant for BrO + BrO owing to low initial stoichiometries of [NO] to [BrO].

(b) Reinterpretation of the same data reported in reference [1].

(c) Discharge flow: mass spectrometric detection of BrO.

(d) Flash photolysis: UV absorption detection of BrO.

(e) Based on the value reported by Clyne and Watson [2].

Preferred Value

$k = 2.1 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K.

$k = 8.7 \times 10^{-12} \exp(260/T)$ cm^{3}molecule^{-1}s^{-1} over range 224-425 K.

Reliability

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

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies [3,4,6] and the high pressure UV absorption study [5], which all used pseudo-first-order conditions, are in excellent agreement at 298 K, and are more reliable than the earlier low pressure UV absorption study [1]. The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in references [3–6]. By combining the data reported in reference [5] with that in references [3,4,6] it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependence for k for the analogous ClO and HO_2 reactions are also negative, and are similar in magnitude.

References

[1] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66**, 2227 (1970).
[2] Cruse, H. W., Ph.D. Thesis, QMC, London University (1971).
[3] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I. **71**, 336 (1975).
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[6] Leu, M. T., Chem. Phys. Lett. **61**, 275 (1979).
[7] NASA, Ref. Pub. #1010, "Chlorofluoromethanes and the Stratosphere," Chapter 1, R. D. Hudson, editor (1977).

$BrO + NO_2 + M \longrightarrow BrO\ NO_2 + M$

$\Delta H° = -138$ kJ mol^{-1}

Low Pressure Rate Coefficient

k_0/cm^{3}molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
3×10^{-31} [N_2]	298	Watson and Sander, 1978 [1]	(a)

Comments

(a) Provisional data between 300 and 700 Torr, to be reconfirmed.

Preferred Value

$k_0 = 3 \times 10^{-31} (T/300)^{-3.0}$ [N_2] cm^{3}molecule^{-1}s^{-1} over range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ over range 200–400 K.

Comments on Preferred Values

More measurements are needed. Value accepted since it is similar to the $ClO + NO_2 + M \longrightarrow ClO\ NO_2 + M$ data; the temperature coefficient is taken from this reaction.

High Pressure Rate Coefficients

No available experimental data. From the measurements in ref. [1] one concludes $k_\infty > 3 \cdot 10^{-12}$ cm^{3}molecule^{-1}s^{-1}. A value of $k_\infty \simeq 1.2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}, as for $ClO + NO_2 + M \longrightarrow ClO\ NO_2 + M$, is adopted tentatively with a value of $F_c \simeq 0.7$ at 300 K.

Reference

[1] Watson, R. T. and Sander, S. P., unpublished data (1978).

$BrO + O_3 \rightarrow Br + 2O_2$

$\Delta H^\circ = -157$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Relative Rate Coefficients			
$<8 \times 10^{-14}$	293	Clyne and Cruse, 1970 [1]	(a)
$<5 \times 10^{-15}$	298	Sander and Watson, 1978 [2]	(b)
Reviews and Evaluations			
$<10^{-14}$	298	NASA, 1977 [3]	(c)

Comments

(a) Discharge flow: UV absorption detection of BrO and O_3. An upper limit was placed on k by monitoring BrO and O_3 in a system where $[O_3]$ is in excess of [BrO]. It was deduced that the rate of disappearance of O_3 could be totally attributed to the regeneration of Br atom from the BrO + BrO reaction. However, as the values of k(BrO + BrO) and σ(BrO) reported in this study are questionable (see BrO + BrO reaction) the upper limit deduced for this rate constant may be in error.

(b) Flash photolysis: UV absorption detection of BrO and O_3. An upper limit was placed on k by monitoring $\Delta[O_3]$ as a function of $[BrO]_0$ in the presence of a large excess concentration of O_3 ($[O_3]_0 > 50[BrO]_0$). The loss of O_3 could be totally attributed to the catalytic destruction of O_3 through the regeneration of Br atoms via the $BrO + BrO \rightarrow 2\,Br + O_2$ reaction, where $BrO + BrO \rightarrow 2Br + O_2$ (1) represents ~85% of the total reaction pathway for the bimolecular disproportionation of BrO radicals. (See the BrO + BrO reaction.) The removal of O_3 was dependent upon $[BrO]_0$ but not $[O_3]_0$.

(c) The entry was meant to read $<8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} as it was based upon the value reported by Clyne and Cruse [1].

Preferred Value

$k < 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = {}^{+0.5}_{-?}$.

Comments on Preferred Value

There is no evidence for this reaction. The analogous ClO reaction has a rate constant of $\sim 10^{-18}$ cm^3 molecule^{-1} s^{-1} [4].

References

[1] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc. **66,** 2214 (1970).
[2] Sander, S. P., and Watson, R. T., Manuscript in preparation (1978).
[3] NASA, Ref. Pub. #1010, "Chlorofluoromethanes and the Stratosphere," R. D. Hudson, editor (1977).
[4] DeMore, W. B., Lin, C. L., and Jaffe, S., results presented at 12th Informal Conference on Photochemistry, Washington, D.C. (1976).

$$\mathrm{BrO + ClO \rightarrow Br + OClO} \quad (1)$$
$$\mathrm{\rightarrow Br + Cl + O_2} \quad (2)$$
$$\mathrm{\rightarrow BrCl + O_2} \quad (3)$$

$\Delta H°(1) = -14.0$ kJ mol^{-1}

$\Delta H°(2) = +4.9$ kJ mol^{-1}

$\Delta H°(3) = -213.8$ 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			
2.5×10^{-12}	300	Basco and Dogra, 1971 [1]	(a)
$(1.34 \pm 0.2) \times 10^{-11}$	298	Clyne and Watson, 1977 [2]	(b)
Reviews and Evaluations			
$k_1 = 6.7 \times 10^{-12}$	298	Watson, 1977 [3]	(c)
$k_2 = 6.7 \times 10^{-12}$	298		
$k_1 = 6.7 \times 10^{-12}$	298	NASA, 1977 [4]	(c)
$k_2 = 6.7 \times 10^{-12}$	298		

Comments

(a) Flash photolysis: UV plate photometric detection of ClO, BrO, OClO. It was assumed that the only reaction channel was (3). This value must be rejected to an erroneous analysis of the kinetic data (see reference [2]).

(b) Discharge flow: mass spectrometric detection of ClO, BrO, and OClO. This study measured k_1 and the sum of $k_2 + k_3$ separately. Even though the results obtained in this study could not be used to differentiate between channels (2) and (3), by analogy with BrO + BrO and ClO + ClO (where it has been demonstrated that the atomic channel dominates) it can be assumed that channel (2) predominates over channel (3). The reported values for k_1 and $k_2 + k_3$ were: $k_1 = (6.7 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and $k_2 + k_3 = (6.7 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Preferred values taken from data of Clyne and Watson [2], k_3 assumed to be zero.

Preferred Value

$k_1 = 6.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 + k_3 = 6.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta \log (k_2 + k_3) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The temperature dependence for such processes is expected to be small, e.g., BrO + BrO. Although channel (2) is shown proceeding directly Br + Cl + O_2, it almost certainly proceeds through Br + ClOO ($\Delta H° = -27.5$ kJ mol^{-1}) or Cl + BrOO ($\Delta H°$ unknown). The preferred values are based on the data reported by Clyne and Watson [2].

References

[1] Basco, N., and Dogra, S. K., Proc. R. Soc. London Ser. A. **323**, 417 (1971).
[2] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I. **73**, 1169 (1977).
[3] Watson, R. T., J. Phys. Chem. Ref. Data **6**, 871 (1977).
[4] NASA Ref. Pub. #1010, "Chlorofluoromethanes and the Stratosphere," Chapter 1, R. D. Hudson, editor (1977).

4.8. Reactions of BrO_x

$BrO + BrO \rightarrow 2\,Br + O_2$ (1)

$\rightarrow Br_2 + O_2$ (2)

ΔH° (1) = − 28 kJ mol^{-1}

ΔH° (2) = −256 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			
0.65×10^{-12}	298	Clyne and Coxon, 1968 [1]	(a,b)
$(2.62 \pm 1.3) \times 10^{-11} \exp(-(450 \pm 300)/T)$	293–573	Clyne and Cruse, 1970 [2]	(a,c)
$(5.2 \pm 0.07) \times 10^{-12}$	293		
$(1.03 \pm 0.13) \times 10^{-12}$	298	Basco and Dogra, 1971 [3]	(a,d)
$(3.17 \pm 0.67) \times 10^{-12}$	298	Clyne and Watson, 1975 [4]	(a,e)
$1.13 \times 10^{-12} \exp((244 \pm 100)/T)$	223–398	Sander and Watson, 1978 [5]	(a,f)
$(2.4 \pm 0.5) \times 10^{-12}$	298		
Reviews and Evaluations			
$1.45 \times 10^{-11} \exp(-450/T)$	293–573	Clyne and Watson, 1975 [4]	(a,g)
$1.45 \times 10^{-11} \exp(-450/T)$	293–573	NASA, 1977 [6]	(a,g)

Comments

(a) The values of k shown in this table are derived using the following equation: $-d[BrO]/dt = 2k[BrO]^2$. In each of the original publications the authors used the following expression: $-d[BrO]/dt = k[BrO]^2$. This results in a difference of a factor of 2 between the values of k and A tabulated above, and those reported by the authors.

(b) Discharge flow: uv absorption detection of BrO using the $A\,(^2\Pi, v' = 6) \leftarrow X\,(^2\Pi, v'' = 0)$ transition. A value of $(2.25 \pm 0.25) \times 10^5$ cm s^{-1} was reported for k/σ. This value of k/σ was combined with the estimated value for σ of $\sim 3.2 \times 10^{-18}$ cm^2 $molecule^{-1}$.

(c) Discharge flow: uv absorption detection of BrO using the $A\,(^2\Pi, v' = 4) \leftarrow X\,(^2\Pi, v'' = 0)$ transition. Values of $(6.6 \pm 0.8) \times 10^5$ cm s^{-1} and $(8.0 \pm 0.9) \times 10^{-18}$ cm^2 $molecule^{-1}$ were reported k/σ and σ, respectively, at 298 K. These values of k/σ and σ result in the value shown for k at 298 K in the table. Clyne and Cruse reported a positive temperature dependence for k/σ, and combined this data with their 298 K value for σ (BrO monitored at room temperature) and obtained the Arrhenius expression shown in the table. Cruse [7] estimated that the value of $k_1/(k_1 + k_2)$ lies between 0.8 and 0.9.

(d) Flash photolysis: ultraviolet absorption detection (plate photometry) of BrO using the $A\,(^2\Pi, v' = 4) \leftarrow X\,(^2\Pi, v'' = 0)$ and $A\,(^2\Pi, v' = 8) \leftarrow X\,(^2\Pi, v'' = 0)$ transitions. Values of $(2.18 \pm 0.08) \times 10^5$ cm s^{-1} and $(2.71 \pm 0.35) \times 10^5$ cm s^{-1} were reported for $k/\sigma_{(4-0)}$ and $k/\sigma_{(8-0)}$, respectively. These values of k/σ were combined with experimentally determined values of $(4.7 \pm 0.4) \times 10^{-18}$ cm^2 $molecule^{-1}$ and $(3.85 \pm 0.4) \times 10^{-18}$ cm^2 $molecule^{-1}$ for $\sigma(4-0)$ and $\sigma(8-0)$, respectively, resulting in values of $(1.02 \pm 0.17) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and $(1.05 \pm 0.15) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for k.

(e) Discharge flow: mass spectrometric detection of BrO. BrO radicals were either detected directly, or stoichiometrically converted to NO_2 (which was then monitored) upon addition of a large excess concentration of NO. Watson [8] deduced from the mass spectrometric behaviour of Br^+, Br_2^+, and BrO^+ that the major reaction pathway was that producing atomic products (1).

(f) Flash photolysis: ultraviolet absorption detection (photoelectric) of BrO using the $A\,(^2\Pi, v' = 4) \leftarrow X\,(^2\Pi, v'' = 0)$ transition. The temperature dependence of both k/σ and σ were monitored. Values of 2.21×10^5 (223 K), 2.07×10^5 (298 K), and 2.25×10^5 (388 K) cm s^{-1} were determined for k/σ. These were combined with values of 1.56×10^{-17} (233 K), 1.17×10^{-17} (298 K) and 9.67×10^{-18} (388 K) cm^2 $molecule^{-1}$ for σ resulting in the Arrhenius expression, and the value of k at 298 K shown in the table. The rate coefficients were shown to be independent of total pressure from 50–600 Torr. Two independent methods were used to determine the separate values of k_1 and k_2. One method required knowledge of σ(BrO) whereas the other did not. A value of 0.85 ± 0.05 was obtained for $k_1/(k_1 + k_2)$ at 298 K.

(g) This evaluation was based on the temperature dependence reported by Clyne and Cruse [2], but the A-factor was adjusted to give the preferred value of 3.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (value reported by Clyne and Watson [4].

Preferred Value

$k = 2.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} over range 200–400 K.

Reliability

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

Comments on Preferred Values

Four of the five studies [1–3,5] monitored the BrO radical concentration using ultraviolet absorption spectrometry. As the reaction being studied was second order in [BrO] knowledge of σ was required in order to determine k. The notes show how there are substantial differences between the value of σ. Although the magnitude of σ is dependent upon the particular transition, and instrumental parameters such as spectral band width, the most probable reason for the differences is that the technique (based on reaction stoichiometry) used to determine σ in the early studies [1–3] was used incorrectly (discussed in reference [4]). It can be seen that in three of the studies [1,3 and 5] there is good agreement in the reported values of k/σ, however, this may be fortuitous as σ is expected to vary somewhat from study to study. The preferred value for k at 298 K is the average of the values reported in references [4,5]. From the values of k reported in references [4] and [5] it can be stated that the BrO + BrO reaction exhibits no pressure dependence within the range 1–600 Torr. The recent flash photolysis study [5] determined in the temperature dependence of both k/σ and σ independently, but more data are required to confirm the temperature dependence of the reaction. Although the partitioning of the total rate constant into its two components, k_1 and k_2, was studied at 298 K [5] and the ratio $k_1/(k_1 + k_2)$ reported to be 0.85 ± 0.05, it is not clear whether this ratio would be expected to exhibit a temperature dependence.

References

[1] Clyne, M. A. A., and Coxon, J. A., Proc. R. Soc. London Ser. A., **303**, 207 (1968).

[2] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc., **66**, 2214 (1970).

[3] Basco, N., and Dogra, S. D., Proc. R. Soc. London Ser. A., **323**, 1 (1971).

[4] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I., **71**, 336 (1975).

[5] Sander, S. P., and Watson, R. T., Manuscript in preparation (1978).

[6] NASA Ref. Pub. #1010. "Chlorofluoromethanes and the Stratosphere", Chapter 1, R. D. Hudson, editor (1977).

[7] Cruse, H. W., Ph.D. Thesis Queen Mary College, London University (1971).

[8] Watson, R. T., Ph.D. Thesis Queen Mary College, London University (1973).

BrO + $h\nu \rightarrow$ 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

Absorption cross section data

Wavelength range/nm	Reference	Comments
310–355	Clyne and Cruse, 1970 [1]	(a)
318–339	Brown and Burns, 1970 [2]	(b)
320.8; 338.3	Basco and Dogra, 1971 [3]	(c)
339	Sander and Watson, 1979 [4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 1$	289-355	Durie and Ramsay, 1958 [5]	(e)

Comments

(a) BrO produced in a discharge flow system using the Br + O_3 reaction. The vibrational bands (1,0–11,0) of the $A^2\Pi$–$X^2\Pi$ system of BrO are shown in a figure at a spectral resolution of 0.15 nm. σ (4–0) at $\lambda = 338.3$ nm was reported to decrease by a factor of 2 as the spectral slit width was increased from 0.25 to 1.5 nm. σ (4–0) was reported to be $(8.1 \pm 0.9) \times 10^{-18}$ cm^2 molecule^{-1} for a spectral slit width of 1 nm. From an expanded version of figure 3 in reference [1] the relative values of σ can, within a factor of ~2, be deduced for the 1–0 to 11–0 transitions. $\sigma(1\text{–}0) : \sigma(2\text{–}0) \ldots \sigma(11\text{–}0) = 0.35 : 0.45 : 0.60 : 1.0 : 0.85 : 0.60 : 0.50 : 0.55 : 0.45 : 0.30 : 0.30$. These values were derived assuming that the baseline is well below the wavelength axis in figure 3 and that I_0 is not varying significantly (< 10% over the complete range). If the baseline were close to the wavelength axis, then I_0 would be showing a significant variation with wavelength and the relative values of $\sigma(\lambda)$ at shorter wavelengths would need to be increased by the factor $I_0(355\ \text{nm})/I_0(\lambda\ \text{nm})$. The FWHM values of these vibrational bands can be estimated to be ~ 1.5 nm from figure 3.

(b) BrO produced from the flash photolysis of Br_2/O_2 mixtures. From a microdensitometer trace of the BrO spectrum, figure 1, the FWHM of the 4–0 to 8–0 vibrational bands can be estimated to be ~ 1.0 nm. No absolute absorption cross sections determined. Assuming a constant plate sensitivity from 318–339 nm, relative values of $\sigma(4-0) : \sigma(5-0) : \ldots \sigma(8-0)$ can be estimated to be 1.0 : 0.6 : 0.5: 0.6 : 1.10.

(c) Flash photolysis of Br_2/OClO mixtures used to generate BrO. BrO, ClO, and OClO monitored using plate photometry. Values of $(4.7 \pm 0.4) \times 10^{-18}$ and $(3.85 \pm 0.4) \times 10^{-18}$ cm^2 molecule^{-1} were reported for $\sigma(4-0)$ at λ = 338.3 nm, and $\sigma(8-0)$ at λ = 320.8 nm, respectively. However, these values should be considered as estimates as the data analysis procedure used is invalid due to assuming an incorrect reaction mechanism.

(d) Flash photolysis of Br_2/O_3 mixtures used to generate known concentrations of BrO. The $A^2\Pi(v' = 4) \leftarrow X^2\Pi(v'' = 0)$ transition was monitored photoelectrically at 339 nm with a spectral bandwidth (FWHM) of 0.2 nm. The temperature dependence of $\sigma(4-0)$ was determined from 223–388 K. Values of 1.56×10^{-17} (233 K), 1.17×10^{-17} (298 K) and 9.67×10^{-18} (388 K) cm^2 molecule^{-1} were reported.

(e) Flash photolysis of Br_2/O_2 mixtures used to generate BrO. High resolution spectra of BrO revealed that of the 20 bands forming a progression between 289 and 355.5 nm 16 bands were completely diffuse, and although the other four bands showed evidence of rotational fine structure, the individual rotational lines were still distinctly diffuse.

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

At present no preferred values are given for the absorption cross sections. The 4–0 band at $\lambda \sim 338$ nm is the only transition for which there have been several [1,3,4] quantitative determinations of the absorption cross section. The notes show how there are substantial differences between the values of σ. Although the magnitude of σ is dependent upon instrumental parameters such as spectral bandwidth, the most probable reason for the differences is that the technique (based on reaction stoichiometry) used to determine σ in the early studies [1,3] was used incorrectly (discussed in reference [6]). The absorption cross section reported for the 4–0 band by Sander and Watson [4] is at present preferred. Measurement of absorption cross section data, such as σ and the FWHM of the vibrational bands in the $A \leftarrow X$ system, was not the prime interest of any of these studies. The data reported by Clyne and Cruse [1], and to a lesser extent Bown and Burns [2], can be used to estimate (to within a factor of ~ 3) atmospheric J values by, (a) combining the relative values of σ with an absolute determination of $\sigma(4-0)$, and (b) assuming a value of 1.25 nm for the FWHM of each of the vibrational bands—this represents a mean of the two derived values [1,2].

The extensive predissociation observed by Durie and Ramsay [5] indicates that the value of Φ_1 should be taken to the unity for all vibrational bands within the $A-X$ system.

References

[1] Clyne, M. A. A., and Cruse, H. W., Trans. Faraday Soc., **66,** 2214 (1970).

[2] Brown, J., and Burns, G., Can. J. Chem., **48,** 3487 (1970).

[3] Basco, N., and Dogra, S. D., Proc. R. Soc. London Ser. A., **323,** 41 (1971).

[4] Sander, S. P., and Watson, R. T., Manuscript in preparation (1979).

[5] Durie, R. A., and Ramsay, D. A., Can. J. Phys., **36,** 35 (1958).

[6] Clyne, M. A. A., and Watson, R. T., J. Chem. Soc. Faraday Trans. I. **71,** 336 (1975).

HOBr + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ mol^{-1}	$\lambda_{threshold}$/nm
HOBr + $h\nu \rightarrow$ HO + Br	(1)	231	518
$\rightarrow$ HBr + O(^{3}P)	(2)	293	409
$\rightarrow$ BrO + H	(3)	423	283
$\rightarrow$ HBr + O(^{1}D)	(4)	483	248

Note: $\Delta H°_{298}$ values are given since the heat of formation of HOBr at 0 K is not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
~210–400	Anbar and Dostrovsky, 1954 [1]	(a)

Quantum Yield Data: No available experimental data.

Comments

(a) The absorption spectrum of HOBr in an aqueous solution, not in the gas phase, was shown graphically. The absorption maximum was reported to occur at 260 nm.

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 Dostrovsky 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's (HOCl (230 nm), HOBr (260 nm)) were displaced by 30 nm. By analogy with HOCl it is probable that $\Phi_1 \sim$ unity for all wavelengths $\geq$ 200 nm.

Reference

[1] Anbar, M., and Dostrovsky, I., J. Chem. Soc., London, Part I, 1105 (1954).

$BrONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{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: ΔH°_{298} values are given since the heat of formation of $BrONO_2$ and BrONO at 0 K are not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
186–390	Spencer and Rowland, 1978 [1]	(a)

Quantum Yield Data: No available experimental data.

Comments

(a) Absorption cross sections measured at 298 K, and tabulated at 5 nm intervals. The estimated uncertainty in the measurements is ±30% for $\lambda \geq 340$ nm, and ±20% for 186 nm $\leq \lambda \leq$ 335 nm.

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 preferred values are taken from the only known study. The spectrum is similar in appearance to that of $ClONO_2$ except that the absorption cross sections of $BrONO_2$ are significantly greater than those of $ClONO_2$ at wavelengths greater than 300 nm. There is a need for additional absorption cross-section studies using longer optical pathlengths for determining σ at longer wavelengths, and for determining σ as a function of temperature. The absorption cross section data of $ClONO_2$ shows a significant temperature dependence over much of the wavelength range, i.e., ~230–400 nm. Although there *have been no quantum yield studies of $BrONO_2$ photolysis*, it is quite likely that it is photodissociated in a manner similar to $ClONO_2$. The absorption spectrum of $BrONO_2$ is a continuum with evidence of several shoulders suggesting an overall quantum yield for destruction of unity, but where the relative importance of the various pathways changes with wavelength. Unfortunately there are conflicting results as to the photolysis products of $ClONO_2$. One study reported the products to *be Cl + NO_3, in contrast to the other study which reported* the products to be ClONO + $O(^3P)$. Direct studies of the photolysis products are required in order to resolve this problem.

Reference

[1] Spencer, J. E., and Rowland, F. S., J. Phys. Chem. **82**, 7 (1978).

5. Summary of Preferred Rate Data

Summary of preferred rate data

Reaction	k_{298} $cm^3 molecule^{-1} s^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/cm^3 molecule^{-1} s^{-1}$	Temp. range/K	$\Delta(E/R)$/ K
O_x Reactions					
$O + O_2 + M \rightarrow O_3 + M$	3.6×10^{-34} [Ar](k_0)	±0.1	$3.6 \times 10^{-34}(T/300)^{-1.93}$ [Ar]	200–1100	
	5.6×10^{-34} [N_2](k_0)	±0.1	$5.6 \times 10^{-34}(T/300)^{-2.36}$ [N_2]	220–300	
	2.8×10^{-12} (k_∞)	±0.3			
$O + O_3 \rightarrow 2O_2$	9.5×10^{-15}	±0.1	$2.0 \times 10^{-11} \exp(-2280/T)$	220–1000	±130
$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	3.7×10^{-11}	±0.15	$3.0 \times 10^{-11} \exp(67/T)$	200–350	±100
$\rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	0.9×10^{-11}	±0.15	$0.7 \times 10^{-11} \exp(67/T)$	200–350	±100
$O_2 + h\nu \rightarrow 2O$	See data sheets				
$O_3 + h\nu \rightarrow O + O_2$	See data sheets				
HO_x Reactions					
$H + HO_2 \rightarrow H_2 + O_2$	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 −?			
$H + O_2 + M \rightarrow HO_2 + M$	1.8×10^{-32} [Ar](k_0)	±0.2	$1.8 \times 10^{-32}(T/300)^{-0.8}$ [Ar]	200–2000	
	5.9×10^{-32} [N_2](k_0)	±0.2	$5.9 \times 10^{-32}(T/300)^{-1.0}$ [N_2]	200–400	
$H + O_3 \rightarrow HO + O_2$	2.8×10^{-11}	±0.2	$1.4 \times 10^{-10} \exp(-480/T)$	220–360	±100
$O + HO \rightarrow O_2 + H$	3.8×10^{-11}	±0.3			
$O + HO_2 \rightarrow HO + O_2$	3.1×10^{-11}	±0.5			
$O + H_2O_2 \rightarrow HO + HO_2$ $\rightarrow O_2 + H_2O$	2.1×10^{-15}	±0.3	$2.7 \times 10^{-12} \exp(-2100/T)$	283–368	±500
$O(^1D) + H_2 \rightarrow HO + H$ $\rightarrow O(^3P) + H_2$	2.0×10^{-10}	±0.3	2.0×10^{-10}	200–350	±100
$O(^1D) + H_2O \rightarrow 2HO$ $\rightarrow O(^3P) + H_2O$	2.8×10^{-10}	±0.3	2.8×10^{-10}	200–350	±100
$HO + H_2 \rightarrow H_2O + H$	7.1×10^{-15}	±0.1	$1.8 \times 10^{-11} \exp(-2330/T)$	210–300	±300
$HO + HO \rightarrow H_2O + O$	1.8×10^{-12}	±0.2			
$HO + HO + M \rightarrow H_2O_2 + M$	6.5×10^{-31} [Ar](k_0)	±0.3	$6.5 \times 10^{-31}(T/300)^{-2.9}$ [Ar]	300–1500	
	6.5×10^{-31} [N_2](k_0)	±0.3			
$HO + HO_2 \rightarrow H_2O + O_2$	3.5×10^{-11}	±0.5			
$HO + H_2O_2 \rightarrow H_2O + HO_2$	8.0×10^{-13}	±0.3	$7.6 \times 10^{-12} \exp(-670/T)$	200–700	±200
$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}	±0.15	$1.9 \times 10^{-12} \exp(-1000/T)$	220–450	$^{+250}_{-100}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.3×10^{-12}	±0.3			
$HO_2 + O_3 \rightarrow HO + 2O_2$	2.0×10^{-15}	±0.2	$1.4 \times 10^{-14} \exp(-600/T)$	250–400	±200
$H_2O + h\nu \rightarrow HO + H$	See data sheets				
$H_2O_2 + h\nu \rightarrow 2HO$	See data sheets				
NO_x Reactions					
$N + O_2 \rightarrow NO + O$	8.9×10^{-17}	±0.1	$4.4 \times 10^{-12} \exp(-3220/T)$	280–333	±350
$N + O_3 \rightarrow NO + O_2$	$\leq 5 \times 10^{-16}$				
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	±0.15	3.4×10^{-11}	200–400	±100
$N + NO_2 \rightarrow N_2O + O$	1.4×10^{-12}	±0.2			
$O + NO + M \rightarrow NO_2 + M$	6.4×10^{-32} [Ar](k_0)	±0.1	$6.4 \times 10^{-32}(T/300)^{-1.80}$ [Ar]	200–2000	
	1.2×10^{-31} [N_2](k_0)	±0.1	$1.2 \times 10^{-31}(T/300)^{-1.82}$ [N_2]	200–300	
	3.0×10^{-11} (k_∞)	±0.2	$3.0 \times 10^{-11}(T/300)^{+0.3}$	300–1500	

Summary of preferred rate data (continued)

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
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	±0.06	9.3×10^{-12}	230–340	$^{+0}_{-150}$
$O + NO_2 + M \rightarrow NO_3 + M$	9×10^{-32} $[N_2](k_0)$	±0.1			
	2.2×10^{-11} (k_∞)	±0.1			
$O + NO_3 \rightarrow O_2 + NO_2$	1×10^{-11}	±0.5			
$O + N_2O_5 \rightarrow$ products	$\leq 3 \times 10^{-16}$		$\leq 3 \times 10^{-16}$	220–300	
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	4.5×10^{-11}	±0.15	$3.2 \times 10^{-11} \exp(107/T)$	200–350	±100
$O(^1D) + N_2O \rightarrow N_2 + O_2$	7.4×10^{-11}	±0.15	7.4×10^{-11}	200–350	±100
$\rightarrow 2NO$	8.6×10^{-11}	±0.15	8.6×10^{-11}	200–350	±100
$\rightarrow O(^3P) + N_2O$	No recommendation (see data sheet)				
$HO + NO + M \rightarrow HONO + M$	6.5×10^{-31} $[N_2](k_0)$	±0.1	$6.5 \times 10^{-31}(T/300)^{-2.4}$ $[N_2]$	220–440	
	1.0×10^{-11} (k_∞)	±0.2	1.0×10^{-11}	220–440	
$HO + NO_2 + M \rightarrow HONO_2 + M$	1.0×10^{-30} $[Ar](k_0)$	±0.1	$1.0 \times 10^{-30}(T/300)^{-2.9}$ $[Ar]$	300–1200	
	2.6×10^{-30} $[N_2](k_0)$	±0.1	$2.6 \times 10^{-30}(T/300)^{-2.7}$ $[N_2]$	220–550	
	1.6×10^{-11} (k_∞)	±0.2	1.6×10^{-11}	200–1200	
$HO + HONO_2 \rightarrow H_2O + NO_3$	8.5×10^{-14}	±0.1	8.5×10^{-14}	240–470	±300
$HO + HO_2NO_2 \rightarrow$ products	No recommendation (see data sheet)				
$HO_2 + NO \rightarrow HO + NO_2$	8.4×10^{-12}	±0.08	$4.3 \times 10^{-12} \exp(200/T)$	230–425	±200
$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	2.1×10^{-31} $[N_2](k_0)$	±0.1			
	5×10^{-12} (k_∞)	±0.4			
$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	1.2×10^{-20} $[N_2](k_0/s^{-1})$	±0.1		298	
	0.09 (k_∞/s^{-1})	±0.6	$1.4 \times 10^{14} \exp(-10420/T)s^{-1}$	250–300	±500
$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}	±0.06	$2.3 \times 10^{-12} \exp(-1450/T)$	200–360	±200
$NO + NO_3 \rightarrow 2NO_2$	2×10^{-11}	±0.5			
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	1.5×10^{-30} $[N_2](k_0)$	±0.3	$1.5 \times 10^{-30}(T/300)^{-4.6}$ $[N_2]$	300–340	
	5×10^{-12} (k_∞)	±0.3	5×10^{-12}	200–400	
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	6.4×10^{-20} $[N_2](k_0/s^{-1})$	±0.3	$8.8 \times 10^{-6} \exp(-9700/T)$ $[N_2]s^{-1}$	300–340	
	0.20 (k_∞/s^{-1})	±0.3	$5.7 \times 10^{14} \exp(-10600/T)s^{-1}$	273–300	
$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}	±0.06	$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	±150
$NO + h\nu \rightarrow$ products	See data sheets				
$NO_2 + h\nu \rightarrow$ products	See data sheets				
$NO_3 + h\nu \rightarrow$ products	See data sheets				
$N_2O + h\nu \rightarrow$ products	See data sheets				
$N_2O_5 + h\nu \rightarrow$ products	See data sheets				
$HONO + h\nu \rightarrow$ products	See data sheets				
$HONO_2 + h\nu \rightarrow$ products	See data sheets				
$HO_2NO_2 + h\nu \rightarrow$ products	See data sheets				
CH$_4$ Reactions					
$O(^1D) + CH_4 \rightarrow HO + CH_3$	2.2×10^{-10}	±0.3	2.2×10^{-10}	200–300	±100
$\rightarrow HCHO + H_2$	2.4×10^{-11}		2.4×10^{-11}	200–300	±100
$HO + CH_4 \rightarrow H_2O + CH_3$	8.0×10^{-15}	±0.1	$2.4 \times 10^{-12} \exp(-1710/T)$	200–300	±200
$HO + CO \rightarrow H + CO_2$	1.5×10^{-13} (≤ 100 Torr)	±0.05	1.5×10^{-13}	200–300	
$HO + CO \rightarrow$ products	2.8×10^{-13} (1 atm air)	±0.1			
$HO + HCHO \rightarrow H_2O + HCO$ $\rightarrow H + HCOOH$	1.3×10^{-11}	±0.15	1.3×10^{-11}	200–400	±200
$HO_2 + CH_3O_2 \rightarrow O_2 + CH_3OOH$ $\rightarrow HO + O_2 + CH_3O$	6.5×10^{-12}	±0.3			
$HCO + O_2 \rightarrow HO_2 + CO$	5.1×10^{-12}	±0.1			
$HCO + O_2 + M \rightarrow HCO_3 + M$	No recommendation (see data sheet)				
$CH_3 + O_2 \rightarrow HCHO + HO$	No recommendation (see data sheet)				
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	2.6×10^{-31} $[N_2](k_0)$	±0.3	$2.6 \times 10^{-31}(T/300)^{-3}$ $[N_2]$	260–340	
	2×10^{-12} (k_∞)	±0.3	2.0×10^{-12}	200–400	
$CH_3O + O_2 \rightarrow HCHO + HO_2$	6×10^{-16}	±0.6	$5 \times 10^{-13} \exp(-2000/T)$	300–450	±1000
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$ $\rightarrow 2\,CH_3O + O_2$ $\rightarrow CH_3OOCH_3 + O_2$	4.6×10^{-13}	±0.1			
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.5×10^{-12}	±0.3	7.5×10^{-12}	200–300	±500
$CH_3O_2 + NO_2 + M \rightarrow CH_3O_2NO_2 + M$	1.6×10^{-12} (1 atm)	±0.5	1.6×10^{-12} (1 atm)	200–300	±500
$HCHO + h\nu \rightarrow$ products	See data sheets				
$CH_3OOH + h\nu \rightarrow$ products	See data sheets				
SO$_x$ Reactions					
$O + H_2S \rightarrow HO + HS$	2.7×10^{-14}	±0.1	$7.2 \times 10^{-12} \exp(-1660/T)$	250–500	±150
$O + CS \rightarrow CO + S$	2.1×10^{-11}	±0.1	$2.7 \times 10^{-10} \exp(-760/T)$	150–300	±250

Summary of preferred rate data (continued)

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
$O + OCS \rightarrow SO + CO$	1.4×10^{-14}	±0.2	$2.6 \times 10^{-11} \exp(-2250/T)$	220–600	±150
$O + CS_2 \rightarrow SO + CS$ $\rightarrow CO + S_2$ $\rightarrow OCS + S$	5.5×10^{-12}	±0.2	$5.8 \times 10^{-11} \exp(-700/T)$	200–500	±100
$O + SO_2 + M \rightarrow SO_3 + M$	1.4×10^{-33} $[N_2](k_0)$	±0.3	$4.0 \times 10^{-32} \exp(-1000/T)$	200–400	$^{+200}_{-100}$
$HO + H_2S \rightarrow H_2O + HS$	5.3×10^{-12}	±0.1	$1.1 \times 10^{-11} \exp(-225/T)$	250–400	±225
$HO + OCS \rightarrow$ products	$\leq 6 \times 10^{-14}$	$^{+0.7}_{-?}$			
$HO + CS_2 \rightarrow$ products	$\leq 2 \times 10^{-13}$	$^{+0.7}_{-?}$			
$HO + SO_2 + M \rightarrow HOSO_2 + M$	3×10^{-31} $[N_2]$ (k_0) 2×10^{-12} (k_∞)	±0.3 ±0.4	$3 \times 10^{-31}(T/300)^{-2.9}$ $[N_2]$ 2×10^{-12}	200–400 200–400	
$HO_2 + SO_2 \rightarrow$ products	No recommendation (see data sheet)				
$S + O_2 \rightarrow SO + O$	2.0×10^{-12}	±0.15	2.0×10^{-12}	230–400	±100
$S + O_3 \rightarrow SO + O_2$	1.2×10^{-11}	±0.3			
$HS + O_2 \rightarrow HO + SO$	No recommendation (see data sheet)				
$CS + O_2 \rightarrow CO + SO$ $\rightarrow OCS + O$	No recommendation (see data sheet)				
$SO + O_2 \rightarrow SO_2 + O$	9×10^{-18}	±0.5	$6 \times 10^{-13} \exp(-3300/T)$	300–1000	±500
$SO + O_3 \rightarrow SO_2 + O_2$	6×10^{-14}	±0.3	$2.5 \times 10^{-12} \exp(-1100/T)$	220–300	±400
$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}	±0.3			
$SO_3 + H_2O \rightarrow$ products	No recommendation (see data sheet)				
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ $\rightarrow CH_3O_2SO_2$	No recommendation (see data sheet)				
$OCS + h\nu \rightarrow$ products	See data sheets				
$CS_2 + h\nu \rightarrow$ products	See data sheets				
FO_x Reactions					
$O + FO \rightarrow O_2 + F$	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			
$F + H_2 \rightarrow HF + H$	2.5×10^{-11}	±0.2	$2.0 \times 10^{-10} \exp(-620/T)$	200–400	±250
$F + O_2 + M \rightarrow FO_2 + M$	1.1×10^{-32} $[N_2](k_0)$ 3×10^{-11} (k_∞)	±0.3 ±0.5	$1.1 \times 10^{-32}(T/300)^{-2.0}$ $[N_2]$ 3×10^{-11}	270–360 200–400	
$F + O_3 \rightarrow FO + O_2$	1.3×10^{-11}	±0.3	$2.8 \times 10^{-11} \exp(-226/T)$	250–365	±200
$F + H_2O \rightarrow HF + HO$	1.1×10^{-11}	±0.5	$2.2 \times 10^{-11} \exp(-200/T)$	240–360	±200
$F + CH_4 \rightarrow HF + CH_3$	8×10^{-11}	±0.2	$3.0 \times 10^{-10} \exp(-400/T)$	250–450	±150
$FO + O_3 \rightarrow F + 2O_2$ $\rightarrow FO_2 + O_2$	No recommendation (see data sheet)				
$FO + NO \rightarrow F + NO_2$	2×10^{-11}	±0.5			
$FO + NO_2 + M \rightarrow FONO_2 + M$	1.7×10^{-31} $[N_2](k_0)$ 1.2×10^{-11} (k_∞)	±0.7 ±0.4	$1.7 \times 10^{-31}(T/300)^{-3.0}$ $[N_2]$ 1.2×10^{-11}	200–400 200–400	
$FO + FO \rightarrow 2F + O_2$ $\rightarrow FO_2 + F$ $\rightarrow F_2 + O_2$	1.5×10^{-11}	±0.3			
$HF + h\nu \rightarrow$ products	See data sheets				
$COF_2 + h\nu \rightarrow$ products	See data sheets				
$FONO_2 + h\nu \rightarrow$ products	See data sheets				
ClO_x Reactions					
$O + HCl \rightarrow HO + Cl$	1.4×10^{-16}	±0.3	$1.1 \times 10^{-11} \exp(-3370/T)$	293–718	±350
$O + ClO \rightarrow O_2 + Cl$	5.0×10^{-11}	±0.1	$7.5 \times 10^{-11} \exp(-120/T)$	220–425	±120
$O + ClONO_2 \rightarrow ClO + NO_3$ $\rightarrow OClO + NO_2$ $\rightarrow O_2 + ClONO$	1.9×10^{-13}	±0.1	$3.0 \times 10^{-12} \exp(-808/T)$	213–295	±200
$O(^1D) + CF_2Cl_2 \rightarrow ClO + CF_2Cl$ $\rightarrow O(^3P) + CF_2Cl_2$	2.8×10^{-10}	±0.3			
$O(^1D) + CFCl_3 \rightarrow ClO + CFCl_2$ $\rightarrow O(^3P) + CFCl_3$	3.5×10^{-10}	±0.2			
$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ $\rightarrow O(^3P) + CCl_4$	4.8×10^{-10}	±0.2			
$Cl + H_2 \rightarrow HCl + H$	1.8×10^{-14}	±0.2	$4.7 \times 10^{-11} \exp(-2340/T)$	210–1070	±200
$Cl + HO_2 \rightarrow HCl + O_2$	4.1×10^{-11}	±0.3			
$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.3×10^{-13}	±0.2	$1.1 \times 10^{-11} \exp(-980/T)$	265–424	±500
$Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}	±0.06	$2.7 \times 10^{-11} \exp(-257/T)$	205–298	±100
$Cl + CH_4 \rightarrow HCl + CH_3$	1.04×10^{-13}	±0.06	$9.9 \times 10^{-12} \exp(-1360/T)$	200–300	±150
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	5.7×10^{-11}	±0.06	$7.7 \times 10^{-11} \exp(-90/T)$	220–350	±100
$Cl + HCHO \rightarrow HCl + HCO$	7.3×10^{-11}	±0.06	$7.9 \times 10^{-11} \exp(-34/T)$	200–500	±100
$Cl + HONO_2 \rightarrow HCl + NO_3$	$\leq 7 \times 10^{-15}$	$^{+0.3}_{-2.5}$			

Summary of reactions and preferred rate data (continued)

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
$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$	4.9×10^{-13}	±0.1	$3.4 \times 10^{-11} \exp(-1260/T)$	233–350	±200
$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$ $\rightarrow ClONO + ClO$	2.2×10^{-13}	±0.3	$1.7 \times 10^{-12} \exp(-610/T)$	224–273	±400
$HO + HCl \rightarrow H_2O + Cl$	6.6×10^{-13}	±0.06	$3.0 \times 10^{-12} \exp(-425/T)$	210–460	±100
$HO + ClO \rightarrow HO_2 + Cl$ $\rightarrow HCl + O_2$	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	$1.2 \times 10^{-12} \exp(-330/T)$	246–387	±200
$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$	4.1×10^{-14}	±0.1	$2.2 \times 10^{-12} \exp(-1140/T)$	240–422	±200
$HO + CHF_2Cl \rightarrow H_2O + CF_2Cl$	4.4×10^{-15}	±0.1	$1.3 \times 10^{-12} \exp(-1670/T)$	240–400	±200
$HO + CHFCl_2 \rightarrow H_2O + CFCl_2$	2.8×10^{-14}	±0.1	$1.5 \times 10^{-12} \exp(-1180/T)$	240–400	±200
$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	1.2×10^{-14}	±0.15	$5.1 \times 10^{-12} \exp(-1800/T)$	250–460	±200
$ClO + HO_2 \rightarrow HOCl + O_2$ $\rightarrow HCl + O_3$	5.2×10^{-12}	±0.2			
$ClO + NO \rightarrow Cl + NO_2$	1.8×10^{-11}	±0.1	$8.9 \times 10^{-12} \exp(+210/T)$	227–415	±100
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.7×10^{-31} $[N_2]$$(k_0)$ 1.2×10^{-11} (k_∞)	±0.1 ±0.4	$1.7 \times 10^{-31}(T/300)^{-3.0}$ $[N_2]$ 1.2×10^{-11}	250–400 200–400	
$HOCl + h\nu \rightarrow$ products	See data sheets				
$COFCl + h\nu \rightarrow$ products	See data sheets				
$ClONO_2 + h\nu \rightarrow$ products	See data sheets				
$COCl_2 + h\nu \rightarrow$ products	See data sheets				
$CF_2Cl_2 + h\nu \rightarrow$ products	See data sheets				
$CFCl_3 + h\nu \rightarrow$ products	See data sheets				
$CCl_4 + h\nu \rightarrow$ products	See data sheets				
<u>BrO_x Reactions</u>					
$O + HBr \rightarrow HO + Br$	3.9×10^{-14}	±0.2	$7.0 \times 10^{-12} \exp(-1560/T)$	250–400	±300
$O + BrO \rightarrow O_2 + Br$	3×10^{-11}	±0.5			
$Br + HO_2 \rightarrow HBr + O_2$	1×10^{-11}	±0.7			
$Br + H_2O_2 \rightarrow HBr + HO_2$	$\leq 2 \times 10^{-14}$	$^{+0.3}_{-1.7}$			
$Br + O_3 \rightarrow BrO + O_2$	1.1×10^{-12}	±0.1	$1.4 \times 10^{-11} \exp(-760/T)$	220–360	±200
$HO + HBr \rightarrow H_2O + Br$	8.5×10^{-12}	±0.3	8.5×10^{-12}	249–416	±250
$HO + CH_3Br \rightarrow H_2O + CH_2Br$	3.8×10^{-14}	±0.1	$7.6 \times 10^{-13} \exp(-890/T)$	244–350	±200
$BrO + HO_2 \rightarrow HOBr + O_2$ $\rightarrow HBr + O_3$	5×10^{-12}	±0.5			
$BrO + NO \rightarrow Br + NO_2$	2.1×10^{-11}	±0.1	$8.7 \times 10^{-12} \exp(+260/T)$	224–425	±100
$BrO + NO_2 + M \rightarrow BrONO_2 + M$	3×10^{-31} $[N_2]$$(k_0)$ 1.2×10^{-11} (k_∞)	±0.4 ±0.4	$3 \times 10^{-31}(T/300)^{-3.0}$ $[N_2]$ 1.2×10^{-11}	200–400 200–400	
$BrO + O_3 \rightarrow Br + 2O_2$	$< 5 \times 10^{-15}$	$^{+0.5}_{-?}$			
$BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}	±0.3			
$\rightarrow Br + Cl + O_2$ $\rightarrow BrCl + O_2$	6.7×10^{-12}	±0.3			
$BrO + BrO \rightarrow 2Br + O_2$ $\rightarrow Br_2 + O_2$	2.8×10^{-12}	±0.1	2.8×10^{-12}	220–440	±500
$BrO + h\nu \rightarrow$ products	See data sheets				
$HOBr + h\nu \rightarrow$ products	See data sheets				
$BrONO_2 + h\nu \rightarrow$ products	See data sheets				

Appendix I

Enthalpy data

Substance	$\Delta H^\circ_f(298)$ kJ mol^{-1}	$\Delta H^\circ_f(0)$ 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

Enthalpy data (continued)

Substance	$\Delta H^\circ_f(298)$ kJ mol^{-1}	$\Delta H^\circ_f(0)$ kJ mol^{-1}	Notes
HO_2	2 ± 8	5 ± 8	2
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	7 ± 8		10
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_5	107.5		2
C_2H_6	− 83.8	− 68.3	2
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
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

Enthalpy data (continued)

Substance	$\Delta H^\circ_f(298)$ kJ mol^{-1}	$\Delta H^\circ_f(0)$ kJ mol^{-1}	Notes
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_2Cl	125		19
CH_2Cl_2	− 95.4	− 88.5	18
CH_3Cl	− 82.0	− 74.0	18
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

Notes

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26. Estimated value. Derived from bond energy considerations for $ClONO_2$.

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} =	$6.91 \times 10^7 T^2$	$6.91 T^2$	$69.1 \times 10^{-5} T^2$	$1.904 \times 10^{-40} T^2$	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.