Survey of Photochemical and Rate Data for Twenty-eight Reactions of Interest in Atmospheric Chemistry

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Photochemical and rate data have been evaluated for 28 gas phase reactions of interest for the chemistry of the stratosphere. The results are presented on data sheets, one per reaction. For each reaction, the available data are summarized. Where possible there is given a preferred value for the rate constant or, for the photochemical reactions, preferred values for primary quantum yields and optical absorption coefficients.

Key words: Atmospheric chemistry; chemical kinetics; data evaluation; gas phase reactions; optical absorption coefficients; photochemistry; quantum yields; rate constants.

Contents

267

J. Phys. Chem. Ref. Data, Vol. 2, No. 2, 1973

Summary of Evaluated Rate Data

Reaction		Rate constant k (cm³ molecule⁻¹ s⁻¹)	Temperature range (K)	Uncertainty in log k
$H + HNO$	$\rightarrow H_2 + NO$	$> 5 \times 10^{-14}$	211–703	
		$7 \times 10^{-12}*$	2000	± 0.3
$H + HNO_2$	$\rightarrow$ Products	No recommendation		
$H + HNO_3$	$\rightarrow$ Products	$< 1 \times 10^{-13}$	300	
$H + H_2O_2$	$\rightarrow H_2 + HO_2$	$2.8 \times 10^{-12} \exp(-1900/T)$	300–800	± 0.3
	$H_2O + HO$	No recommendation		
$H + NO_2$	$\rightarrow HO + NO$	4.8×10^{-11}	300	± 0.1
$H + O_3$	$\rightarrow HO + O_2$	2.6×10^{-11}	300	± 0.1
$HNO + HO$	$\rightarrow H_2O + NO$	$7 \times 10^{-11}*$	1600–2100	± 0.7
$HNO_2 + HO$	$\rightarrow H_2O + NO_2$	No recommendation*		
$HNO_2 + O$	$\rightarrow HO + NO_2$	No recommendation		
$HNO_3 + HO$	$\rightarrow H_2O + NO_3$	$6 \times 10^{-13} \exp(-400/T)*$	300–650	± 0.5
$HNO_3 + O$	$\rightarrow HO + NO_3$	$< 1.5 \times 10^{-14}$	300	
$HO + H_2O_2$	$\rightarrow HO_2 + H_2O$	$1.7 \times 10^{-11} \exp(-910/T)$	300–800	± 0.2
$HO + O_3$	$\rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-1000/T)*$	220–450	± 0.3
$HO_2 + HO_2$	$\rightarrow H_2O_2 + O_2$	$3 \times 10^{-11} \exp(-500/T)$ (a)*	300–1000	± 0.3 (b)
$H_2O + NO + NO_2$	$\rightarrow 2 HNO_2$	$< 1.1 \times 10^{-55}$ (c)*	300	
$H_2O + N_2O_5$	$\rightarrow 2 HNO_3$	$< 1 \times 10^{-20}*$	300	
$H_2O + O(^1D)$	$\rightarrow 2 HO$	$3.5 \times 10^{-10}*$	300	± 0.1
$H_2O_2 + NO$	$\rightarrow HO + HNO_2$	$< 5 \times 10^{-20}*$	300	
		$\sim 2 \times 10^{-20}$	550	
$NO + O_3$	$\rightarrow NO_2 + O_2$	$9 \times 10^{-13} \exp(-1200/T)$	198–330	± 0.11
$NO_2 + O_3$	$\rightarrow NO_3 + O_3$	$5 \times 10^{-17}*$	298	± 0.2
$N_2O + O(^1D)$	$\rightarrow N_2 + O_2$	$1.1 \times 10^{-10}*$	300	± 0.1
	$\rightarrow 2 NO$	$1.1 \times 10^{-10}*$	300	± 0.1
$O + O_3$	$\rightarrow 2 O_2$	$1.9 \times 10^{-11} \exp(-2300/T)*$	200–1000	± 0.1
$O_2(^1\Delta) + M$	$\rightarrow O_2 + M$	$2.2(T/300)^{0.8} \times 10^{-18}(M = O_2)$	285–322	± 0.1
		$< 2 \times 10^{-20}$ $(M = N_2)$	300	
$O_2(^1\Sigma) + M$	$\rightarrow O_2 + M$	$1.5 \times 10^{-16}(M = O_2)$	300	± 0.12
		$2.0 \times 10^{-15}(M = N_2)$	300	± 0.1
		$4 \times 10^{-12}(M = H_2O)$	300	± 0.18

(a) $-d[HO_2]/dt = 2k[HO_2]^2$.

(b) Error in log k increases to ± 1 at 1000 K.

(c) $-d[NO_2]/dt = k[NO][NO_2][H_2O]^2$. Value of k is for a surface reaction. This is adopted as the upper limit for the gas phase rate constant.

  *Changed from value recommended in NBS Reports 10692 (Jan. 1972) and 10828 (April 1972).

Summary of Evaluated Photochemical Data

Reaction	Quantum yield, $\phi(\lambda)$	Wavelength λ, nm	Wavelength range nm, for absorption coefficients
$HNO_3 + h\nu \rightarrow HO + NO_2$	no recommendation*		190–370*
$H_2O_2 + h\nu \rightarrow 2 HO$	1	200–300	185–225
			254
$O_3 + h\nu$ (vis) $\rightarrow O + O_2$	1	450–750	440–850
$O_3 + h\nu$ (uv) $\rightarrow O(^1D) + O_2(^1\Delta)$	1	250–310	200–360
	0	> 310	
$\rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	0	< 350	
$\rightarrow O(^3P) + O_2$ (Singlet)	0	< 310	
	~ 1	310–350	
$\rightarrow O$ (total) $+ O_2$	1	250–350	
$\rightarrow O(^1D) + O_2(^1\Sigma_g^+)$	0	250–350	
$\rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	0	250–350	

  *Changed from value recommended in NBS Report 10828 (April 1972).

1. Introduction

This review presents data sheets on the chemical kinetics and photochemistry of 28 gas phase reactions.

These reactions were selected for review on the basis that they are potentially important reactions in the chemistry and photochemistry of the stratosphere, the values for their rates and quantum yields were needed in models, and what value should be used was uncertain. Some of them had not been reviewed. For others, an updating or validation of an existing evaluation appeared desirable. Most of them also apply to tropospheric chemistry. They are part of a larger set of reactions that must be considered in models of the chemistry of the stratosphere. These data sheets are the first of a group that will cover this larger set of reactions.

The data sheets provide for each reaction:

An estimate, if possible, of the most reliable value for the rate constant or in the case of a photochemical system, for the photoabsorption coefficient and primary quantum yield.

An estimate of the reliability of that value.

Sufficient information to make apparent the basis for that value.

A summary of the available data.

The data sheets were prepared during the period July 1971–January 1973. The conclusions in them are based on the experimental work published or privately communicated to the reviewers or editor in completed manuscript form up to the date of preparation (which is shown on each data sheet). Summaries of data in each evaluation show all the work considered to be pertinent. Reference lists also include other papers examined by the evaluators.

Most of these data sheets were originally issued in references [1] and [2].

In some instances, the recommendation has been changed by consideration of data published since the publication dates of these reports. These changes in preferred values are indicated in the data sheets.

2. Evaluation of Data

Each data sheet has been prepared by chemical kineticists or photochemists who are familiar with the measurement techniques and may have done research on this or closely related reactions. The evaluators are identified on each data sheet. Their conclusions are based on a critical examination of the available experimental data, an assessment of the techniques used, and a consideration of the behavior of related chemical systems.

The reader is warned that the state of the art varies sharply from reaction to reaction. In some cases a firm statement may be made about the rate constant or quantum yield. In others, all the evaluator can do is to point out the lack of data or the low reliability of the existing measurements. That type of information is important and must be considered by the user.

The conclusions of the evaluators are, necessarily, tentative. Atmospheric chemistry is an active research field. New data and new understanding of the experimental techniques will dictate revision of some of the results presented here. All that we can hope is that our recommendations reflect the best judgments of the data evaluators about the current state of the art.

3. Description of Data Sheets

The general form for a data sheet is described immediately below. Although this usually is followed, some modifications have been made, dictated by the type of material to be handled. Some conventions are explained in following section.

3.1. Format of a Typical Data Sheet

a. Statement of the chemical reaction or photochemical process considered and explicit definition of the chemical kinetic rate constant evaluated.

b. Auxiliary data (e.g. thermochemical data) and statement of related chemical reactions.

c. Summary of experimental chemical kinetic or photochemical data. Values of directly measured quantities are given rather than derived values based on auxiliary data. A brief statement of experimental conditions is included.

d. Preferred, selected, or estimated value for the quantity evaluated, i.e. chemical kinetic rate constant, photoabsorption coefficient, or primary photochemical quantum yield. A statement about the reliability of this value follows.

e. Remarks indicating the basis for the preferred value, comments on individual data items, and general discussion of the chemical system. Sometimes specific recommendations are made for additional studies to clarify areas of disagreement.

f. References. The name of the evaluator and the date of preparation follow the reference list.

3.2. General Conventions

a. Each Data Sheet is an independent entity. References to other data sheets are treated on the same basis as those to journal articles and reports.

b. Reactions and photochemical processes are numbered in a single sequence. This numbering is independent of that used in other data sheets. References are keyed by letters.

c. Physical quantities are given in units consistent with the (metric) International System of Units. Occasionally these are supplemented by values in units hallowed by tradition, e.g. kcal mol^{-1} in addition to kJ mol^{-1}. In all cases the units are identified.

The value of a physical quantity shows only the sig-

nificant figures. The last figure shown is, in most cases, subject to some uncertainty.

Charts are included (Appendix) for conversion of quantities from one system of units to another. Definitions and conventions concerning specific properties are given below.

Rate Constant

A rate constant for a chemical reaction, k, is a measure of the change in concentration of a species per unit concentration per unit time.

Almost all of the reactions evaluated here are elementary processes. For them the rate expression is derivable from the statement of the reactions:
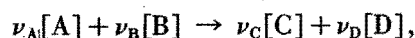
$$\nu_A[A] + \nu_B[B] \rightarrow \nu_C[C] + \nu_D[D],$$

$$k[A]^{\nu_A}[B]^{\nu_B} = (-1/\nu_A)d[A]/dt = (-1/\nu_B)d[B]/dt,$$

$$= (1/\nu_C)d[C]/dt = (1/\nu_D)d[D]/dt,$$

as an example, for the reaction $A + 2B \rightarrow AB_2$,

$$-d[A]/dt = -(1/2)d[B]/dt = d[AB_2]/dt = k[A][B]^2.$$

Wherever there may be any doubt an explicit rate expression is given.

Rate constants are expressed using concentrations in (molecules cm^{-3}) and time in seconds. This means that the units for integral order reactions are:

1st order	s^{-1}
2d order	cm^3 molecule^{-1} s^{-1}
3rd order	cm^6 molecule^{-2} s^{-1}

Tables of conversion factors for units of rate constants are given in the Appendix.

Normally, the temperature dependence of a rate constant is shown using the Arrhenius expression: $k = A \exp(-C/T)$ where C is the activation energy divided by the gas constant, i.e. E^*/R.

Equilibrium Constants

Equilibrium constants, K, are given in concentration units. They are for mixtures of ideal gases. They are related to the usual equilibrium constants for pressure units by

$$\log K = \log K_P - \Delta n \log(RT)$$

where Δn is moles of products minus moles of reactants, R is the gas constant, and T the absolute temperature in Kelvin. The gas constant must have units consistent with the concentration units and the pressure units, e.g. dm^3 atm mol^{-1}K^{-1} or cm^3 atm molecule^{-1}K^{-1}.

Quantum Yield

A quantum yield is a measure of the chemical change per quantum of light absorbed. Overall quantum yields in a system, indicated by the symbol uppercase phi, Φ, include all changes caused by the primary light absorbing process and secondary reactions that follow it. The initial quantum yield, indicated by lowercase phi, ϕ, is a measure of the change occurring solely in a single light absorbing step. Occasionally it is desirable to indicate what species was measured or the formal basis for recording the quantum yield, as for example, $\Phi(-H_2O_2)$, for the total disappearance of hydrogen peroxide in its photolysis, or $\phi(OH)$ for product formation in $H_2O_2 + h\nu \rightarrow 2 OH$.

Optical Absorption Coefficients

Optical absorption coefficients are measures of the fraction of incident light transmitted by a sample per unit concentration and per unit length. They are defined and discussed in the introduction to a conversion chart in the Appendix. They are reported in data sheets either in figures or as numerical values. While we have attempted to use a consistent set of units for the numerical values, the figures retain the ordinates and abscissae used in the original publications.

d. The uncertainty in a preferred value given in a data sheet is the evaluator's estimate of that value's reliability. This is a subjective judgment that, to a high degree of probability, the true value of the quantity lies within the bounds indicated.

Uncertainties are indicated in several ways:

$A < k < B$ means k lies in the range between A and B.

$k < B$ means B is an upper limit.

$k \sim B$ means that B is only a rough guide to the value of k.

$k = A \pm B$ means that a reasonably reliable estimate of the likely error can be stated. This is an estimate by the evaluator of the absolute accuracy of the preferred value. It is a subjective judgment derived from intercomparison of data sets, consideration of related reactions studied with the same technique, estimates of how well the parameters could have been controlled, and comparison with theory. It means that in the evaluators judgment, the true value will lie within the indicated limits to a high level of confidence (90 to 95 percent).

Sometimes it is more appropriate to give $\log_{10} k = C \pm D$, "k uncertain to E percent" or "k uncertain to a factor of F", all three of which are equivalent statements of multiplicative limits. The statement that k has the value k_0 and is uncertain to a factor of F means $k_0/F < k < k_0 F$.

Formally, substantial sets of parentheses are required when stating uncertainties using the plus or minus sign, e.g.

$$k = (1.2 \pm 0.3) \times 10^{-9} \exp((-3.0 \pm 0.5) \times 10^3/T).$$

These conventions are difficult to enforce. Therefore we permit the convention

$$k = 1.2 \pm 0.3 \times 10^{-9} \exp(-3.0 \pm 0.5 \times 10^3/T),$$

based on the hierarchy of operators

$$\pm > (\times, \div) > (+, -).$$

Acknowledgement

In the preparation of these data sheets, it has occasionally been necessary to ask authors to clarify their published work. We wish to thank them for responding to questions and for supplying additional information and data. We are especially grateful to those who supplied data prior to their formal publication.

References

[1] Hampson, R. F., ed., Chemical Kinetics Data Survey I. Rate Data for Twelve Reactions of Interest for Stratospheric Chemistry, NBS Report 10692, National Bureau of Standards, Washington, D.C., Jan. 1972, 44 pp. Unpublished.

[2] Hampson, R. F., ed., Chemical Kinetics Data Survey II. Photochemical and Rate Data for Fifteen Gas Phase Reactions of Interest for Stratospheric Chemistry, NBS Report 10828, National Bureau of Standards, Washington, D.C., April 1972, 91 pp. Unpublished.

4. Data Sheets

4.1. The Reaction Between H and HNO

$$H + HNO \rightarrow H_2 + NO \hspace{4cm} k_1$$
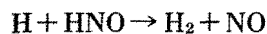
Auxiliary Data

$$\Delta H^\circ_{298} = -227 \text{ kJ/mol } (-54.3 \text{ kcal/mol}) \hspace{2cm} \text{(a)}$$

Data

k_1 (cm^3 molecule^{-1} s^{-1})	System
$> 5 \times 10^{-14}$ (211–703 K)	NO, H$_2$ discharge, flow system. Clyne, Thrush, 1962 (b); Thrush, 1965 (d).
$10 \pm 5 \times 10^{-12}$ (1600–2000 K)	H$_2$, O$_2$, N$_2$, NO flames. Bulewicz, Sugden, 1964 (c).
$8 \pm 2 \times 10^{-12}$ (2000 K)	H$_2$, O$_2$, N$_2$, NO flames. Measured [H] as function of time. Halstead, Jenkins, 1968 (e).
$3.9 \pm 1.9 \times 10^{-12}$ (2117 K)	C$_3$H$_8$, O$_2$, N$_2$, NO flames. Measured [H] as function of time. Smith, 1972 (f).

Preferred Value

Changed from that in NBS Report 10692 (Jan. 1972).)
k_1 (211–703 K) $> 5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.
k_1 (2000 K) $= 7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
k_1 (2000 K) good to a factor of 2 and may be good to a factor of 1.5.

Remarks

Value of k_1 (2000 K) chosen as simple average of values in ref. (c), (e), and (f). The combination of this result with the lower limit from (b, d) leads to an upper limit of 10 kJ/mol (2.3 kcal/mol) for any activation energy.

References

(a) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).
(b) M. A. A. Clyne and B. A. Thrush, Disc. Faraday Soc. **33**, 139 (1962).
(c) E. M. Bulewicz and T. M. Sugden, Proc. Roy. Soc. (London) **A277**, 143 (1964).
(d) B. A. Thrush, Progr. React. Kin. **3**, 63 (1965).
(e) C. J. Halstead and D. R. Jenkins, Chem. Phys. Lettrs. **2**, 281 (1968).
(f) M. Y. Smith, Combustion and Flame **18**, 293 (1972).

R. Brown
July, 1972

4.2. The Reaction Between H and HNO$_2$

$$H + HNO_2 \rightarrow H_2 + NO_2 \hspace{3cm} k_1$$
$$\rightarrow H_2O + NO \hspace{3cm} k_2$$

Auxiliary Data

$$\Delta H_{298} (1) = -105 \text{ kJ/mol } (-25.2 \text{ kcal/mol}) \hspace{1cm} \text{(a)}$$
$$\Delta H_{298} (2) = -290 \text{ kJ/mol } (-69.3 \text{ kcal/mol}) \hspace{1cm} \text{(a)}$$

Data

No data exist on these rate constants.

Preferred Value

None.
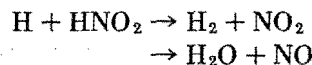
Remarks

No information is available. The upper limit for the reaction k(H + HNO$_3$ $\rightarrow$ products) $< 1 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} by Morris and Niki (b) may be applicable. The only justification is on the basis of structural and energetic similarities. Clearly, if this should turn out to be an important reaction, its rate must be measured.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).
(b) E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **75**, 3193 (1971).

W. Tsang
August, 1971

4.3. The Reaction Between H and HNO₃

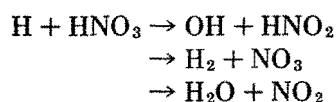$$H + HNO_3 \rightarrow OH + HNO_2 \qquad k_1$$
$$\rightarrow H_2 + NO_3 \qquad k_2$$
$$\rightarrow H_2O + NO_2 \qquad k_3$$

Auxiliary Data

$\Delta H°_{298}$ (1) $= -123$ kJ/mol $(-29.5$ kcal/mol$)$ (a,b)

$\Delta H°_{298}$ (2) $= -12 \pm 21$ kJ/mol $(-3 \pm 5$ kcal/mol$)$

$\Delta H°_{298}$ (3) $= -292$ kJ/mol $(-69.7$ kcal/mol$)$

Data

Quantity measured	System
$\dfrac{k(H + HNO_3) \text{ all channels}}{k (H + \text{trans-2-butene})}$ <0.1	Discharge-flow system coupled with mass spectrometer. Traces of HNO₃ (10^{12} molecule cm⁻³) added to H-atom rich (10^{14} atom cm⁻³) system. Rate of decay of HNO₃ (monitored by $m/e = 46$ peak, NO₂⁺) compared with rate of decay of trans-2-butene under similar conditions. Morris, Niki, 1971 (ref. d).
$k (H + NO_2)/k_1 = 60 \pm 30$ $(k_3 + k_2)/k_1 = 0.06 \pm 0.02$	Photolysis of HNO₃ at 265 nm. in presence of H₂. Relative quantum yield of decomposition of HNO₃ (monitored by meas. of [NO₂]) in presence and absence of H₂ measured. Many step mechanism used to interpret data. Berces, Forgeteg, 1970 (ref. c).

Preferred Value

$(k_1 + k_2 + k_3) < 1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

Remarks

The preferred value is the upper limit derived in (d). It is based on the value of k (H + trans-2-butene)$= 9 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ given in (e).

This relatively low value of k suggests an activation energy in excess of 12 kJ/mol (4 kcal/mol).

Comments on Measurements

Ref. (c)

Rejected.

Johnston (f) has criticized the work in ref. (c) on the grounds of heterogeneity. He claims that the processes $NO_2 + h\nu \rightarrow NO + O$; $4HNO_3 + 2NO \rightarrow 6NO_2 + 2H_2O$ (heterogeneous) are of major importance. Note that the photolytic results are from the latter stages of the reaction and thus a large quantity of NO₂ is in fact present. The HNO₃/H₂ ratio is also very close to the limit above which the authors feel that quantitative results are no longer valid (due to the considerations raised by Johnston).

Ref. (d)

This direct method accepted in preference to indirect method in (c).

It should be noted that the validity of the result in (d) may be affected by the fact that the mass 46 peak is also of importance in the mass spectra of NO₂ and NO₃. However the reaction of H atoms with NO₂ (and possibly with NO₃) is very fast. This will reduce the concentrations of these latter compounds.

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3 (Jan. 1968).

(b) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).

(c) T. Berces, S. Forgeteg, and F. Marta, Trans. Far. Soc. **66**, 648 (1970).

(d) E.D. Morris, Jr. and H. Niki, J. Phys. Chem. **75**, 3193 (1971).

(e) E. E. Daby and H. Niki, J. Chem. Phys. **51**, 1255 (1969).

(f) H. S. Johnston, Formation and Stability of Nitric Acid in the Stratosphere, typescript, University of California, Berkeley, California (1971).

W. Tsang
January, 1972

4.4 The Reaction of H with H₂O₂

Two channels are possible for this reaction; they are

$$H + H_2O_2 \rightarrow H_2 + HO_2 \qquad k_1$$
$$H + H_2O_2 \rightarrow H_2O + HO \qquad k_2$$
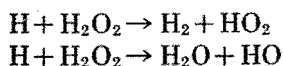
Auxiliary Data

$\Delta H°_{298}$ (1) $= -61 \pm 8$ kJ/mol $(-14.5 \pm 2$ kcal/mol$)$ (a)

$\Delta H°_{298}$ (2) $= -284$ kJ/mol $(-68.0$ kcal/mol$)$ (a)

$\log_{10} K_{eq.}$ (1) $= 0.342 + 3.26$ $(1000/T)$ (b)

$\log_{10} K_{eq.}$ (2) $= 0.877 + 14.98$ $(1000/T)$ (b)

Data

The available rate data have been presented and evaluated by Baulch, Drysdale, Horne, and Lloyd (c). There have been no more recent measurements.

Albers et al. (d) measured the total rate of removal of D atoms in a discharge-flow reactor from 294 to 464 K with 5–8 torr H_2O_2 and added O atoms to suppress the chain decomposition initiated by OH. D atoms were monitored by ESR and mass spectrometry. They estimate the $k_1/k_2 \approx 10$ for D atoms at 421 K. Also they find $k_1^{(H)}/k_1^{(D)} = 0.43$ at 375 K. They give the result that $k_1^{(D)} + k_2^{(D)} = 1.2 \times 10^{-11}$ exp $(-4200/RT)$ cm^3 molecule^{-1} s^{-1}. (294–464 K).

Baldwin et al. (e) studied the decomposition of H_2O_2 in the presence of H_2 from 713–773 K. They report k_1/k_2 to have the value 0.143 over this temperature range (note: in the abstract this is incorrectly given as 0.125). Also they measure the ratio k_2/k_3 where (3) is $H + O_2 + M \rightarrow HO_2 + M$. From this ratio and their previously measured values of k_3/k_4 where (4) is $H + O_2 \rightarrow HO + O$ they derive values of k_2/k_4. Baulch, et al. (c) use the values k_1/k_2 and k_2/k_4 in (e) with their own recommended expression for k_4 to obtain values of k_1. (Note: Because Baulch, et al. used the value of k_1/k_2 in Baldwin's abstract, the calculated values of k_1 given on p. 212 should be increased by 14%; however this will not seriously affect their evaluation).

Preferred Value

$k_1 = 2.8 \times 10^{-12}$ exp $(-1900/T)$ cm^3 molecule^{-1} s^{-1} (300–800 K).

Uncertainty: factor of two.

No value is recommended for k_2.

Remarks

The recommendations of Baulch, et al. have been adopted. The value derived there for $k_2 = 3.7 \times 10^{-9}$ exp $(-5900/T)$ cm^3 molecule^{-1} s^{-1} as noted there can not be recommended with any confidence because of the unreasonably high value of the pre-exponential factor. By extrapolation, k_1 at stratospheric temperatures (220 K) is estimated to be 5×10^{-16} cm^3 molecule^{-1} s^{-1}. From these expressions k_2/k_1 at 220 K is estimated to be 10^{-5}, subject to a large uncertainty.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).
(b) V. N. Kondratiev, Rate Constants of Gas Phase Reactions—Reference Book, R. M. Fristrom, editor. National Technical Information Service, Springfield, Virginia COM–72–10014 (Jan. 1972).
(c) D. L. Baulch, D. D. Drysdale, D. G. Horne, A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions volume 1, Homogeneous gas phase reactions of the H_2-O_2 system, Butterworth & Co., London (1972).
(d) E. A. Albers, K. Hoyermann, H. Gg. Wagner, J. Wolfrum, 13th Combustion Symposium, 81 (1971).
(e) R. R. Baldwin, D. Brattan, B. Tunnicliffe, R. W. Walker, S. J. Webster, Combustion and Flame 15, 133 (1970).

M. D. Scheer
September, 1972

4.5. The Reaction Between H and NO₂

$H + NO_2 \rightarrow OH + NO$ $\qquad\qquad$ k_1

Auxiliary Data

$\Delta H°_{298} = -122$ kJ/mol (−29.1 kcal mol) $\qquad$ (a)

Data

Quantity measured	System
$k_1 = 4.8 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1}	Flow system, NO₂, microwave discharge in H₂/Ar on H₂/He mixt. $\Delta[H]$, $\Delta[NO_2]$ meas. 298 K. Phillips, Schiff, 1962 (b).
k_1/k (H + Cl₂) = 0.16 exp $(1.58 \times 10^3/T)$	H₂, Cl₂, NO₂ (500–540 K). Rosser, Wise, 1961 (c).
k_1/k (H + O₂ + M) = 6 × 10²¹ molecules cm^{-3}	H₂, O₂, NO₂ 633 K, M = H₂. Also values for M = O₂, N₂, CO₂, H₂O, He. Ashmore, Tyler, 1962 (d).

Preferred Value

$k(298$ K$) = 4.8 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1}.

Estimated uncertainty: ±25 percent.

Remarks

The above value and error limits are those given in (b). The rate was measured in Ar and He carriers and is 10 percent larger in He than in Ar. The difference is statistically significant and suggests that the observed reaction rate was partially limited by diffusion mixing of the reactants. An activation energy of 2 kcal/mol^{-1} (8 kJ/mol) results from combining the results at 298 K (b) and 633 K (d) using k (H + O₂ + H₂) = 5 × 10^{-32} cm^6 molecule^{-2} s^{-1} at 633 K (g), following Schofield (f). A lower activation energy, 1.5 kcal/mol^{-1} (6 kJ/mol) results from combining the data in (b) and (c) using k(H + Cl₂) = 4.5 × 10^{-11} cm^3 molecule^{-1} s^{-1}, extrapolating the evaluation in (h). There is no good basis for choosing between these. Measurements at temperatures below 273 K are needed. If the upper limiting value of 2 kcal/mol for the activation energy is used, then the

estimated value for the rate constant at 220 K is one-third the value at 298 K. The uncertainty at this temperature is unknown. A recent mass-spectrometric study of the stoichiometry of the reactions of OH generated by this reaction is reported in (e).

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).

(b) L. F. Phillips and H. I. Schiff, J. Chem. Phys. **37**, 1233 (1962).

(c) W. A. Rosser and H. Wise, J. Phys. Chem. **65**, 532 (1961); **65**, 2277 (1961).

(d) P. G. Ashmore and B. J. Tyler, Trans. Faraday Soc. **58**, 1108 (1962).

(e) M. F. R. Mulcahy and R. H. Smith, J. Chem. Phys. **54**, 5215 (1971).

(f) K. Schofield, Planet. Space Sci. **15**, 643 (1967).

(g) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, High Temperature Reaction Rate Data, Report No. 3 (April 1969), Department of Physical Chemistry, The University, Leeds, England.

(h) V. N. Kondratiev, Rate Constants of Gas Phase Reactions — Reference Book, R. M. Fristrom, editor. National Technical Information Service, Springfield, Virginia, COM–72–10014 (Jan. 1972).

R. L. Brown
February 1972

4.6. The Reaction Between H and O_3

$$H + O_3 \rightarrow OH \ (X \ ^2\Pi, \ v > 0) + O_2 \qquad\qquad k_1$$
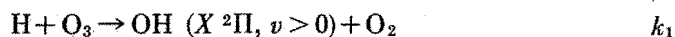
Auxiliary Data

$$\Delta H^\circ_{298} = -322 \ \text{kJ/mol} \ (-76.9 \ \text{kcal/mol}) \qquad (a)$$

Data

k_1 (cm^3 molecule^{-1} s^{-1})	System
$(2.6 \pm 0.5) \times 10^{-11}$	Room temp. flow system. H-atom from electric discharge. O_3 or H at pressure $< 5 \times 10^{-4}$ torr. $0.17 < H/O_3 < 3$. Total pressure 0.5 torr (He or Ar). Mass spec. measurement of H, O_3. Reaction time ~ a few ms. 24 measurements. Phillips, Schiff, 1962 (b).
$\sim 2 \times 10^{-11}$	Room temp. flow system. O_3 (in O_2 mixed with H and H_2 (in Ar) [H] ~ [O_3] ~ 6×10^{11} molecule cm^{-3} with total [M]/[O_3] ~ 100 Emission from HO‡ measured. Potter, Coltharp, Worley, 1971 (f).
$(4 \pm \sim 1) \times 10^{-12}$	Room temp., Polanyi diffusion flame O_3 mixed into H/H_2 atmosphere. Pressure ~ 0.08 torr. $7 < H/O_3 < 20$. Measured spatial distribution of OH emission. 2 measurements. Garvin, McKinley, 1956 (c).

Preferred value

k_1 (298 K) $= 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
Estimated uncertainty: ± 25 percent.

Remarks

The OH is formed to a large extent in vibrational levels 4–9 of the ground state. At ~ 1 torr significant collisional and reactive quenching occurs in the rate experiments. The most recent effort to determine the initial vibrational level populations is by Charters, MacDonald, and Polanyi (d). Earlier work is summarized there.

The suggested rate and uncertainty are quoted from ref. (b), the most extensive study. This value also was selected by Kaufman (e). The validity of the result depends upon whether or not the reaction times (1 to 5 ms) are short enough to support their assumption that reaction (1) is "extremely rapid in comparison with the secondary reactions". $OH^* + O_3 \rightarrow HO_2 + O_2$ is the primary worry (e). The approximate value from ref. (f) supports this selection.

The other rate measurement (ref. c) depends strongly upon the choice of a diffusion coefficient, the precise shape of the distribution of OH radiation, and the extent of rapid secondary reactions (ref. e). (The last would increase the observed rate.) Likely reactions are $OH^* + H_2$ and $OH^* + H$. Because of these uncertainties this measurement is rejected.

References

(a) D. D. Wagman, et al., NBS Tech. Note 270–3 (Jan. 1968).

(b) L. F. Phillips and H. I. Schiff, J. Chem. Phys. **37**, 1233 (1962).

(c) D. Garvin and J. D. McKinley, J. Chem. Phys. **24**, 1256 (1956).

(d) P. E. Charters, R. G. MacDonald, and J. C. Polanyi., Applied Optics **10**, 1747 (1971).

(e) F. Kaufman, Can. J. Chem. **47**, 1917 (1969); F. Kaufman, Ann. Geophys. **20**, 106 (1964).

(f) A. E. Potter, Jr., R. N. Coltharp, and S. D. Worley, J. Chem. Phys **54**, 992 (1971).

J. D. McKinley, D. Garvin
January, 1973

4.7. The Reaction Between HNO and HO

$$HNO + HO \rightarrow H_2O + NO \qquad k_1$$
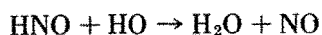
Auxiliary Data

$$\Delta H°_{298} = -290 \text{ kJ/mol} (-69.4 \text{ kcal/mol}) \qquad (a)$$

Data

k_1 (cm^3 molecule^{-1}s^{-1})	System
$1.5 \pm 0.5 \times 10^{-10}$ ($T = 1600-2000$ K)	Flame photometric studies of hydrogen-oxygen-nitrogen flames with added NO. [NO] and [H] measured. Bulewicz, Sugden, 1964 (b).
$0.6 \pm 0.2 \times 10^{-10}$ ($T = 2000$ K)	Flame photometric; same as (b). Halstead, Jenkins, 1968 (c).
$k_1 = 0.18 \pm 0.02 \times 10^{-10}$ ($T = 2117$ K)	Flame photometric studies of propane-oxygen nitrogen flame with added NO. Smith, 1972 (d).

Preferred Value

Changed from that in NBS Report 10692 (Jan. 1972).

$k_1 = 7 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} over temperature range 1600–2100 K. The three reported values have been averaged. Absolute uncertainty is no less than a factor of 5.

Remarks

For all three systems the postulated mechanism is:

$$H + NO + M \rightleftarrows HNO + M \qquad k_3, k_{-3}$$
$$HNO + H \rightarrow H_2 + NO \qquad k_2$$
$$HNO + HO \rightarrow H_2O + NO \qquad k_1$$
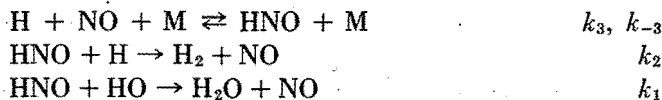
The experimentally determined quantity is K_3k_1. K_3 is derived from JANAF tables (a). The data from ref. (d) is from a more complex system (C, H, O, N) than in (b) and (c) (H, O, N). Thus additional complications may be present. Experiments in (d) are also carried out at considerably higher [OH]/[H] levels than in (b) and (c).

References

(a) D. R. Stull and H. Prophet JANAF Thermochemical Tables 2d Ed. Nat. Stand. Ref. Data Ser., National Bureau of Standards (U.S.), 37 (June 1971).
(b) E. Bulewicz and T. Sugden, Proc. Roy. Soc. (London) A277, 143 (1964).
(c) C. J. Halstead and D. R. Jenkins, Chemical Physics Letters. 2, 281 (1968).
(d) M. Y. Smith, Combustion and Flame, 18, 293 (1972).

W. Tsang
July, 1972

4.8. The Reaction Between HNO$_2$ and HO

$$HNO_2 + HO \rightarrow H_2O + NO_2 \qquad k_1$$
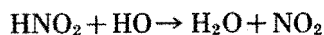
Auxiliary Data

$$\Delta H°_{298} = -168 \text{ kJ/mol} (-40.2 \text{ kcal/mol}) \qquad (a)$$

Data

No data exist on the rate of this reaction.

Preferred Value

(Changed from that in NBS Report 10692 (Jan. 1972).)
None

Remarks

The Arrhenius expression for the rate constant may be similar to that for the reaction of HO with HNO$_3$, for which the rate expression is (see separate data sheet):

$$k(HO + HNO_3 \rightarrow H_2O + NO_3) = 6 \times 10^{-13} \times$$
$$\exp(-400/T), \text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}.$$

Demerjian, Kerr, and Calvert (b) prefer a value of 7×10^{-12} cm^3 molecule^{-1} s^{-1} using as a basis the reported value of 14×10^{-12} cm^3 molecule^{-1} s^{-1} (c) for the reaction $HO + H_2CO \rightarrow H_2O + HCO$ and the argument that since the enthalpies of these hydrogen atom abstraction reactions are similar; the rate constants per abstractable hydrogen atom must be similar.

Clearly, if this reaction is of any importance, a direct measurement of k_1 is needed.

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3 (Jan. 1968).
(b) K. L. Demerjian, J. A. Kerr, and J. G. Calvert, The Mechanism of Photochemical Smog Formation, typescript, Ohio State Univ. (1972) [to appear in Adv. in Environmental Sci. and Technology, J. N. Pitts, Jr., and R. L. Metcalf, editors, Wiley-Interscience (Vol. 4, 1974)].
(c) E. D. Morris and H. Niki, J. Chem. Phys. 55, 1991 (1971).

W. Tsang
August, 1971
Revised: January, 1973

4.9. The Reaction Between HNO_2 and O

$$HNO_2 + O \rightarrow HO + NO_2 \qquad k_{1a}$$
$$HNO_2 + O \rightarrow HNO + O_2 \qquad k_{1b}$$

Auxiliary Data

ΔH°_{298} (a) $= -98$ kJ/mol (-23.3 kcal/mol)   (a)

ΔH°_{298} (b) $= -70$ kJ/mol (-16.8 kcal/mol)   (a)

Data

There are no published data on the rate of this reaction.

Preferred Value

None.
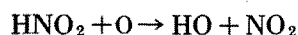
Remarks
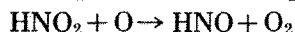
Note that there are two possible reactions: the H-atom abstraction (1a) and the O-atom abstraction (1b).

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968). Data on HNO from D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), **37** (June 1971).

J. T. Herron, R. E. Huie
February, 1972

4.10. Photolysis of HNO_3

Primary Photochemical Transitions

Reaction	ΔH°_0		$\lambda_{threshold}$ (nm)	
	kJ/mol	(kcal/mol)		
$HNO_3 \rightarrow HO + NO_2$	200	(48)	600	(1)
$HNO_3 \rightarrow HNO_2 + O$	298	(71)	400	(2)
$HNO_3 \rightarrow H + NO_3$	418	(100)	286	(3)

ΔH°_0 calculated from ΔH°_f values in ref. (a) except for ΔH°_f (NO$_3$) which is from ref. (b) but is consistent with ref. (a).

Data

Absorption coefficient

370–190 nm	[HNO$_3$] varied between 8×10^{13} and 6×10^{16} molecules cm^{-3}. Path lengths were 8.6 to 34.4 m. Data given in table 1 and shown in fig. 1 for 325–190 nm. Absorption cross section $\sigma \ll 10^{-22}$ cm^2 for 370–330 nm. Johnston, Graham, 1973 (f).
320–168 nm	[HNO$_3$] varied between 2.5×10^{16} and 1.5×10^{18} molecules cm^{-3}. Path length was either 12.31 or 0.97 cm. Schmidt, Amme, Murcray, Goldman, Bonomo, 1972 (h).
300–230 nm	Densitometry of photographic plates. [HNO$_3$] $= 5 \times 10^{16}$ molecules cm^{-3}. Path length $= 75$ cm. See table 1. Dalmon, 1943 (e).
Absorption, cross section $\sigma = 2.6 \times 10^{-20}$ cm^2 at 265, 254 nm	Berces, Forgeteg, 1970 (c).

Quantum yields

λ	$\Phi(-HNO_3)$	
265 nm	0.2 ± 0.03	Steady room temperature photolysis of pure HNO$_3$ and HNO$_3$–O$_2$ mixt. HNO$_3$–NO$_2$, HNO$_3$–H$_2$, and HNO$_3$–CO mixtures photolyzed at 265 nm.
254 nm	0.6 ± 0.07	
		Berces, Forgeteg, 1970 (c).

Preferred Value

(Changed from that in NBS Report 10828 (April 1972).)

Absorption coefficient

370–190 nm	Use data in ref. (f). See figure 1 and table 1 for 325–190 nm. Absorption cross section $\sigma \ll 10^{-22}$ cm^2 for 370–330 nm.

Remarks

Absorption Coefficients

The recent measurements by Johnston and Graham (f) are in good agreement with the earlier results of Dalmon (e) over the common range 300–230 nm except near 300 nm, which it is suggested in (f) can be accounted for by a 1.5 percent NO$_2$ impurity in the nitric acid used in (e).

Schmidt (private communication) has stated that the data shown in ref. (h) for $\lambda > 320$ nm are 2nd order grating spectra and should be disregarded and also that the NO$_2$ impurity in the nitric acid was overestimated. Their results now agree favorably with those of Dalmon (e) and also with those of Johnston and Graham (f). A statistical band model analysis is currently being developed by S. C. Schmidt and A. Goldman to interpret their observed pressure dependence of the absorption coefficient.
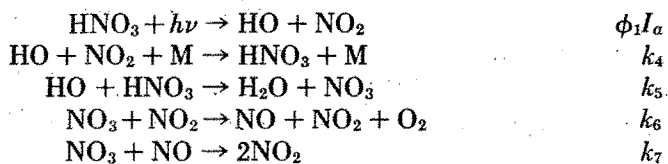
Quantum Yields

No value is recommended for the primary quantum

yield of decomposition of nitric acid. Measurements of this quantity are now in progress ref. (g) and preliminary results indicate that the primary quantum yields ϕ_1 is equal to unity throughout the wavelength region 300–190 nm.

Process (1) appears to be established from the production of HO in the flash photolysis of HNO_3 (3–10 torr) in presence of 500 torr N_2 (ref. d).

There is no positive evidence that processes (2) and (3) are of importance in the region 200–300 nm. Assuming that (1) is the only primary process, the complete mechanism of photolysis is the following:

$$HNO_3 + h\nu \rightarrow HO + NO_2 \qquad \phi_1 I_a$$
$$HO + NO_2 + M \rightarrow HNO_3 + M \qquad k_4$$
$$HO + HNO_3 \rightarrow H_2O + NO_3 \qquad k_5$$
$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2 \qquad k_6$$
$$NO_3 + NO \rightarrow 2NO_2 \qquad k_7$$

The quantum yield of HNO_3 disappearance, $\Phi(-HNO_3)$ is:

$$\Phi(-HNO_3) = \frac{2\phi_1}{1 + (k_4[NO_2][M]/k_5[HNO_3])},$$

where ϕ_1 is the quantum yield of process (1).

In the photolysis of pure HNO_3 at low conversion $k_4[NO_2][M] \ll k_5[HNO_3]$ and therefore,

$$\phi_1 = (1/2) \times \Phi(-HNO_3).$$

References

(a) D. D. Wagman et al., NBS Tech. Note 270–3 (Jan. 1968).
(b) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 37 (June 1971).
(c) T. Berces and S. Forgeteg, Trans. Faraday Soc. **66**, 633, 640, 648 (1970).
(d) D. Husain and R. G. W. Norrish, Proc. Roy. Soc. (London) **A273**, 165 (1963).
(e) R. Dalmon, Mem. serv. chim. etat, **30**, 141 (1943).
(f) H. Johnston and R. Graham, J. Phys. Chem. **77**, 62 (1973).
(g) H. Johnston, private communication.
(h) S. C. Schmidt, R. C. Amme, D. G. Murcray, A. Goldman, and F. S. Bonomo, Nature **238**, 109 (1972).

Acknowledgement

H. Okabe
Dec. 1971
Revised: January, 1973

TABLE 1. Ultraviolet absorption spectrum for nitric acid vapor

λ nm	σ, cm² Dalmon		σ^2 This work		Standard deviation
190			1.32	(−17)*	3
195			9.1	(−18)	3
200			5.5	(−18)	3
205			2.55	(−18)	3
210			9.7	(−19)	3
215			3.28	(−19)	3
220			1.44	(−19)	3
225			8.51	(−20)	1
230	5.35	(−20)*	5.63	(−20)	1
235	3.59	(−20)	3.74	(−20)	1
240	2.56	(−20)	2.60	(−20)	1
245	2.10	(−20)	2.10	(−20)	1
250	1.93	(−20)	1.95	(−20)	1
255	1.91	(−20)	1.94	(−20)	1
260	1.93	(−20)	1.90	(−20)	1
265	1.91	(−20)	1.80	(−20)	1
270	1.64	(−20)	1.63	(−20)	1
275	1.34	(−20)	1.40	(−20)	1
280	1.07	(−20)	1.14	(−20)	1
285	8.79	(−21)	8.77	(−21)	1
290	7.26	(−21)	6.34	(−21)	1
295	5.73	(−21)	4.26	(−21)	5
300	4.59	(−21)	2.76	(−21)	5
305			1.68	(−21)	5
310			9.5	(−22)	5
315			4.7	(−22)	5
320			1.8	(−22)	5
325			2	(−23)	>10

*5.35 (−20) means 5.35×10^{-20}; $\ln(I_0/I) = \sigma[HNO_3]L$.
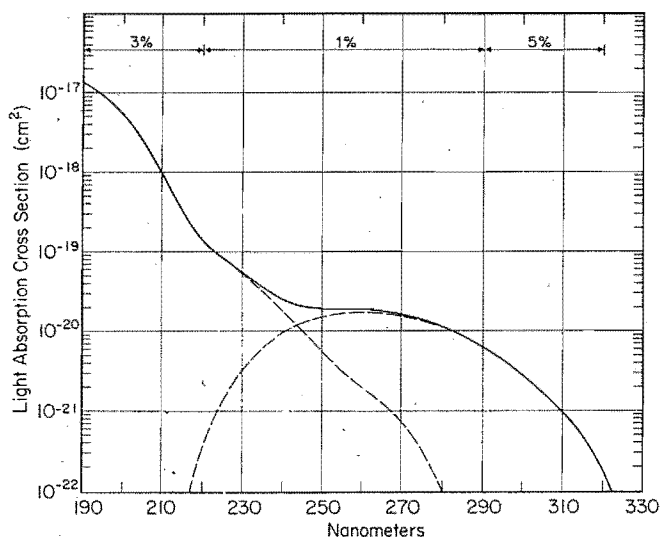From Johnston, Graham (f) with permission of authors.

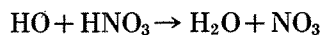FIGURE 1. The ultraviolet absorption spectrum of nitric acid vapor; $\ln(I_0/I) = \sigma[HNO_3]L$, where $[HNO_3]$ is in molecules cm⁻³ and L is optical path in cm. The percentages at the top of the figure refer to the standard deviation based on 15 gas samples (from Johnston, Graham (f) with permission of authors).

4.11. The Reaction Between HNO₃ and HO

$$HNO_3 + HO \rightarrow H_2O + NO_3 \qquad\qquad k_1$$
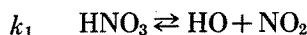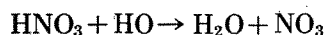
Auxiliary Data

$$\Delta H^\circ_{298} = -76 \pm 21 \text{ kJ/mol} (-18 \pm 5 \text{ kcal/mol}) \qquad (a)$$

Data

Quantity measured	System
$k_1(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	
1.6×10^{-13} ($T = 300$ K)	Flash photolysis of HNO₃ vapor. [OH] measured.
	Husain, Norrish, 1963 (b).
1.3×10^{-13} ($T = 300$ K)	Flash photolysis of HNO₃. [OH] measured.
	Morley, Smith, 1972 (g).
k_1/k (OH + NO₂ → HNO₃)	
0.26 ($T = 670$ K)	Thermal decomposition of HNO₃ vapors. [HNO₃] and [NO₂] measured.
	Johnston, et al., 1953 (c).
0.345 ($T = 622$ K)	Similar to (c).
	Godfrey, et al., 1965 (d).
$k_1/k(\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}) = 0.093$ $k_1/k(\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}) = 1.95$ $k_1/k(\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O})$ < 0.1	Room temperature photolysis at 265 nm. of HNO₃ in presence of additive.
$k_1/k(\text{OH} + i\text{-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9 + \text{H}_2\text{O})$ < 0.02	Berces, et al., 1970 (e).

Preferred Value

(Changed from that in NBS Report 10692 (Jan. 1972).)

$k_1(300 \text{ K}) = 1.4 \times 10^{-13} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
$k_1(650 \text{ K}) = 3 \times 10^{-13}$.
Estimated uncertainty is a factor of three.
Inserting these values into the Arrhenius equation gives:

$$k = 6 \times 10^{-13} \exp[-400/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Remarks

Ref. (b)

Value is undoubtedly a good upper limit.

Ref. (c)

Reaction is homogeneous at $T > 570$ K. The mechanism considered is:

$$HNO_3 \rightleftarrows HO + NO_2 \qquad\qquad k_2, k_3$$

$$HO + HNO_3 \rightarrow H_2O + NO_3 \qquad\qquad k_1$$

At 670 K, $k_2 = 0.16$ s⁻¹ and $k_1/k_3 = 0.26$. From data in ref. (a), $k_2/k_3 = 1.8 \times 10^{11}$ molecules/cm³, and the derived value of k_1 is 2.4×10^{-13} cm³ molecule⁻¹ s⁻¹. This result will not change even if reaction (3) is not truly bimolecular.

Ref. (d)

The mechanism considered is the same as in (c). At 622 K and 680 torr total pressure $k_2 = 0.0125$ s⁻¹ and $k_1/k_3 = 0.345$. From data in ref. (a), $k_2/k_3 = 1 \times 10^{10}$ molecules/cm³, and the derived value of k_1 is 4×10^{-13} cm³ molecule⁻¹ s⁻¹ in excellent agreement with (a). However lowering the total pressure to 230 torr results in a decrease in value of k_1 which conflicts with the mechanism and disagrees with (a).

Ref. (e)

The quantum yields for disappearance of HNO₃ in the presence and absence of added gas were measured. For CO and H₂ as additives, from the measured ratios and the well established values of $k(\text{OH} + \text{CO})$ and $k(\text{OH} + \text{H}_2)(f)$, the value of k_1 is calculated to be 1.3×10^{-14} cm³ molecule⁻¹ s⁻¹. The values based on the reactions with hydrocarbons are rough estimates. The value of the rate constant derived from these experiments is a factor of 10 lower than the direct determinations (b, g). Since it must be derived on the basis of a complex mechanism and difficult experiments, it is rejected in favor of the direct measurements.

References

(a) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).
(b) D. Husain and R. G. W. Norrish, Proc. Roy. Soc. (London) **A165**, 273 (1963).
(c) H. S. Johnston, L. Foering, and R. J. Thompson, J. Phys. Chem. **57**, 390 (1953).
(d) T. S. Godfrey, E. D. Hughes, and C. Ingold, J. Chem. Soc. 1063 (1965).
(e) T. Berces, S. Forgeteg, and F. Marta, Trans. Far. Soc. **66**, 648 (1967).
(f) N. R. Greiner, J. Chem. Phys. **46**, 2795 (1967).
(g) C. Morley and I. W. M. Smith, J. Chem. Soc. Far. Trans. II **68**, 1016 (1972).

W. Tsang
August, 1971
Revised: January, 1973

4.12. The Reaction Between HNO_3 and O

$$HNO_3 + O \rightarrow HO + NO_3 \hspace{4cm} k_1$$

Auxiliary Data

$$\Delta H^\circ_{298} = -4 \pm 21 \text{ kJ/mol} \ (-1 \pm 5 \text{ kcal/mol}) \hspace{1cm} (a)$$

Data

k_1 (cm^3 molecule^{-1} s^{-1})	System
$\sim 10^{-11}$	Photolysis of NO_2 at 366nm in presence of HNO_3. Postulated to occur in multistep mechanism used to interpret overall quantum yield meas. Jaffe, Ford, 1967 (b).
$\sim 10^{-10}$	Photolysis mixtures of HNO_3 and NO_2 at 265nm. Value inferred from overall quantum yield meas. interpreted according to multistep mechanism. Berces, Forgeteg, 1970 (c).
k_1/k ($0 + C_2H_2$) < 0.1 k_1/k ($0 + C_2H_4$) < 0.1	Directly studied at room temp. in flow system with mass spectrometer. Morris, Niki, 1971 (d).
$k_1 < 1.3 \times 10^{-14}$	Flash photolysis of NO_2 in presence of HNO_3 and He. $[NO_2] = 0.1$ torr; $[HNO_3] = 1.8$ torr. Unable to detect OH by resonance absorption. Morley, Smith, 1972 (i).

Preferred Value

$$k_1 \ (298K) \leqslant 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Remarks

The only direct study is that of Morris and Niki (d). Under the experimental conditions $[O] \sim 10^{14}$ molecule cm^{-3}, $[HNO_3] \sim 10^{12}$ molecule cm^{-3}, reaction time as great as 20ms, little or no change in the HNO_3 concentration was observed as monitored by the m/e 46 peak. Comparison with the rate of loss of ethylene and acetylene under identical conditions led to the conclusion that the rate constant k_1 was at least 10 times smaller than the rate constants for the reactions of atomic oxygen with either ethylene or acetylene. The rate constant for the reaction of atomic oxygen with acetylene (which is slower than the corresponding ethylene reaction) is 1.5×10^{-13} cm^3 molecule^{-1} s^{-1} (e) (f), hence $k_1 \leqslant 1.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

This limiting value is supported by the work of Morley and Smith (i) who produced O atoms by the photolysis of NO_2 in a mixture of HNO_3 and He, and were unable to detect any OH by means of resonance absorption. They derived an upper limit to the rate constant $k_1 \leqslant 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Using a pulsed uv photolysis chemiluminescent technique under conditions of excess HNO_3 Stuhl (in a private communication quoted in (d)) observes that k_1 is several orders of magnitude slower than inferred from the photolysis experiments at 366 and 265 nm (b) and (c).

Johnston (g) has argued that this discrepancy in k_1 is a consequence of unrecognized heterogenous reactions occurring, specifically $NO + HNO_3$, in the case of (b) and (c), citing the experience of Smith (h). The direct observations (d) are accepted. Note that there is an alternative path $O + HNO_3 \rightarrow O_2 + HNO_2$, $\Delta H^\circ_{298} = -194$ kJ/mol $(-46.3$ kcal/mol) (a).

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3 (Jan. 1968). Data on NO_3 from D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed., Nat. Stand. Ref. Data. Ser. Nat. Bur. Stand. (U.S.), 37 (June 1971).
(b) S. Jaffe and H. W. Ford, J. Phys. Chem. **71**, 1832 (1967).
(c) T. Berces and S. Forgeteg, Trans. Faraday Soc. **66**, 640 (1970).
(d) E. D. Morris, Jr. and H. Niki, J. Phys. Chem. **75**, 3193 (1971).
(e) K. Hoyerman, H. Gg. Wagner, and J. Wolfrum, Z. Physik, Chem. (Frankfurt) **63**, 193 (1969).
(f) A. A. Westenberg and N. De Haas, J. Phys. Chem. **73**, 1181 (1969).
(g) H. Johnston, Formation and Stability of Nitric Acid in the Stratosphere, typescript, University of California, Berkeley, California (1971).
(h) J. H. Smith, J. Am. Chem. Soc. **69**, 1741 (1947).
(i) C. Morley and I. W. M. Smith, J. Chem. Soc. Faraday Trans. II, **68**, 1016 (1972).

J. T. Herron, R. E. Huie
February, 1972
Revised: January, 1973

4.13. The Reaction of HO with H_2O_2

$$HO + H_2O_2 \rightarrow HO_2 + H_2O \hspace{4cm} k_1$$

Auxiliary Data

$$\Delta H^\circ_{298} = -124.3 \text{ kJ mol}^{-1} \ (-29.7 \text{ kcal mol}^{-1}) \hspace{1cm} (a)$$

$$\log_{10} K_{eq} = -0.329 + 6.612 \ (1000/T) \hspace{2cm} (j)$$

Data

The available data prior to 1972 have been described and evaluated by Baulch et al. (h) and by Drysdale and Lloyd (i).

Upper and lower limits for k_1 at 298 K have been derived from studies employing flash photolysis (b) and electric discharge (c) of H_2O_2.

Absolute values of k_1 over the temperature range $307 - 462$ K have been determined in flash photolysis studies by following the OH decay by kinetic spectroscopy.

Rate ratio data at higher temperatures extends the range. A k_1/k_2 ratio was determined at 798 K using the thermal decomposition of H_2O_2 in the presence CO (d).

$$CO + HO \rightarrow CO_2 + H \qquad (2)$$
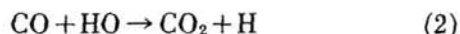
The rate relative to reaction (3),

$$HO + H_2 \rightarrow H + H_2O, \qquad (3)$$
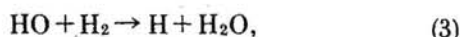
has been determined between 700 and 800 K by examination of the inhibition of the second explosion limit of the H_2/O_2 system by H_2O_2 (e), in studies of the decomposition of H_2O_2 in the presence of H_2 in boric acid coated vessels (f) and from studies of the $H_2/O_2/N_2$ system (g).

Recent Measurements

There has been only one measurement involving the rate of this reaction since the 1972 review by Baulch, et al. (h).

| Quantity measured	System
$k_1/k_2 = 8.13 \pm 0.56$ where k_2: $HO + CO \rightarrow$ $CO_2 + H$	Photolysis of H_2O_2 (0.94 torr) at 254 nm in presence of O_2 (5.4 torr) and CO (3–32 torr). Measured initial rate of formation of CO_2. Gorse, Volman, 1972 (k).

Preferred Value

$k_1 = 1.7 \times 10^{-11}$ exp $(-910/T)$ cm^3 molecule^{-1} s^{-1} for $298 < T < 800$.

$k_1(300$ K$) = 8.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This is the evaluation given in refs. (h, i). It fits the measured data within 50 percent.

Remarks

Reaction 1 is a simple H atom abstraction

$$HO + H\text{-}O_2H \rightarrow H_2O + HO_2,$$
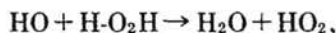
and is the only interaction expected in this system. The evaluation relies heavily on the data of Greiner which are the only absolute rate measurements available. The flash photolysis study is subject to some uncertainty due to the method of temperature measurement. The temperature was varied by changing inert gas pressures thereby lowering the effect of flash heating. This coupled with the normal experimental uncertainties gives a reliability factor of approximately 2 to the data. Thus, the expression given above probably predicts the value for

k_1 within a factor of 2 over the temperature range 298 to 800 K. At stratospheric temperatures 200–240 K the uncertainty is considerably larger (probably at least a factor of 4). Thus a number of lower temperature measurements are in order.

A value of k_1 can be derived from the recent relative rate measurement in ref. (k) by selecting a value for k_2: $HO + CO \rightarrow CO_2 + H$. We select as the best value for k_2 that recently measured directly by Stuhl and Niki (l): $k_2 = 1.35 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Using this value, we derive the value $k_1 = (11 \pm 3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} from the ratio measured in (k). We consider this to be in substantial agreement with the value k_1 (300 K) $= 8.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} recommended in the Preferred Value section. The combined uncertainties in the measured values of (k_1/k_2) and k_2 and the complexity of the mechanism used in (k) do not justify changing the recommended value of k_1.

References

(a) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d. Ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).
(b) N. R. Greiner, J. Chem. Phys. **45**, 99 (1966); ibid, **46**, 2450 (1967) (erratum); superseded by J. Phys. Chem. **72**, 406 (1968).
(c) S. N. Foner and R. L. Hudson, J. Chem. Phys. **36**, 2681 (1962).
(d) D. E. Hoare, Proc. Roy. Soc. (London) **A291**, 73 (1966).
(e) W. Forst and P. A. Giguere, J. Phys. Chem. **62**, 340 (1958), R. R. Baldwin and L. Mayor, Trans. Faraday Soc. **56**, 80 and 103 (1960), R. R. Baldwin, P. Doran, and L. Mayor, Symp. Combust 8th, 103 (1962).
(f) R. R. Baldwin and D. Brattan, Symp. Combust 8th, 110 (1962), R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, Symp. Combust 10th, 423 (1965).
(g) R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, Trans. Faraday Soc. **63**, 1676 (1967).
(h) D. L. Baulch, D. D. Drysdale, D. G. Horne, A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions volume 1, Homogeneous gas phase reactions of the H_2-O_2 system, Butterworth & Co., London (1972); also in D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, High Temperature Reaction Rate Data, Report No. 3 (1969), Dept. of Physical Chemistry, The University, Leeds, England.
(i) D. D. Drysdale and A. C. Lloyd, Oxidation and Combustion Reviews, **4**, 157 (1970).
(j) V. N. Kondratiev, Rate Constants of Gas Phase Reactions—Reference Book, R. M. Fristrom, editor. National Technical Information Service, Springfield, Virginia COM–72–10014 (Jan. 1972).
(k) R. A. Gorse and D. H. Volman, J. Photochem., **1**, 1–10 (1972).
(l) F. Stuhl and H. Niki, J. Chem. Phys. **57**, 3671 (1972).

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July, 1972
Revised: January, 1973

4.14. The Reaction of HO and O₃

	ΔH°_{298} (a)		
	kJ mol⁻¹	(kcal mol⁻¹)	
$HO + O_3 \rightarrow HO_2 + O_2$	-160 ± 8	(-38 ± 2)	k_{1a}
$HO + O_3 \rightarrow H + 2O_2$	$+36.4$	$(+8.7)$	k_{1b}
$HO + O_3 \rightarrow HO + O_2 + O$	106.3	(25.4)	k_{1c}
$HO\dagger + O_3 \rightarrow$ all channels			$k_1\dagger$

†A dagger following a formula or reaction number, e.g. $HO^\dagger$, $k_1{}^\dagger$, means vibrational excitation.

$k_1 = k_{1a} + k_{1b} + k_{1c}$.

Auxiliary Data

Excitation energy of HO in vibrational levels 1–9 of the ground state. No rotational energy included (b).

v	kJ mol⁻¹	kcal mol⁻¹	v	kJ mol⁻¹	kcal mol⁻¹
0	0.0	0.0	5	193.9	46.3
1	42.7	10.2	6	226.8	54.2
2	83.4	19.9	7	257.7	61.6
3	122.2	29.2	8	286.6	68.5
4	159.0	38.0	9	313.4	74.9

Subtract (add) values above to ΔH of reaction if HO is a reactant (product) to obtain ΔH for HO in a specific level.

$\Delta H f^\circ_{298}(HO) = 39.0$ kJ mol⁻¹ (9.31 kcal mol⁻¹) (a).

Closely related reactions

	kJ mol⁻¹	(kcal mol⁻¹)	
$HO + H_2 \rightarrow H_2O + H$	-62.8	(-15.0)	k_2
$HO\,(v') + M \rightarrow HO(v'') + M$			k_3
$HO + H_2O_2 \rightarrow HO_2 + H_2O$	-125 ± 8	(-30 ± 2)	k_4
$HO + O \rightarrow H + O_2$	-70.3	(-16.8)	k_5
$H + O_3 \rightarrow HO + O_2$	-321.7	(-76.9)	k_6
$HO_2 + O_3 \rightarrow HO + 2O_2$	-125 ± 8	(-30 ± 2)	k_7

Data

Measurements

k's in cm³ molecule⁻¹ s⁻¹*	System
$k_1{}^\dagger (HO, v=9) = (7.7 \pm 0.3) \times 10^{-12}$ to $k_1{}^\dagger (HO, v=2) = (1.9 \pm 1.1) \times 10^{-12}$ extrapolating $k_1 (HO, v=0) \sim 10^{-12}$	Flow system, $p \sim 0.3$–0.6 torr, Ar carrier. $H + O_3 \rightarrow HO\dagger + O_2$, $[O_3], [H] \sim 10^{-5} - 10^{-4}$ torr $[O_2]/[O_3] \sim 20$. Emission from HO meas. as fn. of distance. Coltharp, Worley, Potter, 1971 (c).
$k_{1a} \sim 8 \times 10^{-14}$	Steady photolysis of O_2 and H_2O at $\lambda = 184.9$ nm in presence and absence of CO. $P(O_2) = 300$ torr, $P(H_2O) = 4.6$ torr. $[O_3]$ meas. by absorption at $\lambda = 254$ nm, before and at steady state. DeMore, 1972 (m).

Measurements—Continued

k's in cm³ molecule⁻¹ s⁻¹*	System
$k_{1a} = (5.5 \pm 1.5) \times 10^{-14}$ at 298 K $E/R = 0.96 \times 10^3$ $220 < T < 450$ K	Fast flow reactor, $[HO] \sim 3 \times 10^{11}$, $[O_3] = 1$–6×10^{14} molecules cm⁻³, added He to make P(total) = 2–5.5 torr. [HO] vs distance measured by resonance fluorescence at $\lambda = 309$ nm, $[O_3]$ meas. by absorption at $\lambda = 254$ nm. HO from $H + NO_2 \rightarrow HO + NO$. Anderson, Kaufman, 1973 (p).
$k_{1a}/k_4 = 1/12$ See remarks.	Photolysis of O_3, $\lambda = 254$ nm in the presence of H_2O_2 in a flow system, 25 to 100 °C. $[O_3]/[H_2O_2] = 0.7$ to 10, $[O_3] = (2.7$ to $15) \times 10^{-8}$ mol cm⁻³, $[O_2]$ to make up a total pressure of 1 atm, $(4 \times 10^{-5}$ mol/cm³) $\Delta O_3/\Delta t$, $\Delta H_2O_2/\Delta t$ meas. Volman, 1951 (j).
$k_{1a} = 7 \times 10^{-14}$ See remarks.	From data of ref. (j) and an evaluation of $k_4 = 0.16 \times 10^{-10}$ $\exp(-0.9 \times 10^3/T)$. Drysdale, Lloyd, 1970 (k).

Estimates

$k_1 < 5 \times 10^{-13}$	Flow systems, $p \sim 1$ torr. $H + NO_2 \rightarrow HO + NO$. $\Delta[HO]/\Delta t$ meas. in presence and absence of O_3. Kaufman, 1964 (f).
k_1, no reaction $k_1{}^\dagger/k_2{}^\dagger > 10^3$	Liquid phase, photolysis of O_3, $\lambda = 254$ nm, in $H_2/O_3/Ar$ solutions at 87 K. $\phi(O_3)$ meas. in presence and absence of added $O_2 \cdot H_2/O_3 \sim 200$. DeMore, 1967 (g.)
$k_{1a} < 10^{-16}$	Flash photolysis of $O_3/H_2O/Ar$ mixtures. $[O_3] = 1$ torr, $[H_2O] = 1,5,10$ torr, $[Ar] = 100$ torr. $\Delta O_3/\Delta t$ meas. $\Delta O_3/\Delta t$ decreases as $[H_2O]$ increases. Langley, McGrath, 1971 (h).
$k_{1a} > 10^{-16}$	Estimate based on interpretation of quantum yields in the photolysis of O_3 in the presence of water in terms of chain reactions (1) and (7). Johnston, 1968 (i).

* At room temperature unless otherwise indicated.

Preferred Values

(Changed from that in NBS Report 10828 (April 1972).)

$k_{1a} = 1.6 \times 10^{-12} \exp(-1 \times 10^3/T)$ cm^3 molecule^{-1} s^{-1}.
$220 < T < 450$ K, log $k \pm 0.3$.
$k_{1a} = 6 \times 10^{-14}$ at 300 K.

The results in reference (c) may be used as an upper limit for reaction (1†).

$k_1{}^\dagger$(HO, $v=9$) $< 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

This is a sum over all channels, not an elementary process. There are no data on reactions (1b) and (1c).

Remarks

The preferred value is approximately that from the current experiments of Anderson. These are the most direct measurements of k_{1a} and are preferred for that reason. The error limit is broad, and reflects the disagreement between reference (p) and the only other recent quantitative measurement, reference (m). The earlier quantitative result (j) has been reinterpreted to exclude reaction (1a). All of the earlier limit estimates should now be disregarded. Reaction (1a) should be considered an O-atom transfer reaction with a normal rate constant.

DeMore's steady state photolysis experiments (ref. m) yield an approximate value that is fifty percent larger than reported in (p). This is good agreement if the very different technique and greater complexity of the experimental system are considered.

More experiments on reaction (1a) are needed in order to establish the value and narrow the error bounds. A rate constant of this magnitude makes reaction (1) an important component of mechanisms of stratospheric chemistry.

DeMore's work (m) is especially important for an understanding of the O$_3$/HO$_x$ system. It has been evident since the studies of Forbes and Heidt in the early 1930's (q) that there is a chain reaction sequence involving HO$_x$ that destroys ozone. The simplest chain is that proposed by Norrish and Wayne (r)

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (1a)$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \qquad (7)$$
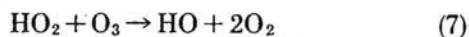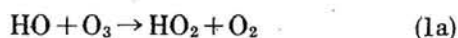
Most studies of the O$_3$/HO$_x$ system have used high [O$_3$]/[O$_2$] ratios and photolysis of O$_3$ of wavelengths less than 300 nm. Energy transfer steps and reactions of electronically excited O and O$_2$ could not be ruled out. DeMore's experiments, in which O(^3P) alone is formed and in which there is a high [O$_2$]/[O$_3$] ratio indicate that the chain must involve only normal (thermally equilibrated) species.

Under his experimental conditions reaction (7) is the most likely step regenerating hydroxyl. The occurrence of this reaction has been questioned, because it is difficult to formulate a transition state. The reaction could be an O-atom transfer followed by rapid decomposition of an unstable O$_4$ complex. Unfortunately, analogous processes cannot be cited. The systems in which the O$_3$/HO$_x$ chain have been studied are complex. They require elaborate mechanisms for complete interpretation. Thus the importance of reaction (7), although probable, is not firmly established. Experiments are needed in which other species than O$_3$ are measured.

Comments on specific studies follow.

Ref. (c)

The total rate of reaction of HO ($v=2$ to 9) in the presence of O$_3$ was measured. This is based on infrared emission bands. Corrections were made for loss by radiation and at the walls. Both corrections are large. Physical quenching appears to be minor (d). Thus, these rates are summations for the chemical reactions in the system.

When extrapolated to HO ($v=0$), $k_1 \sim 10^{-12}$, in reasonable agreement with the experiments in (p), since the extrapolation presupposes no energy barrier. This extrapolation depends heavily on the radiative life time for HO ($v=9$), $\tau_9 = 6.4 \times 10^{-2}$ s, and on the relative transition probabilities for the lower states. τ_9 is surprisingly long.

The experiments are extensive, but are not described in sufficient detail to permit estimates of concentrations in the measurement region of the flow tube. As is the case with most studies of secondary reactions, the measured phenomenon occurs in a region where there is a buildup of product. For HO ($v=9$), 50 percent of reaction (1†) must have occurred before the earliest measurement. Water is an effective quencher (e) and may be troublesome. So might reaction with H$_2$ (reaction (2†) although DeMore's data suggest this is not important (g). Experiments in the absence of excess O$_3$ would be desirable to test this point and to determine the "background" decay rate. Direct, optical, measurements of [O$_3$] also are needed.
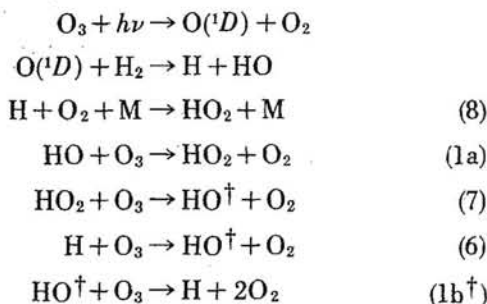
Ref. (f)

This upper limit is based on the *absence* of an effect of O$_3$ on the rate of disappearance of HO and on an estimate of instrumental sensitivity.

Ref. (g)

Absence of a reaction of thermal HO at 87 K does not rule out a gas phase reaction at room temperature if there is an activation energy. However, the experiments suggest that it will be slow.

The two results (no reaction of thermal HO, reaction of excited OH) are based on quantum yields of O_3 destruction and water formation in the presence and absence of small additions of O_2. The pertinent reactions are:

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

$$O(^1D) + H_2 \rightarrow H + HO$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (8)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (1a)$$

$$HO_2 + O_3 \rightarrow HO^\dagger + O_2 \qquad (7)$$

$$H + O_3 \rightarrow HO^\dagger + O_2 \qquad (6)$$

$$HO^\dagger + O_3 \rightarrow H + 2O_2 \qquad (1b^\dagger)$$

The interpretation, which we accept, may be summarized as follows. In the presence of O_2, reaction (8) scavenges H atoms. Then $\Delta O_3 = \Delta H_2O$ where water is the ultimate product formed from radicals and peroxides in the system. This is interpreted to mean that reactions (1a) and (7) do not occur, i.e., HO and HO_2 are unreactive. In the absence of sufficient O_2 to scavenge H atoms, $\Delta O_3 > \Delta H_2O$. This is interpreted as due to the chain (6) followed by some reaction of $HO^\dagger$ with O_3. The chain (6) and $(1b^\dagger)$ is favored over (6), $(1a^\dagger)$, and (7) because (7) is ruled out by the experiments with added O_2.

Ref. (h)

A preliminary report on flash photolysis experiments. Details not given. No evidence was found for a chain reaction in a system containing O_3 and HO, either immediately or at long times after the flash. Hydroxyl is formed in the sequence

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

$$O(^1D) + H_2O \rightarrow HO + HO$$
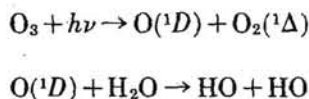
with little, if any excitation of the HO. At short times the quantum yield, $\phi(-O_3)$, is ~ 2. This is in contrast to the steady photolysis of O_3/H_2O mixtures in which high quantum yields are found: $(\Phi(-O_3)$ up to 100). The authors argue that their results rule out reactions (1a) and (7) in both types of photolysis. The upper limit is based on *absence* of an effect and an estimate of instrumental sensitivity. Fortin, et al. (o) have criticized the interpretation given in ref. (h). They studied the flash photolysis of moist ozone, show that a very extensive mechanism must be used to interpret the intermediate quantum yield, and state that reactions (1a) and (7) would contribute very little even if both had rate constants $\sim 5 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

Ref. (i)

This lower limit estimate is based on the chain mechanism (1a, 7) and on an estimate of $[HO_2]$. The estimate

is too indirect to be useful.

Refs. (j and k)

These data were, prior to 1972, the only quantitative measurements on reaction (1a). Volman has recently reexamined and reinterpreted them (n) in the light of the now known kinetics of reactions of $O(^1D)$. He concludes that reaction (1a) is probably not important, but that

$$O(^1D) + H_2O_2 \rightarrow HO + HO_2 \qquad k_{10}$$
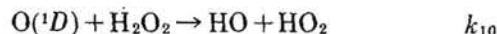
controls the variation of $\Delta[O_3]/\Delta[H_2O_2]$ with reactant concentrations. The rate constant k_{10} may be up to 10 fold faster than $O(^1D) + H_2O$, that is, it occurs essentially at every collision.

We agree with the reinterpretation but also note that we have been unable to model these experiments using modern rate data to the point that the observed concentration changes can be reproduced. The modelling gives smaller O_3 and H_2O_2 destruction.

These experiments remain important for interpretation of the O_3 photolysis in the presence of water. Volman gives evidence that there is no chain process. This is contrary to the results in reference (m). The two studies are sufficiently similar that they should agree on the point. We have no explanation.

Ref. (m)

Steady photolysis of O_2 and H_2O at $\lambda = 184.9$ nm in excess O_2 produces O_3, HO, and HO_2

$$O_2 + h\nu \rightarrow 2O$$

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

$$H_2O + h\nu \rightarrow H + HO$$

$$H + O_2 + M \rightarrow HO_2 + M$$
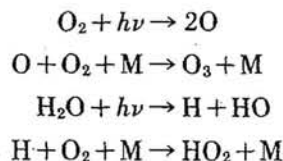
Photon absorption in this optically thick system was determined from rate of O_3 formation in calibration experiments. Only slight O_3 photolysis occurs. Rate of O_2 photolysis is 9 fold greater than that of H_2O for $P(O_2) = 300$ torr and $P(H_2O) = 4.6$ torr. A steady state in O_3 is reached at long times (more than 100 min) that indicates chain destruction of O_3 by HO and HO_2. Interpreted as

$$HO + O_3 \rightarrow HO_2 + O_2, \qquad k_{1a}$$

$$HO_2 + O_3 \rightarrow HO + 2O_2. \qquad k_7$$
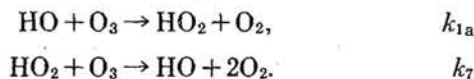
Competition experiments with added CO (removing HO and forming HO_2)

$$CO + HO \rightarrow CO_2 + H, \qquad k_9$$
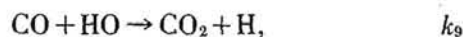
were used to obtain approximate values $k_{1a} \sim 8 \times 10^{-14}$ and $k_7 \sim 3 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. These are only

approximate because the system is optically thick and the concentrations of intermediates are intensity dependent.

Ref. (p)

These experiments measure the total rate of disappearance of HO in the presence of excess O_3. The method is similar to that used by the same authors for studying the reaction of HO with NO_2 (s). Tests indicated no measurable concentration of O atoms. The hydroxyl radicals used should be almost exclusively HO$(v=0)$. The pre-exponential factor is $\sim 10^{-12}$ cm³ molecule⁻¹ s⁻¹ which is consistent with the extrapolated value from reference (c).

These are the most direct measurements, to date, of k_1. Interference from $HO_2 + O_3$ or $NO + O_3$ should be unimportant.

Acknowledgement

Drs. W. B. DeMore and J. Anderson have assisted us by providing information on experiments prior to publication. Discussions with Dr. D. H. Volman about his work and DeMore's have been invaluable in the preparation of this report.

References

(a) D. D. Wagman, et al., NBS Tech. Note 270-3 (Jan. 1968).

(b) R. C. Herman and G. A. Hornbeck, Astrophys. J. **118**, 214 (1953); A. M. Bass and D. Garvin, J. Molec. Spectr. **9**, 114 (1962).

(c) R. N. Coltharp, S. D. Worley, and A. E. Potter, Appl. Optics **10**, 1786 (1971); A. E. Potter, R. N. Coltharp, and S. D. Worley, J. Chem. Phys. **54**, 992 (1971).

(d) S. D. Worley, R. N. Coltharp, and A. E. Potter, J. Chem. Phys. **55**, 2608 (1971); R. N. Coltharp, S. D. Worley, and A. E. Potter, Am. Chem. Soc. 162d Nat. Meeting, Phys. Chem. Paper No. 89 (Washington, Sept. 1971) preprint.

(e) S. D. Worley, R. N. Coltharp, and A. E. Potter, J. Phys. Chem. **76**, 1511 (1972).

(f) F. Kaufman, Annales de Geophys. **20**, 106 (1964).

(g) W. B. DeMore, J. Chem. Phys. **47**, 2777 (1967); **46**, 813 (1967).

(h) K. F. Langley and W. D. McGrath, Planet. Space Sci. **19**, 413 (1971).

(i) H. S. Johnston, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. 20 (1968) footnote 3.

(j) D. H. Volman, J. Am. Chem. Soc. **73**, 1018 (1951).

(k) D. D. Drysdale and A. C. Lloyd, Oxidn. and Comb. Rev. **4**, 157 (1970).
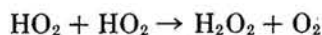
(l) E. A. Albers, K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, Symp. Combustion (International) **13**, 81 (1971).

(m) W. B. DeMore, Rate Constants for the Reactions of OH and HO_2 with Ozone, typescript, Jet Propulsion Laboratory 1972, and related correspondence among W. DeMore, D. Volman, and D. Garvin (Nov. Dec. 1972).

(n) D. Volman, correspondence with D. Garvin (Aug.–Oct. 1972).

(o) C. J. Fortin, D. R. Snelling, and A. Tardif, Can. J. Chem. **50**, 2748 (1972).

(p) J. Anderson and F. Kaufman, private communication (Jan. 1973).

(q) G. S. Forbes and L. J. Heidt, J. Am. Chem. Soc. **56**, 1671 (1934).

(r) R. G. W. Norrish and R. P. Wayne, Proc. Roy. Soc. (London) **A288**, 361 (1965).

(s) J. G. Anderson and F. Kaufman, Chem. Phys. Lettrs **16**, 375 (1972).

D. Garvin
February 1972
Revised: January 1973

4.15. The Reaction of HO_2 with HO_2

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad \qquad k_1$$

Auxiliary Data

$\Delta H^\circ_{298} = -178 \pm 16$ kJ/mol $(-42.6 \pm 4$ kcal/mol) (a)

Preferred value

(Changed from that in NBS Report 10828 (April 1972).

$k_1 (300) = 6 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, estimated uncertainty: a factor of two.

$k_1 = 3 \times 10^{-11}$ exp $(-500/T)$ cm³ molecule⁻¹s⁻¹ (300–1000 K), estimated uncertainty is an order of magnitude at 1000 K.

$-d[HO_2]/dt = 2k_1[HO_2]^2$.

Remarks

There are four studies, three of which (b, c, i) indicate a rate constant in the range $0.3–1.0 \times 10^{-11}$. For this reason the other (d) is rejected. Only the two latest measurements (b, i) need be considered. The techniques are sufficiently difficult and different so that the discrepancy in rates is not surprising. Paukert's rate (b)

Data

k_1 (300K) (cm³molecule⁻¹s⁻¹)	System
$9.5 \pm 0.83 \times 10^{-12}$	Flash photolysis of H_2O/O_2 mixtures in H_2, He, Ar, total pressure: 1 atm. $[HO_2]$ vs time measures. Hochanadel, et al., 1972 (i).
$3.6 \pm 0.5 \times 10^{-12}$	Photolysis of H_2O_2. HO_2 absorption measured. Paukert, Johnston, 1972 (b).
3×10^{-12}	Electrical discharge through H_2O_2. HO_2 detected by mass spectrometry. Foner, Hudson, 1962 (c).
1.1×10^{-10}	Hg photosensitized hydrogen-oxygen reaction 293–319 K. Measured temp. rise. Burgess, Robb, 1957 (d).

depends upon the absolute value of the absorption coefficient for H_2O_2, while Hochanadel's depends upon that for HO_2. Both measured the extinction coefficient of HO_2 at 210 nm in units of $dm^3 mol^{-1} cm^{-1}$ base 10: 1200 (b), 1770 (i). If the former is correct then the rate constant in (i) should be reduced to 6.5×10^{-12} cm^3 molecule$^{-1}s^{-1}$. A similar argument may not be made to raise the rate in (b). That rate is based on ϵ (H_2O_2) at 200 nm reported in ref. (g). A value twice as large has also been reported (h).

Because of the uncertainty in ϵ (HO_2), we simply have averaged the two rates (b, i), and have adopted the activation energy estimated by Lloyd (e). His room temperature rate constant is, however, 3.3×10^{-12} based on (b) and (c).

References

(a) D. D. Wagman, et. al., NBS Technical Note 270-3 (Jan. 1968)

(b) T. T. Paukert and H. S. Johnston, J. Chem. Phys. **56**, 2824 (1972)

(c) Foner, S. N., and Hudson, R. L., Adv. Chem. Series **36**, 34 (1962)

(d) Burgess, R. H., and Robb, J. C., Chem. Soc. Spec. Publ. 9, 16 (1957).

(e) Lloyd, A. C., Evaluated and Estimated Kinetic Data for the Gas Phase Reactions of the Hydroperoxyl Radical, National Bureau of Standards Report 10447 (July 1971).

(f) D. L. Baulch, D. D. Drysdale, D. G. Horne, A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions volume 1, Homogeneous gas phase reactions of the H_2-O_2 system, Butterworth & Co., London (1972).

(g) R. B. Holt, C. K. McLane, and O. Oldenberg, J. Chem. Phys. **16**, 225, 638 (1948).

(h) M. Schürgers and K. H. Welge, Z. Naturforsch **23a**, 1508 (1968).

(i) C. J. Hochanadel, J. A. Ghormley, and P. J. Ogren, J. Chem. Phys. **56**, 4426 (1972).

D. Garvin, R. F. Hampson
June, 1972

4.16. The Overall Reaction of H_2O, NO, and NO_2

$$H_2O + NO + NO_2 \rightarrow 2 HNO_2 \qquad k_1$$

Auxiliary Data

$\Delta H°_{298} = -40.6$ kJ/mol (-9.7 kcal/mol) (a)

$\Delta G°_{298} = -1.34$ kJ/mol (-0.32 kcal/mol)

$K_P = 1.7$ atm^{-1} (value calculated from above value of $\Delta G°_{298}$)

Preferred Value

No recommendation can be made for the value of the rate constant for the homogeneous gas-phase reaction of H_2O, NO, and NO_2 since the only rate data reported (ref. (b) and (c)) refer to the heterogeneous reaction occurring on the vessel walls (see Remarks).

Remarks

All that can be said about the value of the homogeneous gas-phase reaction rate constant is that it must be less than the values in (b) and (c) which pertain to the dominant heterogeneous reaction. Therefore, for the rate expression

$$-dP_{NO_2}/dt = kP_{NO}P_{NO_2}P^2_{H_2O},$$

an upper limiting value for the homogeneous gas-phase reaction rate constant is (from Graham and Tyler):

$$k \leqslant 1.1 \times 10^{-55} \text{ cm}^9 \text{ molecule}^{-3} \text{ s}^{-1}.$$

(Changed from that in NBS Report 10692 (Jan. 1972).)

The following mechanism was considered in both studies:

Data

There are no direct data on the rate of the homogeneous gas phase reaction between H_2O, NO, and NO_2.

However the following data on the rate of the *heterogeneous* reaction can be used to set an upper limit to the rate of the homogeneous reaction.

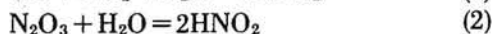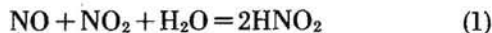|	
$k = 1.1 \times 10^{-55}$ cm^9 molecule^{-3} s^{-1} $-dP_{NO_2}/dt = k P_{NO}P_{NO_2}P^2_{H_2O}$	Cylindrical stirred flow reactor 5.8 cm long, 6.0 cm i.d. P_{NO_2} meas. by optical abs. as fct. of time after introduction of H_2O into stream of NO, NO_2, and N_2. Range of exptl. conditions was: P_{NO_2} 0.002 − .01 atm P_{NO} 0.057 − .27 atm P_{H_2O} 0.0063 − .019 atm and N_2 added to give $P_{total} = 1$ atm. Graham, Tyler, 1972 (b).
$k = 1.2 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1} $-2 dP_{NO_2}/dt = dP_{HNO_2}/dt$ $k PP^2_{H_2O}$ with $P_{NO} = 1$ atm $P = P_{NO_2} + P_{N_2O_3}$	Rate of approach to equilibrium of trapped, non-equil. mixt. of NO, NO_2, and H_2O determined from meas. of P_{NO_2} as fct. of time by optical abs. Capillary tubing. Range of exptl. conditions was: P_{NO_2} 0.005–.033 atm P_{H_2O} .009–.025 atm P_{NO} 1 atm Wayne, Yost, 1951 (c).

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (1)$$
$$N_2O_3 + H_2O = 2HNO_2 \qquad (2)$$
$$NO + NO_2 = N_2O_3 \qquad (3)$$

Neither study distinguished between (1) and (2) because of the rapid attainment of equilibrium in (3).

Remarks on Specific References

Ref. (b)

This study verified the second-order dependence of the rate on $[H_2O]$ suggested in (c). A first-order dependence on $[NO_2]$ and on $[NO]$ was found. The surface-to-volume ratio was (1/40) the value in (c), and the rate constant was (1/36) its value in (c) similarly defined. This strong dependence of k on (s/v) was interpreted as evidence for the heterogeneous nature of the reaction. They attempted to fit the data to the stoichiometry indicated by eqn. (1), i.e. first order in H_2O, NO, and NO_2. Although the derived rate constant was not independent of $[H_2O]$, the values were within a factor of 2 of the mean value of 2.0×10^{-3} m^4 kN^{-2} s^{-1}, equal to 3.4×10^{-38} cm^6 molecule^{-2} s^{-1}. This can be taken as an upper limiting value to the rate constant for the homogeneous gas phase reaction whose stoichiometry is given by eqn. (1). An overall rate in terms of $[N_2O_3]$ is also given.

Ref. (c)

This study was performed in a 1 mm diameter pyrex tube and no precautions were taken to avoid surface reaction. In view of the results in (b) these measurements are rejected as gas phase rate data. They might be useful in defining the rate in a heterogeneous converter. Note that the reported rate does not reflect the dependence on $[NO]$ which was fixed at 1 atm. This is unity (b). If this is introduced:

$$d[HNO_2]/dt = k'[NO][A][H_2O]^2,$$

where

$$k' = 5 \times 10^{-54} \text{ cm}^9 \text{ molecule}^{-3} \text{ s}^{-1},$$

and

$$[A] = [NO_2] + [N_2O_3].$$

Note that the rate quoted from (c) in the Data section has occasionally been cited incorrectly as applicable in the rate expression

$$dP_{HNO_2}/dt = kP_{NO}P_{NO_2}P_{H_2O},$$

that is without the second order dependence on water.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).
(b) R. F. Graham and B. J. Tyler, J. Chem. Soc. Far. Trans I **68**, 683 (1972).
(c) L. G. Wayne and D. M. Yost, J. Chem. Phys. **19**, 41 (1951); ibid **18**, 767 (1950).

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July, 1972

4.17. The Reaction Between H₂O and N₂O₅

$$H_2O + N_2O_5 \rightarrow 2HNO_3 \qquad k_1$$

Auxiliary Data

$$\Delta H^\circ_{298} = -40 \text{ kJ/mol} (-9.5 \text{ kcal/mol}) \qquad (a)$$

Data

There are no published quantitative data on the rate of this reaction.

Preferred Value

(Changed from that in NBS Report 10692 (Jan. 1972).)

$$k_1(300 \text{ K}) < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Remarks

There is no evidence that this reaction occurs. It has been postulated as a possible regenerative step for HNO_3 in the photolysis of mixtures of NO_2 and HNO_3 at 366 nm (b), although it was not considered to be important in a similar study at 265 nm (c). Other homogeneous and heterogeneous reactions may serve the same purpose, so that the value in (b) must be considered an upper limit. It is not clear how this value was obtained.

H. Johnston (d) in a discussion of his earlier work on the effects of foreign gases on the decomposition of N_2O_5 (e) suggests that k_1 (323 K) is less than 2×10^{-19} cm^3 molecule^{-1} s^{-1} and that Jaffe and Ford were observing a heterogeneous reaction. Niki, et al. (f) on the basis of a photochemical smog model estimate $k_1 = 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 300 K, a value supported by preliminary results from a direct study of the reaction which indicate $k_1 < 10^{-20}$ cm^3 molecule^{-1} s^{-1} (g). The latter is tentatively accepted as a realistic upper limit for the rate constant. Assuming a normal pre-exponential factor this reaction would have a rate constant at least 100 times slower at stratospheric temperatures (220 K) than at 300 K.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).
(b) S. Jaffe and H. W. Ford, J. Phys. Chem. **71**, 1832 (1967).
(c) T. Berces and S. Forgeteg, Trans. Faraday Soc. **66**, 640 (1970).
(d) H. S. Johnston, Formation and Stability of Nitric Acid in the Stratosphere, typescript, University of California, Berkeley, California (1971).
(e) H. S. Johnston, J. Am. Chem. Soc. **75**, 1567 (1953).
(f) H. Niki, E. E. Daby, and B. Weinstock, Advan. Chem. Series, to appear.
(g) H. Niki, private communication to D. Garvin, 1972.

J. T. Herron, R. E. Huie
March, 1972
Revised: January, 1973

4.18. The Reaction Between H_2O and $O(^1D)$

	$\Delta H^\circ_{298}(a, b)$		
$H_2O + O(^1D) \rightarrow HO + HO$,	$-119.2\,kJ\,mol^{-1}$	$(-28.50\,kcal\,mol^{-1})$	k_{1a}
$\rightarrow O(^3P) + H_2O$	-189.8	(-45.36)	k_{1b}
$\rightarrow H_2O_2$	-333.4	(-79.69)	k_{1c}
$\rightarrow H_2 + O_2$	-197.1	(-47.11)	k_{1d}

Auxiliary Data

Reaction (1) has been studied only in relative rate experiments.

Comparison reactions are:

	$\Delta H^\circ_{298}(a, b)$		
$N_2 + O(^1D) \rightarrow N_2 + O(^3P)$	$-189.8\,kJ\,mol^{-1}$	$(-45.36)\,kcal\,mol^{-1}$	k_2
$O(^1D) + O_3 \rightarrow O_2 + O_2$	-581.6	(-139.01)	k_3
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	-189.8	(-45.36)	k_4
$C_5H_{12} + O(^1D) \rightarrow C_5H_{11}OH$	-589.1	(-140.8)	k_5
$N_2O + O(^1D) \rightarrow N_2 + O_2$	-521.0	(-124.52)	k_{6a}
$N_2O + O(^1D) \rightarrow NO + NO$	-340.5	(-81.38)	k_{6b}
$CO + O(^1D) \rightarrow CO + O(^3P)$	-189.8	(-45.36)	k_7

Preferred Values

(Changed from that in NBS Report 10828 (April 1972).)

Ratios (o)

$k_1(H_2O)/k_3(O_3) = 0.70$

$k_1(H_2O)/k_4(O_2) = 4.7$

$k_1(H_2O)/k_2(N_2) = 6.4$ at 300 K. Reproducibility 20−30 percent.

Absolute Value

$k_1 = 3.5 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$.

Uncertainty: $\log k \pm 0.1$

Remarks

The preferred values are those developed by Cvetanovic (o), see below, from an analysis of all rate ratio data for reactions of $O(^1D)$. The ratios are more reliable than the absolute value since the uncertainty in the latter must reflect the errors in the available absolute measurements of $O(^1D)$ rate constants.

The rate ratios probably are sufficiently accurate for atmospheric modelling. All of the reactions of $O(^1D)$ with major and trace components of the atmosphere are very fast, only the competition among them is important. For this reason the rate ratios are more important than the absolute values.

Comments on Measurements

Ref. (c)

Large extent of decomposition of O_3 during and immediately after the (relatively long) flash make it difficult to assess the primary quantum yield and contribution from other reactions. (The value 0.45 is not given in the paper. It has been derived from the data and mechanism.

Data

k_1/k_3	Conditions
0.45 ± 0.2	Room temp, uv flash photolysis of $O_3/H_2O/He$ mixtures. O_3 decomp. meas.
	Biedenkapp, et al., 1970 (c).
0.5	Room temp, uv flash photolysis of $O_3/H_2O/Ar$ mixtures. O_3 decomp. meas.
	Langley, McGrath, 1971 (d).
0.25 ± 0.06	Room temp, steady; $\lambda = 253.7$ nm, photolysis of O_3/H_2O^{18} mixtures, ^{18}O exchange meas.
	Katakis, 1967 (e).
1.5	Room temp, steady photolysis of O_3, $\lambda = 228.8,\ 253.7,\ 280.0$ nm in presence of water and He. $\Phi(-O_3)$ obtained from $\Delta[O_3]$ (photometric) and actinometry using HBr photolysis.
	Lissi, Heicklen, 1972 (k).
$k_1/(k_{6a} + k_{6b}) =$ 1.50 ± 0.06	Uv flash photolysis of O_3 in $O_3/N_2O/H_2O$ mixt. vs. the same O_3/N_2O mixt. at 23 ± 1 °C. $[O_3] = 0.4 - 2.3$ torr, $[N_2O] = 25 - 400$ torr, $[H_2O]/[N_2O] < 1$. N_2 production meas.
	Scott, Cvetanovic, 1971 (f).
$k_1/k_5 = 0.38 \pm 0.03$	Steady photolysis of N_2O, $\lambda = 213.9$ nm. in $N_2O/C_5H_{12}/SF_6/H_2O$ mixtures at 25 °C. $[N_2O] = 3$ torr, $[C_5H_{10}] = 10$ torr, $[SF_6] = 300$ torr, $[H_2O] = 5 - 21$ torr. $\Delta C_5H_{11}OH/\Delta N_2$ meas.
$k_{1b} \sim 0$	Same expts, 1-butene added as a test for $O(^3P)$. H_2O had no effect.
	Paraskevopoulos, Cvetanovic, 1971 (g).
$k_1/(k_{6a} + k_{6b}) = 2.1$ $k_{1a}/k_1 > 0.9$	Steady photolysis of N_2O in presence of H_2O and CO. Relative yields of CO_2 and N_2 measured.
	Simonaitis, Heicklen, 1972 (l).
$k_1/k_4 = 5.0$	Quenching of radiation from $O_2(^1\Sigma)$ in 254 nm photolysis of O_3.
	Gauthier, Snelling, 1972 (m).
$k_1/k_2 = 3.5$	Flash photolysis of $O_3/H_2O/N_2$ mixtures. $[O_3]$ vs. t measured.
	Fortin, Snelling, Tardif, 1972 (n).
$k_1/k_7 =$ 3.0 (300 K) 1.67 (423 K) $0.385\,exp\,(+600/T)$	Steady photolysis of NO_2, $\lambda = 228.8$ nm in $NO_2/H_2O/CO/He$ mixtures. Actinometry using NO_2/N_2O mixtures. $\Phi(CO_2)$ meas.
	Simonaitis, Heicklen 1972 (j).

Ref. (*d*)

Pending a more detailed report of the measurements, the [H_2O] at which a limiting quantum yield is reached cannot be assessed. This limit is used in setting the rate ratio.

Ref. (*e*)

O-atom exchange was measured in steady photolysis of O_3/H_2O mixtures. The resultant rate ratio is strongly dependent upon the mechanism and on the efficiency of a chain reaction in recycling the oxygen.

Ref. (*f*)

Simultaneous photolysis of two mixtures, one containing a quenching gas (H_2O, Xe, He, SF_6, O_2, CO_2, neopentane). Results do not depend upon k_{6a}/k_{6b}.

Ref. (*g*)

Water decreases the production of $C_5H_{11}OH$. Effect assigned to competition between reactions (1a) and (5) since reaction (1b) was shown to be unimportant. Results consistent with $k_1/k_5 = 0.35 \pm 0.03$ derived from ref (f). Results do not depend upon k_{6a}/k_{6b}.

Ref. (*j*)

In this study k_1/k_7 and the ratio of rates for

$$HO + NO_2(+M) \rightarrow HNO_3$$
$$HO + CO \rightarrow CO_2 + H$$
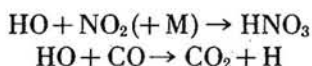
were determined simultaneously. Experiments under extreme conditions permitted both ratios to be established. The temperature coefficient is believed to apply to k_7, not k_1.

Ref. (*k*)

The experiments show $\Phi(-O_3)$ to rise from a minimum value ~ 5.5 when $P(H_2O) = 0$ and pass through a maximum at $P(H_2O) \sim 4$ torr. See fig. 7 in ref. (k). At low [H_2O], Φ is proportional to [H_2O]$^{0.5}$. The authors estimate $k_1/k_3 \sim 1.5$ from Φ at $(\Phi_{max} - \Phi_0)/2$. At this point $k_3[O_3] = 3k_1[H_2O]$. The mechanism is complex, the estimate approximate.

Ref. (*l*)

These experiments determine the relative rates of reaction of H_2O and N_2O with $O(^1D)$ by following CO_2 production from $CO + HO \rightarrow CO_2 + H$ as a function of

[N_2O]/[H_2O]. The ratio applies to the sum of the following four reactions

$$
\begin{aligned}
O(^1D) + H_2O &\rightarrow 2HO & >90\% \\
&\rightarrow H_2O + O(^3P) & <4\% \\
&\rightarrow H_2O_2 & <5\% \\
&\rightarrow H_2 + O_2 & <0.4\%
\end{aligned}
$$
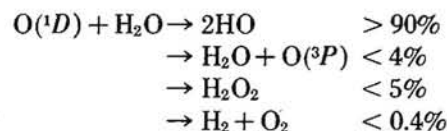
the relative importance of which is shown at the right.

Ref. (*o*)

An evaluation of all data available in Nov. 1972 for reactions of $O(^1D)$ with CH_4, C_2H_6, C_3H_8, C_5H_{12}, CO, CO_2, H_2, H_2O, N_2, NO, NO_2, N_2O, O_2, O_3 and the rare gases. These rate ratio data form an interconnected net, solution of which yields a self consistent set of rate ratios. The data network is displayed in the data sheet on $O(^1D) + N_2O$. The relative rates pertinent to the data listed in this review are 1.0(CO_2), 0.42(O_2), 2.8(O_3), 0.30(N_2), 1.22(N_2O), 0.42(CO), 1.95(H_2O).

References

(a) D. D. Wagman, et al., NBS Tech. Note 270–3 (Jan. 1968).
(b) C. E. Moore, NBS Circular 467. vol. 1 (1949).
(c) D. Biedenkapp, L. G. Hartshorn, and E. J. Bair, Chem. Phys. Lettrs. **5**, 379 (1970).
(d) K. F. Langley and W. D. McGrath, Planet. Space Sci. **19**, 413 (1971).
(e) D. Katakis, J. Chem. Phys. **47**, 541 (1967).
(f) P. M. Scott and R. J. Cvetanovic, J. Chem. Phys. **54**, 1440 (1971).
(g) G. Paraskevopoulos and R. J. Cvetanovic, Chem. Phys. Lettr. **9**, 603 (1971).
(h) J. F. Noxon, J. Chem. Phys. **52**, 1852 (1970).
(i) R. Gilpin, H. I. Schiff, and K. H. Welge, J. Chem. Phys. **55**, 1087 (1971).
(j) R. Simonaitis and J. Heicklen Int. J. Chem. Kinetics **4**, 529 (1972).
(k) E. Lissi and J. Heicklen, J. Photochem **1**, 39 (1972/73).
(l) R. Simonaitis and J. Heicklen, The reaction of $O(^1D)$ with H_2O and the reaction of OH with C_3H_6, (Pennsylvania State University, Ionospheric Research Laboratory Scientific Report 397, Sept 5, 1972).
(m) M. Gauthier and D. R. Snelling, letters to R. F. H. and D. G. (1972).
(n) C. J. Fortin, D. R. Snelling, and A. Tardif, Can. J. Chem. **50**, 2747 (1972).
(o) R. Cvetanovic The Reactions of $O(^1D_2)$, in The Natural Stratosphere, E. Reiter, editor (Climatic Impact Assessment Program, Monograph 1), preliminary draft, November 1972.
(p) R. F. Heidner, D. Husain, and J. R. Wiesenfeld, Chem. Phys. Lett. **16**, 488 (1972).

David Garvin
March, 1972
Revised: January, 1973

4.19. Photolysis of H_2O_2, $\lambda < 300$ nm

Primary Photochemical Transitions

Reaction	ΔH_0°		λ threshold (nm)	
	kJ/mol	kcal/mol		
$H_2O_2 \rightarrow 2HO(X^2\Pi)$	207	(49.6)	577	(1)
$\rightarrow HO(X^2\Pi) + HO(A^2\Sigma)$	598	(142.9)	200	(2)
$\rightarrow H + HO_2$	371	(88.7)	322	(3)
$\rightarrow 2H + O_2(X^3\Sigma_g^-)$	562	(134.3)	213	(4)
$\rightarrow H_2 + O_2(a^1\Delta_g)$	224	(53.6)	533	(5)
$\rightarrow H_2 + O_2(b^1\Sigma_g^+)$	287	(68.6)	417	(6)
$\rightarrow H_2 + 2O(^3P)$	624	(149.0)	192	(7)
$\rightarrow H_2O + O(^1D)$	328	(78.3)	365	(8)

ΔH_0° calculated using ΔH_f° values in (a) and excitation energies of $OH(^2\Sigma)$, $O_2(^1\Delta)$, and $O_2(^1\Sigma)$ from (b).

Data

Absorption spectrum and absorption coefficient

Wavelength range	Observation
275–215 nm	Continuous abs. spectrum; same value of absorption coefficient for vapor and sol'n. Urey, et al., 1929 (c).
225–185 nm 254 nm	Continuous abs. spectrum; value of abs. coefficient increases steadily as λ decreases. See table I and fig. 1. Holt, et al., 1948 (d).
200–120 nm	Some structure. Bands beginning at $\sim$ 185 nm, 165 nm, and possibly at $\sim$ 145 nm. Structure is superimposed on broad underlying continuum resembling H_2O. Contribution of H_2O to absorption for $\lambda < 180$ nm not known. At 200 nm value of abs. coeff. is nearly twice that in (d). Schürgers, Welge, 1968 (e).

Quantum yields

$300 > \lambda > 200$ nm. $\phi_8(O(^1D))/\phi_1(OH) < 0.10$	$[OH]$ and $[OD]$ observed in absorption. $\phi_1(OH) = 2\phi_1(-H_2O_2)$. Greiner, 1966 (f).
$\lambda = 253.7$ nm $\Phi(-H_2O_2) = 1.7 \pm 0.4$	Based on Φ (acetone) = 0.8. Volman, 1949, 1963 (h).
$\phi_8(O(^1D)) < 0.01$	Stief, DeCarlo, 1969 (g).
$\lambda = 147$ nm $\phi_2(HO(A^2\Sigma)) > 0$ $\phi_8(O(^1D)) < 0.01$	HO $(A-X)$ emission obs. Stief, DeCarlo, 1969 (g).
$\lambda = 123.6$ nm $\phi_2(HO(A^2\Sigma)) > 0$ $\phi_8(O(^1D)) < 0.01$ $\phi_5 + \phi_6 + \phi_7 = 0.25$ $\phi_3 + \phi_4 \gtrsim 0.25$ $\phi_1 + \phi_2 \lesssim 0.50$	Inferred from meas. $\Phi_{(H_2)} = 0.50$, half of which is scavenged with C_2D_4. No direct observation of O_2^* in (5) or (6). Stief, DeCarlo, 1969 (g).

Preferred Values

Absorption coefficients, $200 < \lambda < 300$ nm: Data of reference (d) see table I and fig. 1.

Quantum yields, $200 < \lambda < 300$ nm: $\phi_1(-H_2O_2) \sim 1$. $\lambda < 200$ nm: No recommendation.

Remarks

Absorption Coefficients

The corrected data from ref. (d) are selected here. Relative absorption coefficients (i) match the wavelength dependence. There is good agreement between (d) and (c) at 220 nm. Measurements in the vacuum uv (e) give an absorption coefficient 2 times the value in (d) at 200 nm. The cause of the discrepancy is unknown.

Quantum yields

$\lambda > 200$ nm

The only data are from one study (h) in which the overall quantum yield is $\Phi(-H_2O_2) = 1.7 \pm 0.4$ based on the mechanism:

$$H_2O_2 + h\nu \ (\lambda = 253.7 \text{ nm}) \rightarrow 2 HO \qquad (1)$$

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

$$2HO_2 \rightarrow H_2O_2 + O_2$$
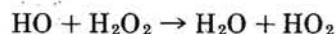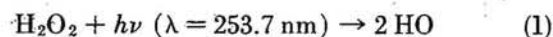
This leads to $\phi_1(-H_2O_2) \sim 1$, which is reasonable. Greiner has criticized some of the tests in support of the above mechanism and suggests that O atoms could be formed in the photolytic step and still give the observed quantum yield. There are no data on this point.

$\lambda < 200$ nm

These data, ref. (g), are important primarily because they indicate what photolytic processes occur. The numerical values are based on H_2 production in the absence and presence of C_2D_4 (which scavenges H atoms), and are put on an absolute basis by using CO_2 as an actinometer. Although the trends reported clearly are present, the absolute values for the ϕ's may have a large uncertainty.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).

(b) G. Herzberg, Spectra of Diatomic Molcules, D. Van Nostrand Co. Inc., New York (1950).

(c) H. C. Urey, L. H. Dawsey, and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

(d) R. B. Holt, C. K. McLane, and O. Oldenberg, J. Chem. Phys. **16**, 225, 638 [erratum] (1948).

(e) M. Schürgers and K. H. Welge, Z. Naturforsch. **23a**, 1508 (1968).

(f) N. R. Greiner, J. Chem. Phys. **45**, 99 (1966).

(g) L. J. Stief, and V. J. DeCarlo, J. Chem. Phys. **50**, 1234 (1969).

(h) D. H. Volman, J. Chem. Phys. **17**, 947 (1949); Adv. Photochem. **1**, 43 (1963).

(i) T. T. Paukert and H. S. Johnston, J. Chem. Phys. **56**, 2824 (1972).

A. H. Laufer, M. J. Kurylo, W. Braun
March, 1972

TABLE I. Values of absorption coefficient of H_2O_2, 185–225 nm. (read from corrected figure 1 of ref. (d), J. Chem. Phys. **16**, 638 (1948))

λ(nm)	$10^{20} \, \sigma$, cm^2
190	80
195	60
200	54
205	46
210	40
215	34
220	28
225	24
254	7.4

The absorption coefficient is defined by the eqn:

$$\sigma = (1/cl) \, \log_e (I_0/I),$$

where c is conc. in molecules/cm^3, l is the path length in cm, I_0 and I are the incident and transmitted light intensities. The value for 254 nm is from the original paper by Holt, et al., J. Chem. Phys. **16**, 225 (1948).
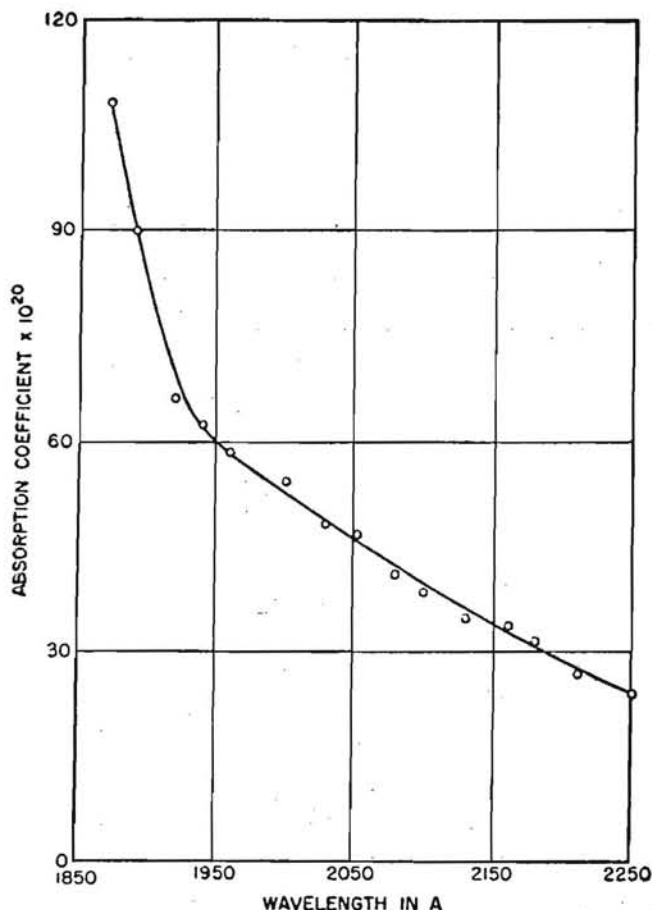
FIGURE 1. Absorption coefficient σ for H_2O_2 vapor. Same data as in table I. Units of σ are cm^2. For definition of σ see footnote to table I. Holt, et al. (corrected fig. 1 of ref. (d), J. Chem. Phys. **16**, 638 (1948)).

4.20. The Reaction Between H_2O_2 and NO

$$H_2O_2 + NO \rightarrow H_2O + NO_2 \quad \text{(overall reaction)} \qquad k_0$$
$$\rightarrow HNO + HO_2 \qquad k_{1a}$$
$$\rightarrow HNO_2 + OH \qquad k_{1b}$$
$$\rightarrow HNO_3 + H \qquad k_{1c}$$
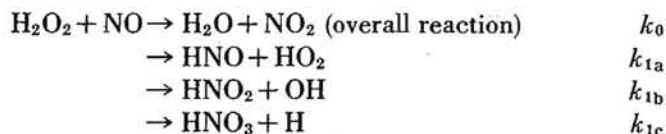
Auxiliary Data

$$\Delta H^\circ_{298}(0) = -163 \text{ kJ/mol} (-38.9 \text{ kcal/mol}) \qquad \text{(a, b)}$$
$$\Delta H^\circ_{298}(1a) = 166 \text{ kJ/mol} (40 \text{ kcal/mol})$$
$$\Delta H^\circ_{298}(1b) = 5.5 \text{ kJ/mol} (1.3 \text{ kcal. mol})$$
$$\Delta H^\circ_{298}(1c) = 129 \text{ kJ/mol} (30.8 \text{ kcal/mol})$$

Data

k(s^{-1})	T(K)	System
0.032	491	H_2O_2 (2–12 torr) and NO (3–40 torr) allowed
.115	521	to react in excess N_2, He, or CO_2. Meas-
.42	550	ured initial $d[NO_2]/dt$ and initial dP/dt.
.76	569	
1.57	588	Asquith, 1969 (c).
2.53	601	

$d[NO_2]/dt$ (initial)$=k[H_2O_2]^2/[M]$. When data for k are expressed in Arrhenius form: $A = 7 \times 10^8$ s^{-1} and $E = 23.4$ kcal/mol (98 kJ/mol) $(k_2/k_4)_{T=550 K} = 3.7 \times 10^{-5}$ mol/cm^3. Asquith, 1969 (c) (see Remarks section for definition of rate constants).

Quantity Measured	System
$k_1 < 5 \times 10^{-20}$ cm^3 molecule^{-1}s^{-1} ($T = 298$ K)	H_2O_2 (0.5–1.5 torr) and NO(1–12 torr) allowed to react in presence of 1–2 torr Ar. [NO], [H_2O_2], [NO_2] followed by mass spectrometry [NO_2] also measured by optical absorption.
	Gray, Lissi, Heicklen, 1972 (g).

Preferred Value

(Changed from that in NBS Report 10828 (April 1972).)

$$k_1 \, (550 \text{ K}) \sim 2 \times 10^{-20} \text{ cm}^3 \text{molecule}^{-1}\text{s}^{-1}.$$
$$k_1 \, (300 \text{ K}) < 5 \times 10^{-20} \text{ cm}^3 \text{molecule}^{-1}\text{s}^{-1}.$$

Remarks

The data in (c) are interpreted according to the following mechanism:

$$H_2O_2 + NO \rightarrow HNO + HO_2$$
$$\rightarrow HNO_2 + OH \qquad k_1$$
$$\rightarrow HNO_3 + H \rightarrow OH \text{ or } HO_2$$

$OH + H_2O_2 \rightarrow HO_2 + H_2O$ k_2
$HO_2 + NO \rightarrow OH + NO_2$ k_3
$OH + NO + M \rightarrow HNO_2 + M$ k_4
$OH + NO_2 + M \rightarrow HNO_3 + M$ k_5
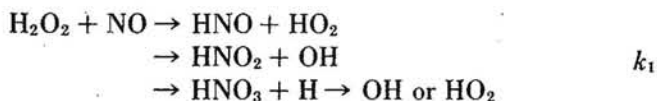
This mechanism leads to the expression:

$$d[NO_2]/dt \text{ (initial)} = (k_1 k_2/k_4) \; ([H_2O_2]^2/[M]).$$

From the measured values of $k = k_1 k_2/k_4$ and of k_2/k_4 at 550 K the value of k_1 at 550 K is obtained. From the measured value of 23.4 kcal/mol for $E = E_1 + E_2 - E_4$ one can get an estimate of E_1. The value of E_2 has been estimated to be 1.8 kcal/mol (e). The author in (c) estimates E_4 to be $\rightarrow 7.5$ kcal/mol assuming it to be equal to the value estimated for E_5 in (f). Although the magnitude of this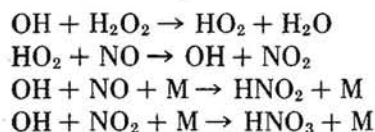 number seems much too large it can be used to set a lower limit to the value of E_1 of 14 kcal/mol. This leads to k_1 (300 K) $< 10^{-24}$ cm^3 molecule^{-1} s^{-1}. Choosing the value of E_4 to be near zero permits one to calculate an upper limit of 22 kcal/mol for the value of E_1. It is likely that reaction (1b) is the initiating step, since it is the only elementary reaction with a ΔH less than the observed E_1.

The mechanism used in (c) was originally used in (d). There, in a detailed study at 572 K, NO (up to 25 torr) and H_2O_2 (up to 14 torr) in excess N_2 were allowed to react and the overall reaction shown to correspond to (1). The initial rate of formation of NO_2 was found to be independent of [NO] and vessel diameter and to be of the form d $NO_2]/dt$ (initial) $= k[H_2O_2]^x/[N_2]$ where $1.6 < x < 1.9$ depending on $[N_2]$. The deviation of x from the value 2 can be accounted for by participation of H_2O_2 as a third body in reaction (4).

The upper limiting value of k_1 (300 K) in (g) is derived on the basis of the observed decay of H_2O_2 in the presence of NO. It is far larger than the upper limit derived from the high temperature data (c). The possibility that the room temperature results are due to heterogeneous reactions cannot be ruled out.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).
(b) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d. Ed. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).
(c) P. L. Asquith, The Gas-Phase Reactions of Hydrogen Peroxide with Oxides of Nitrogen. Thesis submitted to Dept. of Chemistry, University of Manchester (April 1969).
(d) B. J. Tyler, Nature **195**, 279 (1962).
(e) D. D. Drysdale and A. C. Lloyd, Gas Phase Reactions of the Hydroxyl Radical, Oxidation and Combustion Reviews **4**, 157 (1970).
(f) M. G. Burnett, Ph.D. Thesis, University of Cambridge, 1961.
(g) D. Gray, E. Lissi, and J. Heicklen, J. Phys. Chem. **76**, 1919 (1972).

W. Tsang, R. F. Hampson
March, 1972
Revised: January 1973

4.21. The Reaction Between NO and O_3

$NO + O_3 \rightarrow NO_2 + O_2$ k_1
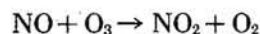
Auxiliary Data

$\Delta H^\circ_{298} = -200$ kJ/mol (-47.7 kcal/mol)   (a)

Data

k_1 (cm^3 molecule^{-1} s^{-1})	System
$1.3 \times 10^{-12} \exp(-1.25 \times 10^3/T)$	Stopped-flow technique. Meas. at 198 and 230 K (total of 65 expts.)
	Johnston, Crosby, 1954 (b).
5×10^{-14}	Photolysis of NO_2 in air, in a 50 liter stirred flow reactor, 302 K.
	Ford, et al., 1957 (c).
$9.5 \times 10^{-13} \exp(-1.23 \times 10^3/T)$	Flow system, infrared chemiluminescence, 216–322 K.
	Clyne, et al., 1964 (d).
1.4×10^{-14}	Flow system, infrared chemiluminescence, 293 K.
	Clough, Thrush, 1967 (e).

Data—Continued

k_1 (cm^3 molecule^{-1} s^{-1})	System
2.1×10^{-14}	Flow system, mass spec. 298 K.
	Phillips, Schiff, 1962 (f).
2.1×10^{-14}	Flow system, mass spec., 296 K.
	Sharma, et al., 1970 (g).
$2.0 \times 10^{-12} \exp(-1.28 \times 10^3/T)$	Supersonic nozzle. Meas. $\Delta[O_3]$ by absorption at 254 nm. 245–345 K (total of 80 expts.).
	Marte, et al., 1963 (h).

Preferred Value

$k(198–330 \text{ K}) = 9 \times 10^{-13}$ exp $(-1.2 \times 10^3/T)$ cm^3 molecule^{-1} s^{-1}, estimated uncertainty: ± 30 percent over indicated temperature range.

$k(298 \text{ K}) = 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.
$k(220 \text{ K}) = 3.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Remarks

The rate constant is given for the overall reaction. There are two reaction channels which have been identified, one leading to ground state NO_2, the other to NO_2^* (probably $NO_2(^2B_1)$) (d, e, i). The rate constant for the latter is reported to be $1.3 \pm 0.2 \times 10^{-12}$ exp $(-2100 \pm 150/T)$ cm^3 molecule^{-1} s^{-1} (e), which corresponds to about 2 percent of the total reaction at 220 K.

The preferred values are derived from an Arrhenius plot of the data in (b) and (d). Although the total pressures used in (b) are not given, in the one case noted the total pressure was 565 torr. In (d) total pressure varied from 0.8 to 3 torr.

The other extensive set of data (h) is in good agreement with the preferred values. Because of the scatter in the data (about a factor of three at any given temperature) it was not used in arriving at the preferred value. With the exception of the data in (c), all the data obtained at or near room temperature (e, f, g) are also in good agreement with the preferred value.

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3 (Jan. 1968).
(b) H. S. Johnston and H. J. Crosby, J. Chem. Phys. **22**, 689 (1954).
(c) H. W. Ford, G. J. Doyle, and N. Endow, J. Chem. Phys. **26**, 1337 (1957).
(d) M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, Trans. Faraday Soc. **60**, 359 (1964).
(e) P. N. Clough and B. A. Thrush, Trans. Faraday Soc. **63**, 915 (1967).
(f) L. F. Phillips and H. I. Schiff, J. Chem. Phys. **36**, 1509 (1962).
(g) H. D. Sharma, R. E. Jervis, and K. Y. Wong, J. Phys. Chem. **74**, 923 (1970).
(h) J. E. Marte, E. Tschuikow-Roux, and H. W. Ford, J. Chem. Phys. **39**, 3277 (1963).
(i) A. E. Redpath and M. Menzinger, Can. J. Chem. **49**, 3063 (1971).

J. T. Herron, R. E. Huie
February, 1972
Revised: January, 1973

4.22. The Reaction Between NO_2 and O_3

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad\qquad k_1$$
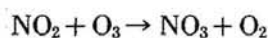
Auxiliary Data

$$\Delta H^\circ_{298} = -105 \pm 21 \text{ kJ/mol } (-25 \pm 5 \text{ kcal/mol}) \qquad (a, b)$$

Data

(cm^3 molecule^{-1} s^{-1})	System
$k = 1 \times 10^{-11}$ exp $(-3.5 \times 10^3/T)$ $k(293-295) = 6.1 \times 10^{-17}$	Stopped-flow technique. $[NO_2] \sim [O_3] \sim 1-10$ torr. $[NO_2]$ measured by optical absorption. 27 experiments at 293–295 K. Arrhenius expression derived from consideration of set of 22 experiments 286–302 K. Johnston, Yost, 1949 (c).
$k_1 = 3.3 \times 10^{-17}$	50 l stirred flow reactor, 298 K. $[NO_2] \sim [O_3] \sim 1$ ppm. $[NO_2]$ and $[O_3]$ followed. Ford, Doyle, Endow, 1957 (d).
$k \approx 1.3 \times 10^{-17}$	Flash photolysis of O_3–N_2O mixture at room temperature. Scott, et al., 1971 (e).
$k_1 = 6.5 \times 10^{-17}$	Photolysis of NO_2 in 1 atm. air at 298 K. $[NO_2] \sim 1-10$ ppm. $[O_3]$ followed by NO/O_3 chemiluminescence detection. Stedman, Niki, 1972 (f).
$k_1 = 4.4 \times 10^{-17}$	Same system as in (f). Niki, 1972 (g).

Preferred Value

(Changed from that in NBS Report 10692 (Jan. 1972).)

$k(298) = 5 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. Estimated uncertainty: $\pm 50\%$.

Remarks

The recommended rate is based on the data of (c, d, and g).

There are no satisfactory data on this reaction extending over a meaningful range of temperature. In the work of Johnston and Yost (c), rate constants were measured over the range 286 to 302 K. The accuracy of the temperature measurements was stated to be ± 2 degrees. From these data they derived the Arrhenius expression $k = 1 \times 10^{-11}$ exp $(-3.5 \times 10^3/T)$ cm^3 molecule^{-1} s^{-1}. Although the pre-exponential factor appears to be reasonable, the uncertainty in the data makes an extrapolation to 220 K extremely unreliable. An uncertainty of $10^{\pm 1}$ is therefore attached to the value of the rate constant at 220 K, about 10^{-18} cm^3 molecule^{-1} s^{-1}.

The other reported values (d, g) for the rate constant are all near room temperature. The preferred value at 298 K is an average of these values and that predicted by the Arrhenius expression given in (c). At present not enough data is available to make a clear choice of the "best" value at 298 K. These data (d, g) however confirm the approximate correctness of the data of (c) near room temperature, and in turn the reasonableness of the derived Arrhenius expression.

In these studies, reaction (1) was assumed to be followed by the reaction: $NO_2 + NO_3 \rightarrow N_2O_5$. Information on the overall stoichiometry, however, is available only in (d), where only two of six runs matched the assumed

stoichiometry, i.e. $\Delta[NO_2]/\Delta[O_3] = 2$. Values of this quantity ranged from 0.9 to 4.8. Thus the interpretation of (c) and (d) is uncertain.

The result in (e) is based on widely scattered data and an assumed stoichiometry determined by a seven-step mechanism for the flash photolysis of O_3 in presence of N_2O.

References

(a) D. D. Wagman, et al., NBS Technical Note 270–3 (Jan. 1968).

(b) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d Ed, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), **37** (June 1971).

(c) H. S. Johnston and D. M. Yost, J. Chem. Phys. **17**, 386 (1949).

(d) H. W. Ford, G. J. Doyle, and N. Endow, J. Chem. Phys. **26**, 1336 (1957).

(e) P. M. Scott, K. F. Preston, R. J. Andersen, and L. M. Quick, Can. J. Chem. **49**, 1808 (1971).

(f) D. H. Stedman and H. Niki, preprint, 1972.

(g) H. Niki, private communication to D. Garvin, 1972.

R. E. Huie, J. T. Herron
January, 1972
Revised: January, 1973

4.23. The Reaction Between N_2O and $O(^1D)$

	ΔH°_{298} (a, b)		
$N_2O + O(^1D) \rightarrow N_2 + O_2$	-521.0 kJ/mol	$(-124.52$ kcal/mol$)$	k_{1a}
$N_2O + O(^1D) \rightarrow 2NO$	-340.5	(-81.38)	k_{1b}

Auxiliary Data

Reaction (1) has been studied in relative rate experiments only. Comparison reactions are:

	ΔH°_{298} (a, b)		
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	-189.8 kJ/mol	$(-45.36$ kcal/mol$)$	k_2
$O(^1D) + O_3 \rightarrow 2O_2$	-581.6	(-139.01)	k_3

In addition to the reactions with O_2 and O_3 for which absolute values of the rate constants are available, reaction (1) has been studied in competition with the deactivation or reaction of $O(^1D)$ with the following species: N_2, CO, CO_2, H_2, H_2O, NO, NO_2, Xe, CH_4, and neopentane.

Data

Note: Only the data comparing k_1 with k_2 or k_3 are given here. They are chosen from the very large set of data for relative values for $k(O(^1D) + N_2O)$ (37 measured values of 12 ratios) because absolute values have been measured only for $k_2(j)$ and $k_3(k, q)$.

$(k_{1a} + k_{1b})/k_2$	Conditions
2.8	~250 nm photolysis of O_3; decrease in yield of N_2 measured.
	Scott, Cvetanovic, 1971 (ref. c).
3.4	228.8 nm photolysis of NO_2; decrease in yield of N_2 measured.
	Paraskevopoulos, et al., 1971 (ref. d).
4.4	147.0 nm photolysis of O_2; change in yield of $O(^3P)$ measured.
	Young, et al., 1968 (ref. e).
5.0	253.7 nm photolysis of O_3; change in yield of N_2O_5 measured.

Data—Continued

$(k_{1a} + k_{1b})/k_2$	Conditions
	De More, 1970 (ref. f).
3.6	Quenching of radiation from $O_2(^1\Sigma)$ in 254 nm photolysis of O_3.
	Gauthier, Snelling, 1972 (ref. n).

$(k_{1a} + k_{1b})/k_3$	
0.39	254 nm photolysis of O_3 in presence of N_2O; $\phi(N_2)$ measured.
	Goldman, et al., 1971 (ref. i).
0.25–0.67	Photolysis of O_3 in presence of N_2O at 228.8, 254, and 280 nm, $\Phi(-O_3)$ measured.
	Lissi, Heicklen, 1972 (ref. o).

k_{1a}/k_{1b}	
1.01 ± 0.06	NO_2 photolysis at 228.8 and 242 nm, yields of NO and N_2 measured.
0.99 ± 0.06	O_3 photolysis at ~250 nm, yields of NO_2 and N_2 measured.
	Scott, et al., 1971 (ref. g).
0.59 ± 0.01	N_2O photolysis at 213.9 nm, quantum yield of O_2 measured.
	Greenberg, Heicklen, 1970 (ref. h).
0.50 ± 0.1; 0.59 ± 0.1	O_3/N_2O mixture photolysis at 228.8 and at 253.7 nm, $\phi(N_2)$ meas.
	Goldman, et al., 1971 (ref. i).
0.69 ± 0.05	N_2O photolysis at 213.9 nm and 184.9 nm. Measured $\Phi(N_2)/\Phi_m(O_2)$ where $\Phi_m(O_2)$ is the measured quantum yield of O_2 formation.
0.83 ± 0.06	Same system as above with excess He added to remove translational energy of $O(^1D)$.
	Simonaitis, Greenberg, Heicklen, 1972 (ref. m).

Preferred Values (300 K)

(Changed from that in NBS Report 10828 (April 1972).)

Ratios (p)

$k_1(N_2O)/k_2(O_2) = 2.9$.

$k_1(N_2O)/k_3(O_3) = 0.44$.

$k_{1a}/k_{1b} = 1.0$.

Absolute Values

$k_1 = 2.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

$k_{1a} = 1.1 \times 10^{-10}$.

$k_{1b} = 1.1 \times 10^{-10}$.

Uncertainty: $\log k \pm 0.1$.

Remarks

The preferred values for k_1/k_2, k_1/k_3, and k_1 are those developed by Cvetanovic (p) from an analysis of all rate ratio data for reactions of $O(^1D)$.

This consisted of an evaluation of all data available in Nov. 1972 for reactions of $O(^1D)$ with CH_4, C_2H_6, C_3H_8, neopentane, CO, CO_2, H_2, H_2O, N_2, NO, NO_2, N_2O, O_2, O_3, and the rare gases. These rate ratio data form an interconnected network, the solution to which yields a self-consistent set of rate ratios. This data network is displayed in fig. 1. The relative rates pertinent to the data listed in this data sheet are: 1.0 (CO_2), 1.22 (N_2O), 0.42 (O_2), 2.8 (O_3), 0.30 (N_2), 0.42(CO), 1.61(H_2), 1.95(H_2O), 1.17(NO), 1.55(NO_2), 0.78(Xe), 2.22(CH_4), 6.8 (neopentane).

k_{1a}/k_{1b} value in (g) selected as best value for thermally equilibrated $O(^1D)$ atoms.

Comments on Measurements

Ref. (e)

Relative values put on an "absolute" basis by taking k_3 to be the mean of estimated upper and lower limits. Reported value for overall rate agrees with value chosen here for $(k_1 + k_2)$.

Ref. (g)

From the limiting relative $\phi(N_2)$ at high additive pressure in the 228.8 nm. photolysis of N_2O, the value of $k_1/(k_2 + k_d)$ was estimated to be 1.08 ± 0.19, where k_d is the rate constant for the deactivation of $O(^1D)$ by N_2O. They take this as confirmation of the two reported values of (k_1/k_2) and also as an indication that k_d is small relative to k_2.

Ref. (h)

A less precise value of $k_1/k_2 = 1.04$ (+0.59, −0.37) based on $\Phi(N_2)$ also reported.

Ref. (m)

Authors conclude that value of $k_1/k_2 = 0.65 \pm 0.07$ for $O(^1D)$ atoms possessing greater than 10 kcal/mol translational energy and that for thermal $O(^1D)$ atoms $k_1/k_2 = 0.90 \pm 0.10$.

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3.

(b) C. E. Moore, NBS Circular 467, vol 1 (1949).

(c) P. M. Scott and R. J. Cvetanovic, J. Chem. Phys. **54**, 1440 (1971).

(d) G. Paraskevopoulos, K. F. Preston, and R. J. Cvetanovic, J. Chem. Phys. **54**, 3907 (1971).

(e) R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. **49**, 4758 (1968).

(f) W. B. DeMore, J. Chem. Phys. **52**, 4309 (1970).

(g) P. M. Scott, K. F. Preston, R. J. Andersen, and L. M. Quick, Can. J. Chem. **49**, 1808 (1971).

(h) R. I. Greenberg and J. Heicklen, Int. J. Chem. Kin. **2**, 185 (1970).

(i) C. S. Goldman, R. I. Greenberg, and J. Heicklen, Int. J. Chem. Kin. **3**, 501 (1971).

(j) J. F. Noxon, J. Chem. Phys. **52**, 1852 (1970).

(k) R. Gilpin, H. I. Schiff, and K. H. Welge, J. Chem. Phys. **55**, 1087 (1971).

(l) G. Paraskevopoulos and R. J. Cvetanovic, Chem. Phys. Lettrs. **9**, 603 (1971).

(m) R. Simonaitis, R. I. Greenberg, and J. Heicklen, Int. J. Chem. Kin. **4**, 497 (1972).

(n) M. Gauthier and D. R. Snelling, letters to R. F. H. and D. G. (1972).

(o) E. Lissi and J. Heicklen, J. Photochem. **1**, 39 (1972).

(p) R. Cvetanovic, The Reactions of $O(^1D_2)$, in The Natural Stratosphere, E. Reiter, editor (Climatic Impact Assessment Program, Monograph 1), preliminary draft, Nov. 1972.

(q) R. F. Heidner, D. Husain, and J. R. Wiesenfeld, Chem. Phys. Lettr. **16**, 488 (1972).
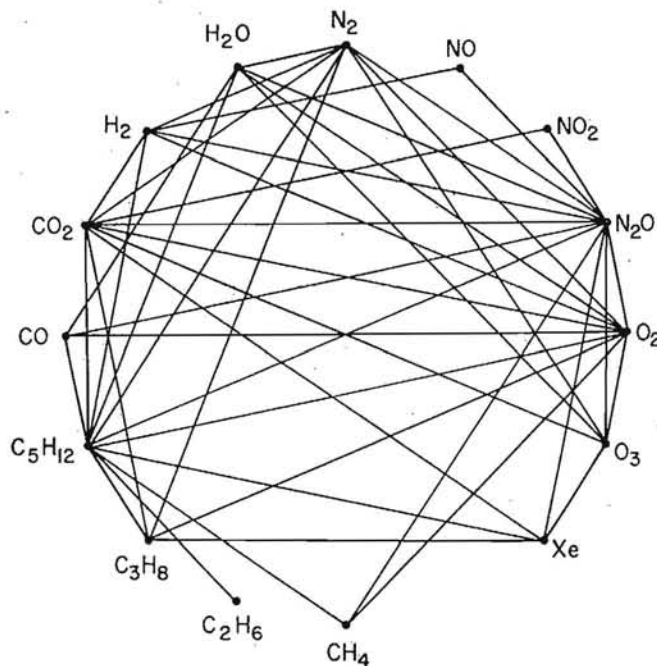
R. F. Hampson
March, 1972
Revised: January, 1973

FIGURE 1. Rate ratio network for $O(^1D)$ reactions. Each line indicates that the ratio of the rates of reaction of $O(^1D)$ with the two species has been measured, e.g. the measured ratio $k(O^* + O_3)/k(O^* + N_2O)$ is indicated by a line between O_3 and N_2O.

4.24. The Reaction of Oxygen Atoms with Ozone

	ΔH°_{298} (a)		
	kJ mol^{-1}	kcal mol^{-1}	
$O(^3P) + O_3 \rightarrow O_2 + O_2$	-391.6	-93.6	k_3^*

*For k_1, k_2, and k_3 the numbering used in NSRDS–NBS 20 (ref. b) is maintained in these data sheets.

Auxiliary Data

Related reactions

			ΔH°_{298}	
$O_3 + M \rightarrow O(^3P) + O_2 + M$	106.3 kJ mol^{-1}		25.4 kcal mol^{-1}	k_1
$O(^3P) + O_2 + M \rightarrow O_3 + M$	-106.3		-25.4	k_2
$O(^3P) + OCS \rightarrow CO + SO$	-211.3		-50.5	k_4

Equilibrium constant: $K_{12} = k_1/k_2$

$\log_{10} K_{12} = 25.565 - 5.422(1000/T)$ molecules cm^{-3} (table III)

Data

Direct measurements

k in cm^3 molecule^{-1} s^{-1}

log k_3 (range) -11.62 to -12.19	Shock wave decomposition of O_3, 769–910 K. [O_3] vs time meas. See table I. Jones, Davidson, 1962 (ref. c).
$k_3 = (1.05 \pm 0.18) \times 10^{-11}$ $\exp[(-2.169 \pm 0.05) \times 10^3/T]$ Uncertainties: 1 σ $k_3(298) = 7.5 \pm 0.6 \times 10^{-15}$	Flow system mixing O, O_3, Ar, and small amounts of NO. 269–409 K. Chemiluminescence of O+NO meas. vs distance. See table I. McCrumb, Kaufman, 1971 (ref. d).
$k_3 = (1.46 \pm 0.06) \times 10^{-14}$ at 296.4 K	Flow system, mixed Ar, O_3, N_2O, and O, with O produced by decomposition of N_2O on Nernst glower. Calorimetric detection of O atoms. Lundell, et al., 1969 (ref. e).
$k_3 = 1.8 \times 10^{-11}$ $\exp(-2.11 \times 10^3/T)$ $247 < T < 345$ K	Quotation, no data points available. Schiff, 1972 (ref. f).

Data—Continued

Direct measurements

k in cm^3 molecule^{-1} s^{-1}

$k_3 = (1.16 \pm 0.1) \times 10^{-11}$ $\exp((-1.93 \pm 0.08) \times 10^3/T)$ $k_3(298) = 1.8 \times 10^{-14}$ (calc.)	Flow system mixing O from discharge in $O_2 + Ar$? with O_3. Press. ~ 0.9 torr, $292 < T < 370$ K. [O_3] ~ 0.1–0.2 torr, [O_3]/[O] > 10. ESR detection of Δ[O]. See table I. Balakhnin, Egorov (ref. g).
$k_3 = 1.3 \pm 0.5 \times 10^{-14}$, $T \sim 300$ K	Ultraviolet flash photolysis of O_3 in ~ 150 torr of N_2. [O] vs time meas. by absn. at 130 nm. See table I. Husain, Kirsch, Donovan, 1972 (ref. l).
$k_3 = 2.02 \pm 0.19 \times 10^{-11}$ $\exp(-2.28 \times 10^3/T)$ $220 < T < 355$ K $k_3 = 1.08 \times 10^{-14}$, $T = 298$ K	Flash (laser) photolysis of O_3 at $\lambda = 590$ nm, $P(O_3) = 0.1$–14 torr, P(He or N_2) $= 50$–300 torr. [O] meas. vs time by atomic resonance fluorescence. See table I. Davis, Wong, Lephardt, 1972 (ref. m).

Indirect measurements in the ozone-oxygen system, k_2/k_3 and $k_J = k_1 k_3/k_2$

$k_2/k_3 = 2.31_5 \times 10^{-24} \times$ $\exp(+3.47 \times 10^3/T)$ cm^3 molecule^{-1} $200 < T < 900$ Uncertainty: log (k_2/k_3) ± 0.3 $k_J = 7.16 \times 10^{14} \times$ $\exp(-14.9 \times 10^3/T)$ s^{-1} $200 < T < 900$ K Uncertainty: log $k_J \pm 0.3$	Data evaluation, based on k_1, k_2, k_2/k_3, k_J and k_3. See ref. (b) for tables of data. Uncertainties are evaluator's overall estimates. Johnston, 1968 (ref. b).
$k_J = (1.7 \pm 0.5) \times 10^{14} \times$ $\exp[(-14.14 \pm 0.1) \times 10^3/T]$ $409 < T < 449$ K Uncertainty: 1 σ	Thermal decomposition of O_3 ($\sim 2.5\%$ in O_2) at atmospheric pressure. ΔO_3 and Δt measured. k_J recalculated here from points and k_1. See table II. Intezarova, Kondratiev, 1967 (ref. h).

Indirect measurements not in the ozone-oxygen system

k_3/k_4	T, K	
0.92 ± 0.03	197	Steady photolysis of O_3 in O_3/OCS mixtures. ϕ(CO) and ϕ(CO_2) measured. Values recalculated here.
1.28 ± 0.10	228	
0.86 ± 0.04	273	
0.88 ± 0.02	298	
Average: 0.98		Krezenski, et al., 1971 (ref. i).

Data — Continued

k in cm³ molecule⁻¹ s⁻¹	

k in cm^3 molecule^{-1} s^{-1}

Data evaluations

$k_3 = 2.00 \times 10^{-11}$ $\exp(-2.41 \times 10^3/T)$ for $200 < T < 1000$ Uncertainty: $\log k_3 \pm 0.2$	Data evaluation based on measurements for k_1, k_2, and k_3 and $K_{eq} = k_1/k_2$ Johnston, 1968 (ref. b).
$k_3 = 1.9 \times 10^{-11}$ $\exp(-2.3 \times 10^3/T)$ $220 < T < 1000$ Uncertainty $\log k_3 \pm 0.1$	Data evaluation based on references c, d, l, and m. Davis, Johnston, Schiff, 1972 (ref n).

Preferred Value

(Changed from that in NBS Report 10828 (April 1972).)

$k_3 = 1.9 \times 10^{-11} \exp(-2.3 \times 10^3/T)$ cm^3 molecule^{-1} s^{-1}.
$E^* = 19.1$ kJ mol^{-1} (4.57 kcal mol^{-1}).
Uncertainty $\log k_3 \pm 0.1$.

Remarks

Recent direct measurements of k_3 (d, e, g, l, m) provide data over the range 220–410 K. In this temperature range only rate ratios, k_2/k_3, were available in 1968 when the ozone data were evaluated by Johnston (b). The preferred value, which is the evaluation by Davis et al. (n), takes into account the new measurements. It is based solely on the direct measurements (c, d, l, m). It emphasizes the low temperature work and uses those near 1000 K (c) only to extend the temperature range.

A least squares fit to the data in table I, excluding those from (g), gives the same result. This k_3 passes through the center of the high temperature data (c) and lies between the results in (d, m). The net result of the new evaluation is to lower the activation energy by about 0.9 kJ (0.2 kcal) and reduce the error bounds. These are now $\log k_3 \pm 0.1$ or $k_3 \pm 25$ percent. They define a range about equal to the spread between the data reported in (d) and (m).

A caveat is in order. These error limits may be optimistic since the other low temperature data (e, g, l) are all higher than those from (d) and (m) by factors of 1.5 to 2.5 in k_3. We believe these other studies are less reliable but that the total spread is not surprising since five different methods have been used.

No significance should be attached to the slightly different activation energies reported in various studies. Temperature coefficients are more likely to be affected by systematic errors than are absolute values of rate constants.

The overall situation is that there are now two quite

consistent studies (d, m) of k_3 covering the temperature range 220–410 K and very rough measurements at 1000 K. The latter should be repeated.

Ref. (b)

Evaluation of data available in 1967. Three rate constants k_1, k_2, and k_3 were derived using the following scheme, after it had been justified. In the chart below k (obs) means data points, $k(T)$ a function. $K_{12} = k_1/k_2$, the equilibrium constant.

k_1 (obs) and k_2 (obs) $K_{12}(T) \rightarrow k_1(T)$.
$k_1(T)/K_{12} \rightarrow k_2(T)$.
k_3 (obs) and $k_2(T)/(k_2/k_3)$ (obs) and k_J (obs)$/K_{12}(T) \rightarrow k_3(T)$.

Ref. (c)

These are the only high temperature measurements for k_3. They scatter badly. Undoubtedly higher precision could be obtained today with the same technique.

Ref. (d)

O atoms (produced by decomposition of O_3 on a Nernst glower) reacted with O_3. NO added (to monitor the O-atom concentration). In all experiments $[NO] < [O] \ll [O_3]$. NO also reacts at an appreciable rate with O_3 and decreases during the reaction. The simultaneous differential equations for the system were integrated and k_3 matched to the observed decay of [O]. This analysis is dependent upon the rate coefficients for $O + NO_2 \rightarrow O_2 + NO$ and $O_3 + NO \rightarrow NO_2 + O_2$. The scatter of the data is small, as shown by the range of rates at 298 K $(0.62 - 0.84 \times 10^{-14})$.

Ref. (e) and (f)

Wall effects (decay of O in the absence of O_3) were observed (25 to 50% of overall rate). $[N_2O]$ probably equals 50–100 [O]. No production of NO was found in the pyrolysis of N_2O. This is contrary to the later experience reported in ref. (d). The two studies would agree if $[NO]/[O] \sim 0.4$ here. This would lower k_3. Other heat producing reactions would raise k_3. Schiff (private communication) believes that the uncertainty in [NO] could not be large enough to account for the discrepancy. He also states any likely impurity reactions would have very little effect on the temperature coefficient although they might raise the absolute value of the rate constant.

Ref. (g)

The information in this paper is insufficient to permit a detailed comparison with other work. Only by inferences drawn from other work by the same authors can the method, gas composition, and contact times be guessed at. The reported rates are 2 to 2.5 times faster than those of McCrumb and Kaufman (ref. d).

These data are not used here primarily because an electric discharge was used to produce the O-atoms: there may be other energetic species present. (The objection may not be as valid as it is for some of the older work since, apparently, only a small percentage of O_2 in Ar was passed through the discharge.)
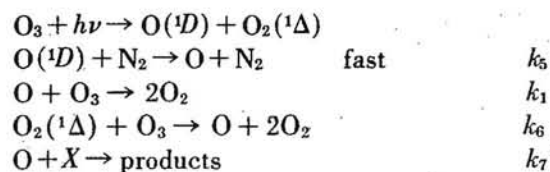
Ref. (h)

Experiments at constant mole fraction of O_3 and constant (NTP) flow rate. Corrections made for reaction being in the intermediate region (both k_1 and k_J important). Because of the constant input conditions and the sharply different percentage conversions at the ends of the temperature range, there could be substantial systematic errors that would affect the results. Authors report k_2/k_3 based on a selected $k_1 = 1.29 \times 10^{-9}$ $\exp(-11.75 \times 10^3/T)$ for $M = O_2$. Expression and points reported here (table II) are calculated $k_J = k_1 k_3/k_2$ using their $k_1(T)$ and k_2/k_3 points. There are insufficient data in these experiments to permit extraction of both k_1 and k_2/k_3. Because k_2/k_3 is a correction term in the analysis, its value is probably less reliable than k_J. The temperature dependence of k_2/k_3 depends strongly on k_1. Using K_{eq} from table III this data set yields log $k_3 = -11.34 - 0.73 (1000/T)$ cm^3 molecule^{-1}s^{-1}.

Ref. (i)

Values for k_3/k_4 recalculated from data in table IV, ref. (h), pooling all data at each temperature and fitting $[\phi(CO) + \phi(CO_2)]^{-1} - 1 = k_3[O_3]/k_4[OCS]$ by least squares. We assign $k_3/k_4 = 0.98$, $197 < T < 298$. (Authors made a different fit, obtaining $k_3/k_4 = 0.98$, 1.05, 0.925, 0.901 at 197, 228, 273, 298 and calculated $k_3/k_4 = 0.64 \exp(+100/T)$.) The available data for reaction (4), measured 298–1100 K are not reliable enough to be extrapolated to lower temperatures. The reported k_3/k_4 should be used to establish k_4, not k_3. See ref. (i) for an analysis, based on the rate of $O + 1$-butene and 3 rate ratios that yields k_3 in agreement with ref. (d).

Ref. (l)

These experiments determine the rate of disappearance of O-atoms after flash photolysis of ozone. They were interpreted using the mechanism

$$O_3 + h\nu \to O(^1D) + O_2(^1\Delta)$$
$$O(^1D) + N_2 \to O + N_2 \quad \text{fast} \quad k_5$$
$$O + O_3 \to 2O_2 \quad k_1$$
$$O_2(^1\Delta) + O_3 \to O + 2O_2 \quad k_6$$
$$O + X \to \text{products} \quad k_7$$

where X is impurities or walls. Corrections were made for $O + O$ and $O + O_2$ combination. Assuming reaction (5) converts all $O(^1D)$ to O, which is reasonable here, $[O] \sim [O_2(^1\Delta)]$ at $t = 0$ and the measured rate constant

is $k_7 + (k_1 - k_6)$. The final value of k_1 depends upon the choice for k_6, here 3×10^{-15} cm^3 molecule^{-1} s^{-1} and, indirectly, upon the absolute value of the absorption coefficient for O-atoms. The undefined path, reaction (7) accounts for more than 50 percent of the O-atom disappearance in 11 of 12 runs. These factors lead us to place little reliance upon the absolute value of k_1. The data are summarized as one point in table I.

Ref. (m)

The rate constant was determined from the time history of [O] determined by atomic resonance fluorescence after flash photolysis of O_3 at 590 nm. This source produces only $O(^3P)$. Variation of total pressure produced no change in k, indicating that combination reactions are unimportant. $[O_2] \sim 0.06 [O_3]$. Precision of 11 percent claimed. The Arrhenius expression quoted in the data section is a weighted least squares fit.

References

(a) D. D. Wagman, et al., NBS Tech. Note 270–3 (1968).

(b) H. S. Johnston, Nat. Stand. Ref. Data Series–NBS 20 (1968).

(c) W. M. Jones and N. Davidson, J. Am. Chem. Soc. **84**, 2868 (1962).

(d) J. L. McCrumb and F. Kaufman, J. Chem. Phys. **57**, 1270 (1972).

(e) O. R. Lundell, R. D. Ketcheson, and H. I. Schiff, Symposium (International) on Combustion **12**, 307 (1969).

(f) H. I. Schiff, Ann. Geophys. **28**, 67 (1972), quoting unpublished work of Lundell, Ketcheson, and Schiff. A slightly different preliminary value was quoted in Can. J. Chem. **47**, 1903 (1969).

(g) V. P. Balakhnin and V. I. Egorov, Kinetika y Kataliz **13**, 282 (1972). Kinetics and Catalysis **13**, 255 (1972).

(h) E. I. Intezarova and V. I. Kondratiev, Bull. Acad. Sci. USSR, Div. Chem. Sci., p. 2326 (1967). (English translation of Izvest. Akad. Nauk SSSR, Ser. Khim., p. 2440 (1967)).

(i) D. C. Krezenski, R. Simonaitis, and J. Heicklen, Int. J. Chem. Kinetics **3**, 467 (1971).

(j) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2d edition, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) 37 (June 1971).

(k) E. S. Castellano and H. J. Schumacher, Z. Phys. Chem. N. F. **34**, 198 (1962).

(l) D. Husain, L. J. Kirsch, and R. J. Donovan, J. Photochem. **1**, 69 (1972/73).

(m) D. D. Davis, W. Wong, and Lephardt, private communication, January, 1973.

(n) D. D. Davis, H. S. Johnston, and H. I. Schiff in The Natural Stratosphere, E. Reiter, editor (preliminary draft, Climatic Impact Assessment Program Monograph 1, November, 1972).

TABLE I. Observed values of k_3, cm³ molecule⁻¹ s⁻¹. This table incorporates table 25, ref. (b), and the later measurements in refs. (d), (e), (g), (l) and (m).

T/K	$1000/T$	M	$\log k_3$	Ref.	T/K	$1000/T$	M	$\log k_3$	Ref.
769	1.300	Ar	−11.98	(c)	330	3.030		−13.812	(d)
812	1.230		−12.19		338	2.956		−13.708	
827	1.209		−11.89		347	2.882		−13.728	
840	1.190		−12.16		359	2.786		−13.578	
846	1.181		−11.85		363	2.755		−13.587	
876	1.140		−11.62						
910	1.098		−11.74		378	2.646		−13.462	
					384	2.604		−13.446	
788	1.269	N₂	−11.90	(c)	388	2.577		−13.424	
831	1.202		−11.80		409	2.445		−13.315	
837	1.193		−11.87						
863	1.158		−11.82		296.4	3.374		−13.836	(e)
298	3.356	Ar	−14.102	(d)	292	3.424	Ar?	−13.80	(g)
298	3.356		−14.114		311	3.215		−13.63	
298	3.356		−14.114		316	3.165		−13.56	
298	3.356		−14.076		334	2.994		−13.46	
298	3.356		−14.137		370	2.703		−13.19	
298	3.356		−14.119		∼300	3.33	N₂	−13.89	(l)
298	3.356		−14.149						
298	3.356		−14.125		220	4.545	He	−15.222	(m)
298	3.356		−14.108		240	4.167		−14.780	
298	3.356		−14.180		266	3.759		−14.439	
					298	3.356		−13.979	
298	3.356		−14.167		298	3.356		−13.987	
298	3.356		−14.208		298	3.356		−13.947	
269	3.717		−14.539		353	2.833		−13.544	
273	3.663		−14.457		353	2.833		−13.527	
314	3.185		−13.941						

$\log k_3 = (-10.712 \pm 0.05) - (1.007 \pm 0.017)$ $(1000/T)$. Uncertainty: 1 σ. Residual standard deviation: 0.11.

$E^* = 18.8$ kJ mol⁻¹ (4.50 kcal mol⁻¹). Data from ref. (g) were not used in deriving $\log k_3$ above.

TABLE II. Observed values of the Jahn rate constant, $k_1 k_3 / k_2$. This table supplements, but does not incorporate, table 22, ref (b). $\log k_3$ was calculated using the equilibrium data in table III (2 constant equation).

T^*	$1000/T$	$\log k_J^{**}$	$\log k_3$(calc)	Ref.	T^*	$1000/T$	$\log k_J^{**}$	$\log k_3$(calc)	Ref.
498	2.005	1.885	−12.809	(h)	446	2.240	0.437	−12.983	
498	2.010	1.833	−12.833	M = O₂					
485	2.060	1.611	−12.784		435	2.300	0.061	−13.033	
484	2.065	1.590	−12.779		435	2.300	0.083	−13.011	
472	2.120	1.175	−12.895		429	2.330	−0.104	−13.036	
					429	2.330	−0.092	−13.024	
472	2.120	1.195	−12.875		427	2.340	−0.093	−12.971	
472	2.120	1.161	−12.909						
467	2.140	1.041	−12.921		426	2.350	−0.144	−12.967	
464	2.155	0.945	−12.936		425	2.355	−0.260	−13.056	
458	2.185	0.794	−12.924		417	2.400	−0.547	−13.099	
					417	2.400	−0.535	−13.087	
458	2.185	0.852	−12.866		410	2.440	−0.889	−13.244	
458	2.185	0.768	−12.950						
446	2.240	0.381	−13.039		409	2.445	−0.879	−13.127	
446	2.240	0.423	−12.997		409	2.445	−0.741	−13.049	

*Calculated from $1000/T$, rounded to nearest degree.

**See note on reference (h) for method of calculation.
$\log k_{Jahn} = (14.23 \pm 0.15) - (6.151 \pm 0.065)(1000/T)$ for k_{Jahn} in s⁻¹.
Uncertainty: 1 σ. Residual standard deviation 0.045.

TABLE III. Equilibrium constant, K_1 for the reaction $O_3 = O_2 + O$ (molecules cm^{-3}) based on log K_1 from the JANAF Tables (ref. j) with additional points calculated at 188 and 250 K. This replaces table 16 (ref. b) in which the points at 400 and 500 K are incorrect. The two functions, log $K_{12}(T)$ have been recalculated, and are improved fits to the tabulated values.

T	$1000/T$	log K_{12}
188	5.319	-3.271
200	5.000	-1.548
250	4.000	3.866
300	3.333	7.485
400	2.500	12.018
500	2.000	14.738
600	1.667	16.546
700	1.429	17.831
800	1.250	18.789
900	1.111	19.528
1000	1.000	20.117

log $K_{12} = 25.565 - 5.422$ $(1000/T)$. Residual standard deviation: 0.014. Range of deviations $+0.017$ (600 K) to -0.026 (1000 K).

log $K_{12} = 25.982 - 5.444$ $(1000/T) - 0.136$ log T. Residual standard deviation: 0.013. Range of deviations $+0.0124$ (188K) to -0.0153 (at 250 K).

log $K_{12} \equiv$ log $K_p -$ log $RT +$ log N_A, where K_p is the thermodynamic equilibrium constant in atmospheres, $N_A = 6.02 \times 10^{23}$ molecules mol^{-1} and $R = 82.05$ cm^3 atm mol^{-1} K^{-1}.

4.25. Collisional Quenching of O_2 $(a\ ^1\Delta g)$

$$O_2\ (a\ ^1\Delta g) + M \rightarrow O_2(X\ ^3\Sigma_g^-) + M \qquad\qquad k_1$$
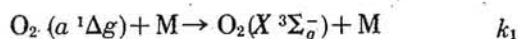
Auxiliary Data

$$\Delta H^\circ_{298} = -94\ kJ/mol\ (-22.5\ kcal/mol \qquad\qquad (a)$$

Data

Units of k_1 are cm^3 molecule^{-1} s^{-1}; all data at 300 K except in (f)

$k_1(M = O_2)$	System
$2.4 \pm 0.2 \times 10^{-18}$	$O_2(^1\Delta)$ produced by electric discharge in O_2 and detected by photoionization with argon resonance lamp. Flow system. Clark, Wayne, 1969 (b).
$2.04 \pm 0.23 \times 10^{-18}$	$O_2(^1\Delta)$ produced by electric discharge in O_2 and detected by emission at 1.27 μm. Flow system. Steer, et al., 1969 (c).
$1.7 \pm 0.1 \times 10^{-18}$	$O_2(^1\Delta)$ produced by electric discharge in O_2. Static system. Measured exponential time decay of 1.27 μm emission. Becker, et al., 1971 (d).

Data—Continued

Units of k_1 are cm^3 molecule^{-1} s^{-1}; all data at 300 K except in (f)

$k_1(M = O_2)$	System
$2.17 \pm 0.12 \times 10^{-18}$	$O_2(^1\Delta)$ produced by benzene photosensitization. Static system. Measured exponential time decay of 1.27 μm emission. Findlay, et al., 1969 (e).
$2.22 \times (T/300)^{0.78} \times 10^{-18}$ (285 – 322 K)	Same conditions as (e). Findlay, Snelling, 1971 (f).

$k_1(M = N_2)$	References
$\leqslant 1.1 \times 10^{-19}$	Clark, Wayne, 1969 (b).
$\leqslant 1.4 \times 10^{-19}$	Steer, et al., 1969 (c).
$\leqslant 1 \times 10^{-20}$	Becker, et al., 1971 (d).
$\leqslant 3 \times 10^{-21}$	Findlay, et al., 1971 (e).

Preferred Value

k_1 (M = O_2) = 2.2 ± 0.5 × $(T/300)^{0.8}$ × 10^{-18} cm^3 molecule^{-1} s^{-1}, over temperature range 285–322K.

Estimated uncertainty in k: ±25 percent throughout this temp. range.

Although the temperature dependence has not been determined over a large temperature range, because this dependence is very small the above expression can probably be safely extrapolated to stratospheric temperatures.

k_1 (M = N_2) ≤ 2 × 10^{-20} cm^3 molecule^{-1}s^{-1} at 300 K.

Remarks

For M = O_2, all the recent room temperature measurements (b), (c), (d), (e), (f), are in good agreement. A simple average is given as the preferred rate at 300 K and the temperature dependence in (f) is accepted. Preliminary data given in (g) were not used nor were the earlier discordant data of (h).

For M = N_2 values from 10^{-19} to 10^{-21} are reported. Only an upper limit is given here. Data in support of the lower value in (d) are not given in sufficient detail to permit reevaluation, and the very low value in (e) can not be substantiated by the data.

References

(a) G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand, Princeton, N.J., 1950.

(b) I. D. Clark and R. P. Wayne, Proc. Roy. Soc. (London) A314, 111 (1969).

(c) R. P. Steer, R. A. Ackerman, and J. N. Pitts, Jr., J. Chem. Phys. 51, 843 (1969).

(d) K. H. Becker, W. Groth, and U. Schurath, Chem. Phys. Letters 8, 259 (1971).

(e) F. D. Findlay, C. J. Fortin, and D. R. Snelling, Chem. Phys. Letters 3, 204 (1969).

(f) F. D. Findlay and D. R. Snelling, J. Chem. Phys. 55, 545 (1971).

(g) I. D. Clark and R. P. Wayne, Chem. Phys. Letters 3, 93 (1969). Superseded by (b).

(h) A. M. Winer and K. D. Bayes, J. Phys. Chem. 70, 302 (1966).

J. T. Herron, R. E. Huie
March 1972

4.26. Collisional Quenching of O_2 $(^1\Sigma_g^+)$

O_2 $(b^1\Sigma_g^+)$ + M → O_2 $(^3\Sigma_g^-)$ + M k_1
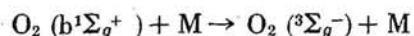
Auxiliary Data

$\Delta H°_{298}$ = −157 kJ mol^{-1} (−37.5 kcal mol^{-1})   (a)

Data

Units of k are cm^3 molecule^{-1}s^{-1}; all data at 300 K; $(O_2(^1\Sigma))$ determined from intensity of 762 nm emission ($b^1\Sigma-X^3\Sigma$)

k_1(M = O_2)	Conditions
1.5 ± 0.5 × 10^{-16}	$O_2(^1\Sigma)$ produced by vacuum uv photolysis of O_2 to give $O(^1D)$, then $O(^1D)$ + O_2 → $O(^3P)$ + $O_2(^1\Sigma)$. Steady state $(O_2(^1\Sigma))$ measured. Noxon, 1970 (b).
4.5 × 10^{-16}	Flash photolysis of O_2 in vacuum uv. Followed decay of $(O_2(^1\Sigma))$. Filseth, et al., 1970 (d).
~ 1 × 10^{-15}	Flow system. $O_2(^1\Sigma)$ produced by microwave discharge in O_2. Measured relaxation rate of $(O_2(^1\Sigma))$. O'Brien, Myers, 1970 (e).

Data—Continued

Units of k are cm^3 molecule^{-1} s^{-1}; all data at 300 K; $(O_2(^1\Sigma)$ determined from intensity of 762 nm emission ($b^1\Sigma - X^3\Sigma$)

k_1 (M = N_2)	Conditions
2.0 ± 0.5 × 10^{-15}	Noxon, 1970 (b).
1.8 × 10^{-15}	Filseth, et al., 1970 (d).
3 ± 1 × 10^{-15}	O'Brien, Myers, 1970 (e).
k_1 (N_2)/k_1 (O_2) = 1.5	Stopped flow reactor. Microwave discharge in O_2. Steady state (O_2 ($^1\Sigma$)) measured. Relative values of k_M converted to absolute values by adopting value of k (M=O_2) in (b). Becker, et al., 1971 (g).
k_1 (M = H_2O)	
3.3 × 10^{-12}	Filseth, et al., 1970 (d).
4 ± 0.6 × 10^{-12}	O'Brien, Myers, 1970 (e).
5.5 × 10^{-12}	Same conditions as (d). Stuhl, Niki, 1970 (f).
k_1(H_2O)/k_1(O_2) = 3.3 ± 0.7 × 10^4	Becker, et al., 1971 (g).

| M	k_M	Estimated uncertainty
O_2	1.5×10^{-16} cm³ molecule⁻¹ s⁻¹	± 33%
N_2	2.0×10^{-15}	± 25%
H_2O	4×10^{-12}	± 50%

Remarks

The values in (b) are adopted for M=N_2 and O_2. The value for H_2O is based on (d) and (f). The preferred values are supported by both the photolysis and flow type experiments. A possible source of uncertainty in the value of k_1 (M=O_2) is the observed pressure effect on the quenching rate (d). Filseth, et al. (d) recommend the value

4.5×10^{-16} for k (M=O_2). However stopped flow experiments (g give the relative rate ratio for O_2 and N_2 the same as in (b). Earlie literature is discussed in (b) and (d).

References

(a) G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand and Co., Princeton, N.J., 1950.
(b) J. F. Noxon, J. Chem. Phys., **52**, 1852 (1970).
(c) F. Stuhl and K. H. Welge, Can. J. Chem., **47**, 1870 (1969).
(d) S. V. Filseth, A. Zia, and K. H. Welge, J. Chem. Phys., **52**, 5502 (1970).
(e) R. J. O'Brien, Jr., and G. H. Myers, J. Chem. Phys., **53**, 3832 (1970).
(f) F. Stuhl and H. Niki, Chem. Phys. Letters, **7**, 473 (1970).
(g) K. H. Becker, W. Groth, and U. Schurath, Chem. Phys. Letters, **8**, 259 (1971).

J. T. Herron, R. E. Huie
December 1971

4.27. Photolysis of Ozone in Red Light ($\lambda \sim 600$ nm)

$$O_3 + h\nu \rightarrow O(^3P) + O_2(X\,^3\Sigma_g^-), \qquad k_1.$$
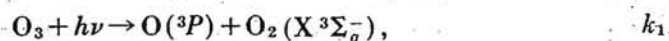
which is followed by the reactions

$$O + O_2 + M \rightarrow O_3 + M, \qquad k_2$$

$$O + O_3 \rightarrow O_2 + O_2. \qquad k_3$$

Auxiliary Data

$$\Delta H_0^\circ(1) = -\Delta H_0^\circ(2) = +101.4 \text{ kJ/mol} \ (=24.24 \text{ kcal/mol})$$
(a)

Thermodynamic threshold: $\lambda = 1180$ nm.

$$\Delta H_0^\circ(3) = -392.1 \text{ kJ/mol} \ (=-93.72 \text{ kcal/mol})$$
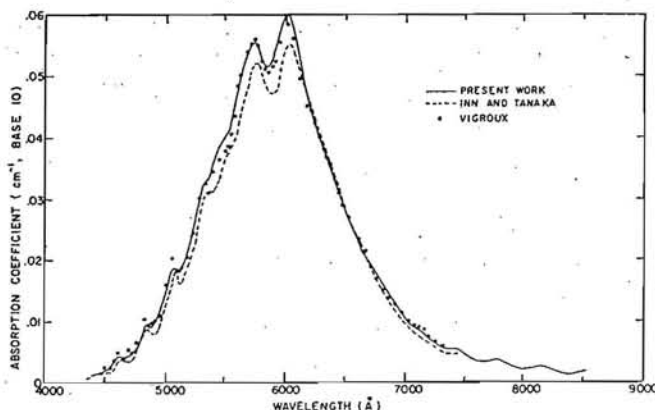
Absorption Spectrum 440–850 nm. (figure 1).

FIGURE 1. Absorption coefficient of ozone, 440–850 nm (Chappuis bands). Absorption coefficient in units of cm⁻¹ (atm at 273 K)⁻¹ base 10, i.e. $k = (1/p \cdot l) \log_{10} (I_0/I)$. (Figure 4 from M. Griggs, J. Chem. Phys. **49**, 857 (1968) with consent of the author.)

Hearn (e) measured the absorption coefficient at the Hg line, $\lambda = 576.95$ nm, to be 0.0555 ± 0.0010. This agrees well with the solid trace in figure 1.

Data

Quantum Yield (overall) maximum: 2.0	$570 < \lambda < 630$ nm, steady photolysis at 5, 18, and 25 °C. $25 < P(O_3) < 200$ torr. $1 < P(O_2) < 250$ torr. With and without added He, Ar, N_2, CO_2 Δ press. vs. Δt measured.
	Castellano, Schumacher, 1962 (b).
Presence of excited ground state O_2	$\lambda = 595$ nm, flash photolysis [O_2^*] vs. time meas.
	Ellis, McGarvey, McGrath, 1971 (c).

Recommendation

Primary quantum yield, reaction (1) = 1.0, for 580 $< \lambda < 620$ nm. It probably is the same throughout the Chappuis band. Mechanism as given in the first section, above.

Expression for quantum yield (steady state in [O]), from (b) is

$$Q.Y. = 2/(1 + (k_2[O_2]/k_3[O_3])[M]),$$

where

$$[M] = [O_3] + \alpha_{O_2}[O_2] + \alpha_X[X],$$

in which α_X is the efficiency of molecule X relative to $\alpha_{O_3} = 1$ in reaction (2).

For O_2, N_2, CO_2, He, Ar, α = 0.44, 0.39, 0.96, 0.34, 0.25 at 291 K. $\log_{10}[(k_2/k_3)/\text{cm}^3 \text{ molecule}^{-1}] = (23.64 \pm 0.25) + 1.506 (1000/T)$ for $200 < T < 1000$ K (from ref. (f)).

Comments

Steady laboratory photolysis in the Chappuis bands is explainable on basis of the mechanism in the first sec-

tion and q.y. expression in "Recommendation" above. The observed quantum yield is well fit by the expression for $0.01 < [O_2]/[O_3] < 40$. Extrapolation to higher ratios is expected to be good.

Although vibrationally excited ground state O_2 has been observed, (c), with sufficient energy to decompose O_3, no effect has been found in the photolysis. Presumably energy transfer is inefficient.

Although the process: $O_3 + h\nu \rightarrow O_2 (^1\Delta) + O(^3P)$ has a thermodynamic threshold of $\lambda = 611.0$ nm, no effect on the q.y. from the reaction of $O_2(^1\Delta)$ with O_3 has been observed. (In contrast, such an effect is postulated in the uv photolysis.) For this reason the primary process is given as in the first section above. If $O_2(^1\Delta)$ were demonstrated to be a primary product from absorption in the Chappuis bands, the uv photolysis mechanisms would have to be reconsidered.

Ref. (b)

Absolute quantum yields determined by a difference method for many points in each run for up to 25 percent conversion. This means that the $[O_2]/[O_3]$ ratio varies sharply in each run. Data fit to the mechanism in

"Recommendation" (above) to obtain k_3/k_2. The mechanism reproduces the observed Φ's to better than ± 0.1. The effect of O_2 is to decrease the quantum yield, via reaction (2). Limit at high $[O_2]/[O_3]$: Φ tends to zero. Earlier studies showing higher q.y. discussed and refuted.

Ref. (c)

Presence of $O_2(X^3\Sigma_g^-, v > 0)$ demonstrated with a vibrational distribution similar to that observed in uv photolysis, both during photolysis and as a slow process afterwards. Due to reaction (3).

References

(a) D. D. Wagman, et al., Nat. Bur. Stand. Tech. Note 270-3 (1968).
(b) E. Castellano and H. J. Schumacher, J. Chem. Phys. **36**, 2238 (1962); Z. fur phys. Chem. N.F. **34**, 198 (1962).
(c) D. M. Ellis, J. J. McGarvey, and W. D. McGrath, Nature Physical Science **229**, 153 (1971).
(d) M. Griggs, J. Chem. Phys. **49**, 857 (1968).
(e) A. G. Hearn, Proc. Phys. Soc. **78**, 932 (1961).
(f) H. S. Johnston, Nat. Stand. Ref. Data Series-Nat. Bur. Stand. No. 20 (1968) Table 17 (essentially quoting ref. b), and Table 28.

David Garvin
March 1972

4.28. Ultraviolet Photolysis of O_3: Quantum Yields

Photolysis reactions of ozone pertinent to laboratory studies, $\lambda \leqq 334$ nm, with their enthalpies of reaction

	$\Delta H^\circ_{(298)}$ (a, b)		
	kJ mol^{-1}	(kcal mol^{-1})	
$O_3 + h\nu \rightarrow O(^1D) + O_2(X^3\Sigma_g^-)$	296.6	(70.9)	1a
$O(^1D) + O_2(^1\Delta)$	390.4	(93.3)	1b
$O(^1D) + O_2(^1\Sigma_g^+)$	453.1	(108.3)	1c
$O(^3P) + O_2(X^3\Sigma_g^-)$	106.3	(25.4)	1d
$O(^3P) + O_2(^1\Delta)$	200.8	(48.0)	1e
$O(^3P) + O_2(^1\Sigma_g^+)$	263.6	(63.0)	1f

Secondary reactions considered in laboratory studies of ozone photolysis

$O_2(^1\Delta) + O_3 \rightarrow O(^3P) + 2O_2$	12.6	(3.0)	2a
$O_2(^1\Delta) + M \rightarrow O_2 + M$	-94.3	(-22.5)	2b
$O(^1D) + O_3 \rightarrow O_2^* + O_2$	-581.6	(-139.0)	3a
$\rightarrow 2O(^3P) + O_2$	-83.3	(-19.9)	3b
$O_2^* + O_3 \rightarrow O(^3P) + 2O_2$	106.3	(25.4)	4a
$\rightarrow O(^1D) + 2O_2$	296.2	(70.8)	4b
$O(^1D) + M \rightarrow O(^3P) + M$	-189.8	(-45.4)	5
$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	-32.8	(-7.8)	6a
$\rightarrow O(^3P) + O_2$	-189.8	(-45.4)	6b
$O_2(^1\Sigma_g^+) + O_3 \rightarrow O(^3P) + 2O_2$	-50.2	(-12.0)	7a
$O_2(^1\Sigma_g^+) + M \rightarrow O_2 + M$	-156.9	(-37.5)	7b
$O(^3P) + O_3 \rightarrow O_2^{**} + O_2$	-391.6	(-93.6)	8
$O(^3P) + O_2 + M \rightarrow O_3 + M$	-106.3	(-25.4)	9

Notes: Enthalpies for reactions 3a, 4a, and 8 are calculated using $\Delta H_f = 0$ for O_2^* and O_2^{**}. When an electronic state designation is not shown, the ground state is implied.

Auxiliary Data

Threshold wavelengths, at 0 K for reactions 1a–f, in nm (c)

O_2:	$X^3\Sigma_g^-$	$^1\Delta_g$	$^1\Sigma_g^+$
O: ^3P	1180	611	463
^1D	411	310	266

Enthalpies of formation of species (a, b)

	ΔH°_0		ΔH°_{298}	
	kJ mol^{-1}	(kcal mol^{-1})	kJ mol^{-1}	(kcal mol^{-1})
$O_2: X^3\Sigma_g^-$	0.0	(0.0)	0.0	(0.0)
$^1\Delta$	94.30	(22.54)	94.30	(22.54)
$^1\Sigma_g^+$	156.9	(37.51)	156.9	(37.51)
O : ^3P	246.8	(58.98)	249.2	(59.55)
^1D	436.5	(104.34)	438.94	(104.91)

Absorption Spectra and Coefficients
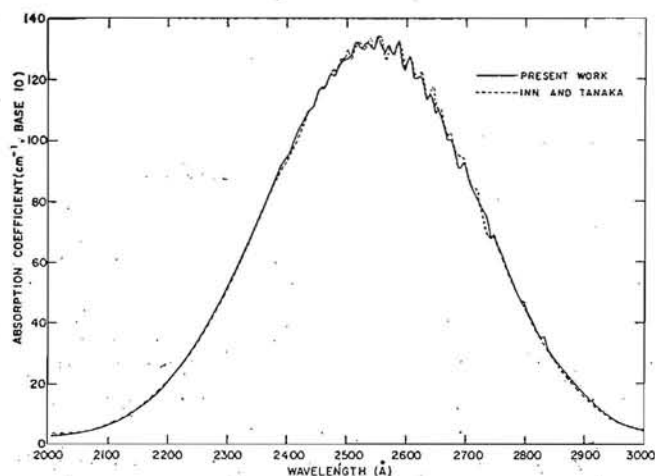

FIGURE 1. Absorption coefficient of ozone, 200–300 nm (Hartley band). k in cm^{-1} (atm at 273 K)$^{-1}$ base 10. (Figure 2 from M. Griggs, J. Chem. Phys. **49**, 857 (1968), reprinted with consent of the author.)

FIGURE 2. Absorption coefficient of ozone, 300–360 nm (Huggins band), k in cm^{-1} (atm at 273 K)$^{-1}$ base 10. (Figure 3 from M. Griggs, J. Chem. Phys. **49**, 857 (1968), reprinted with consent of the author.)

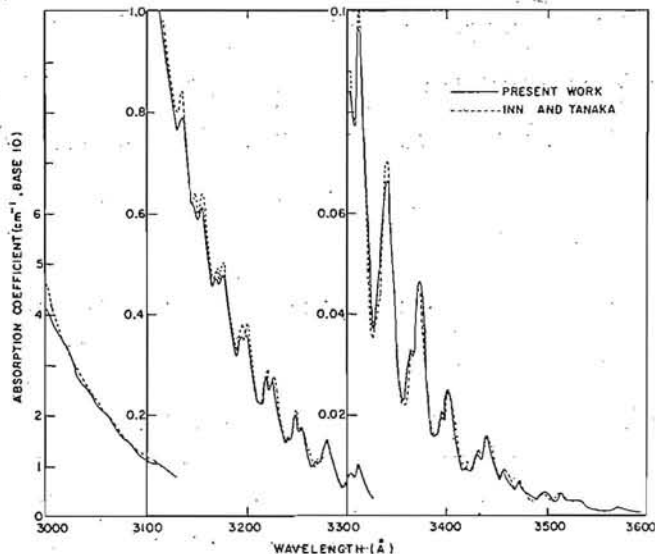Absorption Coefficients at Hg lines (d)

λ (nm)	Absorption coefficient cm^{-1} (atm at 273)$^{-1}$ base 10
253.65	133.9 ± 1.9
289.36	17.2 ± 0.3
296.73	6.969 ± 0.030
302.15	3.340 ± 0.014
334.15	0.0498 ± 0.0007

These values measured by Hearn agree well with the traces marked "Inn and Tanaka" in figures 1 and 2.

Photochemical Data

Spectroscopic Evidence for Photolytic Formation of $O(^1D)$, $\lambda < 300$ nm.

Time rate of decay of $O(^1D)$ emission immediately following flash photolysis (f). Quenching of emission by N_2 in flash (f) and steady photolysis (e), due to reaction (5). Appearance and growth of emission from $O_2(^1\Sigma_g^+)$ with addition of O_2 to systems (e, f), due to reaction 6a.

$\phi(O(^1D)) \sim 1$	$\lambda = 254$ nm steady.
	Gauthier, Snelling, 1971 (e).
$\phi(O(^1D))/\phi(O_2(^1\Sigma_g^+))$ $\geqslant 20$	$\lambda = 254$ nm flash.
	Gilpin, Schiff, Welge, 1971 (f).

Chemical Evidence on Photolytic Formation of $O(^1D)$ *as a Function of Wavelength*

Liquid phase steady photolysis of O_3 in Ar, at 87 K (g), and in N_2, at 95 K (h). Measurement of quantum yields for ozone disappearance, atom exchange (total atom production) and N_2O formation. These show sharp drops in $\Phi(O_3)$ and $\Phi(N_2O)$ at $\lambda > 300$ nm, but no change in Φ (exchange). Higher Φ's for $\lambda < 300$ nm are attributed to $O(^1D)$, assuming that excited molecules are quenched by the solvent and that $O(^3P) + O_3 \rightarrow 2O_2$ does not occur at these temperatures. See also section on total gas phase quantum yields.

$\Phi(O_3) = 0.5$	Liq. Ar, $\lambda = 313$, high $[O_3]$ limit.
$\Phi(O_3) = 2.0$ $\phi(O(^1D)) = 0.25$ at $\lambda = 313$ nm. $\phi(O(^1D), \lambda = 254)/\phi(\lambda = 313) = 3.7$ Φ (exchange) $= 0.70-0.97$	Liq. Ar, $\lambda = 254$, high $[O_3]$ limit. Liq. Ar, $\lambda = 297-334$ nm.
	DeMore, Raper, 1966 (g).
$\Phi(N_2O)$ $= 0.013-0.016$, $\lambda \leqslant 300$ nm $= 0.0035-0.007$, $\lambda = 302-334$ nm Φ (exchange) $= 0.64-0.78$, $\lambda = 300$ nm	Liq. N_2, $\lambda = 248-334$ nm. DeMore, Raper, 1962 (h).
$\phi(O(^1D)) \sim 1$, $\lambda < 300$ nm $\phi(O(^1D)) \sim 0.4$, $\lambda > 300$ nm	Evaluation of data in refs. (g, h), and those in aq. soln. (i). DeMore, Raper, 1966 (g).

Spectroscopic Evidence for the Photolytic formation of $O_2(^1\Delta)$

Steady photolysis of O_3, $\lambda = 254$ nm, and measurement of the emission from $O_2(^1\Delta)$, $\lambda = 1270$ nm. Two studies (e, j) show the emission to be proportional to $[O_3]$. It is independent of added O_2 and N_2 (e). This indicates that $O(^1D)$ is not a precursor, as for example in reac-

tions (3) and (6). The studies suggest that $\phi(O_2^1\Delta)$ is close to unity. For other evidence of the presence of $O_2(^1\Delta)$ in ozone photolysis see (hh, ii).

Total Quantum Yields, Gas Phase Photolysis of O_3 at high O_3/O_2 Ratios

Absolute quantum yields for ozone decomposition in steady photolysis experiments, at various wavelengths, measured as a function of $[O_3]$. Two distinct sets of experiments, show sharply different results. In one (k, l, ff), $\Phi(O_3) = 6$, $\lambda < 310$ nm independent of $[O_3]$ and $\phi = 4$, $\lambda = 334$ nm. In the other (c, m, n), Φ is ~ 4 at low $[O_3]$ and increases with $[O_3]$ for $\lambda < 300$ nm. This increase in Φ is proportional to the surface/volume ratio of the photolysis cell. In both sets added N_2 and O_2 reduced the quantum yield in a manner consistent with other experiments, $\lambda < 310$ nm. However N_2 had no effect at $\lambda = 334$ nm (ff). Both sets used filtered Hg light sources, and similar actinometry.

$\Phi(O_3)$	System
6	Steady photolysis, $\lambda = 254$ nm. $10 < [O_3] < 100$ torr.
	Ellenrieder, Castellano, Schumacher, 1971 (k).
6 (initial value)	Steady photolysis, $\lambda = 308 \pm 24$ nm. $15 < [O_3] < 300$ torr.
	Castellano, Schumacher, 1969 (l).
$\sim 4 + a[O_3]$ $a(297) \sim a(254)$ $a(313)/a(297) \sim 0.1$	Steady photolysis, $\lambda = 248$, 254, 289/292, 297/302, 313, 334 nm. $10 < [O_3] < 50$ torr.
	Jones, Wayne, 1970 (c).
$\sim 4 + a[O_3]$	Steady photolysis, $\lambda = 254$ nm. $2 < [O_3] < 50$ torr.
	Norrish, Wayne, 1965 (m).
~ 4	Steady photolysis, $\lambda = 254$ nm, flow system. $5 \times 10^{-2} < [O_3] < 2$ torr.
	Jones, Kaczmar, Wayne, 1970 (n).
4 (initial value)	Steady photolysis, $\lambda = 334$ nm. $50 < P(O_3) < 300$ torr, $P(O_2)$, $P(N_2)$ to 500 torr. Δ Press/Δt meas.
	Castellano, Schumacher, 1972 (ff).
4.7	Deduced from "intermediate" q.y. $\lambda = 254$ nm and study of $O(^1D)$ reactions. $[O_3] < 10^{-6}$ mol dm^{-3}.
	Giachardi, Wayne, 1972 (gg).

Effect of Non-Reactive Gases on the Photolysis of O_3

Inert gases have several effects. First they reduce the total quantum yield. $\Delta\Phi(O_3) \sim 2$ for high enough pressures (k, l, o, p, s). The efficiency varies considerably with the identity of the added gas (l, p, q). This effect,

due to reaction with $O(^1D)$, has been observed only below $\lambda = 310$ nm. At the same time they quench emission from $O(^1D)$ (e, f). This effect is attributed to reaction (5). The reactions with N_2 and CO_2 are the most effective. In flash photolysis experiments added N_2 changes markedly the concentration-time pattern immediately after the flash (q). In the gas phase only traces of N_2O are formed (m). Rate ratios, k_5/k_3, are reported in references (e, k, l, r).

Second, they reduce the quantum yield via the three body reaction (9). This effect is the same, quantitatively, as in the photolysis of O_3 in red light (l, t).

Third they quench $O_2(^1\Delta)$, reaction (2b), and $O_2(^1\Sigma_g^+)$, reaction (7b). These are slow reactions that are relatively unimportant in the steady state photolysis of high concentration ozone and which occur at long times after flash photolysis.

Effect of Added O_2 on the Photolysis of O_3

Molecular oxygen has two important effects. First it quenches emission from $O(^1D)$ and, at the same time, produces emission from $O_2(^1\Sigma_g^+)$ (e, f). This is due to reaction (6a). Because (7b) is slow, this changes the concentration-time pattern after flash photolysis (q) without affecting the quantum yield (reaction (6a) followed by (7a)). Rate ratios, k_6/k_3, are reported in references (e, f, k, l).

Second, it reduces the quantum yield principally by reformation of O_3 in reaction (9), but also via quenching of $O(^1D)$, reaction (6b) (k, l, m).

Vibrationally Excited Molecular Oxygen

Absorption from ground state molecular oxygen in vibrational levels up to $v = 30$ has been observed following flash photolysis of ozone. (o, s, u, v, x, y). Attributed to products of reactions (3) and (8). In one study (y) using a monochromatic flash source at $\lambda = 595$ nm, excited ground state O_2 was observed. At this wavelength only reaction (8) can occur. To date, there is no clear, quantitative evidence that these excited molecules affect the quantum yield for O_3 photolysis.

Effect of Reactive Molecules-Impurities

The principal impurities expected in high concentration O_3 are H_2O, N_2O_5, CO_2, and hydrocarbons. These either are present in the O_2 from which the O_3 is made or are produced in the electric discharge of the ozonizer. They may be concentrated along with the O_3.

Photolysis of O_3 in the presence of H_2 and H_2O and other hydrogen containing molecules shows formation of OH and a Φ indicating a chain reaction (c, z, aa, bb). An increased Φ also occurs with CO_2 (cc). Nitrogen dioxide (rapidly converted to N_2O_5) is reported (m) to have only a small effect on the photolytic yields in high concentration O_3 but at the same time introduces an important "dark reaction." This is undoubtedly the N_2O_5 catalyzed decomposition of O_3 (dd).

Preferred Values

Quantum yields for primary processes.
These are arbitrary, rounded values.

$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$	(1b)
$250 < \lambda < 310$ nm $\phi = 1$	
$310 < \lambda$ $\phi = 0$	
$O_3 + h\nu \rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	(1a)
$\lambda < 350$ nm $\phi = 0$	
$O_3 + h\nu \rightarrow O(^3P) + O_2(^1\Delta)$ or $O_2(^1\Sigma_g^+)$	(1e, 1
$\lambda < 310$ nm $\phi = 0$	
$310 < \lambda < 350$ nm $\phi \sim 1$	
$O_3 + h\nu \rightarrow O$ (total) $+ O_2$	
$250 < \lambda < 350$ nm $\phi = 1$	
Other processes (1c, 1d) $\phi = 0$	

Remarks

Only the quantum yield is assessed here. uv photolysis of O_3 is complex. It provides information on and is explained in terms of an extensive mechanism of secondary reactions. See reference (ee) for a recent review.

The preferred quantum yields are quite arbitrary. They are step functions (although there must be some wavelength region in which there is a gradual transition) because the data cannot support anything else. More studies of ϕ as a function of λ 290–330 nm are badly needed.

Photolysis Below 310 nm

The photolytic products at $\lambda = 254$ nm are $O(^1D)$ and $O_2(^1\Delta)$. There is no evidence for $O_2(^1\Sigma_g^+)$ as a primary product, although the threshold for reaction (1c) is at $\lambda = 266$ nm.

Schumacher's experiments (k, l) show the same total quantum yield at $\lambda = 254$, ~ 313 nm. DeMore's (h, g) show a change in quantum yield at $\lambda = 300$ nm. Wayne's show a change between $\lambda = 297/302$ and 313 nm, as evidenced by the decreased "chain reaction" contribution. (c).

These are combined to indicate that reaction (1b) is effective at all λ shorter than its threshold.

This choice for the q.y. of (1b) has two assumptions behind it: (1) that the break in q.y. in DeMore's experiments at $\lambda = 300$ nm (as opposed to $\lambda = 310$ nm) is due to solvent effects, and (2) that wavelengths above $\lambda = 305$ nm (particularly $\lambda = 313$ nm) are effective in Schumacher's even though the absorption coefficient is changing rapidly. If either of these assumptions is incorrect, ϕ for reaction (1b) will start to drop at about $\lambda = 300$ nm.

There is no evidence concerning ϕ for $\lambda < 248$ nm. Presumably it remains unity throughout the rest of the Hartley bands.

Photolysis Above 310 nm

Two processes are assumed to occur (1a) and either (1e) or possibly (1f) subject to these constraints:

(1) The total atom production is the same above and below $\lambda = 310$ nm. This means that quenching of O_3^* is unimportant.

(2) A quantum yield of 3–4 has been observed at $\lambda = 313, 334$ nm (c). This means that one product of photolysis must be excited. It may be either O or O_2.

DeMore's estimate (g) for $\phi(^1D)$ is an upper bound. This quantum yield decreases slowly with increasing λ (above 310 nm). The recent gas phase measurements at $\lambda = 334$ nm (ff) show no effect of N_2 on Φ. This indicates that $O(^1D)$ is absent. Therefore the preferred value for $O(^1D)$ production is given as 0 for $\lambda > 310$ nm.

Total Quantum Yields

No recommendation is made for expressions relating the total quantum yield to the composition of a system containing O_3, O_2, and inert gas. We prefer the results in ref. (k, l) to those in (c). This preference rests solely on suspicion that the evidence for a chain reaction in (c) may be faulty. (See ref. (f) for data on reactions in the chain: (3a) and (4b).) However, we can offer no reasonable alternative interpretation.

The discrepancies can be resolved only by new experiments. It would be important in them to use monochromatic light sources, measure the absorption coefficient, analyze the gas samples for impurities, stir the gases in optically thick systems, and report in detail on "dark" reactions.

Ref. (k, l)

The papers in Z. fur Phys. Chem. vol. 76 treat the 313 and 254 nm data according to the same mechanism and revise earlier numerical values and correct equations. This mechanism is 1b, 2a, 3a, 4a, 5, 6a, 6b, 7a, 8, 9. The experiments measure $(k_{6a} + k_{6b})/k_{3a}$ and k_5/k_{3a}. They use values for k_9/k_8 from red light photolysis (ref. t). The deactivation rate ratios measured are sensitive functions of k_9/k_8. Using values from (w) for k_9/k_8, $k_6/k_{3a} \sim 0.15$ as opposed to 0.23. The expressions for Φ should not be used far outside the $[M]/[O_3]$ used in the studies. At higher values deactivation reactions such as (2b) and (7b) must enter. They would *raise* Φ. Since similar results were obtained at $\lambda = 254$ and 313 nm, the fact that the system at 254 nm was optically thick probably is unimportant.

Ref. (c, m, n)

That this work shows a dependence of Φ on $[O_3]$ suggesting a chain reaction (3a, 4b) and wall deactivation of $O(^1D)$ leads one to suspect impurities. They could be concentrated when the O_3 is condensed or absorbed on silica gel. However, a variety of preparative

methods, analytical techniques, and actinometry were used, making this impurity thesis improbable. The presence of NO_2 (m) has only a slight effect (as it should by any mechanism). Water, if present, would be there at about 2 torr, which is unreasonably high (calculated from data in ref. (z)).

Ref. (cc)

The quantum yields in the presence of high pressures of N_2 are, in 3 cases, of the same order of magnitude as those calculable from the expressions for Φ in refs. (k, l). One run without added O_2, however, gives a Φ much smaller than it should from the same calculation. The authors feel that little weight should be given to these Φ.

Acknowledgement

We wish to thank Drs. DeMore, Schumacher, Wayne, and Bair for their assistance. They have supplied additional information and data, answered questions, and made suggestions about the various experiments and this analysis.

References

(a) D. D. Wagman, et al., NBS Technical Note 270-3 (Jan. 1968).
(b) C. E. Moore, NBS Circular 467, Vol. 1 (1949).
(c) I. T. N. Jones and R. P. Wayne, Proc. Roy. Soc. A319, 273 (1970).
(d) W. Griggs, J. Chem. Phys. 49, 857 (1968), A. G. Hearn, Proc. Phys. Soc. 78, 932 (1961).
(e) M. Gauthier and D. R. Snelling, J. Chem. Phys. 54, 4317 (1971), Chem. Phys. Letters 5, 93 (1970).
(f) R. Gilpin, H. I. Schiff, and K. H. Welge, J. Chem. Phys. 55, 1087 (1971).
(g) W. B. DeMore and O. F. Raper, J. Chem. Phys. 44, 1780 (1966).
(h) W. B. DeMore and O. F. Raper, J. Chem. Phys. 37, 2048 (1962).
(i) H. Taube, Trans. Faraday Soc. 53, 656 (1957).
(j) I. T. N. Jones and R. P. Wayne, Proc. Roy. Soc. A321, 409 (1971).
(k) G. von Ellenrieder, E. Castellano, and H. J. Schumacher, Chem. Phys. Letters 9, 152 (1971), Z. fur Phys. Chem. Neue Folge 76, 240 (1971).
(l) E. Castellano and H. J. Schumacher, Z. fur Phys. Chem. Neue Folge 65, 62 (1969), Z. fur Phys. Chem. Neue Folge 76, 258 (1971).
(m) R. G. W. Norrish and R. P. Wayne, Proc. Roy. Soc. A288, 200 (1965).
(n) I. T. N. Jones, U. B. Kaczmar, and R. P. Wayne, Proc. Roy. Soc. A316, 431 (1970).
(o) V. D. Baiamonte, L. G. Hartshorn, and E. J. Bair, J. Chem. Phys. 55, 3617 (1971).
(p) H. Webster and E. J. Bair, J. Chem. Phys. 53, 4532 (1970).
(q) D. Biedenkapp and E. J. Bair, J. Chem. Phys. 52, 6119 (1970).
(r) D. R. Snelling and E. J. Bair, J. Chem. Phys. 47, 228 (1967).
(s) D. R. Snelling, V. D. Baiamonte, and E. J. Bair, J. Chem. Phys. 44, 4137 (1966).
(t) E. Castellano and H. J. Schumacher, Z. Phys. Chemie Neue Folge 34, 198 (1962).
(u) W. D. McGrath and R. G. W. Norrish, Proc. Roy. Soc. A242, 265 (1957), A254, 317 (1960).
(v) R. V. Fitzsimmons and E. J. Bair, J. Chem. Phys. 40, 451 (1964).
(w) H. S. Johnston, Nat. Stand. Ref. Data Series-Nat. Bur. Stand. 20 (1968).
(x) V. D. Baiamonte, D. R. Snelling, and E. J. Bair, J. Chem. Phys. 44, 673 (1966).
(y) D. M. Ellis, J. J. McGarvey, and W. D. McGrath, Nature Phys. Sci. 229, 153 (1971).
(z) R. G. W. Norrish and R. P. Wayne, Proc. Roy. Soc. A288, 361 (1965).
(aa) L. J. Heidt and G. S. Forbes, J. Am. Chem. Soc. 56, 1617, 2365 (1934).
(bb) D. Katakis, J. Chem. Phys. 47, 541 (1967).
(cc) W. B. DeMore and C. Dede, J. Phys. Chem. 74, 2621 (1970).
(dd) Discussed in S. W. Benson, The Foundation of Chemical Kinetics (McGraw-Hill Book Co., 1960), p 417, and in H. S. Johnston, Gas Phase Reaction Rate Theory (Ronald Press 1966) Chapter I, especially Tables 1-1, 1-2 and pages 30-32.
(ee) K. F. Preston and R. J. Cvetanovic, Decomposition of Inorganic Oxides and Sulfides, in Comprehensive Chemical Kinetics, ed. C. H. Bamford and C. F. H. Tipper (Elsevier Publishing Co., 1972) volume 4, pages 47-141.
(ff) E. Castellano and H. J. Schumacher, Chem. Phys. Lett. 13, 625 (1972).
(gg) D. J. Giachardi and R. P. Wayne, Proc. Roy. Soc. A330, 131 (1972).
(hh) R. J. Donovan, L. J. Kirsch, and D. Husain, Chem. Phys. Lett. 7, 453 (1970).
(ii) R. E. Huffman, J. C. Larrabee, and V. C. Baisley, J. Chem. Phys. 50, 4594 (1969).

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July 1972

Notes Added in Proof

Additional measurements have been reported or brought to our attention since the preparation of these data sheets. The following notes summarize these points. Where a recommendation has been changed, the revised value is incorporated in the summary table and in the data sheets, but no attempt has been made to discuss these new data in the body of the text.

Section 4.5.   The Reaction Between H and NO_2

The activation energy that results from combining the room temperature value of k_1 by Phillips and Schiff (b)

with the 633 K data of Ashmore and Tyler (d) is changed from 2.0 to 1.5 kcal/mol when one uses the newer recommendation of 3×10^{-32} cm^6 $molecule^{-2}$ s^{-1} for $k(H + O_2 + H_2)$ at 633 K.* This improves the agreement with the value of the activation energy resulting from combining the room temperature results (b) with the 500–540 K data in (c). Using $E = 1.5$ kcal/mol, then $k(220)/k(300) \sim 0.4$.

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*D. L. Baulch, D. D. Drysdale, D. G. Horne, A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions volume 1, Homogenous gas phase reactions of the H-O₂ systems, Butterworth & Co., London (1972).

Section 4.18.   The Reaction between H_2O and $O(^1D)$

and

Section 4.23.   The Reaction between N_2O and $O(^1D)$

Since the preparation of these data sheets, there has appeared a preliminary note (a) reporting the following values of the rate constants for the quenching (or reaction) of $O(^1D)$ at 300 K in units of 10^{-10} cm^3 molecule^{-1} s^{-1}: O_2 (0.70); N_2 (0.69); CO (0.73); CO_2 (2.1); H_2O (3.0); and O_3 (2.7). Each is an absolute value determined by the technique of time-resolved atomic absorption spectroscopy in the vacuum ultraviolet (b).

Although these data are not included in the data sheets, the preferred values given take them into account. These preferred values are Cvetanovic's revisions of his earlier evaluated values in (c).

(a) R. F. Heidner and D. Husain, Nature Phys. Science **241**, 10 (1973).
(b) R. F. Heidner, D. Husain and J. R. Wiesenfeld, Chem. Phys. Lett. **16**, 530 (1972).
(c) R. J. Cvetanovic, The Reaction of $O(^1D_2)$, in The Natural Stratosphere, E. Reiter, editor (Climatic Impact Assessment Program, Monograph 1), preliminary draft, Nov. 1972.

Section 4.19.   Photolysis of H_2O_2, $\lambda < 300$ nm

We are grateful to Professor J. Troe for the following comments on this data sheet:

(1) Data on the absorption coefficient of H_2O_2 in the wavelength range 195–290 nm at higher temperatures (650 and 1100 K) are given in H. Kijewski and J. Troe, Helv. Chim. Acta. **55**, 205 (1972).

(2) The temperature dependence of the absorption coefficient suggest the contribution of a second channel for photolysis (in addition to reaction (1)) for $\lambda < 195$ nm.

Section 4.21.   The Reaction between NO and O_3

D. H. Stedman and H. Niki (preprint, 1972) have measured a value of $1.73 \pm 0.09 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for k_1 by photolysis of NO_2 (< 100 ppm) in air. The reaction was studied by NO/O_3 chemiluminescence. This is in good agreement with other measurements. Our recommendation is unchanged.

Section 4.22.   The Reaction between NO_2 and O_3

References (f) and (g) are both unpublished. There is less scatter to the data in (g). The results in (f) should probably be considered as preliminary data.

Section 4.25.   Collisional Quenching of O_2 $(a^1\Delta g)$

Findlay and Snelling (private communication) have reconsidered the data in Findlay, Fortin, and Snelling, Chem. Phys. Lett. **3**, 204 (1969). They now interpret their results to give the firm upper limit: k_1 (M = N_2) $\leqslant$ 2×10^{-20} cm^3 molecule^{-1} s^{-1}. We agree with their new interpretation and accept this revised value.

Appendix

Conversion Tables

Equivalent second order rate constants

A \ B	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

A \ B	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 molecular energy

	J/mol	cal/mol	cm³ atm/mol	kWh/mol	Btu/lb-mol	cm⁻¹/molecule	eV/molecule
1 J/mol =	1	2.390057×10^{-1}	9.86923	2.77778×10^{-7}	0.429923	8.35940×10^{-2}	1.036409×10^{-5}
1 cal/mol =	4.18400	1	41.2929	1.162222×10^{-6}	1.798796	3.49757×10^{-1}	4.33634×10^{-5}
1 cm³ atm/mol =	0.1013250	2.42173×10^{-2}	1	2.81458×10^{-8}	4.35619×10^{-2}	8.47016×10^{-3}	1.050141×10^{-6}
1 kWh/mol =	3,600,000	860,421	3.55292×10^{7}	1	1,547,721	300,938	37.3107
1 Btu/lb-mol =	2.32600	5.55927×10^{-1}	22.9558	6.46111×10^{-7}	1	1.944396×10^{-1}	2.41069×10^{-5}
1 cm⁻¹/molecule =	11.96258	2.85912	118.0614	3.32294×10^{-6}	5.14299	1	1.239812×10^{-4}
1 eV/molecule =	96487.0	23060.9	952,252	2.68019×10^{-2}	41482.0	8065.73	1

The underlined numbers represent the fundamental values used in deriving this table. The remaining factors were obtained by applying the relationships: $n_{ij} = n_{ik} \cdot n_{kj}$, $n_{ii} = n_{ik} \cdot n_{ki} = 1$.

Gas constant. $R = 8.3143 \pm 0.0012$ J/K mol $= 1.98717$ cal/K mol $= 82.056$ cm³atm/K mol $= 0.69502$ cm⁻¹/K molecule $= 8.6170 \times 10^{-5}$ ev/K molecule. (From NBS Technical Note 270-3.)

Units of Optical Absorption Coefficients

The molar (linear) absorption coefficient ϵ is defined by the Lambert-Beer equation: $\epsilon = (1/lc) \log_{10} (I_0/I_t)$ where I_0 and I_t are incident and transmitted intensity, l is the path length, and c is the concentration.* The units for ϵ are (concentration⁻¹ length⁻¹).

A variety of equivalent forms of this equation have been used to define reported values of ϵ. Both logarithmic bases e and 10 have been used. Length has invariably been expressed in cm. Concentration has usually been expressed in (mol/liter). Often a pressure unit has been used instead of a concentration unit, in which case the temperature to which the value of the pressure is referred must be specified. When pressure units are used the absorption coefficient is usually denoted by k (or α) with units of [(pressure (T))⁻¹ (length)⁻¹].

* Commission on Symbols, Terminology, and Units, I.U.P.A.C., M. L. McGlashan, chairman, Pure and Applied Chemistry, 21, 1 (1970).

When the pressure unit used is (1 atmosphere at 273 K), the value of k is expressed in any of the numerically equivalent forms: [(atm at 273 K)⁻¹ cm⁻¹]; [NTP]⁻¹ cm⁻¹]; or cm⁻¹. This last form is equivalent to converting the measured value of l at T and P to its corresponding value l_0 at the reference state $T_0 = 273$ K and $P_0 = 1$ atm ($l_0 = l \times (P/P_0) \times T_0/T$) and using the eqn: $k = (1/l_0) \log (I_0/I_t)$.

Alternatively the molecular concentration, n, expressed in (molecules/cm³) may be used. Then the molecular "cross-section", σ, is defined as $\sigma = (1/nl) \log_e (I_0/I_t)$.

Because of the diversity of units, when using reported values in numerical calculations one must always determine what defining equation was used. When reporting absorption coefficients it is recommended that the units be given explicitly and that the defining equation appear in table and figure captions.

A table of conversion factors is shown below.

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 dm³ mol⁻¹ cm⁻¹ base 10 to (atm at 273)⁻¹ cm⁻¹ base e, multiply by 0.103.