Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions

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The available information, up to mid-1972, for the rate constants of a series of gas phase chemical reactions has been evaluated critically. For each reaction, relevant thermodynamic data are presented and values for the equilibrium constant expressed in mathematical form. Kinetic data are presented in tabular and graphical form together with a discussion of the pertinent details. Recommended rate constant values are presented wherever possible with suggested error limits. The reactions considered involve the species H, O, C, N, S, OH, HS, S_2, CS, SO, HSO_2, NH_2, NH_3, NO, N_2O, NO_2, N_2O_4, N_2, O_2, O_3, H_2, H_2O, SO_2, SO_3, CS_2, OCS, H_2S, and CO. Particular emphasis is given to reactions involving sulfur chemistry. The best available data for these reactions have been summarized in a table at the end of the paper. An appendix discussing the available evaluations and review articles published since 1960 also has been included to publicize these sources of either evaluated data or of extensive reference bibliographies.

Key words: Activation energies; evaluation; gaseous reactions; radical reactions; rate constants; review; sulfur chemistry; tables.

Contents

1. Introduction

The available information on a series of gas phase chemical reactions has been carefully evaluated and tabulated. An effort has been made to include all pertinent references up to mid-1972. The aim of this publication is to provide a useful reference source of data against which new information can be compared and added at a later time. Also, it is hoped that it will better illustrate those areas of greatest uncertainty where further effort is needed and possibly dissuade researchers from repeating measurements of established values unless well justified.

A number of factors influenced the choice of reactions included in this review. They are frequently

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encountered reactions that have not been evaluated elsewhere, and many of them are relevant to current research and development programs. The majority emphasize reactions of importance in the gas phase chemistry of sulfur compounds. Others were added to round off more completely the coverage of previously published evaluations. Nineteen related reactions for which very little information is available have been listed together in a miscellaneous reactions section. These frequently appear in chemical kinetic models. The extent and limit of our knowledge of their rate constants is outlined.

An evaluation of experimental data in chemical kinetics centers on various important facets. Judgments have to be made, based on present knowledge, as to whether the techniques used and the assumptions made were valid; whether it is necessary to reanalyze the primary experimental data using parameters that have since been improved on; and whether the reported rate constants actually refer to the reaction claimed. Assessments can only be fair if comparisons are truly valid. Frequently, it appears that only during the compilation of such tables does the opportunity arise to assess the available data carefully. To indulge in this time-consuming activity is not generally possible, and often is not of particular interest, to the average experimental investigator. Unfortunately, insufficient information still exists in many current publications, so that only a cursory evaluation can be made. Authors should be reminded that for others to judge their work, certain inclusions have to be made. For example, it is not unusual for an uncertainty to arise simply through the omission of the basic definition of the rate constant.

Inevitably, in spite of the strenuous efforts made to eliminate mistakes and omissions in such a collection of data, some may have occurred. The author hopes to be notified of any such findings.

2. Presentation of Data

The presentation of the available rate information, for the various chemical reactions considered, is based upon a style similar to that of the Leeds University Reports on High Temperature Reaction Rate Data by Baulch, et al. Each reaction is considered separately. A table of pertinent thermodynamic data is given, derived from the JANAF Thermochemical Tables.[1]

Where applicable, values of the equilibrium constants are given in both pressure (atm) and concentration (molecule cm^{-3}) units. In addition, the equilibrium constant has been expressed in the mathematical form

$$K=BT^{n} \exp (C/RT)$$

so that the rate constant for the reverse reaction can be calculated if required. The values for B, n, and C have been determined by taking the equilibrium constant data derived from the JANAF Tables at 100 K intervals over the range specified, and calculating a least squares fit. The temperature range has been restricted in some cases to minimize the deviation between the expression for K and the data points. The maximum deviation within the temperature range is specified.

The available rate data have been listed, and where possible original data points have been preferred. cm^3 molecule^{-1} s^{-1} and cm^6 molecule^{-2} s^{-1} units have been used throughout for bi- and termolecular rate constants, respectively. The experimental temperature range, a brief description of the method used with some experimental conditions, and brief comments are given. Occasionally, to facilitate comparison of data measured in similar temperature regimes, values for k have been calculated for a common temperature. Generally, the data have been plotted to better illustrate the extent of the scatter and the agreement between various studies. The values are then discussed in more detail and the reliability assessed. The data which form the basis for the recommended values are identified. The recommended value is listed separately with suggested error limits. It is based either on the most reliable single set of measurements or, where several sources of data are available, of similar uncertainty, an equally weighted least squares fit. Unreliable sources of data are not included in such an assessment. Error limits are approximately estimated as those which appear most reasonable considering the total available information. In instances where sufficient data permitted, standard deviations of the activation energy and the preexponential factor have been calculated.

The Arrhenius expression for the rate constants

$$k=A \exp (-E/RT),$$

is used in most cases. The activation energy, E, is expressed in cal mol^{-1}. Occasionally, values have been expressed in the theoretical form

$$k=\frac{Z}{(s-1)!}\left(\frac{\Delta E_0^\circ}{RT}\right)^{s-1} \exp (-\Delta E_0^\circ/RT),$$

where s represents the number of oscillator terms contributing to the dissociation process of unimolecular reactions.

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[1] Data were obtained from the JANAF Thermochemical Tables, PB 168370 (1965); 1st, 2nd, and 3rd Addenda, PB 168370-1, 2, 3 (1966–1968). A revision of these tables has recently been published as JANAF Thermochemical Tables, 2nd Edition (NSRDS-NBS 37), D.R. Stull and H. Prophet, Project Directors. (Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402; Catalog No. C 13.48:37, Price $9.75). The revisions do not significantly affect the thermodynamic data presented in this review.

Care has been taken to define the rate constant in a uniform way for reactions involving common species such as

$$X+X \rightarrow Y+Z,$$

for which

$$d[Y]/dt=-0.5\ d[X]/dt=k[X]^2.$$

Unimolecular reactions present certain problems in displaying the available data. The low pressure region where the chemistry is described by 2nd order kinetics and the high pressure 1st order regimes can be handled conventionally. It is the intermediate fall-off region for which k is both a function of concentration and temperature that can be difficult for collectively illustrating the available data. However, this was not a severe problem in the cases considered here.

Where necessary, sensible guesses have been made for the temperature of certain measurements for which the investigator merely reported "room-temperature."

References pertaining to a particular reaction are listed at the end of each section.

3. Symbols and Conversion Factors

K, K_{eq}	equilibrium constant
K_p	equilibrium constant in terms of partial pressures (atm)
K_c	equilibrium constant in terms of concentrations (molecule cm^{-3})
k, $k_{T\ K}$	reaction rate constant
k_{A+B}	rate constant for the reaction A+B→
M	unchanged reactant in termolecular recombination reactions or their reverse bimolecular dissociation.
k_M	rate constant with M as the chaperon third body
k_∞	unimolecular rate constant (s^{-1}) at its infinite pressure limit
[A]	concentration of A
A	pre-exponential factor of a rate constant
E	activation energy of a reaction
R	gas constant, equal to 1.987 cal deg^{-1} mol^{-1}
T	temperature in Kelvins (K)

Avogadro's Number $=6.0225\times10^{23}$ particle mol^{-1}

1 cal $=4.184$ joules

1 mm Hg $=1$ torr$=1/760$ atm

millitorr $=10^{-3}$ torr

1 atm $=7.3395\times10^{21}/T$ particles cm^{-3}$=0.012187/T$ mol cm^{-3} $=1.01325\times10^{5}$ Newtons meter^{-2}

1 molecule cm^{-3} $=1.6604\times10^{-21}$ mol l^{-1}

1 cm^3 molecule^{-1} s^{-1} $=6.0225\times10^{23}$ cm^3 mol^{-1} s^{-1} $=6.0225\times10^{20}$ l mol^{-1} s^{-1}

1 cm^6 molecule^{-2} s^{-1} $=3.6270\times10^{47}$ cm^6 mol^{-2} s^{-1} $=3.6270\times10^{41}$ l^2 mol^{-2} s^{-1}

4. Detailed Rate Constant Evaluations

4.1. O+H+M⇆OH+M

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm^{-1}	$\log_{10}K_c$ cm^3 molecule^{-1}
0	−101. 331	—	—	—
100	−101. 630	−18. 705	218. 012	198. 146
298	−102. 227	−21. 980	70. 127	50. 736
300	−102. 233	−21. 999	69. 665	50. 277
500	−102. 836	−23. 541	39. 802	20. 635
1000	−104. 262	−25. 532	17. 206	−1. 660
1500	−105. 439	−26. 495	9. 571	−9. 119
2000	−106. 369	−27. 031	5. 715	−12. 850
2500	−107. 123	−27. 369	3. 383	−15. 085
3000	−107. 761	−27. 603	1. 817	−16. 571
3500	−108. 327	−27. 777	0. 694	−17. 628
4000	−108. 846	−27. 916	−0. 155	−18. 419
4500	−109. 337	−28. 032	−0. 816	−19. 028
5000	−109. 813	−28. 132	−1. 348	−19. 515
5500	−110. 279	−28. 221	−1. 786	−19. 911
6000	−110. 735	−28. 300	−2. 151	−20. 238

Equilibrium Constant

$$K_p=0.313T^{-1.481}\exp(101{,}350/RT)\ \text{atm}^{-1}\quad(300\text{–}1000\ \text{K range}),$$

$$=3.89\times10^{-3}T^{-0.934}\exp(102{,}580/RT)\quad(1000\text{–}3000\ \text{K range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–1000 K) and 0.6 percent (1000–3000 K).

Recommended Rate Constant

No reliable data are available for this reaction. A value $k_{Ar}\sim2\times10^{-32}$ cm^6 molecule^{-2} s^{-1} for the 1000–3000 K temperature range with a possible error of a factor of 10 would be compatible with observations. No information has been published for the reverse reaction, the dissociation of OH.

Discussion

For several years now, in spite of the scant data available, this reaction has been included in performance calculations of supersonic combustors [Da-Riva, 1966], rocket and ramjet nozzle expansions [Boynton, 1964; Franciscus and Lezberg, 1963; Baulknight, 1965; Westenberg and Favin, 1963], hypersonic wake flow fields [Langan et al., 1965], and shock tube kinetic schemes [Duff, 1958; Schott, 1960]. Also, it has appeared in various

Reported rate constants

Rate constant k (cm^6 molecule^{-2} s^{-1})	k_{1500K}	M	Exp. temp. (K)	Method & reference	Comments
$\leq 2.7 \times 10^{-32}$	$\leq 2.7 \times 10^{-32}$	Ar	1750	Shock tube study of highly diluted lean $H_2/O_2/Ar$ mixtures. [OH] followed by uv absorption. Getzinger and Schott 1965.	Very approximate assessment.
1.17×10^{-31} exp $(+2780/RT)$	3.0×10^{-31}	H_2O	1330–1560	3.7 and 5.7 cm^3 quartz adiabatic stirred flow reactor studies of approximately $2H_2:O_2:10H_2O$ and $H_2:6O_2$ mixtures at atm pressure. Temperature in the reactor measured with a thermocouple and compared with that calculated from an assumed mechanism. Rate constants adjusted for best agreement with the data. Jenkins, Yumlu, and Spalding 1967.	Adjusted rates for other reactions in the kinetic scheme are all higher than generally accepted. This value likewise may be too high. $k_{H_2O} \sim k_{O_2}$
$1.1 \times 10^{-29} T^{-1}$	7.3×10^{-33}	Ar	1000–3000	Used in rocket engine performance calculations and consistent with their kinetic mechanisms. Bahn, Cherry, Gold, et al. 1969.	Too complex a way to establish rate constants.

kinetic rate data tabulations [Kaskan and Browne, 1964; Cherry et al., 1967, 1968; Jensen and Kurzius, 1967; Tunder et al., 1967] although there is no foundation for any of the values quoted or used. In all these cases it has been common to assume a value comparable to those for the O+O+M and H+H+M reactions. However, closer inspection of the rate constants for the latter two shows that a mean value would be too low. The oxygen atom recombination has been extensively evaluated by Johnston (1968) who recommends $k_{O+O+Ar} = 3.55 \times 10^{-31}\ T^{-1}$ exp $(-340/RT)$, (300–15,000 K). At present no evaluation has been published for the H atom recombination but a preliminary analysis of the available data supports a value of $k_{H+H+Ar} = 2.75 \times 10^{-30}\ T^{-1}$, (300–5000 K). Although the room temperature value is known to be about ±40 percent, the available high temperature data (1700–7000 K) are scattered a factor of 2 to 3 about this mean value. At 1500 K these give $k_{O+O+Ar} = 2.1 \times 10^{-34}$ and $k_{H+H+Ar} = 1.8 \times 10^{-33}$. Taking their mean value as a measure of k_{O+H+Ar} gives 1×10^{-33}, an order of magnitude smaller than other estimates.

Getzinger and Schott (1965) made a crude estimate of k_{O+H+Ar} assuming that this was responsible for the slight enhancement in decay rate observed in their shock tube study at temperatures above 1750 K over that accounted for by other hydrogen, oxygen reactions.

Bahn, Cherry, Gold et al. (1969) recommended a set of recombination rates for use in rocket engine nozzle performance calculations. The rates quoted are compatible with their performance data but such a force fitting of rates to a rocket kinetic scheme cannot produce reliable data at this stage, especially for reactions of minor importance.

At present the most extensive study has been carried out by Jenkins, Yumlu, and Spalding (1967). A nine-reaction mechanism was found to describe the enthalpy production of a $H_2/O_2/H_2O$ reactor quite well, provided that the initially chosen reaction rates were adjusted slightly. A series of sensitivity calculations was the guide for adjusting the various rates to minimize the difference between observed and predicted enthalpy curves. However, the changes in the rate constants for reactions 1–4, listed in table 1, were such as to increase their values over the generally accepted ones [Baulch, et al., 1968, 1969]. The rate constant taken for reaction 5 and not adjusted owing to its insensitivity was too low.

TABLE 1

Reaction	T K	Rate constants	
		[Jenkins, et al., 1967]	Recommended value [Baulch et al., 1968, 1969]
1. $OH + H_2 = H_2O + H$	1350 1550	1.10×10^{-11} 1.80×10^{-11}	5.33×10^{-12} 6.83×10^{-12}
2. $H + O_2 = O + OH$	1350 1550	9.98×10^{-13} 2.36×10^{-12}	7.08×10^{-13} 1.59×10^{-12}
3. $O + H_2O = OH + OH$	1350 1550	2.43×10^{-13} 5.79×10^{-13}	1.16×10^{-13} 2.76×10^{-13}
4. $H + OH + M = H_2O + M$	1350 1550	7.97×10^{-31} 7.78×10^{-31}	3.22×10^{-31}
5. $O + H_2 = OH + H$	1350 1550	2.08×10^{-13} 3.02×10^{-13}	8.52×10^{-13} 1.34×10^{-12}

It appears that the nine-reaction mechanism used is not sufficient to fully describe the system and additional reactions of HO_2, H_2O_2, and O_3 need to be considered.

From effects of composition Jenkins et al. (1967) conclude that H_2O and O_2 are equally efficient third bodies for this reaction.

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4.2. $CO+M \rightleftarrows C+O+M$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm	$\log_{10}K_c$ molecule cm^{-3}
0	255. 765	—	—	—
100	256. 168	25. 136	−554. 335	−534. 46
298	256. 862	29. 015	−181. 935	−162. 54
300	256. 867	29. 036	−180. 773	−161. 385
500	257. 487	30. 624	−105. 850	−86. 683
1000	258. 720	32. 370	−49. 466	−30. 600
1500	259. 598	33. 088	−30. 590	−11. 900
2000	260. 305	33. 496	−21. 123	−2. 558
2500	260. 945	33. 783	−15. 428	3. 040
3000	261. 576	34. 013	−11. 621	6. 767
3500	262. 229	34. 215	−8. 896	9. 426
4000	262. 920	34. 399	−6. 847	11. 417
4500	263. 651	34. 571	−5. 249	12. 963
5000	264. 423	34. 734	−3. 966	14. 201
5500	265. 229	34. 887	−2. 915	15. 210
6000	266. 060	35. 032	−2. 036	16. 051
7000	267. 901	35. 318	−0. 645	17. 375
8000	269. 622	35. 548	0. 403	18. 366
9000	271. 187	35. 732	1. 224	19. 135
10, 000	272. 449	35. 865	1. 884	19. 750
11, 000	273. 260	35. 943	2. 426	20. 250
12, 000	273. 493	35. 964	2. 879	20. 665
13, 000	273. 059	35. 929	3. 262	21. 014
14, 000	271. 919	35. 845	3. 589	21. 308
15, 000	270. 085	35. 719	3. 871	21. 561

The thermodynamic data for 7000 to 15,000 K have been calculated using the JANAF program.

Equilibrium Constant

$$K_p = 2.18 \times 10^5 \, T^{0.560} \exp(-260{,}550/RT) \text{ atm}$$

(6000–14,000 K range).

This reproduces the 1000 K interval equilibrium data with deviations of up to 0.8 percent in the range specified.

Recommended Rate Constant

Fairbairn's work (1969) provides the only available data relating directly to this reaction (see discussion). It infers a value of $\lesssim 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 8000 K, with a quoted uncertainty of ±50 percent. Further work is obviously necessary.

Third body efficiencies: $k_{Ar} \sim k_{Ne}$

No experimental data other than these are available for the reverse three body recombination reaction.

Discussion

The rate for the one-step reaction

$$(1) \qquad CO+M \xrightarrow{k_1} C+O+M,$$

has not yet been satisfactorily measured. Fairbairn's (1968, 1969) observation of an induction period in the shock tube dissociation of CO, since confirmed

Reported rate constants

Rate constant k (cm^3 molecule^{-1}s^{-1})	$k_{8000 K}$	Exp. temp. (K)	Method & reference	Comments
$\leq 4.6\times10^{-16}$ M = Ar or Ne		8000	Shock tube study of 0.005–10 percent CO/Ar and 0.5–2.0 percent CO/Ne mixtures. [CO] monitored by 4.65 μ emission behind incident shock waves at 6000–11,000 K. C_2 emission 5088–5200 Å and C emission 2478 Å monitored. Fairbairn 1969.	Identified as the rate constant for this single step reaction. ±50 percent uncertainty stated. 1 percent CO mixture data analyzed for k.
$8.3\times10^{-32}T^{-1/2}K_{eq}$	2.1×10^{-15}		Order of magnitude estimate of the recombination rate from a comparison with other termolecular reaction rates. Cherry, Gold, and Van Nice 1967.	Factor of 25 given as the uncertainty.
$2.7\times10^{-32}T^{-1/2}K_{eq}$	7.2×10^{-16}		Order of magnitude estimate of the recombination rate from a comparison with other termolecular reaction rates. Tunder, Mayer, Cook, and Schieler 1967.	

by Appleton, Steinberg and Liquornik (1970), established that the dissociation mechanism cannot be described by such a one-stage process, but is rather a series of reactions involving an intermediate. Therefore, although the steady state dissociation rate after the induction period can be represented by the expression

$$-d[\mathrm{CO}]/dt=k[\mathrm{CO}]\,[\mathrm{M}].$$

The rate constant so derived has only empirical meaning as it refers to the overall mechanism involved rather than k_1.

Fairbairn (1969) reports that the reactions (2) to (4)

$$\mathrm{CO+M\rightleftarrows C+O+M}, \tag{2}$$

$$\mathrm{C+CO\rightleftarrows C_2+O}, \tag{3}$$

$$\mathrm{C_2+M\rightleftarrows C+C+M}, \tag{4}$$

can account for the essential features of the dissociation process.

At 8000 K he has obtained estimates for the rate constants which reproduce the observed C_2 and CO emission profiles. He reports a value of $\leq 2\times10^{-34}$ cm^6 molecule^{-2} s^{-1} for the reverse three-body recombination $\mathrm{C+O+M\rightarrow CO+M}$ which converts to the value of k_1 $\leq 4.6\times10^{-16}$ cm^3 molecule^{-1} s^{-1} quoted here. However, the conclusions are based on limited data and it would be premature to accept this mechanism over others which invoke electronically excited CO state intermediates [Fairbairn, 1968; Appleton et al., 1970]. It must be regarded as approximate until further measurements are made. He reports also, values derived from the initial reaction rate during the induction period of CO/Ne mixtures (9.2×10^{-16} at 8000 K), but these are subject to an error of about a factor of four owing to the difficulties in the data reduction. Similar slow decays of CO during the induction period were not reported by Appleton et al. (1970).

Little difference was found between Ar or Ne as third bodies [Fairbairn, 1969].

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Tunder, R., S. Mayer, E. Cook, and L. Schieler, "Compilation of reaction rate data for nonequilibrium performance and reentry calculation programs," Aerospace Corp., Report No. TR-1001 (9210-02)-1 (1967), AD 813485.

4.3. $\mathrm{CO+M/C+O+M}$

Values for the rate constant measured from the steady state dissociation of CO *and defined by* $d[\mathrm{CO}]/dt=-k[\mathrm{CO}][\mathrm{M}]$ *but which are identified solely as values that relate to the overall mechanism.*

Thermodynamic Data and Equilibrium Constant

Listed under the $\mathrm{CO+M\rightarrow C+O+M}$ reaction.

Recommended Rate Constant

$k_{\mathrm{Ar}}=1.46\times10^{6}T^{-3.52}\exp(-255,760/RT)$ cm^3 molecule^{-1} s^{-1}.

Temperature range: 7000–15,000 K.

Suggested error limits:

±75 percent (7000–10,000 K),
±50 percent (10,000–15,000 K).

Third body efficiencies:

$$k_{\mathrm{CO}}\leq 2k_{\mathrm{Ar}} \qquad k_{\mathrm{O}}=15k_{\mathrm{Ar}}.$$

The available rate constant data are shown in figure 1.

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	$k_{9000\ K}$	M	Exp. temp. (K)	Method & reference	Comments
$5.80\times10^{-12}T^{1/2}\exp(-184{,}500/RT)$	1.82×10^{-14}	Ar	7000–9200	Shock tube study, 2 percent CO in Ar. Observed decay of 4.65μ fundamental band of CO in emission behind reflected shock waves. Davies 1964.	
or					
$6.25\times10^{7}T^{-3.88}\exp(-255{,}540/RT)$	1.77×10^{-14}				
$2.62\times10^{-13}T^{1/2}\exp(-126{,}850/RT)$	2.06×10^{-14}		9500–12, 000		
5.3×10^{-16} (7000 K) 3.7×10^{-15} (8000 K) 1.4×10^{-14} (9000 K) 3.9×10^{-14} (10,000 K) 8.3×10^{-14} (11,000 K) 1.9×10^{-13} (12,000 K) 3.2×10^{-13} (13,000 K) 5.0×10^{-13} (14,000 K) 7.5×10^{-13} (15,000 K)	$1.4\ \times10^{-14}$	CO+ C+O	7000–15, 000	Shock tube study in pure CO. Emission of the 1st overtone band followed in the 1.9–4.2μ region behind incident shock waves. Presley, Chackerian, and Watson 1966.	Data points taken from a graphical plot.
$4.4\times10^{-10}\exp(-195{,}900/RT)$	$7.7\ \times10^{-15}$	Ar	8000–15, 000	Shock tube study of 0.5–5 percent CO/Ar and CO/4–8 percent O$_2$/Ar mixtures. [CO] decay followed by vacuum uv absorption at 1176 Å behind reflected shock waves. Appleton, Steinberg, and Liquornik 1970.	$k_{CO}\leq 2k_{Ar}$ $k_O=15k_{Ar}$
or					
$2.8\times10^{3}T^{-2.86}\exp(-256{,}300/RT)$	$8.2\ \times10^{-15}$				
$6.86\times10^{-9}\exp(-194{,}800/RT)$	$1.3\ \times10^{-13}$	O	7000–14, 000		

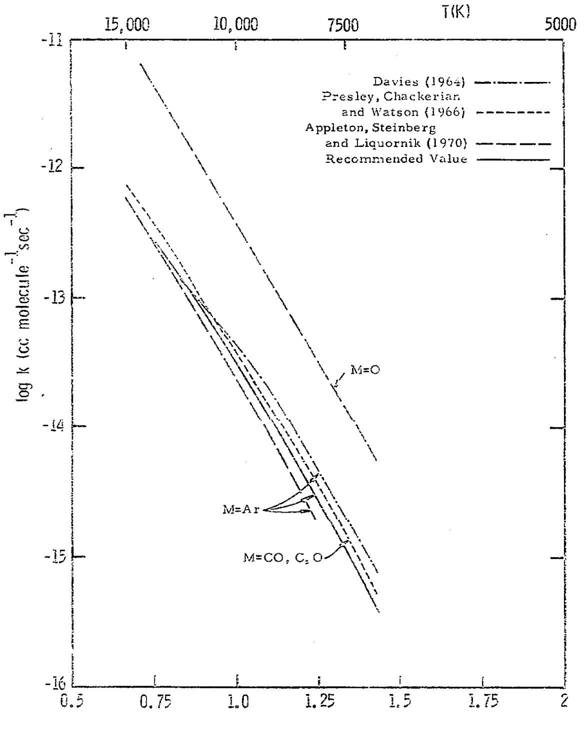

FIGURE 1. Experimental values of $k_{CO+M/C+O+M}$.

Discussion

Although the rate constants derived from the steady state dissociation of CO do not refer to the elementary step $CO+M\rightarrow C+O+M$ but rather to the overall process, which is also described by the expression $d[CO]/dt=-k[CO][M]$, it may be of some use to evaluate the available data. Three shock tube studies constitute the sources of data and are in good agreement which is reassuring since different methods of monitoring the [CO] decay were used in each.

Davies (1964) monitored the infra-red fundamental band of CO at 4.65 μ and also the emission at 6433 Å, which he claimed to be from the (3,0) triplet band of the CO ($d^3\Delta\rightarrow a^3\Pi$) system. Fairbairn (1969), more recently, looked unsuccessfully for this same triplet emission. Both emissions were found to decay similarly and postulating the establishment of a steady state non-equilibrium population in the CO $d^3\Delta$ ($\nu'=3$) level proportional to the total CO concentration, he managed to obtain rate constants only 20–50 percent higher than those obtained from the 4.65 μ measurements. However, owing to the assumptions involved, the 4.65 μ data are considered the more reliable and are quoted here.

Presley, et al. (1966) express their dissociation rate in the form of the recombination coefficient, a practice unfortunately quite common in many shock tube studies of dissociation rates and one which should be dissuaded. They report $k_{\mathrm{recomb}}=6.89\times10^{-20}T^{-7/2}$ for the temperature range studied. However, an error in their published expression for the equilibrium constant has made it preferable to read the data points directly off their plot of $k_{\mathrm{dissociation}}$ rather than use this expression and an equilibrium constant.

Appleton, et al. (1970) conclude that CO and Ar have similar third body effects and show the high efficiency of O atoms as a collision partner. However, it is surprising that such a large efficiency has not shown up as an autocatalytic effect in other CO/Ar studies.

Except for Davies' high temperature results, all the rate expressions show nearly the same temperature dependence and appear to be independent of the nature of M. This tends to suggest a common mechanism independent of the nature of the collision partner.

Davies and Appleton, et al. have fit their data to both an Arrhenius type expression and also to the theoretical form which allows for the participation of several classical harmonic oscillators and fixes the activation energy equal to the dissociation energy.

The recommended value for k_{Ar} is based on the data of Davies (1964) and Appleton, Steinberg and Liquornik (1970) giving slightly more weight to the latter investigation. From the spread of the data it appears accurate to better than ± 75 percent ($<10{,}000$ K) and ± 50 percent ($>10{,}000$ K).

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4.4. $N_2O+M \rightarrow N_2+O+M$

Thermodynamic data

T K	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm	$\log_{10}K_c$ molecule cm^{-3}
0	38. 559	—	—	—
100	39. 076	26. 648	−79. 585	−59. 719
298	39. 949	31. 692	−22. 356	−2. 965
300	39. 954	31. 711	−22. 175	−2. 787
500	40. 350	32. 756	−10. 477	8. 690
1000	40. 477	32. 993	−1. 636	17. 230
1500	40. 222	32. 791	1. 306	19. 996
2000	39. 865	32. 586	2. 765	21. 330
2500	39. 477	32. 412	3. 633	22. 101
3000	39. 083	32. 270	4. 205	22. 593
3500	38. 702	32. 152	4. 610	22. 932
4000	38. 347	32. 057	4. 911	23. 175
4500	38. 026	31. 981	5. 142	23. 354
5000	37. 744	31. 922	5. 327	23. 494
5500	37. 505	31. 876	5. 476	23. 601
6000	37. 308	31. 842	5. 600	23. 687

Equilibrium Constant

$$K_p=4.00\times 10^5 T^{0.488} \exp(-39{,}790/RT) \text{ atm} \quad (300\text{–}1000 \text{ K range}),$$

$$=2.68\times 10^8 T^{-0.350} \exp(-41{,}240/RT) \quad (1000\text{–}3000 \text{ K range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.6 percent (300–1000 K) and 0.4 percent (1000–3000 K).

Recommended Rate Constant

Low Concentration Region 2nd order kinetics

M=Ar $k=7.8\times 10^{-10} \exp(-58{,}000/RT)$ cm^3 molecule^{-1} s^{-1} (1500–2500 K).
Concentration: $<6\times 10^{-5}$ mol cm^{-3}.
Suggested error limits: ± 25 percent.

M=Ne $k=4.2\times 10^{-11} \exp(-43{,}600/RT)$ (1500–2600 K).
Concentration: $<10^{-5}$ mol cm^{-3}.
Suggested error limits: ± 50 percent.

M=Kr $k=1.2\times 10^{-11} \exp(-40{,}700/RT)$ (1750–2800 K).
Concentration: $<10^{-5}$ mole cm^{-3}.
Suggested error limits: within a factor of 2.

M=N_2O $k=4.7\times 10^{-9} \exp(-59{,}400/RT)$ (850–1050 K).
Concentration: $<10^{-6}$ mol cm^{-3}.
Suggested error limits: within a factor of 2 to 3.

Intermediate Concentrations

5×10^{-5} to 10^{-3} mol cm^{-3}. The plotted data of Olschewski, et al. (1965, 1966) (M=Ar, 1500–2100 K) and Johnston (1951) (M=N_2O, 888 K) are preferred.

High Concentrations 1st order kinetics

${}_{\infty}k=1.4\times 10^{11} \exp(-59{,}500/RT)$ s^{-1} (800–2100K).
Concentration: $>10^{-3}$ mol cm^{-3}.
Suggested error limits: ± 50 percent.

The available rate constant data are presented in six plots, figures 2 to 7, which illustrate the character of the dissociation in the various pressure regimes.

Discussion

That the chemistry of even simple systems can be complex is well illustrated by studies of the unimolecular decomposition of the N_2O linear triatomic molecule. This dissociation became of considerable interest because of its simple molecular nature and the fact that the entire unimolecular fall-off region was experimentally accessible, making it attractive for testing various theories. However, the dissociation is not without complications and our quantitative understanding is still somewhat unsatisfactory in spite of a multitude of investigations spanning several generations of chemists.

Original studies were based on static thermal systems whereas emphasis, more recently, has centered on exploiting the high temperature shock tube techniques. Data have been collected over a four decade range of total concentration or pressure

$$(2\times 10^{-7}-2\times 10^{-3} \text{ mol cm}^{-3}/0.01\text{–}300 \text{ atm})$$

2nd order rate constant

Rate constant k (cm^3 molecule^{-1} s^{-1})	M	Exp. temp. (K)	Pressure/ Concentration (atm/mol cm^{-3})	Method & reference	Comments
1.2×10^{-9} exp $(-60{,}000/RT)$	Ar	1530–1820 1640–1690	$5.6–6.7/0.45\times10^{-4}$ $20.4–21.1/1.52\times10^{-4}$	0.8 percent (higher pressures) and 1.8 percent (lower pressures) mole fraction of N_2O in Ar. Shock tube study, $[N_2O]$ monitored by uv absorption at 2250–2400 Å behind reflected shock waves. Jost, Michel, Troe, and Wagner 1963.	Initial rates measured to avoid thermal effects. k taken as $\frac{1}{2}k_{exp}$. Appears bimolecular in this region.
1.7×10^{-9} exp $(-61{,}000/RT)$	Ar	1500–2500	$2–20/(0.15–1.4)\times10^{-4}$	0.5–3 percent N_2O/Ar mixtures studied by the shock tube method. $[N_2O]$ and [NO] monitored behind reflected shock waves using uv absorption at 2300 and 2260 Å, respectively. Jost, Michel, Troe, and Wagner 1964.	Initial rates of decomposition measured. k taken as $\frac{1}{2}k_{exp}$. Bimolecular in this region.
7.8×10^{-10} exp $(-58{,}000/RT)$	Ar	1480–2530	$0.8–12/(0.5–6)\times10^{-5}$	Shock tube study of 0.02–1 percent N_2O/Ar mixtures. $[N_2O]$ followed by IR emission at 4.5μ; agrees with uv absorption measurements at 2300–2500Å. Both incident and reflected shock waves investigated. Olschewski, Troe, and Wagner 1966.	Low pressure region $<6\times10^{-6}$ mol cm^{-3}. Bimolecular kinetics. k taken as $\frac{1}{2}k_{exp}$. Incident and reflected shock wave results agree.
8.3×10^{-19} 3.5×10^{-19} 1.8×10^{-19} 9.5×10^{-20}	Ar	1428 1390 1357 1323	Low pressure region	Rapid adiabatic compression of 0.3% N_2O/Ar mixtures. $[N_2O]$ followed by the 4.5μ IR emission. Martinego, Troe, and Wagner 1966.	Bimolecular kinetics. Question as to whether k_{exp} represents k or $2k$. $k=\frac{1}{2}k_{exp}$ taken.
8.2×10^{-11} exp $(-49{,}500/RT)$ 1.1×10^{-10} exp $(-51{,}400/RT)$ 1.2×10^{-10} exp $(-52{,}400/RT)$ 1.4×10^{-10} exp $(-55{,}000/RT)$ 1.3×10^{-10} exp $(-55{,}700/RT)$ 6.9×10^{-11} exp $(-48{,}200/RT)$ 9.5×10^{-11} exp $(-50{,}000/RT)$ $k_{O_2}=1.4\ k_{Ar}$	Ar Ar Ar Ar Ar O_2 O_2	1908–2160 1738–2060 1748–2020 1728–2190 1640–2195 1550–2175 1545–2155 1900	$2.0–2.3/0.13\times10^{-4}$ $2.7–3.2/0.19\times10^{-4}$ $4.0–4.6/0.28\times10^{-4}$ $10.6–13.5/0.75\times10^{-4}$ $20.2–27.0/1.50\times10^{-4}$ $1.4–2.0/0.11\times10^{-4}$ $2.2–3.0/0.17\times10^{-4}$ $2.2/0.14\times10^{-4}$	Shock tube study of 2 percent N_2O/Ar mixtures. $[N_2O]$ followed behind incident shock waves using IR emission at 3.9 and 4.4μ and absorption at 2536Å. Experiments also with reflected shock waves and some with 2 percent N_2O/O_2 mixtures. Fishburne, et al. 1964.	Emission and absorption measurements in agreement. Reflected shock wave values slightly higher than those from incident shock waves. The rate constants for concentrations of 0.75 and 1.5×10^{-4} mol cm^{-3} fall below the others and lie in the intermediate pressure region. $k=1/2k_{exp}$ taken.

2nd order rate constant—Continued

Rate constant k (cm^3 $molecule^{-1}$ s^{-1})	M	Exp. temp. (K)	Pressure/ Concentration (atm/mol cm^{-3})	Method & reference	Comments
$2.1\times10^{-17}T^{1/2}(60{,}000/RT)^{5.09}\exp(-60{,}000/RT)$ $2.7\times10^{-18}T^{1/2}(60{,}000/RT)^{5.84}\exp(-60{,}000/RT)$	Ar	1877–2500 1877–3421	$0.15–0.86/(0.8–4.3)\times10^{-6}$ $0.15–1.0/(0.8–4.5)\times10^{-6}$	Reflected shock waves in 4 percent N_2O/Ar mixtures sampled through an orifice on the end flange of the shock tube into a quadrupole mass filter. [N_2O], [O_2], [N_2], and [NO] monitored in different experiments. Gutman, Belford, Hay, and Pancirov 1966.	E assumed to be 60 kcal mol^{-1}. Time resolution ~10μsec. Values extrapolated to $t=0$ to eliminate temperature and boundary layer effects. Steady state [O] rapidly established below 2500 K but some uncertainty concerning this at higher temperatures. $k=1/2k_{exp}$ taken.
$5.2\times10^{-10}\exp(-56{,}800/RT)$	Ar	1665–1919	$3.2–4.0/{\sim}2.4\times10^{-5}$	Shock tube study of reflected shock waves in 6 percent N_2O/Ar mixtures. [N_2O] followed in absorption at 2590Å. Drummond and Hiscock 1967.	$k=1/2k_{exp}$ taken. Measurements made 14 and 75 mm from the reflecting end plate agree. Temperatures calculated from the flow parameters assuming no reaction (frozen equilibrium).
3.15×10^{-16} 3.65×10^{-16} 5.31×10^{-16} 1.31×10^{-15} 2.21×10^{-15} 9.63×10^{-16} 2.74×10^{-15} 3.98×10^{-15}	Ne	1815 1890 1985 2010 2020 2050 2180 2330	$0.55/3.7\times10^{-6}$ $0.85/5.5\times10^{-6}$ $0.93/5.7\times10^{-6}$ $0.63/3.8\times10^{-6}$ $0.35/2.1\times10^{-6}$* $0.64/3.8\times10^{-6}$ $0.70/3.9\times10^{-6}$ $0.76/4.0\times10^{-6}$	Reflected shock waves sampled with a nozzle and TOF mass analyzed for N_2O, N_2, O_2, NO. 2 percent N_2O/Ne mixtures studied (and one 5 percent mixture*). Nonstationary solution of the kinetic equations. Borisov 1968.	20–50 μs time resolution. Since an allowance is made in the analysis for the subsequent reactions $k=k_{exp}$.
$2.6\times10^{-10}\exp(-50{,}600/RT)$ $2.8\times10^{-10}\exp(-52{,}500/RT)$	Ne	1920–2350 1880–2360	$0.47–0.58/3\times10^{-6}$ $0.31–0.39/2\times10^{-6}$	Shock tube study of the reflected shock wave in 5 percent N_2O/Ne mixtures. Sampled with a conical orifice into a TOF mass spectrometer. Gay, Kistiakowsky, Michael, and Niki 1965.	20 μs resolution, $k=1/2k_{exp}$ taken.
1.99×10^{-16} 3.64×10^{-16} 1.50×10^{-15} 1.50×10^{-15} 1.54×10^{-15} 1.18×10^{-15} 3.64×10^{-15} 3.77×10^{-15} 5.18×10^{-15} 5.86×10^{-15} 7.45×10^{-15}	Ne	1820 1935 2015 2150 2170 2205 2350 2370 2420 2550 2600	$\sim0.3/1.8\times10^{-6}$	Shock tube study of the reflected wave in 0.3–0.9 percent N_2O/Ne mixtures. Sampled by TOF mass spectrometer. Garnett, Kistiakowsky, and O'Grady 1969.	16–20 μs time resolution. $[O]\propto t$ for <2000 K during the observed time period (400 μs). $k=1/2k_{exp}$ taken.

2nd order rate constant—Continued

Rate constant k (cm^3 molecule^{-1} s^{-1})	M	Exp. temp. (K)	Pressure/ Concentration (atm/mol cm^{-3})	Method & reference	Comments
$3.0\times10^{-11}\exp(-41{,}000/RT)$	Ne	1600–2100	$\sim0.3/2\times10^{-6}$	Shock tube study of the reflected wave in ~1 percent N_2O/Ne mixtures containing small amounts of SO_2 and O_2. Sampled by TOF mass spectrometer. Clark, Garnett, and Kistiakowsky 1970.	Rate constant refers to initial reaction. N_2O used as the source of O atoms in a study of the $^{18}O+S^{16}O_2$ reaction. $[O]\propto t$ during the observed time period (400 μs).
$1.2\times10^{-11}\exp(-40{,}700/RT)$	Kr	1780–2790	$0.2\text{–}0.4/(1.4-1.8)\times10^{-6}$	Shock tube study of the reflected shock wave in 2.1 percent N_2O/Kr mixtures. Sampled via orifice on the end plate into a TOF mass spectrometer. Analyzed for N_2O, O_2, NO, and N_2. Data fit to numerical solutions of the kinetic rate expressions. Barton and Dove 1969.	$k=(0.55-0.6)\,k_{exp}$ established for various experiments using Fenimore and Jones' (1962) value for k_{O+N_2O}. 20 μs time resolution.
$4.7\times10^{-9}\exp(-59{,}400/RT)$	N_2O	841–1052	$\sim0.02\text{–}0.08/(0.25-1)\times10^{-6}$	Reanalysis and synopsis of five earlier studies by Nagasako and Volmer (1930), Volmer and Froehlich (1932a), Musgrave and Hinshelwood (1932), Hunter (1934), Lewis and Hinshelwood (1938), of the thermal dissociation of pure N_2O in static systems. The reaction was followed by measuring the pressure change resulting from the dissociation process. Data corrected for a 1st order contribution in the low pressure region assumed to result from a heterogeneous reaction. Johnston 1951.	$k=1/2k_{exp}$ taken. Bimolecular region $<1\times10^{-6}$ mol cm^{-3} at 888 K(~55 torr) $E\sim60$ kcal mol^{-1} for concentrations up to 5×10^{-4} mol cm^{-3}. A particularly high value for the preexponential factor.
1.27×10^{-21} 9.94×10^{-22} 7.21×10^{-22} 4.50×10^{-22} 3.27×10^{-22} 2.81×10^{-22} 2.57×10^{-22} 2.42×10^{-22} 2.12×10^{-22}	N_2O	993	$0.013/1.6\times10^{-7}$ $0.026/3.2\times10^{-7}$ $0.053/6.5\times10^{-7}$ $0.13/1.6\times10^{-6}$ $0.26/3.2\times10^{-6}$ $0.39/4.8\times10^{-6}$ $0.53/6.5\times10^{-6}$ $0.66/8.1\times10^{-6}$ $1.31/1.6\times10^{-5}$	Thermal dissociation of 10–1000 torr N_2O in several reactions vessels. The reaction followed by monitoring the increase in pressure in the system. Lindars and Hinshelwood 1955.	Rate constants converted to 2nd order. $k=1/2k_{exp}$ taken. Do not appear to be true bimolecular rate constants although they are in the low pressure region. Shown to be homogeneous.

2nd order rate constant—Continued

Rate constant k (cm^3 molecule^{-1} s^{-1})	M	Exp. temp. (K)	Pressure/ Concentration (atm/mol cm^{-3})	Method & reference	Comments
$k_{O_2}:k_{N_2}:k_{CO_2}:k_{He}:k_{N_2O}=$ 0.21:0.26:1.2:1.0:1.0		913	~1.5/~2×10^{-5}(O$_2$) 0.5–1.4/(0.7–1.9) ×10^{-5} (N$_2$) 0.8–1.0/(1.1–1.4)× 10^{-5} (CO$_2$) 0.03–1.2/(0.04–1.6)× 10^{-5} (He) 0.1–1.2/(0.14–1.6)× 10^{-5} (N_2O)	Thermal dissociation of N_2O/M gas mixtures in a 0.7 liter quartz vessel. N_2O condensed out and its concentration measured after reaction times of 10–30 min. Nagasako 1931. Volmer and Kummerow 1930.	Gas mixtures studied: 1 N_2O:8–33 O_2 :2.4–13 N_2 :1–20 CO_2 :0.7–4 He
$k_{O_2}:k_{He}:k_{Ar}:k_{N_2O}=$ 0.21:1.0:0.1:1.0		895–953	0.1–1.4/(0.14–1.8)× 10^{-5} (O$_2$) 0.01–1.3/(0.01–1.7) ×10^{-5} (He) 0.01–1.5/(0.01–1.9) ×10^{-5} (Ar)	Thermal dissociation of N_2O/M mixtures in 0.7 liter quartz vessel. N_2O condensed out and its concentration measured after reaction times of 12–34 min. Volmer and Froehlich 1932b.	Gas mixtures studied: 1 N_2O:10 O_2 :0.7–12 He :0.7–10 Ar
$k_{Ne}:k_{Ar}:k_{Kr}:k_{Xe}:k_{N_2O}=$ 0.44:0.183:0.236:0.147:1.0		926	0.2–0.8/(0.3–1.1)× 10^{-5} (Ne) 0.3–1.2/(0.4–1.5)× 10^{-5} (Ar) 0.2–0.5/(0.2–0.6)× 10^{-5} (Kr) 0.2–1.1/(0.3–1.4)× 10^{-5} (Xe)	Thermal dissociation of about 33 percent N_2O/M mixtures. N_2O condensed out and its concentration measured after a certain reaction time. Volmer and Bogdan 1933.	
$k_{He}>k_{N_2,O_2}>k_{Ar}$		937	0.33/4.3×10^{-6}	Thermal decomposition of 50 torr N_2O/200 torr M mixtures in 0.5 liter quartz vessel. Initial rates of N_2O decomposition measured from the increase in pressure. Kaufman, Gerri, and Bowman 1956.	Initial rates of decomposition 50 torr N_2O/200 torr M: M $-d[N_2O]/dt$ mm/min — 1.07 He 1.72 Ar 1.09 N$_2$ 1.21 O$_2$ 1.22
$k_{CO_2}:k_{CF_4}:k_{SO_2}:k_{N_2O}=$ 0.46:0.85:0.59:1.0		925–1020	~0.06–0.26/(0.8–3.3)×10^{-6}	Homogeneous thermal dissociation studied in a 240 cm^3 silica vessel. 50, 100 torr N_2O in the presence of various third bodies. Initial rate of decomposition measured either by following the resulting pressure change or by analysis of the mixture after a certain reaction time using condensation-separation techniques. Bell, Robinson, and Trenwith 1957.	The rate of dissociation is fit to the empirical relationship $-d[N_2O]/dt=k'[N_2O]^{1.55}+k''[N_2O]^{0.55}[X]$ where X represents a particular third body other than N_2O.
$k_{He}:k_{Ne}:k_{Ar}:k_{Kr}:k_{Xe}:k_{N_2O}=$ 0.488:0.261:0.149: 0.079:0.176:1.0		981	~0.13–0.39/(1.6–4.9)×10^{-6}		

1st order rate constant

Rate constant k_∞ (s^{-1})	k_∞ 1000 K	Exp. temp. (K)	Pressure/ concentration (atm/mol cm^{-3})	Method & reference	Comments
$1.38\times10^{11}\exp(-59{,}500/RT)$	1.37×10^{-2}	1410–2080	115–300/ $10^{-3}-2\times10^{-3}$	Shock tube study of 0.02–0.2 percent N_2O/Ar mixtures. [N_2O] followed by IR emission at 4.5μ. Both incident and reflected shock waves investigated. Olschewski, Troe, and Wagner 1965, 1966.	M=Ar High pressure region $>10^{-3}$ mol cm^{-3}. (140 atm). Unimolecular kinetics. k taken as $\frac{1}{2}k_{exp}$.
$2.31\times10^{11}\exp(-60{,}600/RT)$	1.32×10^{-2}	840–930	40/$\sim5\times10^{-4}$	Reanalysis of an earlier study by Hunter (1934) of the thermal dissociation of pure N_2O in a high pressure static system. The reaction was monitored by measuring the resulting pressure change. Johnston 1951.	A levelling off of the 1st order rate constant was noted at this high pressure. k—$\frac{1}{2}k_{exp}$ taken. M=N_2O

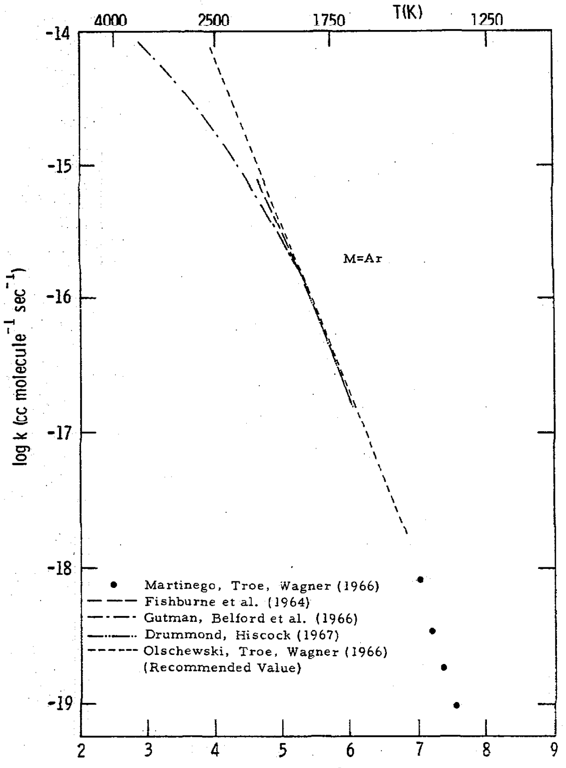

FIGURE 2. Experimental values of $k_{N_2O+Ar\rightarrow N_2+O+Ar}$.

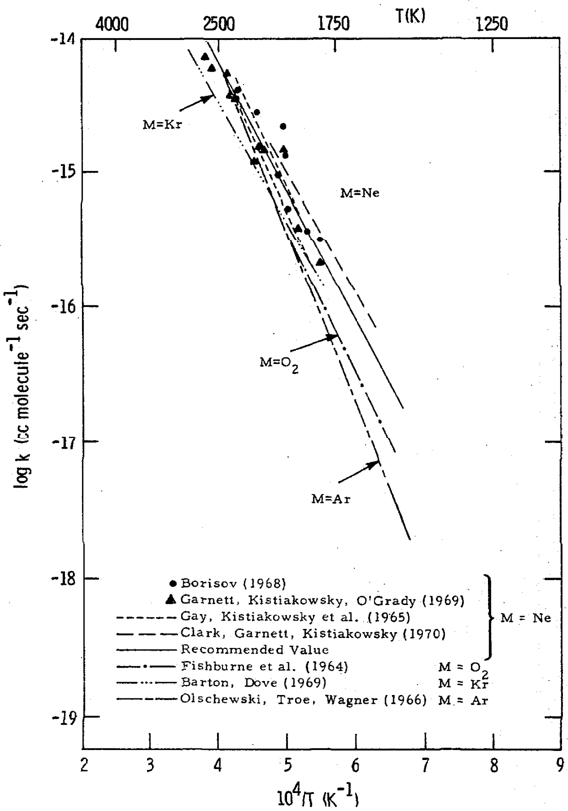

FIGURE 3. Experimental values of k_{N_2O+M}, M=Ne, Kr, and O_2, together with the recommended values for k_{N_2O+Ar}.

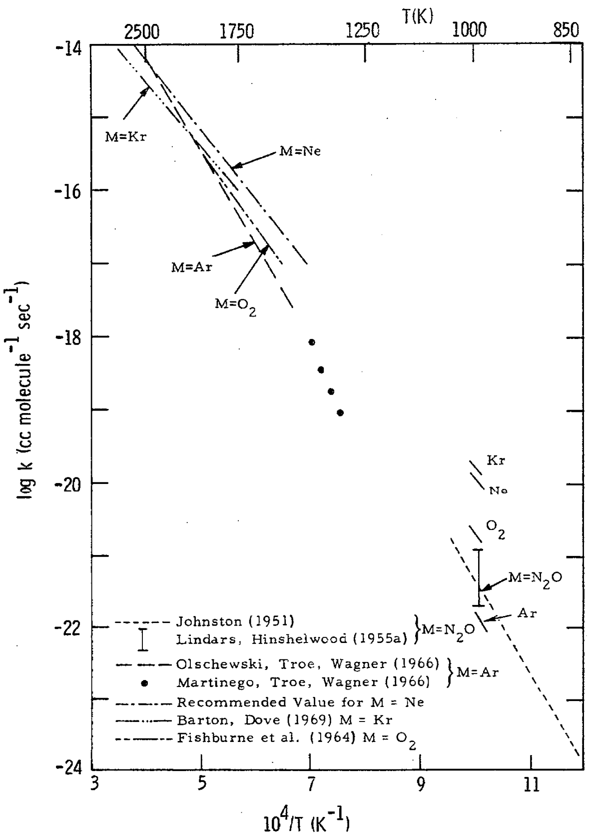

FIGURE 4. Comparison of high and lower temperature values for k_{N_2O+M}.

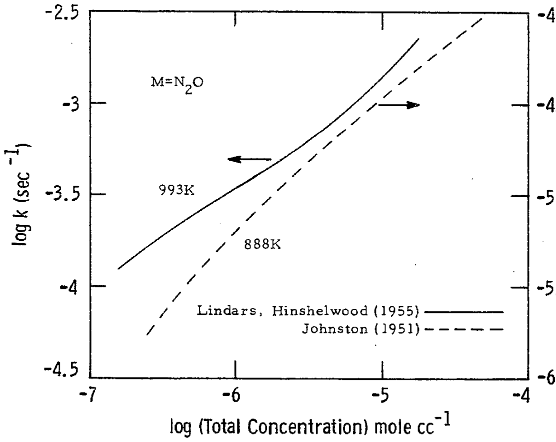

FIGURE 6. Low temperature 1st order experimental data for k_{N_2O} in the intermediate concentration/pressure region.

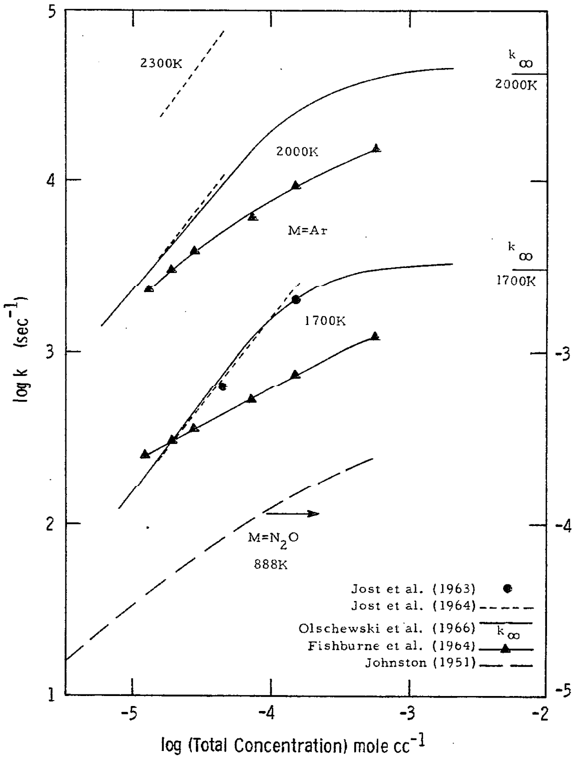

FIGURE 5. 1st order data for k_{N_2O+M} in the intermediate concentration/pressure region.

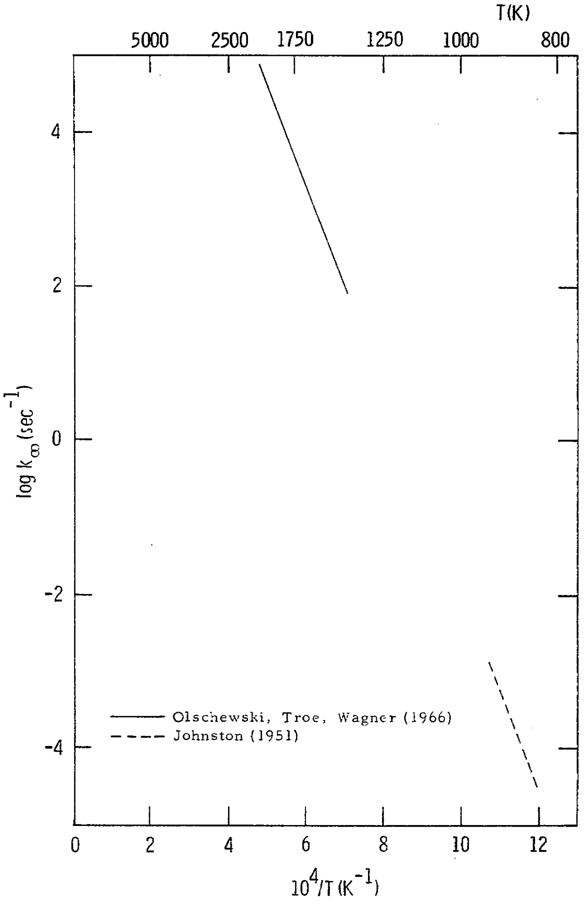

FIGURE 7. 1st order values for k_{N_2O+M} from high concentration/pressure studies.

at temperatures between 850–1050 and 1350–3400 K. Experimentally measured rate constants refer to the rate of disappearance of N_2O and are reported as 1st or 2nd order constants.

$$-d[N_2O]/dt=k_{exp}[N_2O][M] \quad \text{2nd order,}$$
$$=k_{exp}[N_2O] \quad \text{1st order.}$$

One complication of the dissociation results from the subsequent reactions (2) and (3) which immediately follow the primary dissociation process, reaction (1):

$$(1) \quad N_2O+M \xrightarrow{k_1} N_2+O+M \qquad \Delta H^\circ_{298\,K}=39.9 \text{ kcal mol}^{-1}$$
$$(2) \quad O+N_2O \xrightarrow{k_2} N_2+O_2 \qquad =-79.2$$
$$(3) \quad O+N_2O \xrightarrow{k_3} NO+NO \qquad =-36.0$$

Owing to this possible loss of a second N_2O molecule, the measured rate at low concentrations refers either to $2k_1$ or k_1 according to whether the consecutive reactions are sufficiently fast or not to establish a steady state concentration of atomic oxygen before the observation period. This problem is aggravated by an uncertainty in the values of k_2 and k_3 [Baulch, et al., 1969]. Olschewski, Troe, and Wagner (1966), in a shock tube study, report that at 2000 K and above, with a very dilute mixture of 0.02 percent N_2O in argon that k_{exp} was a factor of two lower than its value for mixtures of 0.1 percent N_2O/Ar and larger. It is possible that they observed k_1 directly at this very low mixture strength. Barton and Dove (1969) derived numerical solutions to the kinetic rate expressions for their shock tube experiments with N_2O/Kr mixtures. Fenimore and Jones' (1962) values for k_{O+N_2O} were more consistent with their data than those of Fishburne and Edse (1966). k_1 was found to be about (0.55-0.6) k_{exp} for their temperature range 1780–2790 K. Borisov (1968) obtained approximate analytical solutions to the non-linear differential kinetic equations describing the N_2O/Ne dissociation. Using shock tube TOF mass spectrometric techniques to monitor $[N_2]$ $[O_2]$, [NO], and $[N_2O]$ he derived values for k_1, k_2, and k_3. The values for the latter two lie between those of Fenimore and Jones (1962) and Fishburne and Edse (1966), [Baulch et al., 1969]. Gutman et al. (1966) also have reported that below 2500 K it appears that a steady state O atom concentration is rapidly established. However, Clark, Garnett, and Kistiakowsky (1970) and Garnett, Kistiakowsky, and O'Grady (1969) have calculated that the O atom concentration for N_2O/Ne mixtures at ≤ 2100 K can be described as a linear function of time, indicating insufficient time (~ 400 μs) for it to equilibrate. At lower temperatures the formation of NO is evidence for some contribution from reaction (3). Kaufman, Gerri, and Bowman (1956) found large amounts of NO formed in the initial stages of the dissociation. Up to about 60 percent of the dissociating N_2O produced NO at 876–1031 K (10–760 torr N_2O, $1.5\times10^{-7}-1.3\times10^{-5}$mol cm^{-3}). Consequently the contribution from reactions (2) and (3) appears to be of some importance at all temperatures. Unless derived directly from analytical solutions of the rate expressions it has been assumed throughout this evaluation that the rate of disappearance of N_2O is doubled as a result of these secondary reactions.

A second complicating feature that has been discussed occasionally and was studied in detail by Drummond and Hiscock (1967) pertains to shock tube studies of systems where the released enthalpy affects the shock wave parameters. Owing to the enthalpy changes in reactions (1) to (3) the overall reaction will be either endo- or exothermic according to the relative contributions of (2) and (3). Drummond and Hiscock (1967) discuss the difficulty in establishing the exact shock speed and temperature in a reacting system where the enthalpy changes are not negligible. In order to minimize the problem they recommended that observations be made as close to the reflecting end plate as possible so that the speed and temperature differ little from frozen equilibrium values. The fact that measurements at 14 mm and 75 mm from the end plate agreed for their relatively N_2O rich mixtures (6% N_2O/Ar) tends to confirm Barton and Dove's calculation (1969) that the overall enthalpy change for the reaction is small. Jost, et al. (1963, 1964) and Olschewski, et al. (1966) collected their data 10 cm and 2.5 cm upstream from the end plate, respectively, and the data appeared not to have suffered from thermal effects at these positions. They also used dilute mixtures. The very good agreement between the 2nd order data of Olschewski, et al. (1966), Fishburne, et al. (1964), and Drummond and Hiscock (1967) for M=Ar, figure 2, suggests that the data are not degraded by any such thermal problems.

The dissociation is a unimolecular process but the reaction kinetics appear quite complex. If the rate of dissociation is expressed in terms of a 1st order rate constant it varies with pressure according to an expression of the type:

$$k(\mathrm{s}^{-1})=\sum_i \frac{A_i[M]}{1+B_i[M]}.$$

To account for the changes in $k(\mathrm{s}^{-1})$ over the full pressure range studied at least three separate terms have to be included. A simplistic scheme to illustrate such a general form is:

$$N_2O+M \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} N_2O^*+M \qquad K=k_4/k_{-4},$$
$$N_2O^* \xrightarrow{k_5} N_2+O,$$
$$O+N_2O \xrightarrow{k_6} 2NO \text{ or } N_2+O_2.$$

Making the usual steady state assumptions, this predicts a rate of dissociation given by

$$\frac{-d[N_2O]}{dt}=\frac{2k_4[N_2O]\,[M]}{(1+k_{-4}[M]/k_5)}$$

so that at low concentrations the rate tends to $2k_4$ $[N_2O]$ $[M]$ and at the high concentration limit a 1st order expression $2Kk_5[N_2O]$. However, this scheme oversimplifies the decomposition since an allowance for its forbidden nature must be considered. Friedman and Bigeleisen (1953) removed any doubts as to the dissociation products by showing that no N atoms were formed in the initial bond rupturing. Consequently two overall processes are possible

$$N_2O(^1\Sigma)\rightarrow N_2(^1\Sigma)+O(^3P)\Delta H^0_{298K}=-39.9\text{ kcal mol}^{-1},$$
$$\rightarrow N_2(^1\Sigma)+O(^1D)\qquad =-85.3.$$

The former, although spin forbidden, now is generally accepted as the process. The mechanism depends on a transition from the N_2O $(^1\Sigma)$ ground electronic state to either one of the $^3\Pi$ or $^3\Sigma$ repulsive excited states which correlate to the observed dissociation products [Reuben and Linnett, 1959; Gill and Laidler, 1958]. A scheme involving the energization of N_2O, its transformation to these triplet states followed by their decomposition appears to fit the observed features of the dissociation [Reuben and Linnett, 1959]. It also suggests that since the cross-over point lies above the heat of dissociation of N_2O, that the dissociation products, particularly the O-atom, initially will contain a large fraction of the excess energy. However, no evidence for the presence of such "hot" O atoms has been reported.

Low Pressures—2nd Order Data

M—Argon

The data of five independent studies have been plotted in figure 2. The values of Jost, et al. (1963, 1964) and Olschewski, Troe, and Wagner (1966) are in very close agreement differing at the most by 25 percent over the temperature ranges studied. Because of this only their later data have been plotted [Olschewski, et al., 1966]. This refers also to lower total concentrations where the kinetics are bimolecular. The data of Fishburne, et al. (1964) shows a larger sensitivity to concentration and as seen in the 1st order plot, figure 5, has a more pronounced fall-off. Their five expressions lie almost parallel to one another when plotted as a function of T^{-1}. Values for k cm^3 molecule^{-1} s^{-1} gradually decrease with increasing total concentration. Their lowest concentration data has been taken. The values of Martinego, Troe, and Wagner (1966) appear too low at their lower temperatures. Drummond and Hiscock's data (1967) is in excellent agreement with that of Olschewski, et al. (1966) and Fishburne, et al. (1964). The higher temperature values of Gutman, et al. (1966) appear questionable.

Because of the observed agreement and since their data refers to very dilute mixtures of N_2O/Ar the values of Olschewski, et al. (1966) are recommended for M=Ar. However, values around 2500 K require confirmation. Earlier data by Modica (1965) and Bradley and Kistiakowsky (1961) have not been included since they constituted an evaluation and development of the shock tube-TOF mass spectrometer technique rather than a source of reliable values for k_{Ar}.

M=Neon

The data of Borisov (1968), Gay, Kistiakowsky, et al. (1965), Garnett, Kistiakowsky, et al. (1969), and Clark, Garnett, and Kistiakowsky (1970) are in good agreement as illustrated in figure 3. A line best fitting the four corresponds to a value

$$k_{Ne}=4.1_6\times10^{-11}\ \exp\ (-43{,}600/RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

This is considered accurate to within about 50 percent in the temperature range 1500–2600 K, and the activation energy should be within ±4 kcal mol^{-1}. Only the concentration range $\leq 6\times10^{-6}$ mol cm^{-3} has been studied with neon. Clark, Garnett, and Kistiakowsky (1970) used N_2O as a source of O atoms to study the $^{18}O+S^{16}O_2$ exchange reaction. Olschewski, Troe, and Wagner's value for k_{Ar} (1966) was not compatible with their observations and a much lower value for the activation energy of k_{Ne} was clearly evident.

Other Third Bodies

Values are reported also for k_{O_2}, k_{Kr}, and k_{N_2O}. The lower concentration data of Fishburne, et al. (1964) for $M=O_2$, values for k_{Kr} [Barton and Dove, 1969] and the lower temperature studies of k_{N_2O} have been plotted in figures 3 and 4. The activation energy of the dissociation in the low concentration region appears to increase from Kr (40.7 kcal mol^{-1}) to Ne (43.6), O_2 (48.2), Ar (58), and N_2O (59.4). Although these values may be in error to various extents the differences appear definitely significant.

Additional data for M=Kr and O_2 are required. Johnston's values for $M=N_2O$ (1951) are probably reliable to within a factor of 2–3. The pre-exponential in their expression seems particularly high. Bell, Robinson, and Trenwith (1957) studied the effects of differing third bodies in a static system at 925–1025 K and with low concentrations. They noted that the activation energies for $M=CO_2$ or CF_4 were greater by about 3 kcal mol^{-1} than for $M=N_2O$. Although in the 2000–2500 K region the rates for various third bodies (Ne, Ar, Kr, O_2) do not differ by more than about a factor of two, at low temperatures the effects appear more pronounced. The available data, illustrated in table 2, shows discrepancies particularly for He, Kr, and CO_2.

Table 2. Relative efficiencies of differing third bodies

M	He	Ne	Ar	Kr	Xe	O_2	N_2	CO_2	N_2O	CF_4	SO_2
Volmer & Kummerow (1930); Nagasako (1931)	*1. 0	-------	-------	-------	-------	*0. 21	*0. 26	*1. 2	*1. 0	-------	-------
Volmer & Froehlich (1932b)	1. 0	-------	0. 1	-------	-------	0. 21	-------	-------	1. 0	-------	-------
Volmer & Bogdan (1933)	-------	*0. 44	*0. 18	*0. 24	*0. 15	-------	-------	-------	1. 0	-------	-------
Bell, et al. (1957)	0. 49	0. 26	0. 15	0. 08	0. 18	-------	-------	0. 46	1. 0	*0. 85	*0. 59
Kaufman, et al. (1956)	$k_{He} > k_{N_2, O_2} > k_{Ar}$										

T=895–1020 K.
*Preferred values.

At 1900 K, Fishburne, et al. (1964) report $k_{O_2} = 1.4\ k_{Ar}$, not too different from the ratio at lower temperatures. The fact that $k_{Kr} > k_{Ar}$ (2000 K) makes Volmer and Bogdan's (1933) higher value more appealing. Extrapolation of the high temperature rate constants down to 1000 K, figure 4, does not reflect the established third body effects at that temperature with the one exception of argon.

Intermediate Pressures—Fall-Off Region

The available data in this region are expressed in 1st order form and shown in figure 5 as a function of the total concentration. The trend from 2nd to 1st order kinetics is clearly defined. The data of Jost, et al. (1963, 1964) appears bimolecular. Olschewski, et al. (1965, 1966) extended the studies of 0.1 percent N_2O/Ar mixtures to higher pressures (1–340 atm) and also obtained values for k_∞ which are shown for the two temperatures 1700 and 2000 K.

The data of Fishburne, et al. (1964) appear questionable since they do not tend to a 2nd order dependence at lower concentrations and values seem to be low. Johnston's analysis (1951) involved correcting the older data for what was interpreted as a heterogeneous contribution. His reported values have also been plotted in figure 6 with those of Lindars and Hinshelwood (1955). The latter established that the reaction was homogeneous and that the variation of the 1st order rate constant at low concentrations was a definite feature of the N_2O dissociation. Consesequently there are certain doubts as to the validity of Johnston's corrections and whether at low concentrations, $<3\times10^{-6}$ mol cm^{-3} ($<$200 torr at 1000 K) the kinetics do approximate to a 2nd order dependence.

At present the data of Olschewski, et al. (1965, 1966) and Johnston (1951) are preferred in this intermediate region.

High Pressures—1st Order Data

Olschewski, et al. (1965, 1966) have obtained what appears to be reliable data up to 300 atm (2×10^{-3} mol cm^{-3}). The only other high pressure study was by Hunter (1934) at 40 atm pressure (5×10^{-4} mol cm^{-3}), later reanalyzed by Johnston (1951). This borders on the fall-off region and consequently values are expected to be slightly low. The agreement between the two sets of data acquired for different temperature regimes is extremely good as seen in figure 7 and suggests that some reliability can be placed on the values given by Olschewski, et al. (1965, 1966). Their values are recommended for the 800–2100 K range with a suggested uncertainty of ±50 percent. k_∞ should of course be independent of the nature of M. The low pre-exponential factor is considered a reflexion of the forbidden nature of the dissociation process.

Olschewski, et al. (1965) studied the N_2O dissociation over a wide range of concentrations and reported no significant change in the activation energy (M= Ar) from 1.4×10^{-5} to 1.9×10^{-3} mol cm^{-3}. Although Fishburne, et al. (1964) did find a sensitivity to concentrations their data are questionable for various reasons. Consequently we see that the activation energies for k_{N_2O}, k_{Ar}, and k_∞ are all about 58–59.5 kcal mol^{-1} while those for k_{O_2}, k_{Ne}, and k_{Kr} appear significantly lower.

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4.5. $O+N_2+M\rightarrow N_2O+M$

Thermodynamic Data and Equilibrium Constant

Listed under the reverse dissociation reaction.

Recommended Rate Constant

The reaction appears to be slow as may be expected. It is not possible to recommend a rate because of insufficient data.

Discussion

$$(1)\qquad O(^3P)+N_2(^1\Sigma)+M\rightarrow N_2O(^1\Sigma)+M,$$
$$(2)\qquad O(^1D)+N_2(^1\Sigma)+M\rightarrow N_2O(^1\Sigma)+M.$$

The ground electronic state of N_2O correlates to O (^1D) and so based on spin correlation considerations reaction (1) is forbidden and (2) allowed. In Harteck and Dondes' experiment (1954, 1957) only a trace of N_2O was detected, corresponding to about a 10^{-4} conversion of O_3 to N_2O. At the low temperature used, the approximate value that can be derived from their results refers to reaction (1). Recently, Stuhl and Niki (1971) also were able to place an upper limit on the room temperature value for $k_{O+N_2+N_2}$. Their value confirms the earlier estimate. Since the reverse reaction, the dissociation of N_2O has an activation energy in excess of the enthalpy change, the slowness of reaction (1) is not unexpected.

Groth and Schierholz (1957) photolysed a mixture of 7 torr O_2 and 419 torr N_2 at room temperature with 1295 and 1470 Å radiation. About 10^{-3} to 10^{-4} of the O atoms formed were converted to N_2O. The O(^1D) formed at these wavelengths either reacts

Reported rate constants

Rate constant k (cm ^{6} molecule^{-2} s^{-1})	Exp. temp. (K)	Method & reference	Comments
$\sim 5\times 10^{-38}$	568	A mixture at atm pressure of N_2 and O_2 containing 5 percent O_3 heated at 568 K. Only a trace of N_2O detected ($\sim 2\times 10^{-3}$ torr). Harteck 1957. Harteck and Dondes 1954.	
$\leq 5\times 10^{-38}$ $M=N_2$	300	O atoms generated by pulsed (2 μs half width) vacuum uv photolysis of 1 torr CO_2/19 torr CO/0–345 torr N_2 mixtures. [O] monitored by CO_2 chemiluminescence at 4000 Å (80 Å half bandwidth) filter. [O] $10^{10}-2\times 10^{12}$ atoms cm^{-3}. Measurements delayed 100–1000 μs after the pulse. Reaction followed for up to a few tenths of a second. Stuhl and Niki 1971.	The negligible contribution from this reaction permits an upper limit estimate. Singlet O atom states produced initially are quenched in the delay period before data acquisition.

to produce N_2O or is lost by predominant collisional quenching, reaction (3)

$$(3)\quad O(^1D)+M=O(^3P)+M \qquad k_{O_2,N_2}\sim 6\times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

[Noxon, 1970; Gilpin, et al., 1971; Biedenkapp and Bair, 1970].

From their results, k_2 can be estimated by setting the relative rates of reaction and quenching equal to the observed factor.

$$\frac{k_2[O^1D]\,[N_2][M]}{k_3[O^1D]\,[M]}=\frac{1}{10^4}.$$

This gives a value for k_2 of about 4×10^{-34} cm^6 molecule^{-2} s^{-1}.

Simonaitis et al. (1972) find no evidence for N_2O formation on photolyzing 6–12 torr O_3 at 2537Å for 12–24 hours with 42–115 torr O_2 and 870–900 torr N_2. They estimate an upper limit $k_2[M]/k_3<2.5\times 10^{-6}$ which infers a value for $k_2<5\times 10^{-36}$, two orders of magnitude lower than the estimate had from Groth and Schierholz's work.

Any contribution from reaction (2) will always be overshadowed by the rapid quenching. It could only become important at extremely high pressures. The dominance of the quenching reaction was also noted by DeMore and Raper (1962, 1963) studying the interaction of $O(^1D)$ and N_2 in the liquid phase. They photolyzed a solution of O_3 in liquid N_2 at several wavelengths (2480–3340 Å) and liquid O_2/N_2 mixtures (1849, 2537 Å). The spin forbidden quenching of $O(^1D)$ to $O(^3P)$ by N_2 was about 75 times faster than the formation of N_2O and had a zero or low activation energy. The low efficiency of N_2O formation results from a feature of the potential energy surfaces which allow the vibrationally excited N_2O intermediate to predissociate predominantly. The transition probability for a cross over between the vibrationally excited $^1\Sigma$ state and the $^3\Pi$ or $^3\Sigma$ repulsive states of N_2O must be relatively high.

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4.6. $N_2O_4+M\rightleftarrows NO_2+NO_2+M$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10} K_p$ atm	$\log_{10} K_c$ molecule cm^{-3}
0	12. 699	—	—	—
100	13. 333	39. 636	−20. 474	−0. 608
200	13. 635	41. 871	−5. 747	13. 818
298	13. 650	41. 962	−0. 835	18. 556
300	13. 649	41. 958	−0. 773	18. 615
400	13. 505	41. 550	1. 702	20. 966
500	13. 274	41. 040	3. 167	22. 334

Equilibrium Constant

$$K_p=1.08\times10^{13}\,T^{-1.304}\exp(-14{,}520/RT)\text{ atm}\quad(300\text{–}900\text{ K range}).$$

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.0 percent in this temperature range.

Recommended Rate Constant

The rate and rate constant are defined by

$$-d[N_2O_4]/dt=0.5\,d[NO_2]/dt=k[N_2O_4][M]\quad\text{2nd order,}$$
$$=k_\infty[N_2O_4]\quad\text{1st order.}$$

At high concentrations $>4\times10^{-4}$ mol cm^{-3} (10 atm, 298 K) no data yet are available for this pressure region where the decomposition tends to unimolecular kinetics. Only approximate assessments of k_∞ have been made.

Intermediate concentrations $(0.5\text{–}4)\times10^{-4}$ mol cm^{-3} (1–10 atm, 298 K). The plotted data of Carrington and Davidson (1953) are the only available information. They are probably reliable to ±50 percent considering the accuracy of their lower concentration studies.

Low concentrations $<5\times10^{-5}$ mol cm^{-3} (1 atm, 298 K) the kinetics are 2nd order. $k_{N_2}=3.3\times10^{-7}$

1st order rate constant

Rate constant k (s^{-1})	Exp. temp. (K)	Pressure/concentration (atm/mol cm^{-3})	Method & reference	Comments
7.8×10^4	303	$0.45/1.8\times10^{-5}$	Velocity of sound in N_2O_4, measured using a tube type CW sonic interferometer (9–451 kc s^{-1}, 132–668 torr pressure). Richards and Reid 1933a.	Noted that the 1st order rate constant was a function of pressure. Original values have been increased by 9 percent, Richards and Reid 1933b.
6.9×10^4	303	$0.34/1.4\times10^{-5}$		
5.3×10^4	303	$0.31/1.2\times10^{-5}$		
6.6×10^4	298	$0.88/3.6\times10^{-5}$		
5.3×10^4	298	$0.34/1.4\times10^{-5}$		
4.9×10^4	298	$0.21/8.7\times10^{-6}$		
2.8×10^4	288	$0.34/1.4\times10^{-5}$		
6.9×10^3	274	$0.34/1.5\times10^{-5}$		
4.6×10^3	274	$0.20/9.1\times10^{-6}$		
3.7×10^3	274	$0.17/7.7\times10^{-6}$		
$k_\infty=3\times10^{16}\exp(-13{,}650/RT)$ $=3\times10^6$ (298 K) Values at intermediate pressures are plotted in figure 8.	253–301	$0.8\text{–}6.6/3.2\times10^{-5}-2.7\times10^{-4}$ (N_2) $1.4\text{–}8.4/6.3\times10^{-5}-3.8\times10^{-4}$ (CO_2)	Weak shock waves through 1 percent N_2O_4 in N_2 or CO_2. $[NO_2]$ monitored by 4358Å absorption. N_2O_4 absorption at 2537Å in agreement. The lower limit of k_∞ calculated by the method of Johnston (1952) using data near the low concentration limit. Carrington and Davidson 1953.	This lower limit value of k_∞ was increased by a factor of 3, the justification for which is questionable. Consequently, this is only a very approximate value. The activation energy taken as the dissociation energy at 298 K. Results for CO_2 and N_2 in agreement.
1.7×10^5	293	$1/4.2\times10^{-5}$	Sound absorption measurements at 1–200 torr (20–500 kc s^{-1} frequency). Sessler 1960.	Extrapolated to 1 atm pressure.
8.4×10^5	326	$1/3.7\times10^{-5}$		
$k_\infty=1.7\times10^5$	298	$0.17\text{–}1.1/6.9\times10^{-6}-4.5\times10^{-5}$	Sound absorption measurements with pulsed waves at frequencies of 78–394 kc s^{-1}. Mixtures of N_2O_4/NO_2 alone and with N_2, Ar, or CO_2. Cher 1962.	Values for k_∞ are only very approximate and are obtained by extrapolation to infinite pressure. *This value was derived using Johnston's method (1952) for estimating k_∞.
2.4	303	$0.11\text{–}0.69/4.6\times10^{-6}-2.8\times10^{-5}$		
4.2	308	$0.12\text{–}0.69/4.6\times10^{-6}-2.7\times10^{-5}$		
5.3	313.5	$0.17\text{–}0.69/6.8\times10^{-6}-2.7\times10^{-5}$		
3×10^5*	298	$0.17\text{–}1.1/6.9\times10^{-6}-4.5\times10^{-5}$		
2.29×10^5	303	$1/4\times10^{-5}$	Velocity of acoustic waves in N_2O_4, using a pulsed technique, measured as a function of frequency (1–100 kc s^{-1}) and pressure (10–325 torr). Blend 1970.	Experimental result extrapolated to 1 atm pressure.

2nd order rate constant

Rate constant k (cm ^{3} molecule^{-1} s^{-1})	M	Exp. temp. (K)	Method & reference	Comments
7.1×10^{-15} 8.3×10^{-15} 7.1×10^{-15} 3.0×10^{-15} 6.3×10^{-15} 9.3×10^{-15} 3.2×10^{-15} 7.5×10^{-16} 8.4×10^{-16} 7.9×10^{-16}	$NO_2+N_2O_4$	303 303 303 298 298 298 288 274 274 274	Velocity of sound in N_2O_4 measured using tube type CW sonic interferometer (9–451 kc s^{-1} and at 132–668 torr pressure). Richards and Reid 1933a.	Rate constants have been increased by 9 percent (Richards and Reid 1933b) and interpreted as 2nd order constants.
$3.3\times10^{-7}\exp(-11{,}000/RT)$ or $\frac{8.81\times10^{-11}T^{1/2}}{11.38}\left(\frac{12{,}700}{RT}\right)^{3.484}$ $\exp(-12{,}700/RT)$	N_2	253–301	Weak shock waves through 1 percent N_2O_4 in N_2 or CO_2. Followed by 4358 Å absorption of NO_2. N_2O_4 absorption at 2537 Å in agreement. Studied at 0.8–6.6 atm pressure (N_2) and 1.4–8.5 atm (CO_2). Carrington and Davidson 1953.	$k_{N_2}\sim k_{CO_2}$ Activation energy determined from data at around 1 atm pressure.
3.4×10^{-15} 1.9×10^{-14}	$NO_2+N_2O_4$	293 326	Sound absorption measurements at 1–200 torr and 20–500 kc s^{-1} frequency. Sessler 1960.	Interpreted in terms of a 2nd order rate constant.
7.5×10^{-15} 9.0×10^{-15} 1.04×10^{-14} 1.23×10^{-14}	$NO_2+N_2O_4$	298 303 308 313.5	Sound absorption measurements with pulsed waves at frequencies 78–394 kc s^{-1}. Mixtures of N_2O_4/NO_2 alone and with N_2, Ar, or CO_2 (0.1–1.2 atm pressures). Cher 1962.	$k_{N_2O_4}:k_{NO_2}:k_{CO_2}:k_{N_2}:k_{Ar}$ $=1.0:1.0:1.0:0.5:0.3$
$3.7\times10^{-7}\exp(-11{,}000/RT)$	Ar	280–350	NO_2 absorption at 4350 Å monitored in weak shock waves. N_2O_4 mole fraction <0.1 in Ar or N_2 at pressures <0.5 atm. Zimet 1970.	$k_{N_2}=1.3k_{Ar}$ Activation energy taken from Carrington and Davidson (1953). 2nd order kinetics assumed.
9.4×10^{-15}	$NO_2+N_2O_4$	303	Velocity of acoustic waves in N_2O_4, pulsed technique, measured as a function of frequency (1–100 kc s^{-1}) and pressure (10–325 torr). Blend 1970.	Extrapolated to 1 atm pressure. Interpreted as a 2nd order rate constant.

$\exp(-11{,}000/RT)$ cm^3 molecule^{-1} s^{-1}. Temperature range: 250–350 K. Suggested error limits: ±40 percent.

Discussion

The N_2O_4 dissociation typifies a unimolecular process that has been observed only in its low or intermediate pressure regions where the kinetics tend towards a 2nd order dependence. If the mechanism is described by the simple scheme

$$N_2O_4+M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_4^*+M,\ K_1=k_1/k_{-1};$$

$$N_2O_4^* \xrightarrow{k_2} 2NO_2,$$

the rate of decomposition is given by

$$-d[N_2O_4]/dt=\frac{k_1[N_2O_4][M]}{\left(\frac{k_{-1}}{k_2}[M]+1\right)}.$$

In the two pressure extremes, that is when the pressure tends to either zero or infinity, this reduces to the two limits

$$-d[N_2O_4]/dt=k_1[N_2O_4][M] \text{ or } K_1k_2[N_2O_4], \text{ respectively.}$$

Carrington and Davidson (1953) found that in N_2 at pressures below about 1.2 atm the dissociation was 2nd order. However, at higher pressure the rate fell below that predicted from 2nd order kinetics. No investigations yet have been carried out at a sufficiently high pressure to observe the 1st order dependence. Except for this study (1953) all others have been in the low pressure region and rates are more appropriately described by 2nd order kinetics. The experimental values were expressed invariably in 1st order form and have been plotted so in the 1st order rate constant graph, figure 8,

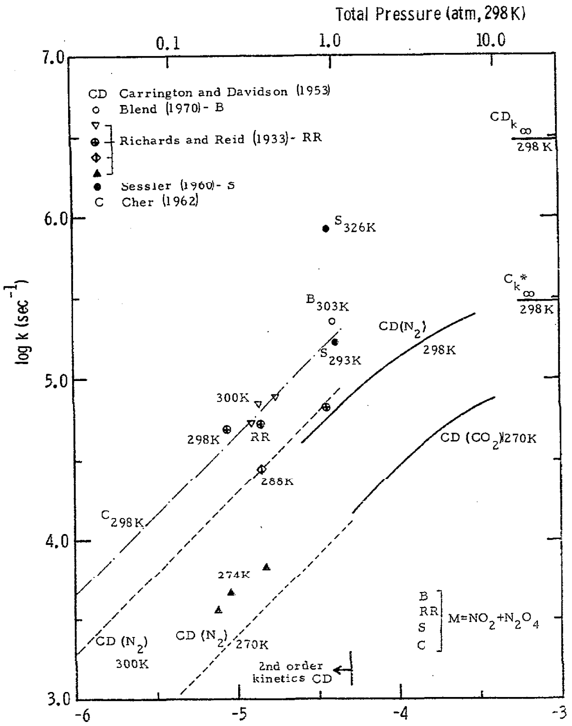

FIGURE 8. 1st order data for $k_{N_2O_4+M \rightarrow NO_2+NO_2+M}$ in the low and intermediate concentration/pressure regimes.

showing the available data. The trend towards the 2nd order dependence is quite clear.

Carrington and Davidson's data (1953) is useful for intermediate pressures. Carrington and Davidson (1953) and Cher (1962) have used the method proposed by Johnston (1952) to obtain a lower limit for the high pressure/concentration 1st order value, k_∞, from data taken in the low concentration region. However, the values for k_∞ appear to be very approximate and differ by an order of magnitude at 298 K. It may be noted that Carrington and Davidson (1953) arbitrarily increased their value by a factor of 3 so that the two estimates only differ in fact by about a factor of 3. Their justification for this was that Johnston's method had been found to underestimate k_∞ for the unimolecular decomposition of N_2O_5 and N_2O by factors of 11 and 3, respectively. Cher (1962) also obtained very approximate estimates for k_∞ by extrapolating the 1st order data to infinite pressure. This gave a value slightly less than that from Johnston's method, and does not agree with the intermediate pressure trend of the 1st order constant of Carrington and Davidson.

By setting the activation energy of the limiting 1st order rate constant equal to the dissociation energy, Carrington and Davidson have expressed their very approximate k_∞ in Arrhenius form.

No satisfactory values for k_∞ can yet be considered available.

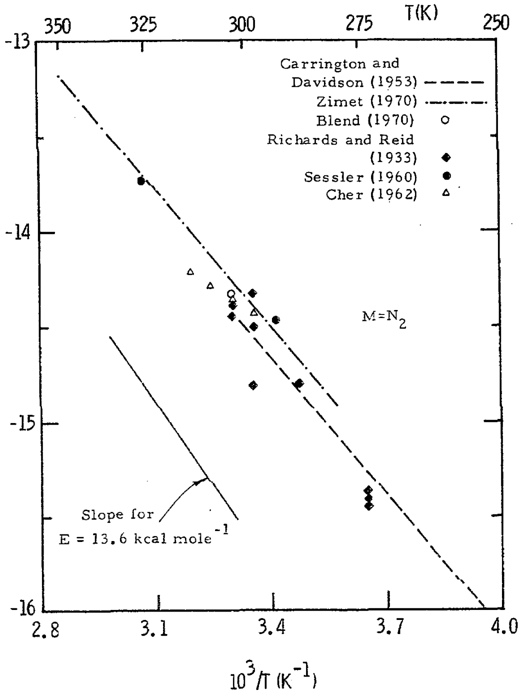

FIGURE 9. Experimental values of $k_{N_2O_4+N_2}$.

2nd Order Rate Constant

Below about 1.2 atm total pressure the rate of dissociation of N_2O_4 is described by 2nd order kinetics. Based on this, the acoustic measurements of Cher (1962), Blend (1970), Richards and Reid (1933a), and Sessler (1960) have been reinterpreted and the resulting values compared for $M=N_2$ in figure 9, assuming that

$$k_{N_2O_4}:k_{NO_2}:k_{N_2}=1.0:1.0:0.5,$$

from Cher (1962). Over the observed temperature range, 253–350 K there is reasonably good agreement among the six independent studies.

Values quoted in the work of Wegener (1958, 1959, 1960) and Bauer and Gustavson (1954) have not been considered here since these involve highly sophisticated aerodynamic flow techniques which at best can only serve to confirm the values obtained from simpler systems.

The various efficiencies of differing third bodies have been reported in several studies. Carrington and Davidson (1953) give $k_{N_2} \sim k_{CO_2}$; Zimet (1970) $k_{N_2}=1.3k_{Ar}$ and Cher (1962),

$$k_{N_2O_4}:k_{NO_2}:k_{CO_2}:k_{N_2}:k_{Ar} = 1.0:1.0:1.0:0.5:0.3,$$

which differ slightly from the others.

It appears that the activation energy is less than the dissociation energy. The data conceivably can be fit to a slope corresponding to the dissociation energy but the trend and particularly the studies of Carrington and Davidson (1953), and Richards and

Reid (1933a) suggest a lower value. This predicts a negative activation energy for the reverse recombination reaction.

Carrington and Davidson's value is recommended for the 250–350 K temperature range for pressures <1.2 atm and is considered accurate to about ±40 percent. The reaction has a very high preexponential factor.

According to the classical coupled oscillator model of a unimolecular reaction, their value for the 2nd order rate constant can be expressed in the form

$$k=\frac{1}{11.38}\,(8.81\times10^{-11}T^{1/2})\left(\frac{12{,}700}{RT}\right)^{3.48}\exp\,(-12{,}700/RT),$$

which suggests the participation of four and a half oscillators in the dissociation process. If this expression is coupled with the equilibrium constant (molecule cm^{-3} units) it predicts the following value for the recombination reaction

$$k_{\mathrm{NO_2+NO_2+M}}=1.7\times10^{-33}T^{-0.68}\ \exp\ (1820/RT)\ \mathrm{cm}^6\ \mathrm{molecule}^{-2}\mathrm{s}^{-1}.$$

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4.7. $NH_3 + M \rightarrow NH_2 + H + M$

Thermodynamic data

T K	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm	$\log_{10}K_c$ molecule cm^{-3}
0	101. 690	—	—	—
100	102. 186	22. 547	−218. 390	−198. 524
298	103. 140	27. 847	−69. 514	−50. 123
300	103. 148	27. 876	−69. 048	−49. 660
500	103. 938	29. 914	−38. 891	−19. 724
1000	105. 162	31. 680	−16. 059	2. 807
1500	105. 727	32. 154	−8. 376	10. 314
2000	105. 903	32. 257	−4. 522	14. 043
2500	105. 835	32. 230	−2. 208	16. 260
3000	105. 511	32. 112	−0. 668	17. 720
3500	104. 972	31. 947	0. 427	18. 749
4000	104. 235	31. 751	1. 245	19. 509
4500	103. 290	31. 529	1. 875	20. 087
5000	102. 134	31. 286	2. 373	20. 540
5500	100. 772	31. 026	2. 776	20. 901
6000	99. 205	30. 754	3. 108	21. 195

Equilibrium Constant

$$K_p=34.4\ T^{1.589}\exp\,(-102{,}290/RT)\ \mathrm{atm}\quad(300\text{–}1000\ \mathrm{K\ range})$$
$$=2.45\times10^6T^{0.174}\exp\,(-105{,}110/RT)\quad(1000\text{–}3000\ \mathrm{K\ range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.4 percent (300–1000 K) and 0.9 percent (1000–3000 K).

Recommended Rate Constant

$k_{\mathrm{Ar}}=7.2\times10^{-9}\exp\,(-79{,}500/RT)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1}$.

Temperature range: 1800–3200 K.

Suggested error limits: within a factor of 2.5 in this range.

$\log_{10}A=\bar{9}.86\pm0.22\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$.

$E=79{,}500\pm2000$ cals.

Discussion

The thermal decomposition of NH_3, even at temperatures as high as 1000 °C is heterogeneous [Szwarc, 1949]. Successful measurements of the homogeneous gas phase dissociation rate have been obtained only in shock tube studies in the 2000–3000 K range. Four such studies have provided data in reasonable accord, differing at the most by a factor of about 5 and all yield similar activation energies, 20–30 kcal mol^{-1} below the NH_2–H bond strength. Experimental conditions vary from pressures of 0.08 to 20 atm and in this region the 2nd order nature of the dissociation appears predominant. The $[NH_3]$ decay has been followed in both emission and absorption. Jacobs' earlier work (1960) was in error possibly because of gas contamination. His more reliable experiments (1963) differ from those of Michel and Wagner (1965) and Bradley, Butlin,

Reported rate constants

Rate constant k (cm ^{3} molecule $^{-1}$s $^{-1}$)	k_{2500K}	Exp. temp. (K)	Pressure/ concentration (atm/mol cm^{-3})	Method & reference	Comments
4.1×10^{-8} $\exp(-77{,}700/RT)$* $(4.2\text{–}12.2)\times 10^{-9}$ $\exp(-77{,}700/RT)$† M=Ar	6.7×10^{-15}* 6.7×10^{-16}† -2.0×10^{-15}	2100–3100	1–1.4/~6×10^{-6}	Shock tube study of 1 and 8 percent NH_3/Ar mixtures. [NH_3] followed in emission at 2.7–3.2μ. Jacobs 1963.	*Defined by $d[NH_3]/dt = k[NH_3]^{1.5}[Ar]^{0.5}$. †Recalculated assuming $-d[NH_3]/dt = k[NH_3]\,[Ar]$.
7.2×10^{-9} $\exp(-79{,}500/RT)$ M=Ar	8.1×10^{-16}	2100–2940	~2–20/(1.2–10.0) $\times 10^{-5}$	Shock tube study of ~0.1–1 percent NH_3/Ar mixtures. [NH_3] decay followed in absorption at 2300–2500 Å behind incident and reflected shock waves. Michel and Wagner 1965.	1st order dependence on [NH_3] and [M] observed. NH detected during the decomposition.
3.8×10^{-9} $\exp(-71{,}100/RT)$ M=Ar	2.3×10^{-15}	2480–2970	~7/~3×10^{-5}	Shock tube study of 1 percent NH_3 in Ar. [NH_3] followed in absorption at 2245 Å. Initial rate of decomposition measured. No induction period observed at these temperatures. Takeyama and Miyama 1966.	Assume 1st order dependence on [NH_3] and [Ar].
6.6×10^{-9} $\exp(-83{,}000/RT)$ M=Ar	3.7×10^{-16}	1925–2960	0.08–0.53/(4.7–20.5)$\times 10^{-7}$	Shock tube study of 5, 10, and 20 percent NH_3/Ar mixtures. [NH_3] monitored in emission at 3μ and [NH] in absorption at 3360 Å. Bradley, Butlin, and Lewis 1967.	Decomposition 1st order in [NH_3] and [Ar].

and Lewis (1967) in that the data appeared better fit to the rate expression

$$-d[NH_3]/dt=k[NH_3]^{1.5}[Ar]^{0.5}.$$

All four studies clearly refer to the same dissociation mechanism and differ only in their interpretation. As to why Jacobs observed a different dependence still is not quite clear. Mechanisms can be invoked as suggested by Bradley, et al. (1967) which predict such a relationship and which also satisfactorily explain the NH behavior and the low activation energy observed. For example,

$$\begin{aligned} NH_3+M &\rightarrow NH_2+H+M,\\ NH_2+NH_3 &\rightarrow N_2H_3+H_2,\\ N_2H_3 &\rightarrow NH+NH_2,\\ NH_2+NH_2 &\rightarrow \text{products}. \end{aligned}$$

More work is required in this area to resolve the problem. Recalculation of Jacobs' data (1963) assuming a 1st order dependence on [NH_3] and [Ar] leads to values in very good agreement with the other studies.

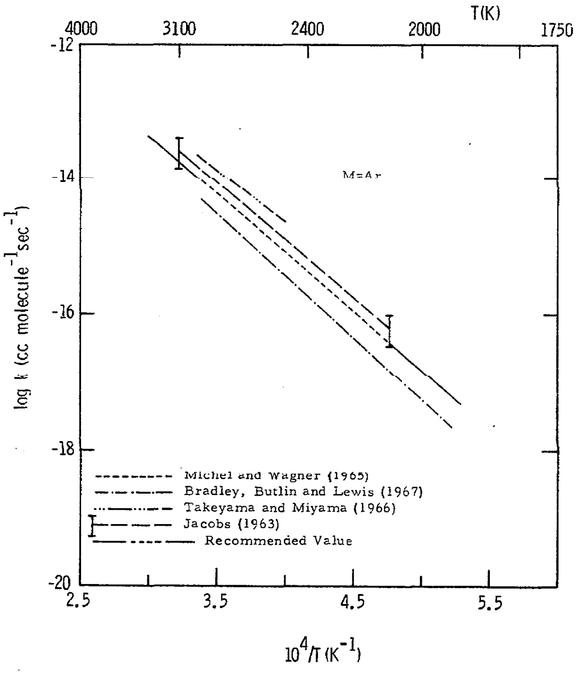

FIGURE 10. Experimental values of $k_{NH_3+Ar\rightarrow NH_2+H+Ar}$.

All the data refer to M=Ar and no information on the effect of different third bodies is available.

Takeyama and Miyama (1966) have noted a temperature dependent induction period below 2400 K when the rate of decomposition is quite slow.

It appears that the values of Michel and Wagner (1965) provide a good mean value to the available data. Their value is recommended. From the spread of the other data it is expected to be accurate to within a factor of 2–2.5 in this temperature range.

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4.8. $NH_2+H+M \rightarrow NH_3+M$

Thermodynamic Data and Equilibrium Constant

Listed under the reverse dissociation reaction.

Recommended Rate Constant

Owing to the limited data available no recommendation can be presented for this reaction.

Discussion

Rather limited data are available at present for this recombination reaction. Two radiolysis studies of pure ammonia provide room temperature values which must be regarded as approximate, until confirmed, owing to the technique used and the assumptions made in the analyses.

The value of 0.8×10^{-33} for k_{H+H+NH_3} used in the analysis of Gordon, Mulac, and Nangia (1971) is probably too low by an order of magnitude. Although information on the behavior of NH_3 as a third body is sparse and no information is available for its effect on the recombination of H atoms, typical room temperature values for polyatomic chaperons are $k_{H+H+H_2O}=1.2\times10^{-31}$ (Eberius, et al., 1969), $k_{H+H+CH_4}=1.4\times10^{-32}$, $k_{H+H+CO_2}=1.3\times10^{-32}$ [Ham, et al., 1970; Bennett and Blackmore, 1970]. However, it is true that the analysis is not particularly sensitive to its value.

The analysis of Boyd, et al. (1971) is rather involved and depends on the mechanism assumed and on the value for $k_{NH_2+NH_2+M}$. Both studies refer to $M=NH_3$. A lack of data for the dissociation of NH_3 at low temperatures eliminates the possibility of an estimate via the equilibrium constant.

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Reported rate constants

Rate constant k (cm^6 molecule^{-2} s^{-1})	Exp. temp. (K)	Method & reference	Comments
5×10^{-30} $M=NH_3$	298	Radiolysis of pure NH_3 at 250–1520 torr in a 950 cm^3 cell with a 30-50 ns pulse of 2 Mev electrons. $[NH_2]$ and $[NH]$ monitored in absorption at 5976 and 3360 Å respectively. Gordon, Mulac, and Nangia 1971.	The $[NH_2]$ decay was fit to a 2 reaction loss mechanism $NH_2+H+M\rightarrow$ $NH_2+NH_2+M\rightarrow$ A value of $k_{H+H+NH_3}=0.8\times10^{-33}$ was used in the analysis.
1.3×10^{-30} $M=NH_3$	298	Radiolysis of pure NH_3 at 700 torr using a Febetron 60 ns pulse. The numerical integration of the rate expressions for the proposed simple mechanism is compared with the measured yields of N_2H_4, H_2, and N_2 and the rate constants adjusted for a best fit. The yield of N_2H_4 is mainly dependent on the NH_2+NH_2 and NH_2+H recombination reactions. Boyd, Willis, and Miller 1971.	Uses a value of $k_{H+H+NH_3}=1.1\times10^{-32}$ in the analysis. The major reaction is the recombination of $H+NH_2$ to reform NH_3. Assume $k_{NH_2+NH_2+(M)}=3\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

4. 9. $SO+O+M \rightarrow SO_2+M$

Thermodynamic data

TK	ΔH° kcal mol^{-1}	ΔS° cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm^{-1}	$\log_{10}K_c$ cm^3 $molecule^{-1}$
0	−130. 970	—	—	—
100	−131. 399	−27. 900	281. 061	261. 195
298	−132. 146	−32. 191	89. 826	70. 435
300	−132. 151	−32. 210	89. 228	69. 840
500	−132. 613	−33. 411	50. 661	31. 494
1000	−133. 143	−34. 196	21. 624	2. 758
1500	−133. 322	−34. 345	11. 918	−6. 772
2000	−133. 367	−34. 372	7. 062	−11. 503
2500	−133. 343	−34. 362	4. 147	−14. 321
3000	−133. 279	−34. 339	2. 205	−16. 183
3500	−133. 193	−34. 313	0. 818	−17. 504
4000	−133. 097	−34. 287	−0. 222	−18. 486
4500	−133. 000	−34. 264	−1. 028	−19. 240
5000	−132. 906	−34. 245	−1. 675	−19. 842
5500	−132. 815	−34. 227	−2. 203	−20. 328
6000	−132. 728	−34. 212	−2. 642	−20. 729

Equilibrium Constant

$$K_p=1.87\times10^{-5}T^{-0.815}\exp(131,740/RT)\ \mathrm{atm}^{-1}\quad(300\text{–}1000\ \mathrm{K\ range}),$$

$$=2.35\times10^{-8}T^{0.033}\exp(133,410/RT)\quad(1000\text{–}6000\ \mathrm{K\ range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.3 percent (300–1000 K) and 1.2 percent (1000–6000 K).

Recommended Rate Constant

Only one value at room temperature is available. This requires confirmation.

Discussion

This is the only published value unearthed and was measured at only the one temperature. Data are not sufficiently firm to allow a value to be calculated from the equilibrium constant and the rate constant for the dissociation of SO_2 studied at higher temperatures.

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4.10. $SO_2+M \rightarrow SO+O+M$

Thermodynamic Data and Equilibrium Constant

Listed under the reverse recombination reaction.

Recommended Rate Constant

With some reservation the following value may be recommended as being the most appropriate at present for this reaction in the temperature range 4500–7500 K, M=Ar (see discussion).

$$4.2\times10^{-10}\exp(-110,000/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Further work is needed to confirm this sole determination which may be reliable to within a factor of two.

4. 9. Reported rate constants

Rate constant k (cm^6 $molecule^{-2}$ s^{-1})	M	Exp. temp. (K)	Method & reference	Comments
8.8×10^{-31}	Ar	300	Low power RF discharge in flowing SO_2/Ar mixtures. [O] and [SO] monitored by the intensities of the air and SO_2 afterglows. Halstead and Thrush 1966.	

4. 10. Reported rate constants

Rate constant k (cm^3 $molecule^{-1}$ s^{-1})	Exp. temp. (K)	Pressure/concentration (atm/mol cm^{-3})	Method & reference	Comments
$4.17\times10^{-10}\exp(-110,000/RT)$ or $\frac{1}{2.11}(4.71\times10^{-13}T^{1/2})\left(\frac{130,970}{RT}\right)^{2.06}$ $\exp(-130,970/RT)$ M=Ar	4500–7500	$\sim$5–40/(1.5–7.0)$\times10^{-5}$	Shock tube study of mixtures of 0.05–1 percent SO_2 in Ar. [SO] and [SO_2] monitored behind reflected shock waves. Olschewski, Troe, and Wagner 1965.	Requires a low concentration of SO_2 and a high temperature and pressure to observe this reaction. Appears to be in the 2nd order "low pressure" regime of a unimolecular decomposition.

Discussion

Using very low SO_2 concentrations, high temperatures, and a total pressure in the range of about 5–40 atm, Olschewski, et al. (1965) obtained a rate constant for the dissociation of SO_2 which most probably refers to this reaction.

Although the observed activation energy falls below the known bond strength of (SO–O) this is not uncommon and by invoking the participation of about three classical harmonic oscillator terms the rate can be expressed in the usual form

$$Z\left(\frac{\Delta E_0^\circ}{RT}\right)^{s-1}(s-1)!^{-1}\exp\left(-\Delta E_0^\circ/RT\right).$$

At temperatures below 4500 K and with higher concentrations of SO_2 in an Ar mixture and lower total pressures (1 atm or less) the kinetics of the dissociation become more involved as inferred by a decrease in the activation energy to about 56–75 kcal mol^{-1} [Gaydon, et al., 1963; Levitt and Sheen, 1967; Olschewski, et al., 1965]. Explanations based on the participation of electronically excited states of SO_2 seem the most probable and a scheme of the following type is envisioned.

(1) $SO_2+Ar \rightarrow SO+O+Ar,$

(2) $SO_2+Ar \rightleftarrows SO_2^*+Ar,$

(3) $SO_2+SO_2 \rightleftarrows SO_2^*+SO_2,$

(4) $SO_2^*+SO_2 \rightarrow SO_3+SO,$

(5) $SO_2^*+Ar \rightarrow SO+O+Ar.$

Reactions (2) and/or (3) become rate determining and explain the lower activation energies observed. Gaydon, Kimball, and Palmer (1963) studied SO_2 dissociation by shock heating 4–32 percent SO_2/Ar mixtures at total pressures around 1 atm and at temperatures of 3000–4000 K. They monitored [SO] in absorption and proposed reaction (4) for its formation. Olschewski, et al. (1965), using 0.36–1 percent SO_2/Ar mixtures at 3000–4000 K and a lower pressure, and Levitt and Sheen (1967) using 1–40 percent SO_2/Ar mixtures at 3000–5000 K and a total pressure of about 1 atm obtained similar results. Levitt and Sheen (1967) observed an induction period for the dissociation. A certain build up of SO or O may be necessary before the dissociation can proceed at the measured rate. Obviously the dissociation of SO_2 is complicated and dependent on SO_2 concentration, total pressure, and the temperature. The system is still far from understood.

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4.11. $SO+O_2 \rightarrow SO_2+O$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−12. 992	—	—
100	−13. 079	−4. 363	27. 601
298	−13. 028	−4. 259	8. 618
300	−13. 027	−4. 255	8. 560
500	−12. 873	−3. 871	4. 781
1000	−12. 349	−3. 150	2. 010
1500	−11. 818	−2. 717	1. 128
2000	−11. 327	−2. 434	0. 706
2500	−10. 905	−2. 246	0. 463
3000	−10. 563	−2. 120	0. 307
3500	−10. 285	−2. 034	0. 198
4000	−10. 049	−1. 971	0. 118
4500	−9. 832	−1. 920	0. 058
5000	−9. 614	−1. 874	0. 011
5500	−9. 379	−1. 830	−0. 027
6000	−9. 122	−1. 785	−0. 058

Equilibrium Constant

$K=3.60\times10^{-3}T^{0.511}\exp(13{,}370/RT)$
(300–3000 K range)

This expression, obtained from a least squares fit to the 100 K interval data derived from the JANAF Thermochemical tables, reproduces the data with deviations of up to 0.7 percent in this temperature range.

Recommended Rate Constant

$k=3.0\times10^{-13}\exp(-5600/RT)$ cm^3 molecule^{-1} s^{-1}.
Temperature range: 400–2500 K.
Suggested error limits: factor of 2 in this range.

$$\log_{10}A=\overline{13}.47\pm0.20 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
$$E=5600\pm700 \text{ cals.}$$

Discussion

As observed from a comparison of the various studies of this reaction, a large discrepancy exists as to its activation energy. The absolute values for the rate constant are in somewhat better agreement however, as seen in figure 11, and suggest a value of about 5600 cals mol^{-1} based on the values of Sheen (1970), Homann, et al. (1968), and Williams (1968). The latter's repetition of Halstead and Thrush's measurement (1966) but at slightly higher temperatures provides evidence for a low activation energy. Oxygen was added to a heated flow system containing only the reactive species SO (free of atomic oxygen). The observation of the SO_2 afterglow and the air afterglow if a trace of NO was added establishes the formation of O atoms. The $SO+O_2$ reaction appears the only likely explanation.

The low activation energy is supported most closely by the work of Homann, Krome, and Wagner (1968) where analysis was by mass spectrometer rather than by optical spectroscopy. There is no obvious expla-

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
2.2×10^{-15}	1255	$H_2S/O_2/N_2$ or Ar atm pressure flames sampled by microprobe, analysed by wet chemistry and by mass spectrometer. Difficulty in measuring SO and SO_2 concentrations. This reaction assumed to be the major source of SO_2 in the flame. Levy and Merryman 1965.	Values must be regarded as only very approximate owing to the difficulties encountered in measuring SO and SO_2 concentrations.
$4.7,\ 10.8\times10^{-15}$	1260		
$9.3,\ 34.0\times10^{-15}$	1350		
$8.6\times10^{-10}\exp(-19{,}300/RT)$	840–1123	Lean $H_2S/O_2/N_2$ flames burnt at 0.1 and 0.05 atm pressure. Sampled by microprobe and analysed by mass spectrometer and by wet chemistry. [SO_2] and [SO] monitored but the latter values are questionable. This reaction assumed to be the major source of SO_2 in the flame. Merryman and Levy 1967.	Values must be regarded as being very approximate owing to the uncertainties in the [SO] measurements.
3.4×10^{-14}	840		
1.1	847		
1.4	855		
1.5	895		
2.4	895		
6.5	990		
6.5	990		
8.5	1055		
5.6×10^{-13}	1055		
1.5	1095		
3.9	1123		
$<3\times10^{-16}$	298	No SO–O afterglow observed when O_2 added at a point in a flow tube where SO present in the absence of O. SO formed from RF discharge in SO_2/Ar mixtures. Halstead and Thrush 1966.	
$5.8\times10^{-13}\exp(-6500/RT)$	580–1145	SO formed from excess OCS and atomic oxygen (from N/NO titration) in a mixture highly diluted with Ar. Mixed with excess O_2/Ar in a heated flow tube at 1.8–24 torr, sampled with a probe and SO_2, CO, OCS, O, SO, and O_2 concentrations analysed with a TOF mass spectrometer. [SO] calibrated by titration with NO_2. Homann, Krome, and Wagner 1968.	
$3.3\times10^{-11}\exp(-10{,}000/RT)$	440–530	SO formed from a microwave discharge in SO_2/Ar mixtures. Sufficient SO_2 added after the discharge to remove O atoms. Passed into heated flow tube and O_2 added. SO_2 afterglow observed and the air afterglow produced if a trace of NO added. Rate extracted from time taken for chemiluminescence to reach its maximum intensity after O_2 addition. Williams 1968.	Dependent on rates of removal of O atoms by other processes. Wall recombination and removal by SO_2 measured in subsequent experiments with the same equipment.
$1.6\times10^{-10}\exp(-29{,}000/RT)$	1600–2100	Shock tube study of CS_2/O_2 mixtures diluted with Ar. SO+O chemiluminescence and SO absorption at 2832 Å monitored for incident and reflected shock waves. Sheen 1970.	
$<8\times10^{-17}$	297	SO formed by RF discharge of dilute SO_2/He mixtures. HgO film used to remove O atoms. O_2 added downstream. Total pressures around 0.5 torr. [SO] monitored by ESR. Breckenridge and Miller 1972.	Reaction occurs only to negligibly small extent.

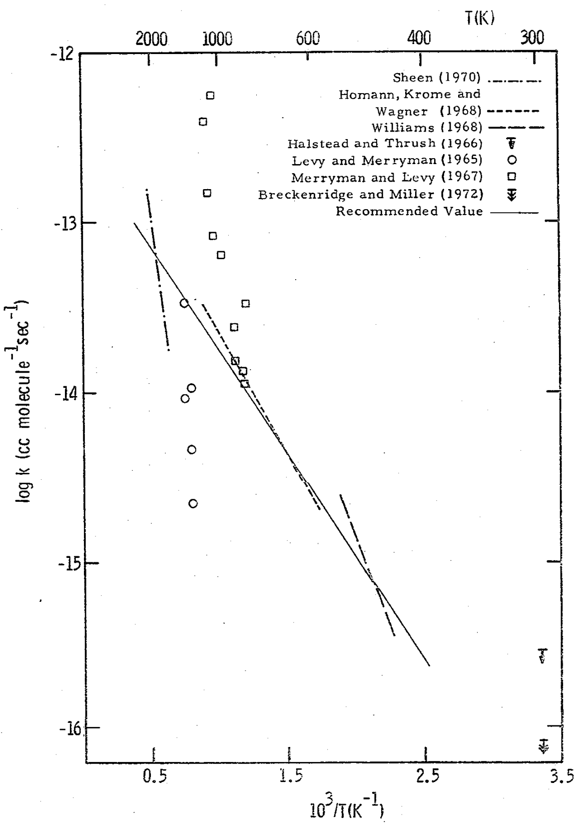

FIGURE 11. Experimental values of $k_{SO+O_2\rightarrow SO_2+O}$.

nation as to why the shock tube measurements [Sheen, 1970] gave a high value. However the CS_2/O_2 system is complicated and additional reactions should have been included in his analysis.

The results of Levy and Merryman (1965) and Merryman and Levy (1967) are of little value since they encountered great difficulty in monitoring SO and SO_2 concentrations by their microprobe/analysis method. The results are probably no better than to an order of magnitude.

The recommended value is based on the data of Sheen (1970), Homann, Krome, and Wagner (1968) and Williams (1968), weighted equally. It will be noted that the reaction appears to have a particularly low preexponential factor.

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4.12. $SO_2+O+M\rightarrow SO_3+M$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K_p$ atm^{-1}	$\log_{10}K_c$ cm^3 molecule^{-1}
0	−81. 868	—	—	—
100	−82. 395	−31. 665	173. 146	153. 280
298	−83. 202	−36. 422	53. 026	33. 635
300	−83. 207	−36. 439	52. 650	33. 262
500	−83. 566	−37. 387	28. 354	0. 187
1000	−83. 735	−37. 672	10. 066	−8. 800
1500	−83. 576	−37. 547	3. 971	−14. 719
2000	−83. 338	−37. 411	0. 930	−17. 635
2500	−83. 091	−37. 299	−0. 888	−19. 356
3000	−82. 861	−37. 217	−2. 098	−20. 486
3500	−82. 669	−37. 157	−2. 958	−21. 280
4000	−82. 527	−37. 118	−3. 603	−21. 867
4500	−82. 443	−37. 099	−4. 104	−22. 316
5000	−82. 422	−37. 094	−4. 504	−22. 671
5500	−82. 466	−37. 102	−4. 832	−22. 957
6000	−82. 571	−37. 121	−5. 104	−23. 191

Equilibrium Constant

$$K_p=2.18\times 10^{-7}T^{-0.475}\ \exp\ (83{,}030/RT)\ \text{atm}^{-1}\quad (300\text{–}1000\ \text{K range})$$
$$=1.05\times 10^{-9}T^{0.215}\ \exp\ (84{,}190/RT)\quad (1000\text{–}3000\ \text{K range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.2 percent (300–1000 K) and 0. 3 percent (1000–3000 K).

Recommended Rate Constant

$$k=1\times 10^{-33}\ \exp\ (+1000/RT)\ \text{for } M=\text{Ar, } O_2,\ N_2,\ \text{He.}$$
Temperature range: 250–1000 K.

This recommendation must be regarded as very tentative and is accurate to no better than a factor of two at room temperature. Until the activation energy is measured, a larger uncertainty will exist at other temperatures.

Very approximate third body efficiencies:

$$k_{(Ar\sim O_2\sim N_2\sim He)}:k_{(SO_2\sim NO_2\sim N_2O)}=1:(6\text{–}40).$$

Discussion

The data for this reaction have all been obtained from room temperature studies and, if nothing else, do show a general trend of k_{SO_2}, $k_{N_2O} > k_{O_2,\ N_2,\ Ar,\ He}$. Discharge flow system, stirred reactor, and static photolysis techniques have been used but the data are still full of inconsistencies and discrepancies such that k is not confidently known to better than a factor of 3 to 4.

Reported rate constants

Rate constant k (cm^6 molecule$^{-2}s^{-1}$)	M	Exp. temp. (K)	Method & reference	Comments
1.3×10^{-32} 1.2×10^{-32}	O_2 N_2	208 298	O atoms produced from N/NO titration (O_2 free) or from a microwave discharge in O_2 or an O_2/Ar mixture. Decay followed in flow tube by air afterglow intensity. SO_2 concentration measured gas chromatographically at various points. Allen and Cadle 1965. Cadle and Powers 1966.	Activation energy zero or very small. 3rd order reaction kinetics established.
1.3×10^{-32}	Ar	293	RF discharge of O_2 or 1–2 percent O_2/Ar mixtures; trace of NO added and the O-atom decay followed in a flow tube by the intensity of the air afterglow. Excess SO_2 added at either of two entry ports past the discharge. Halstead and Thrush 1966.	$k_{Ar}=k_{O_2}$
3.9×10^{-32}	SO_2+NO_2	300	3360 Å photolysis of 3–10 torr NO_2 in the presence of 4–740 torr SO_2. [NO_2] followed spectrophotometrically. Quantum yields for loss of NO_2 measured as a function of SO_2 pressure. Jaffe and Klein 1966.	Based on a comparison of the photolysis of NO_2 with and without SO_2. Value based on $[SO_2]+[NO_2]=2$ torr data.
7.4×10^{-33} 6.6×10^{-33} 2.7×10^{-32}	O_2 Ar SO_2	299 299 299	Microwave discharge in O_2 or 2 percent O_2/Ar mixtures. Products mixed with SO_2 in a 285 cm^3 stirred flow reactor at total pressures of 0.7 to 3.0 torr. [O] monitored by ESR at the inlet and outlet of the reactor. $[SO_2]/[O_2]\sim5$–1000. Surface aged to give reproducible results. Mulcahy, Steven, and Ward 1967.	Efficiencies: $k_{Ar}:k_{O_2}:k_{SO_2}=1.0:1.1:4.2$
3.8×10^{-33}	Ar	300	O atoms generated by a microwave discharge in 1.5 percent O_2/Ar and mixed with SO_2 in a 290 cm^3 stirred pyrex reactor. Total pressures about 2 torr. [O] at inlet and outlet monitored by ESR detection.	Relative efficiencies $k_{Ar}:k_{SO_2}=1:6$ assumed in the analysis. This is most consistent with the data.
2.7×10^{-33}	Ar	300	O atoms generated by a microwave discharge in 0.015–0.1 percent O_2/Ar mixtures. [O] at inlet and outlet of a 2234 cm^3 Teflon coated reactor measured by comparing air afterglow intensities resulting from addition of a trace of NO. Total pressures about 6 torr. Mulcahy, Steven, Ward, and Williams 1969.	Contribution of SO_2 to M is negligible in this case.
1.1×10^{-31} 2.2×10^{-33} 2.7×10^{-33} $E=3400$ cals	SO_2 He Ar SO_2+He	298 298 298 205–298	Electrodeless discharge of 1 percent or less O_2 in He or Ar at 3.4–4.1 torr in a flow system. 0.09–0.28 torr SO_2 added after the discharge through moveable inlet. [O] measured by ESR as a function of inlet position. $[SO_2]/[O_2]\sim6$–24. Timmons, Lefevre, and Hollinden 1969.	Third body effects of both SO_2 and He or Ar considered in the analysis owing to the higher value of k_{SO_2}. $k_{SO_2}:k_{He}:k_{Ar}=41:0.8:1$ Determination of E assumes $E_{SO_2}=E_{He}$. Positive E value reported.

Reported rate constants—Continued

Rate constant k (cm^6 molecule^{-2}s^{-1})	M	Exp. temp. (K)	Method & reference	Comments
$\sim 1\times10^{-31}$	N_2O	298	O atoms generated by the Hg photosensitized decomposition (>2200 Å) of 100–481 torr N_2O in the presence of 1.2–52 torr OCS. Absorbed intensity varied by a factor of 156 and the extent of the conversion by a factor of 13. [CO] and $[N_2]$ analyzed gas chromatographically. Heicklen, Wood, Olszyna, and Cehelnik 1969.	The ratio $\frac{k_{O+SO_2+N_2O}}{k_{O+OCS}} \sim 8\times10^{-18}$ cm^3 molecule^{-1} determined. A very crude estimate however since it is very sensitive to the accuracy of the $[CO]/[N_2]$ measurement from which it is determined. Values fell in the range 1.3×10^{-18} to 2.5×10^{-17}. A value of $k^{298\text{ K}}_{O+OCS}=1.3\times10^{-14}$ has been taken here (q.v.). The measurement can only be considered accurate to within a factor of 2–3.
$E\sim-2000$ cals	O_2+SO_2	440–530	Decay of O atoms in O_2 mixtures containing SO_2 in a heated flow tube. Followed by chemiluminescent emission. Williams 1968.	Negative activation energy reported.
8.3×10^{-32}	O_2	295	High-power microwave discharge in O_2 mixed with 4 percent NO and SO_2 in a flow tube. O-atom decay followed by intensity of the air afterglow and calibrated with NO_2 titration method. Kaufman 1958.	Approximate value. From room temperature measurements the $O+SO_3$ reaction appears to have an activation energy greater than 7 kcal mol^{-1}.
$\geq10^{-32}$	H_2	784	SO_2 inhibition of the H_2/O_2 second pressure limit of explosion in KCl coated vessels. Webster and Walsh 1965.	An involved analysis, should be treated with some reserve.

Halstead and Thrush (1966), Allen and Cadle (1965), and Cadle and Powers (1966) have obtained similar values for k_{Ar}, k_{O_2}, and k_{N_2} using flow tube methods at room temperature. However, they give few details of the experimental conditions and a larger than expected contribution from k_{SO_2} may have been overlooked in their analyses. Their values may be too high.

The reaction of $O+SO_3$ (q.v.) is negligible at room temperature, having an activation energy ≥7 kcal mol^{-1}. Consequently, no correction is necessary for this in the work of Mulcahy, et al. (1967, 1969) or in the other low temperature studies. Mulcahy, et al. (1969) found that wall effects in the stirred-flow reactor were of major importance since the efficiency of recombination on the walls varied with the gas phase composition. Their gas phase and wall effects were not independent variables and the data had to be extrapolated to zero [O] in order to obtain values for the three body gas phase recombination. Using the same technique Mulcahy and Williams (1968) also have derived rates for the $O+O_2+M$ recombination. However, since their values for this fall about a factor of two above the general trend of other available room temperature data, some doubt as to the reliability of their k_{SO_2+O+M} values has to be expressed. They did attempt to separate the relative contributions of k_{O_2}, k_{Ar}, and k_{SO_2}.

The discharge flow study of Timmons, et al. (1969) has not clarified the picture. They report a very high ratio for $k_{SO_2}:k_{He,\ Ar}$ and a positive activation energy of 3.4 kcal mol^{-1} which would seem highly questionable for such a three body recombination. Williams (1968) gave a value of -2 kcal mol^{-1} while Allen and Cadle (1965), and Cadle and Powers (1966) reported it as small or zero. Further studies at different temperatures are obviously needed to remove this severe discrepancy. A very tentative value of -1 kcal mol^{-1} is recommended but this is based more on intuition than actual data.

Heicklen, et al. (1969) have obtained a very approximate value by estimating the ratio

$$k_{O+SO_2+N_2O}/k_{O+OCS},$$

from a photolysis study. This is uncertain by at least a factor of 2–3 but even so it appears that k_{N_2O} may be quite similar in value to k_{SO_2}.

The study of Jaffe and Klein (1966) is an involved photolysis based on previous knowledge of the NO_2

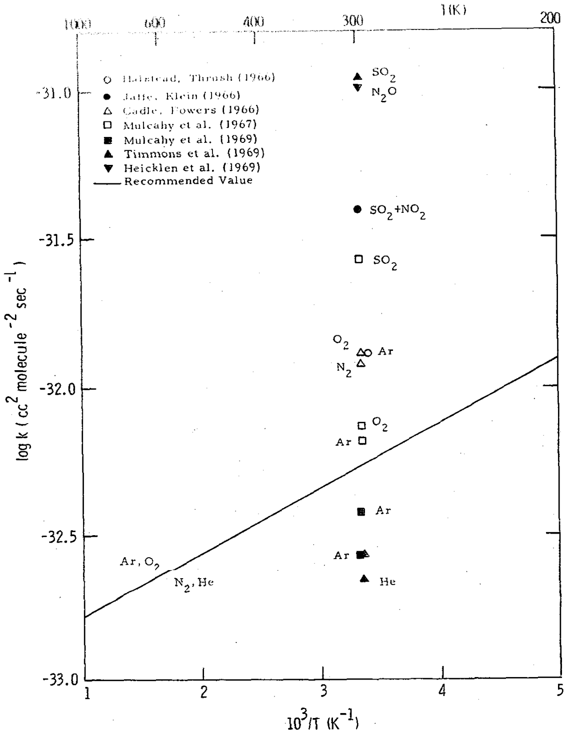

FIGURE 12. Experimental values of $k_{SO_2+O+M \rightarrow SO_3+M}$.

photolysis. Addition of SO_2 makes it a rather complicated system from which to extract data for specific reactions. Their values may only be approximate.

Several other investigations have been reported in the literature which invoke this reaction but are not considered as contributing any further information as to its rate constant value. Webster and Walsh (1965) interpreted the inhibiting effect of small amounts of SO_2 on the H_2/O_2 second pressure limit explosion as resulting from the removal of H atoms by the $H+SO_2+M$ reaction. For larger amounts of SO_2 they also had to invoke a mechanism for removing O atoms and proposed this reaction. Nettleton and Stirling (1969) burned $CH_4/O_2/SO_2$ mixtures diluted with N_2 in an atmospheric pressure flow reactor. SO_2 and SO_3 concentrations were measured in the burnt gases by probe sampling followed by wet analysis. Values for [O] had to be assumed from the work of others. It appeared from the study that the effects of the reaction $O+SO_3 \rightarrow SO_2+O_2$ had to be considered at 2150 K and using reasonable values for this and the three body recombination of $O+SO_2+M$ they could explain their results in a semi-quantitative manner. No independent value can be obtained from their work. Similarly, Levy and Merryman (1965) attempted to extract a value from $H_2S/O_2/N_2$ or Ar atmospheric pressure flames sampled with a microprobe and analysed by wet chemistry or mass spectrometrically. They had difficulty measuring $[SO_2]$ absolutely and had to assume [O] based on certain flame equilibrations. Because of this and the complexity of such flames no reliance can be placed on their values.

Kaufman's early study of this reaction (1958) now is considered to be only approximate.

Although none of the data can be recommended at present, a very tentative value for $k_{Ar,\ O_2,\ N_2,\ He}$ has been quoted. This is based on those values plotted in figure 12.

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4.13. $SO_3+M \rightarrow SO_2+O+M$

Thermodynamic Data and Equilibrium Constant

Listed under the reverse recombination reaction.

Recommended Rate Constant

The available information for this reaction is too limited and too speculative for any recommendation to be made at present.

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	M	Exp. temp. (K)	Method & reference	Comments
1.7×10^{-16}	Ar	1740	SO_2 emission monitored at 4150 Å behind incident shock waves in 10 percent SO_3/Ar mixtures using a glass shock tube. Nettleton and Stirling 1969.	Assumed 90 percent of SO_3 decomposed behind incident shock.
1.3×10^{-15}	N_2	1740	CO/O_2/N_2 mixtures containing a little SO_2 burned in an atm pressure flow reactor. Burnt gases sampled by a probe and analysed for SO_2, SO_3, O_2, CO, CO_2. Wet chemistry was used for SO_2 and SO_3 concentrations. Nettleton and Stirling 1969.	Assumes that the steady state level of the SO_3 concentration represents the equilibration of this reaction. A value of 5.5×10^{-33} cm^6 molecule^{-2} s^{-1} is assumed for the reverse reaction and that [O] is its equilibrium value.

Discussion

These values represent the only available information found for this reaction and are highly speculative in nature. The shock tube experiments were analysed assuming this to be the decomposition mechanism. The analysis of the flame reactor experiments is based on many assumptions, the main one being that this reaction is responsible for the equilibration of SO_2 and SO_3 in the burnt gases of flames.

If the values are correct the apparent activation energy that can be inferred would fall at least 40 kcal mol^{-1} below the 82 kcal mol^{-1} needed to rupture the SO_2–O bond.

It may be noted that the reaction violates the spin correlation rule

$$SO_3(^1A) \rightarrow SO_2(^1A_1)+O(^3P_g),$$

but from studies of the reverse recombination process it does not appear that spin reversal is rate determining in this case.

Reference

Nettleton, M. A., and R. Stirling, 12th Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, Pennsylvania 1969) p. 635.

4.14. $SO+SO\rightarrow SO_2+S$

Thermodynamic data

T K	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−7.459	—	—
100	−7.580	−6.673	15.106
298	−7.547	−6.658	4.076
300	−7.546	−6.654	4.043
500	−7.376	−6.221	1.865
1000	−6.920	−5.593	0.289

Equilibrium Constant

$$K=1.38\times10^{-3}T^{0.478}\exp(7850/RT)$$

(300–2500 K range.)

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.8 percent in this temperature range.

Recommended Rate Constant

The only available data are upper limit estimates

$\leq3\times10^{-15}$ cm^3 molecule^{-1}s^{-1} (300 K),

$\leq2\times10^{-13}$ (1000 K).

The rate and rate constant are defined by

$$d[SO_2]/dt=k[SO]^2=-0.5d[SO]/dt.$$

Discussion

Information for this reaction has come largely from SO/O flow systems. Unfortunately, for these the predominant decay mechanism is the $SO+O+M\rightarrow SO_2+M$ reaction and this overshadows other contributing processes. An initial study by Sullivan and Warneck (1965) failed to realize this and consequently does not give a reliable value. Halstead and Thrush (1966) measuring the decay of [SO] could only estimate an upper limit value. Hoyermann, et al. (1967) and Homann, et al. (1968) similarly were able to derive only upper limit estimates at room temperature and at 1000K, respectively, from rates of formation of SO_2.

More recently, Breckenridge and Miller (1972) have measured the [SO] decay in an SO/O_2/He mixture free of atomic oxygen. However, the time scale of a flow system appears to be insufficiently long at room temperature and they could derive only an upper limit estimate for the rate constant.

Donovan, Husain, and Jackson (1969) observed the decay of [SO] in an $SOCl_2$/Ar photolysis study and could find no significant contribution from this reaction. However, their observation of traces of S_2O and S_2 was considered indicative of such reactions as

$$SO+SO\rightarrow SO_2+S,$$
$$S+SO\rightarrow S_2O,$$
$$S+S+M\rightarrow S_2+M.$$

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
(*)	298	Flow system at 1 torr or less sampled by mass spectrometer. O_2 dissociated by microwave discharge, OCS added in approximately equal amount to [O]. Initial [O] measured from decrease in O_2 mass peak on initiating discharge and from NO_2 titration. Mass spectrometer sensitivity to SO assessed by comparing initial SO and CO productions. Sullivan and Warneck 1965.	*Value obtained not reliable. Interpretation did not include the SO+O+M reaction which is dominant in this system. [Halstead and Thrush, 1966; Sharma, et al., 1967] SO formed from the O+OCS reaction.
$<3.3\times10^{-15}$	300	Flow tube, weak RF discharge through SO_2/Ar mixtures. [O] and [SO] monitored by air (trace of NO added) and SO_2 afterglows. Halstead and Thrush 1966.	Plays a very minor role in the SO/O system. k has been divided by 2 to correct for the rate constant definition.
$<1.7\times10^{-14}$	298	Flow system at 0.5-5 torr pressure. SO formed from excess OCS and O (from N/NO titration). Analyzed with TOF mass spectrometer, SO, SO_2 measured. [SO] calibrated by NO_2 titration. Hoyermann, Wagner, and Wolfrum 1967.	
$<1.7\times10^{-13}$	1000	Heated flow tube at a few torr pressure. SO formed from excess OCS and O atoms (from N/NO titration) diluted in Ar. Sampled by TOF mass spectrometer, SO_2 monitored. Homann, Krome, and Wagner 1968.	
$<6\times10^{-14}$	300	Flash photolysis of $SOCl_2$/Ar mixtures. [SO] measured in absorption using extinction coefficient. Estimated from amount of S_2 and S_2O observed assuming subsequent reactions. Donovan, Husain, and Jackson 1969.	Very approximate assessment. This reaction plays a very minor role in their system. k has been divided by 2 to correct for the rate constant definition.
$<5\times10^{-14}$	297	SO formed by RF discharge of dilute SO_2/He mixtures. HgO film used to remove O atoms. O_2 added downstream, total pressures around 0.5 torr. [SO] decay monitored by ESR. Breckenridge and Miller 1972.	Reaction occurs only to negligible extent.

They obtained an upper limit estimate by taking an approximate value for the extinction coefficient of S_2O.

k_{SO+SO} appears to be $\lesssim 3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K and $\lesssim 2\times10^{-13}$ at 1000 K. Exact values may be considerably below these upper limits.

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4.15. $S+O_2\rightarrow SO+O$

Thermodynamic data

TK	ΔH° kcal mol^{-1}	ΔS° cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−5.513	—	—
100	−5.499	2.310	12.495
298	−5.481	2.399	4.542
300	−5.481	2.399	4.517
500	−5.497	2.350	2.916
1000	−5.429	2.443	1.721
1500	−5.389	2.477	1.326

Equilibrium Constant

$K=2.53\ T^{0.037}\ \exp\ (5520/RT)$ (300–2500 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.6 percent in this temperature range.

Recommended Rate Constant

$k=2.2\times10^{-12}\ \exp\ (-0/RT)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$.

Temperature range: 250–450 K.

Suggested error limits: ±30 percent.

$\log_{10}A=\overline{12}.34\pm0.06\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$,

$E=0\pm100$ cals.

Discussion

The agreement between the low temperature values of Fair and Thrush (1969), Fair, Van Roodselaar, and Strausz (1971), Donovan and Little (1972), and Davis, Klemm, and Pilling (1972) casts grave doubts on the reliability of the higher temperature measurements of Homann, Krome, and Wagner (1968). Although it is desirable to obtain further values at elevated temperatures it appears now that the reaction proceeds with a near zero activation energy. Fair and Thrush (1969) produced S atoms via the reactions

$$H+H_2S\rightarrow HS+H_2,$$

$$H+HS\rightarrow H_2+S,$$

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
$1.7\times10^{-11}\exp(-5600/RT)$	657–1120	Heated flow tube, sulfur vapor S_2/Ar mixture in excess reacted with O atoms (from N/NO titration) to form S atoms at few torr total pressure. O_2/Ar mix added downstream. Monitored with TOF mass spectrometer. S atoms also produced from a microwave discharge of S_2/Ar vapor at a few torr. Homann, Krome, and Wagner 1968.	Data from the two sources of S atoms in agreement. Extrapolation to 298 K gives $k=1.3\times10^{-15}$. Values appear very questionable at this time.
2×10^{-12}	298	1–5 percent H_2/Ar mixture subjected to 100 watt/20 MHz discharge. H_2S added to flow system, usually <5 percent of H_2 flow so that maintain excess H atoms. Total pressure 1–4 torr. O_2 added upstream of H_2S and in 1–10 times its concentration. [SO] monitored from SO_2 afterglow. [O] from air afterglow or addition of trace of NO. Fair and Thrush 1969.	
2.8×10^{-12}	298	Flash photolysis (1900–2600Å) of mixtures of 0.1 torr OCS/0.06–0. 29 torr O_2 with either 60, 100, or 200 torr of CO_2 or a 2.4 Ar: CO_2 mix at 100 or 200 torr. $S(^3P_{2,1})$ followed in absorption at 1807 and 1820 Å. Qualitative measurements also made on the weaker 1826 Å ($^3P_0$) line. [O_2] assumed constant since <5 percent consumed. Fair, Van Roodselaar, and Strausz 1971.	The observed $S(^3P_{2,1})$ decays were 1st order in [S] and [O_2]. k independent of flash energy over a 3-fold change and also for the different pressures studied. If OCS pressure increased to 0.3 torr SO observed weakly in absorption.
1.7×10^{-12}	295	Flash photolysis of 0.03 torr OCS/0.003–0.019 torr O_2/112. 5 torr Ar or N_2 mixtures. [O_2] ~ 9–64 fold [S]. [S] monitored by atomic absorption at 1820Å of the 3^3P_1 state. Donovan and Little 1972.	96 percent of the $S(^1D)$ initially formed will be quenched to $S(^3P)$ during the flash period under these conditions.
$2.24\times10^{-12}\exp(-0/RT)$	252–423	Flash photolysis, >1650 Å, of 0.06–0.10 torr OCS, 25 torr CO_2 and 0.004–0.040 torr O_2 mixtures. [S] and [O] monitored by resonance fluorescence following a 200μs delay. [S] ~ 10^{11}–10^{12} atoms/cm^3. Data also obtained for 0.100 torr OCS, 20 and 200 torr He, and 0.011–0.021 torr O_2 mixtures. Davis, Klemm, and Pilling 1972.	[S] decay follows 1st order kinetics. $S(^1D, ^1S)$ quenched before data collection. No indication of any pressure dependence. CO_2 data appears uncomplicated by any side reactions.

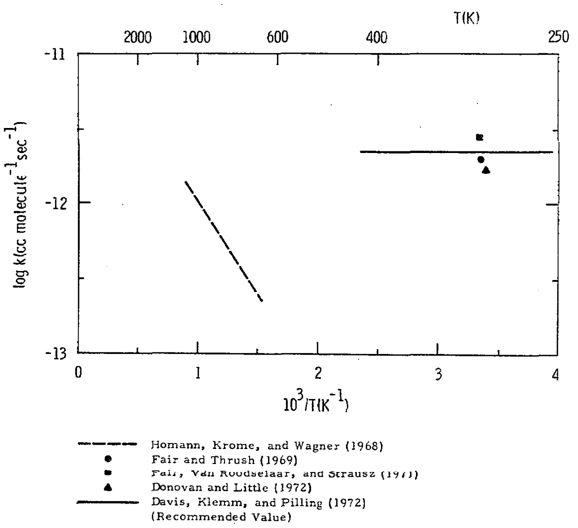

FIGURE 13. Experimental values of $k_{S+O_2\rightarrow SO+O}$.

and followed the interaction with O_2 spectroscopically. This method for the formation of S atoms has been confirmed by Cupitt and Glass (1971) who used ESR detection to establish that, indeed, for conditions where H atoms are in excess, H_2S is converted almost quantitatively into S atoms and can be pumped through a flow system with little loss.

Fair, et al. (1971), Donovan and Little (1972), and Davis, et al. (1972) flash photolysed highly diluted mixtures containing OCS. Under their experimental conditions the $S(^1D,^1S)$ initially formed in the photodissociation is rapidly quenched to ground state $S(^3P_{2,1,0})$ to provide a clean source of S atoms. Davis, et al. (1972) prefer their data utilizing CO_2 as inert diluent. That with helium may have been slightly complicated by formation of some S_2 since in this case $S(^1D,^1S)$ quenching may be partially via reaction with OCS. Even so, the values are scarcely outside their quoted error and are well within the ±30 percent error limits suggested here. They also found that values derived from the rate of appearance of [O] were in good agreement with [S] decay data. Based on this and the other values, a confidence level of ±30 percent seems quite appropriate particularly since three different monitoring techniques were used; chemiluminesence, atomic absorption and atomic fluorescence. The value of Davis, et al. (1972) is recommended.

Homann, et al. (1968) used both the reaction $S_2+O\rightarrow SO+S$, and a discharge through sulfur vapor as separate methods of producing S atoms. The species were monitored with a TOF mass spectrometer. As to how the discrepancy arises in their results is not clear. No reliance can be placed on their values at this time.

It may be noted that Cupitt and Glass (1971) have observed that at room temperatures when $[O_2]>>[H]>[H_2S]$, all of the H_2S is converted to SO. This is explained by a reasonably fast rate of reaction between S and O_2 and is further confirmation of the low temperature values.

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4.16. $H+SO_2+M\rightarrow HSO_2+M$

Thermodynamic Data

The thermodynamic properties of the HSO_2 radical still are unknown.

Recommended Rate Constant

The systems in which this reaction is thought to participate have not been sufficiently well characterized to enable reliable values to be recommended for this rate constant.

Discussion

Webster and Walsh (1965) found that the effect of small amounts of SO_2 on the second pressure limit of explosion for H_2/O_2 mixtures could be satisfactorily explained if this reaction was included in the kinetic scheme. Its rate constant was derived relative to that for the $H+O_2+M$ reaction, the value for which here has been taken as 3×10^{-32} cm^6 molecule^{-2} s^{-1} (784 K). This is based on the values 2.8×10^{-32}, obtained from the ratio $k_{H+O_2}/k_{H+O_2+H_2}=22.5$ mm Hg (784 K)$=2.8\times10^{17}$ molecule cm^{-3} [Baldwin, et al., 1967] using $k_{H+O_2}=7.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} [Baulch, et al., 1969] and 3.1×10^{-32} obtained by Kurzius (1964) at this temperature.

Fenimore and Jones (1965) determined the heat release profile in low pressure flames with and without the presence of small amounts of SO_2. The difference was associated with the extra heat released by a catalytic recombination mechanism

$$H+SO_2+M\rightarrow HSO_2+M,$$
$$H+HSO_2\rightarrow H_2+SO_2,$$
$$OH+HSO_2\rightarrow H_2O+SO_2.$$

This value sets an upper limit since additional heat release processes not considered may occur. Kallend (1967) confirmed this mechanism and found the rate of catalytic recombination to have a first order dependence on [H], the case if the first reaction is rate determining. However, Halstead and Jenkins (1969), using higher temperature flames, found it to be a second order dependence on [H], since con-

Reported rate constants

Rate constant k (cm^6 $molecule^{-2}$ s^{-1})	M	Exp. temp. (K)	Method & reference	Comments
6×10^{-32}	H_2	784	SO_2 inhibition of H_2/O_2 second explosive limit in KCl coated vessels. Webster and Walsh 1965.	$\frac{k_{H+SO_2+H_2}}{k_{H+O_2+H_2}}=2.0$ obtained. This has been coupled with a value of $k_{H+O_2+H_2}=3\times10^{-32}$ (784K).
$\leq2\times10^{-31}$	Burnt flame gases≈ 1 $Ar:0.7H_2:0.6H_2O$	1480–1660	Fuel rich $H_2/O_2/Ar/SO_2$ or H_2S flames burnt at 50–100 torr. Sampled by microprobe-mass spectrometric analysis. [H] measured from HD formation on adding a trace of D_2O to unburnt gases. Heat release profile calculated from temperature measurements. Fenimore and Jones 1965.	Upper limit value. Obtained by assuming no additional reactions but this contribute to the heat release profile.
2×10^{-32}	$H_2+N_2+H_2O$	1647	Fuel rich atm pressure $H_2/O_2/N_2$ flames with addition of up to 1.5 percent SO_2. Microprobe sampler established the SO_2 dominance in the flames over other S compounds. [H] measured from intensity of 4280 Å CuH band.	1st order dependence on [H]. This reaction appears to be the rate determining step.
3.7×10^{-32}	$H_2+N_2+H_2O$	1620–1720	[H] measured by monitoring the intensity of the sodium chemiluminescence. Kallend 1967.	H_2, N_2, H_2O third body efficiencies cannot differ substantially.
1.1×10^{-31}	$0.68N_2+0.15H_2O+0.08CO_2+0.06CO$	2080	Small amounts of up to about 1 percent SO_2 added to fuel rich C_3H_8/air atm pressure flames. [H] measured by the Na/Li method. Wheeler 1968.	Questionable analysis. Assumes a 1st order dependence on H which is not experimentally found.
		1940–90	Fuel rich $H_2/O_2/N_2$ atm pressure flames with up to 1 percent SO_2 added, [H] measured by the Li absorption method with and without SO_2 in the flame. Halstead and Jenkins 1969.	Confirms SO_2 mechanism of catalytic removal of H atoms proposed by Fenimore and Jones (1965).
$<1.4\times10^{-33}$	Ar	298	H atoms produced by RF discharge of 1–5 percent H_2/Ar mixtures in flow tube and measured by the intensity of the HNO emission from a trace of added NO. SO_2 added at entry ports after the discharge. Blue S_2 chemiluminescence observed. Fair and Thrush 1969.	No clear evidence for this reaction. The observed H atom decay attributed to the previously observed sulfur catalysed heterogeneous decay.
		2110	Seven isothermal fuel rich $C_3H_8/O_2/N_2$ atm pressure flames with addition of 0.1–1 percent SO_2. [H] measured by Li absorption method. Included flames of higher [OH] than previously, $[OH]/[H]\sim0.4$–3.8. Duric, Johnson, and Smith 1971.	Recombination kinetics 2nd order in [H]. Confirms findings of Halstead and Jenkins (1969). $OH+SO_2+M$ reaction appears unimportant in flames.

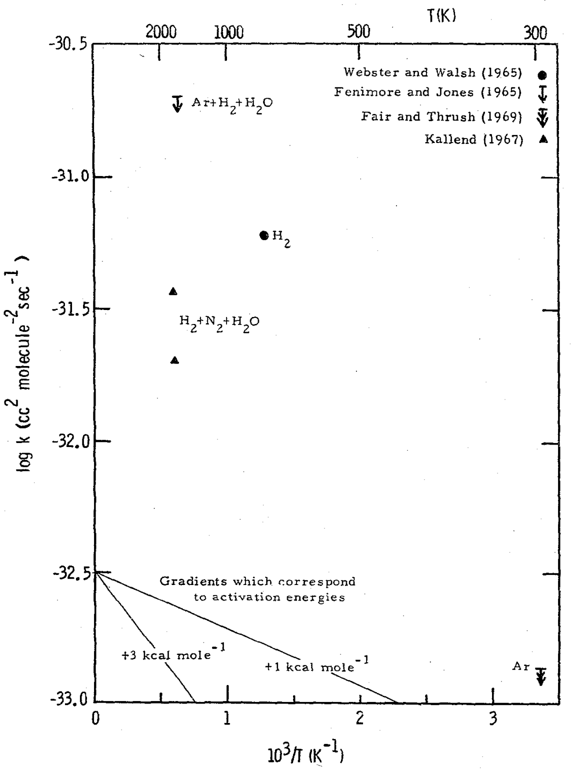

FIGURE 14. Experimental values of $k_{H+SO_2+M \to HSO_2+M}$.

firmed by Durie, et al. (1971), which is explained by including the reverse of the first reaction. At their temperatures (1940–1990 K and 2110 K, respectively) it appears that the first reaction can become essentially balanced so that the rate is then controlled by the subsequent reactions. This second order dependence previously had also been reported by McAndrew and Wheeler (1962) for propane-air flames at a similar temperature. Halstead and Jenkins (1969) suggest that it may not be unreasonable for the order of the reaction to change over to 1st at lower temperatures in agreement with the interpretation of Fenimore and Jones (1965) and possibly also with Kallend's findings (1967). The recalculation by Wheeler (1968) of their previous data [McAndrew and Wheeler, 1962] but assuming a 1st order dependence on [H] appears unjustified and consequently the value is highly questionable.

Kallend (1967) used flames for which $M=H_2+H_2O+N_2$. The rate constant did not significantly vary for changes in $[N_2]$ by a factor of 3, $[H_2]$ by a factor of 2 or $[H_2O]$ by 20 percent inferring that none of these is particularly more efficient than another.

A major difficulty is to reconcile the high temperature data with the negative results of Fair and Thrush (1969) who attempted to observe this reaction at room temperature. It would be necessary for the reaction to have a positive activation energy of about 3 kcal mol⁻¹ which seems unlikely. Consequently, the rate is still very uncertain and further work is necessary using more easily interpreted systems to better specify the observed reactions.

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4.17. $O+CS_2 \to CS+SO$

Thermodynamic data*

TK	ΔH^0 kcal mol⁻¹	ΔS^0 cal deg⁻¹ mol⁻¹	$\log_{10}K$
0	−30.912	—	—
100	−30.750	8.554	69.070
298	−30.899	8.020	24.401
300	−30.902	8.009	24.261
500	−31.297	7.004	15.210
1000	−32.278	5.640	8.287
1500	−33.224	4.872	5.905

*Recent data of Hildenbrand [Chem. Phys. Letters **15**, 379 (1972)] indicate that the values for ΔH^0 and K given in this table should be modified.

Equilibrium Constant

$$K=3.75\times10^4\,T^{-0.972}\exp(30{,}330/RT)$$
(300–2500 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations up to 0.6 percent in this temperature range.

Recommended Rate Constant

$k=2.0\times10^{-11}\exp(-1030/RT)$ cm^3 molecule^{-1} s^{-1}.
Temperature range: 200–1000 K.
Suggested error limits: ±20 percent in this temperature range.

$\log_{10}A=\overline{11}.29_4\pm0.06_0$ cm^3 molecule^{-1} s^{-1},
$E=1030\pm80$ cals.

Discussion

Three independent investigations have produced values for this rate constant. Those of Smith (1968), Westenberg and DeHaas (1969), and the two low temperature datum points of Homann, Krome, and Wagner (1968) are in good agreement, considering the different techniques and analyses involved. These form the basis for the recommended value which appears quite reliable. The high temperature values of Homann, et al. (1968) are suspect and appear to be about a factor of two high. Smith (1968) and Westenberg and DeHaas (1969) had concentrations of CS_2 in excess of the O atom concentration. Homann, et al. (1968) maintained an excess of O atoms. They appear to have measured *k* by following both the decrease in [CS_2] and the rate of increase in [SO] and so an explanation for the twofold discrepancy is not easy. A better understanding of the system at high temperatures is required.

Reported rate constants

Rate constant *k* (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
4.17×10^{-12} 5.35×10^{-12}	305 410	Flash photolysis of $CS_2/NO_2/Ar$ mixtures with wavelengths >3000Å. [CS_2] ~0.1 torr and CS_2/NO_2 ~10:1. Total pressure ~80 torr. [CS] monitored in absorption. SO also detected. *k* refers to the rate of production of ground state CS. Smith 1968.	Only the NO_2 photodissociated. Rather complex analysis but CS_2/NO_2 ratio chosen to minimize complications. O reacts almost exclusively with CS_2. Experimental time appears to have been too short for complications from the O+CS reaction.
3.19×10^{-11} 2.97×10^{-11} 2.37×10^{-11} 1.91×10^{-11} 3.68×10^{-12} 3.35×10^{-12}	917 930 866 704 302 303	Heated flow tube at 3–6 torr total pressure. O_2/Ar subjected to microwave discharge or O from N/NO titration. 0.03 percent CS_2/Ar added downstream such that O atoms about 6 times in excess. Sampled with TOF mass spectrometer. Homann, Krome, and Wagner 1968.	*k* derived from decrease in [CS_2] and increase in [SO]. [O] taken as its mean value.
2.07×10^{-12} 2.99×10^{-12} 7.80×10^{-12}	227 297 538	Flow system, O atoms from discharged 0.03 percent O_2/He mixture. CS_2 added downstream in amounts 5 to 10 times [O]. [O] measured by ESR, SO formation also observed. Stable products mass analyzed. Pressure ~2 torr. Westenberg and De Haas 1969.	Established a value of 2 for the O/CS_2 stoichiometry. Initial reaction followed by the fast $O+CS\rightarrow CO+S$ reaction.

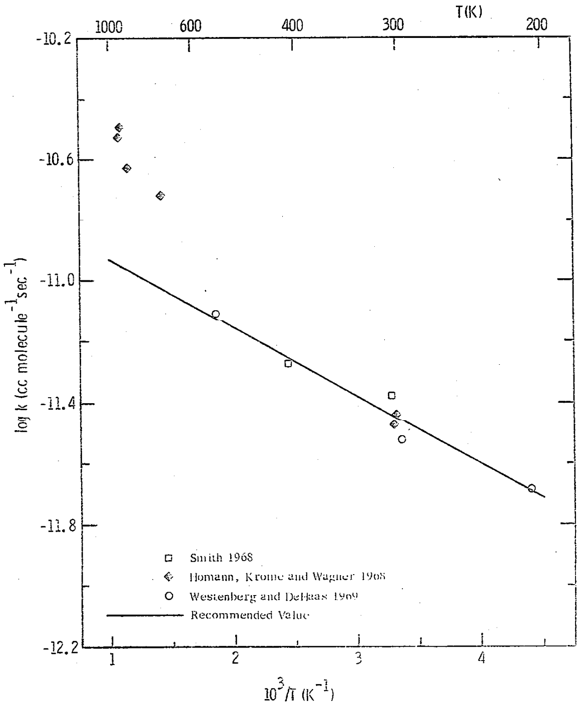

FIGURE 15. Experimental values of $k_{O+CS_2\rightarrow CS+SO}$.

Sheen (1970) has studied the oxidation of CS_2 in a shock tube, monitoring CS and SO in emission and absorption and the SO_2 afterglow. However, the analysis of the data is complex and reactions such as

$$O+CS\rightarrow CO+S,$$
$$S+O_2\rightarrow SO+O,$$

were not included. No reliable values can be derived from his analysis.

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4.18. O+OCS→CO+SO

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−51. 438	—	—
100	−51. 270	6. 126	113. 385
298	−51. 256	6. 444	38. 978
300	−51. 257	6. 438	38. 745
500	−51. 556	5. 693	23. 778
1000	−52. 557	4. 315	12. 429
1500	−53. 608	3. 463	8. 566

Equilibrium Constant

$K=1.28\text{x}10^4\ T^{-0.917}\ \exp\ (50{,}660/RT)$ (300–1000 K range),

$=4.20\text{x}10^4\ T^{-1.071}\ \exp\ (50{,}410/RT)$ (1000–3000 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–1000 K) and 0.3 percent (1000–3000 K).

Recommended Rate Constant

$k=6.8\text{x}10^{-11}\ \exp\ (-5080/RT)$ cm^3 molecule $^{-1}$ s^{-1}.
Temperature range: 270–1500 K.
Suggested error limits: ±35 percent.

$\log_{10}A=\overline{11}.83_3\pm0.08_0$ cm^3 molecule^{-1}s^{-1},
$E=5080\pm140$ cals.

Discussion

It is most gratifying when the values of five independent studies agree so well as is the situation for this reaction. Although investigated in each case by a flow tube technique, the experimental conditions differ considerably from an excess of OCS at one extreme to an excess of O atoms at the other.

The reaction appears very well established and there is no evidence for the alternate displacement reaction [Westenberg and DeHaas, 1969; Rolfes, Reeves, and Harteck, 1965],

$$O+OCS\rightarrow CO_2+S,$$

which would be about 54 kcal mol^{-1} exothermic.

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
0.91×10^{-14}	298	Flow system at about 1 torr or less sampled with a mass spectrometer. O_2 dissociated in a microwave discharge and OCS added in concentrations similar to [O]. Initial [O] calibrated either by NO_2 titration or by the change in mass 32 peak on initiating the discharge. Sullivan and Warneck 1965.	Production of CO equals loss of OCS. O_2 was the carrier gas.
$2.0\times10^{-10}\ \exp\ (-5800/RT)$	290–465	Flow system at 0.5–5 torr. Small [O] from N/NO titration; excess of OCS relative to O added. [O] monitored by ESR, stable products and SO by mass spectrometer. [SO] calibrated by the NO_2 titration. k derived from the decrease in O and the increase in SO. Hoyermann, Wagner, and Wolfrum 1967.	Secondary reactions minimized by operating with low concentrations.
1.06×10^{-11} 4.00×10^{-12} 3.10×10^{-12}	1123 869 794	Heated flow tube at about 3–6 torr total pressure. O_2/Ar mixture subjected to microwave discharge. 0.06 percent OCS/Ar mix added downstream, O-atoms in excess. Sampled with TOF mass spectrometer. k derived from decrease in [OCS] and growth of [SO]. Homann, Krome, and Wagner 1968.	

See footnote at end of table.

Reported rate constants—Continued

Rate constant k (cm ^{3} molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
8.96×10^{-15}	273	Flow system at 0.5–2.5 torr. O from discharge in <0.1 percent O_2/He or Ar mix or from N/NO titration with N_2 carrier gas. OCS concentration in large excess added downstream. O, SO detected by ESR. Stable products mass analyzed. k derived from decay of [O]. Westenberg and De Haas 1969.	1 oxygen atom consumed per OCS molecule.
1.41×10^{-14}	297		
7.14×10^{-14}	374		
3.49×10^{-13}	508		
9.46×10^{-13}	658		
2.06×10^{-12}	808		
$3.15\times10^{-11}\exp(-4530/RT)$	273–808		
1.19×10^{-14}	297	O atoms produced in a flow system by microwave discharge of O_2/He mixtures. OCS added downstream. Pressures around 0.5 torr. [O], [SO] monitored by ESR. Breckenridge and Miller 1972.	Procedure similar to that used by Westenberg and De Haas (1969).
$A_{O+O_3}/A_{O+OCS}=0.671$ $E_{O+OCS}-E_{O+O_3}=170$ cals	197–299	Photolysis of 3 and 12 torr. O_3/1–223 torr OCS mixtures with 5461 (85 percent) + 4358 Å (15 percent) radiation. Gas chromatographic analysis for CO and CO_2.	Independent of radiation time, absorbed intensity or presence of third body. Taking $k_{O+O_3}=1.7\times10^{-11}\exp(-4415/RT)$ Schofield (1972) this gives $k_{O+OCS}=2.5\times10^{-11}\exp(-4580/RT)$.
$A_{O+TMP^*}/A_{O+OCS}=0.928$ $E_{O+OCS}-E_{O+TMP}=2280$ cals	298–523	2537 Å Hg photosensitized decomposition of 500–700 torr N_2O in the presence of 0.7–4.7 torr TMP/1.4–18.3 torr OCS. Analyzed the gas mixture chromatographically for CO and other products. Krezenski, Simonaitis, and Heicklen 1971.	Taking $k_{O+TMP}=1.5\times10^{-11}\exp(-2200/RT)$ Simonaitis and Heicklen (1972) this gives $k_{O+OCS}=1.6\times10^{-11}\exp(-4500/RT)$.

*TMP is 2-Trifluoromethylpropene

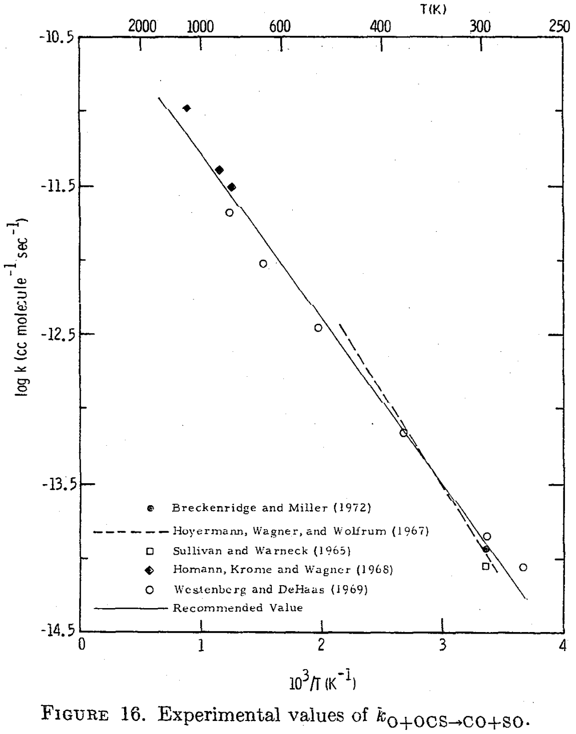

FIGURE 16. Experimental values of $k_{O+OCS\rightarrow CO+SO}$.

Because of the excellent agreement between studies, a best fit to all the available data is the basis for the recommended value. A recent photolysis study by Krezenski, Simonaitis, and Heicklen (1971) measured the rate of this reaction relative to those of $O+O_3$ and O+TMP (2-trifluoromethylpropene). This has not been included owing to the uncertainties in the rates of these reactions. Using the most reliable data for their rate constants, values for k_{O+OCS} are 1.32 times higher than that here recommended at 197 K and 1.17 times too low at 299 K ($O+O_3$ data). Similarly the calculated values are 1.59 (298 K) and 2.43 (523 K) times too low based on the O+TMP data. The latter probably infers a too low literature value for k_{O+TMP}.

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4.19. $O+H_2S \rightarrow OH+HS$

Thermodynamic data

TK	ΔH° kcal mol^{-1}	ΔS° cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−11. 067	—	—
100	−10. 974	1. 279	24. 256
298	−10. 647	2. 990	8. 456
300	−10. 644	2. 999	8. 407
500	−10. 438	3. 546	5. 337
1000	−10. 549	3. 444	3. 058

Equilibrium Constant

$K=1.72\,T^{0.166}\exp(10{,}650/RT)$ (300–1000 K range),
$=3.44\times10^{2}T^{-0.517}\exp(9480/RT)$
(1000–2500 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.4 percent (300–1000 K) and 0.3 percent (1000–2500 K).

Recommended Rate Constant

$k=6.3\times10^{-13}\exp(-1830/RT)$ cm^3 molecule^{-1} s^{-1}.
Temperature range: 200–350 K.
Suggested error limits: better than a factor of two in this range.

$$\log_{10}A=\overline{13}.80\pm0.20 \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1},$$
$$E=1830\pm250 \text{ cals.}$$

Discussion

This reaction has been studied successfully only in discharge flow systems with either mass spectrometric or ESR detection. However, the experimental conditions are different for each of the investigations.

Liuti, Dondes, and Harteck (1966) operated at a total pressure of about 0.5 torr and had similar concentrations of O and H_2S. Their results could be explained in terms of the three reactions

$$O+H_2S\rightarrow OH+HS,$$
$$O+HS\rightarrow H+SO,$$
$$H+H_2S\rightarrow H_2+HS.$$

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
4×10^{-14}	295	Flow system at pressures ~0.5 torr, sampled by TOF mass spectrometer. DC discharge in O_2 or 10 percent O_2/Ar mixtures. O also produced from N/NO titration. H_2S/Ar mixture added downstream. [O] measured from initial decrease in O_2 at mass 32 when the discharge initiated and also from the NO_2 titration. O and H_2S concentrations small and of a similar magnitude. Liuti, Dondes, and Harteck 1966.	Estimates made concerning the average reaction chain length required in the analysis.
4.8×10^{-14}	300	Discharge flow system at about 10 torr, sampled by a TOF mass spectrometer. Low concentrations of O and H_2S, low conversions. $[O]>[H_2S]$. Niki and Weinstock 1967.	No information available about the assumptions made in reducing the data.
8.11×10^{-15} 1.09×10^{-14} 1.58×10^{-14} 2.81×10^{-14} $2.9\times10^{-13}\exp(-1500/RT)$	205 234 273 300 205–300	Flow system at pressures of about 2 torr. Electrodeless discharge in 0.3–1.4 percent O_2/He mixtures. Small additions of H_2S downstream. $[H_2S]>[O]$. Assume $[H_2S]$ constant, decay of O-atoms monitored by ESR. Hollinden, Kurylo, and Timmons 1970.	Assume a 3.5 O atoms:1 H_2S stoichiometry.
1.51×10^{-14}	295	5 percent O_2/He mixtures subjected to a microwave discharge in a flow system at 0.5–1 torr. H_2S added downstream in amounts similar to [O]. [O], [H], [SO] monitored by ESR. Cupitt and Glass 1970.	Computer fit of the experimental data to that calculated assuming a 7 stage mechanism. Agreement for cases of $O>H_2S$. Error found recently in the original analysis leads to a slightly higher value than initially published.

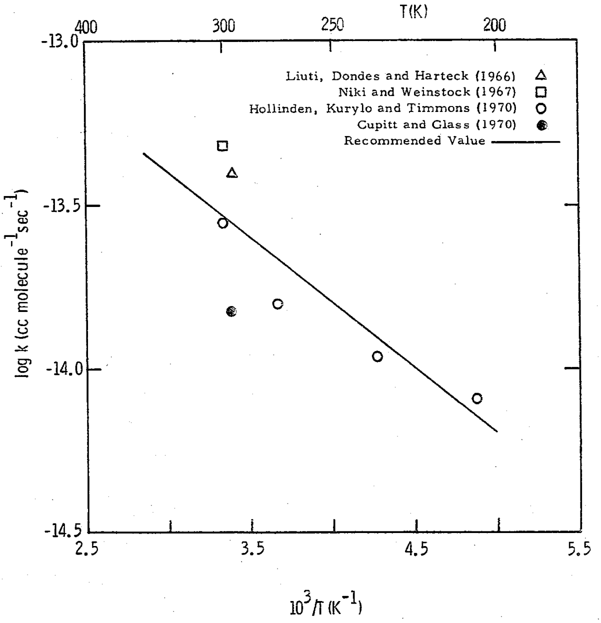

FIGURE 17. Experimental values of $k_{O+H_2S \rightarrow OH+HS}$.

The latter two form a chain mechanism. OH appeared to play no major role in their system and only 1.1–1.25 O atoms were consumed per H_2S. For each H_2S consumed about 0.8 molecule of H_2 was formed. Therefore it was estimated that the average chain length, that is the number of H_2S molecules consumed before either the HS or the H is lost to the walls, was about 5±1.5. The overall rate of consumption of H_2S and O occurred with a reaction rate of 2×10^{-13} cm^3 molecule^{-1} s^{-1} at 295 K. This was corrected by the chain factor to obtain the rate constant for the initiating reaction. Niki and Weinstock (1967) used a similar technique but with differing experimental conditions. Unfortunately, no details have been published of their analysis and so the assumptions made remain unknown.

Hollinden, Kurylo, and Timmons (1970), in a system at about 2 torr, operated with $[H_2S] > [O]$ and monitored only [O]. However, there were experimental limitations as to how much in excess the H_2S could be. Since $[H_2S]$ was assumed constant, although on occassion it appears to have been in only slight excess, there may be some question as to the accuracy of particularly the higher temperature data. Their system was described by the kinetic scheme

$$\mathrm{O+H_2S \rightarrow OH+HS},$$
$$\mathrm{O+OH \rightarrow O_2+H},$$
$$\mathrm{O+HS \rightarrow H+SO},$$

with some contribution from $\mathrm{O+SO+M \rightarrow SO_2+M}$. Based on this they took a value of 3.5 O atoms: 1 H_2S as the stoichiometry of the overall reaction. The $\mathrm{H+H_2S \rightarrow H_2+HS}$ reaction was considered insignificant. This has since been questioned by Cupitt and Glass (1970) who find that the [O]/[H] ratio is not large in H_2S rich mixtures yet k_{H+H_2S}/k_{O+H_2S} is about a factor of 30. Therefore it would seem that their data must have been influenced somewhat by this reaction. Its inclusion though would set up the same chain mechanism considered by Liuti, et al. (1966) and result in a lower value for k.

Cupitt and Glass (1970) by systematically varying the rate constants in the seven step mechanism

$$\mathrm{O+H_2S} \overset{k_1}{\rightarrow} \mathrm{OH+HS},$$
$$\mathrm{O+OH} \overset{k_2}{\rightarrow} \mathrm{H+O_2},$$
$$\mathrm{H+H_2S} \overset{k_3}{\rightarrow} \mathrm{H_2+HS},$$
$$\mathrm{HS+O} \overset{k_4}{\rightarrow} \mathrm{H+SO},$$
$$\mathrm{H+HS} \overset{k_5}{\rightarrow} \mathrm{H_2+S},$$
$$\mathrm{SO+OH} \overset{k_6}{\rightarrow} \mathrm{SO_2+H},$$
$$\mathrm{S+O_2} \overset{k_7}{\rightarrow} \mathrm{SO+O},$$

managed to reproduce the experimental data for cases where $[O] > [H_2S]$. However, the values used in their analysis differ somewhat from those currently recommended. The value for k_2 (4.3×10^{-11}) possibly is too high by a factor of 2, Baulch, et al. (1969) recommend 2.2×10^{-11}. This also is the case for k_6. The calculations were insensitive to k_4 and k_5 but these rates likewise were taken at about 2.5 and 4 times too fast, respectively. k_7 was taken as 1.2×10^{-12} rather than 2.2×10^{-12} (see $S+O_2$ evaluation). Moreover, it appears that the value derived for k_3 is too high by about a factor of 1.8 (see $H+H_2S$ evaluation). This is the same factor by which k_{O+H_2S} falls below the value recommended here. This allows for an arithmetic error found in their original analysis. The SO concentrations originally reported were too high. Their value is the lowest reported at room temperature.

Levy and Merryman (1965) and Merryman and Levy (1967) investigated $H_2S/O_2/N_2$ or Ar flames at atmospheric and reduced pressures. The gases were analysed by microprobe sampling and wet chemical or mass spectrometric methods. However, the system is very complicated and because of insufficient experimental data it is not possible to estimate with any certainty the rate constants of the dominant reactions.

The rate constant recommended for this reaction is based on the 5 datum points obtained by Liuti, Dondes, and Harteck (1966) and Hollinden, Kurylo, and Timmons (1970). These have been weighted equally and give a value in this rather restricted temperature range that should be accurate to better than a factor of two. The reaction has a low pre-exponential factor.

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4.20. $H+H_2S \rightarrow H_2+HS$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−12. 998	—	—
100	−12. 840	0. 441	28. 152
298	−12. 620	1. 394	9. 553
300	−12. 617	1. 403	9. 496
500	−12. 402	1. 971	5. 851
1000	−12. 517	1. 870	3. 144

Equilibrium Constant

$K=0.672\ T^{0.187}\exp(12{,}630/RT)$ (300–1000 K range).

This expression reproduces the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.1 percent.

Recommended Rate Constant

$k=1.5\times10^{-11}\exp(-1700/RT)$ cm^3 molecule^{-1} s^{-1}.
Temperature range: 190–500 K.
Suggested error limits: ±30 percent in this range.

$$\log_{10}A=\overline{11}.18\pm0.07\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},$$
$$E=1700\pm90\ \text{cals.}$$

Discussion

Perner and Franken (1969) determined a value for this rate constant from the maximum in the growth and decay profile of the HS concentration after an energizing pulse. HS is formed by this reaction and had a second order decay in their system which was attributed to the reaction of two HS radicals. The HS absolute concentration had to be estimated indirectly from the yield of H_2 in pure H_2S assuming 85 percent of the HS was formed by this rather than alternate reactions.

Kurylo, et al. (1971) obtained most of their data using flash wavelengths >2000 Å. However, they did investigate the system with wavelengths <2000 Å but found agreement only at low flash intensities where it appeared that competing reactions were unimportant.

Cupitt and Glass' (1970) analysis to derive values for both k_{O+H_2S} and k_{H+H_2S} has been commented upon

Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	$k_{298\text{ K}}$	Exp. temp. (K)	Method & reference	Comments
1.3×10^{-12}		298	Pulsed radiolysis study of H_2S mixtures at total pressures ~0.5–1 atm. A large excess of xenon added to thermalize H atoms. [HS] monitored in absorption. Extent of dissociation $<10^{-3}$ percent. Perner and Franken 1969.	
$1.7\times10^{-11}\exp(-1680/RT)$	1.0×10^{-12}	243–368	Flow system, 1–20 torr pressure. H formed by microwave discharge in H_2/Ar, He, or Xe mixtures. H_2S added downstream in concentrations similar to [H]. [H], [HS], and [S] monitored by ESR. Mass spectral analysis of stable products. Mihelcic and Schindler 1970.	Values derived from H decay and HS growth in agreement.
1.53×10^{-12}		295	Low pressure flow system, O atoms produced by microwave discharge in 5 percent O_2/He mixtures. Small addition of H_2S downstream. ESR detection of O, H, and SO. Concentration profiles followed with reaction time. Cupitt and Glass 1970.	Experimental and computed profiles matched by adjusting the reaction rates for a 7 stage mechanism. Best agreement for [O]>[H_2S] case. An error found in the original analysis leads to a lower value than initially published.

Reported rate constants—Continued

Rate constant k (cm^3 molecule^{-1} s^{-1})	$k_{298\ K}$	Exp. temp. (K)	Method & reference	Comments
$1.3\times10^{-11}\exp(-1709/RT)$	7.2×10^{-13}	190–464	Flash photolysis with wavelengths >2000 Å of 40–125 millitorr H_2S in ~50 torr He. [H] followed by Lyman α resonance fluorescence at 1216 Å. Kurylo, Peterson, and Braun 1971.	
$\frac{k_{H+I_2}}{k_{H+H_2S}}=166$		323	Photolysis of 9.5 torr H_2S/689 torr CO_2/0.2 torr I_2 and 9.0 torr H_2S/600 torr CO_2/1.0 torr Br_2 mixtures with >2000 Å (mainly 2537 Å). Quantum yields of H_2 used as a measure of the reaction in presence and absence of halogen. Darwent, Wadlinger, and Allard 1967.	Gives values for $k_{H+H_2S}\sim(1.8\text{–}5.2)\times10^{-12}$.
$\frac{k_{H+Br_2}}{k_{H+H_2S}}=11.7$		323		
$\frac{k_{H+H_2S}}{k_{H+C_2H_4}}=0.828$		296. 5	2490 Å photolysis of about 12 torr H_2S/1–60 torr C_2H_4 diluted to about 1 atm with CO_2 to thermalize H atoms. Decomposition <1 percent. Rate of production of H_2 measured. Woolley and Cvetanovic 1969.	Gives a value $k_{H+H_2S}\sim1\times10^{-12}$.
$E_{H+H_2S}-E_{H+O_2+M}=2700$ cals		323, 373, 423	Mercury arc photolysis of $H_2S/O_2/CO_2$ mixtures. Quantum yield of H_2 formation measured. H assumed to disappear via $H+H_2S$ and $H+O_2+M$ reactions. Conversion kept to ≤1 percent. Wadlinger and Darwent 1967.	Taking $E_{H+O_2+M}=-1000$ Baulch, et al. (1969) gives $E_{H+H_2S}=1700$ cal mol^{-1}.

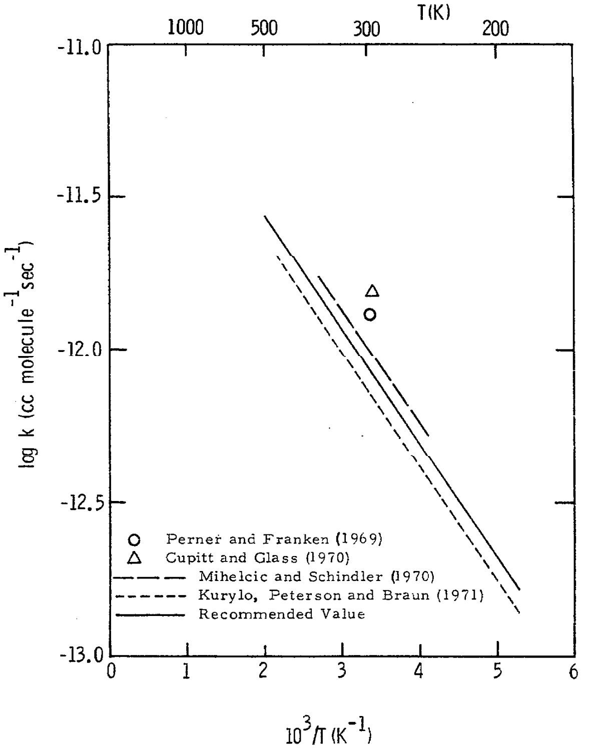

FIGURE 18. Experimental values of $k_{H+H_2S\rightarrow H_2+HS}$.

already in the evaluation of the k_{O+H_2S} data. The remarks made there apply equally well to their value quoted here. Their values for k_{H+H_2S} and k_{O+H_2S} appear too high and too low, respectively. Allowance has been made for an arithmetic error found in the original analysis which resulted in too high SO concentrations.

Earlier photochemical studies of D_2S by Darwent and Roberts (1953) were complicated by "hot" D atom effects and do not provide reliable data. Later work utilized mixtures diluted with excess CO_2 to thermalize the H atoms.

Woolley and Cvetanovic (1969) measured the ratio $k_{H+H_2S}/k_{H+C_2H_4}=0.828$ at 296.5 K. The value for $k_{H+C_2H_4}$ has not been evaluated yet but is known to be a function of pressure. At this temperature the mean of five references [Braun and Lenzi, 1967; Dodonov, et al., 1969; Barker and Michael, 1969; Eyre, et al., 1970; Kurylo, et al., 1970] which report a value for its high pressure limit is 1.2×10^{-12} cm^3 molecule^{-1}s $^{-1}$. This gives $k_{H+H_2S}\sim1\times10^{-12}$ in agreement with the recommended value, figure 18. Similarly Darwent, et al. (1967) obtained values relative to k_{H+I_2} and k_{H+Br_2} at 323 K. Taking the latter two as 3×10^{-10}

[Sullivan, 1959] and 6×10^{-11} [Thrush, 1965] gives values for $k_{\mathrm{H}+\mathrm{H_2S}}$ of 1.8 and 5.2×10^{-12}, respectively, a little on the high side. Both the latter studies assume that no hydrogen results from reactions other than that of $H+H_2S$.

Wadlinger and Darwent (1967) derived an estimate for the activation energy which is in remarkedly good agreement with that recommended here.

At present, the data of Mihelcic and Schindler (1970) and Kurylo, Peterson, and Braun (1971) seem least questionable. A mean value based on their measurements is recommended.

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4.21. $H+HS+M \leftrightarrows H_2S+M$

Thermodynamic data

T K	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10} K_p$ atm^{-1}	$\log_{10} K_c$ cm^3 molecule^{-1}
0	−90. 264	—	—	—
100	−90. 656	−19. 984	193. 756	173. 890
298	−91. 580	−24. 970	61. 671	42. 280
300	−91. 589	−24. 998	61. 258	41. 870
500	−92. 398	−27. 087	34. 465	15. 298
1000	−93. 713	−28. 976	14. 148	−4. 718
1500	−94. 415	−29. 558	7. 296	−11. 394
2000	−94. 810	−29. 788	3. 849	−14. 716
2500	−95. 038	−29. 891	1. 775	−16. 693
3000	−95. 167	−29. 938	0. 390	−17. 998
3500	−95. 230	−29. 958	−0. 601	−18. 923
4000	−95. 248	−29. 963	−1. 345	−19. 609
4500	−95. 229	−29. 959	−1. 923	−20. 135
5000	−95. 185	−29. 949	−2. 385	−20. 552
5500	−95. 122	−29. 937	−2. 763	−20. 888
6000	−95. 041	−29. 923	−3. 077	−21. 164

Equilibrium Constant

$$K_p=0.182\ T^{-1.047}\exp(90{,}700/RT)\ \mathrm{atm}^{-1}$$

(300–1000 K range),

$$=9.88\times10^{-6}T^{-0.401}\exp(93{,}150/RT)$$

(1000–3000 K range).

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.5 percent (300–1000 K) and 0.8 percent (1000–3000 K).

Recommended Rate Constant

Reliable rate constants for this, and the reverse dissociation reaction, appear to be unreported in the literature.

Discussion

Reliable rate constants for this reaction and its reverse appear unreported in the literature. Gas phase studies of H_2S, until recently, mainly have been photochemical in nature. Owing to the difficulties of interpreting such data because of complicating 'hot' H-atom effects [Darwent, et al., 1967; Gann and Dubrin, 1967; Sturm and White, 1969; Compton, et al., 1969, 1970] information, particularly on the reactions of H_2S and HS has been slow in emerging and still requires more extensive investigations.

Darwent and Roberts (1953) studied the thermal dissociation of H_2S and measured the rate of hydrogen production at 760–975 K with initial H_2S pressures of 30–300 torr. They established that above 870 K the decomposition became homogeneous and was second order with respect to the H_2S concentration. The hydrogen production had an apparent activation energy of about 50 kcal mol^{-1}. A scheme involving such reactions as

$H_2S+M \rightarrow H+HS+M$	$\Delta H^0_{298\,K} = +91.58$ kcal mol^{-1}
$H+H_2S \rightarrow H_2+HS$	-12.62
$HS+HS \rightarrow H_2S+S$	-7.40
$HS+HS \rightarrow H_2+S_2$	-38.36
$H+HS \rightarrow H_2+S$	-20.02
$S+HS \rightarrow S_2+H$	-18.34

probably is involved but cannot explain the low activation energy observed.

Levy and Merryman (1965) included the bimolecular dissociation reaction of H_2S in their kinetic scheme describing H_2S/O_2 atm pressure flames. However, such flames propagate via fast atom and radical attack of H_2S such that it is impossible to study the thermal dissociation of H_2S in their system.

References

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4.22. $HS+HS \rightarrow H_2S+S$

Thermodynamic data

*T*K	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−6.940	—	—
100	−7.027	−2.270	14.870
298	−7.400	−4.221	4.504
300	−7.404	−4.231	4.472
500	−7.627	−4.826	2.279
1000	−7.632	−4.871	0.603

Equilibrium Constant

$$K=0.478\ T^{-0.229} \exp\,(7360/RT)\ \text{(300–1000 K range)},$$
$$=6.73\times10^{-3}T^{0.320} \exp\,(8310/RT)\ \text{(1000–2500 K range)}.$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 1.0 percent (300–1000 K) and 0.4 percent (1000–2500 K).

Recommended Rate Constant

There is a large uncertainty in the magnitude of the rate constant for this reaction. At room temperature a value is suggested of about 1.5×10^{-11} cm^3 molecule^{-1}s^{-1} which is probably reliable to within a factor of 4.

A small or zero activation energy is probable. The rate and rate constant are defined by

$$d[H_2S]/dt=k[HS]^2=-0.5\ d[HS]/dt.$$

Reported rate constants

Rate constant *k* (cm^3 molecule^{-1}s^{-1})	Exp. temp. (K)	Method & reference	Comments
1.2×10^{-10}	298	Flash photolysis of 30 torr H_2S and 30 torr H_2S/100–400 torr CO_2 mixtures. [SH], [S_2] followed in aborption. Strausz, Donovan, and De Sorgo 1968.	Stated to be reliable to within a factor of 3. *k* has been divided by 2 to correct for the rate constant definition.
2.7×10^{-11}	298	Pulsed radiolysis study of H_2S in excess Xe. [HS] followed in absorption and products analysed for H_2 formation. HS absolute concentrations had to be estimated approximately from the H_2 yields. Perner and Franken 1969.	2nd order decay observed. *k* determined from the maximum HS concentration. *k* has been divided by 2 to correct for the rate constant definition.
1.1×10^{-11}	295	Flow system, H formed by microwave discharge of H_2/Ar, He, or Xe mixtures. H_2S added downstream in amounts comparable to [H]. H, HS, and S concentrations monitored by ESR. Mass spectral analysis also of stable products. Mihelcic and Schindler 1970.	2nd order decay observed. *k* determined from the HS peak concentration.

Discussion

The three measured rate constants vary by an order of magnitude at room temperature. Mihelcic and Schindler (1970) defined their rate according to

$$-\mathrm{d}[\mathrm{HS}]/dt=2k[\mathrm{HS}]^2.$$

Strausz, et al. (1968), and Perner and Franken (1969) did not define their rate constants but it appears that their values are for $2k$. Consequently, they have been halved in this tabulation.

The reaction is fast at room temperature and the activation energy is either very small or zero [Dzantiev and Shishkov, 1967; Darwent and Roberts, 1953].

Disagreement possibly stems from the difficulties of measuring HS concentrations absolutely. Strausz, et al. (1968) quote an extinction coefficient for the (1, 0) band of HS used in their analysis. Perner and Franken (1969) calibrated the HS concentrations in a very approximate way by measuring the hydrogen formation in the case of pure H_2S. From this, by assuming 85 percent of the H_2 was formed from the $H+H_2S \rightarrow H_2+HS$ reaction, values were estimated for the diluted systems. Mihelcic and Schindler (1970) used an analysis similar to that of Westenberg (1965) for OH to calibrate the HS ESR signals. The latter may be the most reliable and is heavily weighted in the assessment of the recommended value.

The recombination of two HS radicals can occur via two exothermic reaction paths

$$(1)\qquad HS+HS \rightarrow H_2S+S,$$
$$(2)\qquad \rightarrow H_2+S_2.$$

The former of these is the predominant mechanism, probably owing to the four center nature of the other. All the studies above measured the sum k_1+k_2. These have been taken as k_1 values owing to the difference in magnitude between the two. Reaction (2) is discussed more fully next in this paper.

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4.23. $HS+HS \rightarrow H_2+S_2$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−38.093	—	—
100	−38.019	−5.746	81.840
298	−38.360	−7.740	26.428
300	−38.362	−7.745	26.255
500	−38.381	−7.825	15.066
1000	−38.106	−7.439	6.702

Equilibrium Constant

$$K=4.77\times10^{-3}T^{0.199}\ \exp\ (38{,}550/RT)\quad (300\text{–}1000\ \mathrm{K\ range}),$$
$$=3.39\times10^{-2}T^{-0.041}\ \exp\ (37{,}950/RT)\quad (1000\text{–}2500\ \mathrm{K\ range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.6 percent (300–1000 K) and 0.2 percent (1000–2500 K).

Recommended Rate Constant

Very little information is available for this reaction. Further studies are necessary. The rate and rate constant are defined as

$$d[H_2]/dt=k[\mathrm{HS}]^2=-0.5\ d[\mathrm{HS}]/dt.$$

Discussion

This reaction is sufficiently energetic that the S_2 produced can be in its $^1\Delta_g$ or $^1\Sigma_g{}^+$ electronic states, both of which are allowed from spin correlation considerations. They require about 14.6 and 26.0 kcal mol^{-1} energy of excitation [Barrow and DuParcq, 1968]. Strausz, et al. (1968) have monitored $S_2(^1\Delta_g)$ in absorption following the flash photolysis of H_2S_2 and H_2S and identify its formation with this reaction.

Mihelcic and Schindler (1970) studying a D_2/H_2S system at room temperature detected small amounts of H_2 which probably result from this reaction. However, Darwent, Wadlinger, and Allard (1967) found no evidence for it at slightly higher temperatures.

Darwent and Roberts (1953) in a study of the 2288 Å photolysis of H_2S reported that for the two possible reactions

$$(1)\qquad HS+HS \rightarrow H_2S+S$$
$$(2)\qquad \rightarrow H_2+S_2$$

87 percent proceeded via reaction (1). Similar findings were reported by Dzantiev and Shishkov (1967) for a 2537 Å photolysis. These estimates are undoubtedly too low. Like the similar reactions for OH it would appear that the former route is predominant and the four center reaction relatively slow.

Reported rate constants

Rate constant k (cm^3 $molecule^{-1}$ s^{-1})	Exp. temp. (K)	Method & reference	Comments
$<5\times10^{-14}$	295	Flow system, D atoms formed by microwave discharge of D_2/Ar, He, or Xe mixtures at about 2 torr. H_2S added downstream in amounts comparable to [D]. [D] monitored by ESR and stable products analysed by mass spectrometer. Mihelcic and Schindler 1970.	Small amounts of H_2 detected in the products appear to result from this reaction.
	410–500	HS radicals formed from the reaction of CH_3 with H_2S. Acetone was used as the source of CH_3 being photolysed in the presence of H_2S. Darwent, Wadlinger, and Allard 1967.	No H_2 could be detected.

References

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4.24. $H+HS\rightarrow H_2+S$

Thermodynamic data

TK	ΔH^0 kcal mol^{-1}	ΔS^0 cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−19. 938	—	—
100	−19. 867	−1. 829	43. 022
298	−20. 020	−2. 827	14. 057
300	−20. 021	−2. 828	13. 968
500	−20. 029	−2. 855	8. 130
1000	−20. 149	−3. 001	3. 747

Equilibrium Constant

$$K=0.318\ T^{-0.042}\exp(20{,}000/RT)\quad (300\text{–}1000\ \text{K range}),$$

$$=1.67\ T^{-0.257}\exp(19{,}660/RT)\quad (1000\text{–}2500\ \text{K range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.4 percent (300–2500 K).

Recommended Rate Constant

No recommendation is possible at present but the reaction does appear to be fast at room temperature. It is much faster than theoretically predicted.

Discussion

Recently, Cupitt and Glass (1971) have studied the $H/H_2S/O_2$ system in a flow tube. Under the conditions of excess O_2 and $[H]>[H_2S]$ it was found that the measurements could be described by the four reactions

$$H+H_2S\xrightarrow{k_1}H_2+HS,$$

$$H+HS\xrightarrow{k_2}H_2+S,$$

$$S+O_2\xrightarrow{k_3}SO+O,$$

$$HS+O\xrightarrow{k_4}H+SO.$$

By applying the steady state approximation for HS this gives the expression

$$k_1[H]\,[H_2S]=[HS](k_2[H]+k_4[O]).$$

It was possible to determine k_2/k_1 from this by using their measured value of $k_4/k_2=6.5$. $[H_2S]$ was not monitored directly but based on $[H_2S]_0-[SO]$ measurements since at these high O_2 concentrations H_2S appeared to be quantitatively converted into SO. Their assumptions are reasonably well substantiated and the values they also report for k_{H+H_2S} and k_{O+H_2S} are within a factor of two of those currently recommended.

A very preliminary value for $k_{H+HS}\sim2\times10^{-11}$ derived from flash photolysis studies of H_2S [Oldershaw, 1972] confirms Cupitt and Glass' measurements.

It appears that the theoretical calculation of Mayer and Schieler (1968) which at room temperature predicts a value of 3×10^{-13} is in error.

References

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Mayer, S. W., and L. Schieler, "Computed activation energies and rate constants for forward and reverse transfers of H atoms," J. Phys. Chem. **72,** 236 (1968).

Oldershaw, G. A., private communication (1972).

4.24 Reported rate constants

Rate constant k (cm^3 molecule^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
$7.7\times10^{-13}T^{0.67}\exp(-2800/RT)$	298–2500	Theoretical computation based on a modified Johnston-Parr method. Mayer and Schieler 1968.	$k_{300\text{ K}}=3.2\times10^{-13}$
3.1×10^{-11}	295	5 percent H_2/Ar mixture discharged, O_2 added after the discharge followed by H_2S addition further downstream at a total pressure ≤1.7 torr. [H]>[H_2S] with O_2 in excess. [H], [HS], [S], [O], and [SO] monitored by ESR. Cupitt and Glass 1971.	The value $\frac{k_{H+HS}}{k_{H+H_2S}}=37.8\pm7$ was determined. The recommended value for k_{H+H_2S} has been taken as 8.25×10^{-13} at this temperature.

4.25. $S+HS\rightarrow S_2+H$

Thermodynamic data

TK	ΔH° kcal mol^{-1}	ΔS° cal deg^{-1} mol^{-1}	$\log_{10}K$
0	−18. 155	—	—
100	−18. 152	−3. 917	38. 818
298	−18. 340	−4. 913	12. 371
300	−18. 341	−4. 917	12. 287
500	−18. 352	−4. 970	6. 936
1000	−17. 957	−4. 438	2. 955

Equilibrium Constant

$$K=1.50\times10^{-2}T^{0.241}\exp(18{,}550/RT)\quad(300\text{–}1000\text{ K range}),$$
$$=2.04\times10^{-2}T^{0.215}\exp(18{,}300/RT)\quad(1000\text{–}2500\text{ K range}).$$

These expressions reproduce the 100 K interval data derived from the JANAF Thermochemical tables with deviations of up to 0.9 percent (300–1000 K) and 0.4 percent (1000–2500 K).

Recommended Rate Constant

The reaction most probably is fast at room temperature but has been insufficiently studied and no recommendation is yet possible.

Discussion

The reaction is sufficiently energetic and spin allowed to leave the S_2 in the ($^1\Delta_g$) electronic state (about 14.6 kcal mol^{-1} above the ground state) but little is known yet of its dynamics. The value of Mihelcic and Schindler (1970) is dependent on k_{HS+HS} which is still quite uncertain. The two estimates differ by a factor of about seven at room temperature.

References

Mayer, S. W., and L. Schieler, "Computed activation energies and rate constants for forward and reverse transfers of H atoms," J. Phys. Chem. **72,** 236 (1968).

Mihelcic, D., and R. N. Schindler, "Electron spin resonance study of the reaction between atomic hydrogen and hydrogen sulfide," Ber. Bunsenges. Physik. Chem. **74,** 1280 (1970).

Reported rate constants

Rate constant k (cm^3 molecuie^{-1} s^{-1})	Exp. temp. (K)	Method & reference	Comments
4.5×10^{-11}	295	Flow system, H formed by a microwave discharge in H_2/Ar, He, or Xe mixtures at about 2 torr. H_2S added downstream in amounts comparable to H. [H], [HS], [S] monitored by ESR. Mass spectral analysis of stable products. Mihelcic and Schindler 1970.	Value obtained from the peak S concentration. Equate rates of the reactions $HS+HS=H_2S+S$, $S+HS=S_2+H$, and use $k_{HS+HS}=1.1\times10^{-11}$ (295 K).
$6.85\times10^{-13}T^{0.67}\exp(-900/RT)$	298–2500	Theoretical computation based on a modified Johnston-Parr method. Mayer and Schieler 1968.	$k_{295\text{K}}=6.7\times10^{-12}$.

4.26 Miscellaneous Reactions

These are reactions for which only limited information, if any, is yet available

Reaction	$\Delta H^0_{298\ K}$	Comments
$O+H_2+M\rightarrow H_2O+M$	-117.3	This reaction is spin forbidden and not observed experimentally. The third body is not capable of spin-flipping the activated complex. The reaction appears unlikely since it involves the formation of 2 O–H bonds with an H–H bond breakage.
$O(^1D)+H_2+M\rightarrow H_2O+M$	-162.7	Is an allowed reaction [De More, 1967] but necessarily competes with $O(^1D)+H_2\rightarrow OH+H$ which is known to proceed at near collision frequency [Schofield, 1972].
$N+NO+M\rightarrow N_2O+M$ $N(^2D)+NO+M\rightarrow N_2O+M$	-114.9 -169.9	$k_{343\ K}<10^{-35}$ cm^6 molecule^{-2} s^{-1} [Harteck and Dondes, 1957]. Harteck [1957; Harteck and Dondes, 1957] studied the NO decomposition at 343 K resulting from the energy released on fission of $^{235}UO_2$ in a quartz vessel initially filled with 500 torr of gas at 294 K. During the initial stages of radiation when this reaction could be observed, if it were occurring, no N_2O was detectable. The quoted k was derived from this negative result. Both $N(^4S)$ and $N(^2D)$ will be produced in the experiment. Verbeke and Winkler (1960) found no N_2O on interacting NO at temperatures up to 673 K with 'active' nitrogen produced by an electric discharge. These reactions will always be overshadowed by the extremely rapid corresponding bimolecular interactions between N and NO.
$SO+O_2+M\rightarrow SO_3+M$	-96.23	SO_3 is a symmetrical, planar molecule. Consequently, this reaction would involve formation of two S–O linkages with a breaking of the O–O bond. The reaction seems unlikely and is equivalent to the reactions $H_2+O+M\rightarrow H_2O+M,$ $NO+O_2+M\rightarrow NO_3+M,$ $NH+H_2+M\rightarrow NH_3+M,$ which have not been observed. No information is available for the reaction or the reverse dissociation as might be expected.
$SO+O_3\rightarrow SO_2+O_2$	-106.7	$k=(2.5\pm0.3)\times10^{-12}\exp(-2100\pm400/RT)$, 223–303 K. Halstead and Thrush (1965, 1966) have studied this reaction in detail, and the rate constant is reliable in this low temperature range to within a factor of 2 to 3. 1–5 percent SO_2/Ar mixtures were subjected to RF discharge. O_3 added in excess of the SO in the region where O atoms had decayed. Total pressures 0.3–3 torr in the flow system. [SO] measured by titration with NO_2 and the reaction was followed by monitoring the SO_2 chemiluminescence which is proportional to [SO]. Rates of production of electronically excited states of SO_2 were also derived.
$O+SO_3\rightarrow SO_2+O_2$	-35.92	Kaufman (1958), studying the effect at room temperature of added SO_3 on the air afterglow, reported that the activation energy must be equal to or greater than 7 kcal mol^{-1}. More recently Merryman and Levy (1971) have measured $[SO_3]$ and [O] concentration profiles in $OCS/O_2/N_2$ premixed flames at pressures of 75 and 245 torr. The flames were sampled with a quartz microprobe. $[SO_3]$ was determined by wet chemical analysis and [O] by the addition of excess NO_2 to the sample followed by mass spectral analysis. Based on the assumption that the predominant formation/loss mechanisms in these flames are the $O+SO_2+M$ and $O+SO_3$ reactions and taking a value of $k_{O+SO_2+M}=6.6\times10^{-31}\exp(-2500/RT)$ cm^6 molecule^{-2} s^{-1} (200 fold larger at 1500 K than the value currently recommended in this report for $M=O_2,N_2$) they measure $k_{O+SO_3}=4.6\times10^{-10}\exp(-12{,}000/RT)$ cm^3 molecule^{-1} s^{-1} (1480–1550 K). Owing to the complexity of the system studied, the narrow temperature range and the uncertainty of k_{O+SO_2+M} this can only be very tentatively accepted until confirmed.

These are reactions for which only limited information, if any, is yet available—Continued

Reaction	$\Delta H^0_{298\ K}$	Comments
$SO+OH \rightarrow SO_2+H$	−29.92	This reaction has been studied in a flow system at room temperature [Fair and Thrush, 1969]. H_2/Ar mixtures were discharged and O_2 and H_2S added. H atoms were in excess. NO_2 added further downstream to form OH. Measured from the decays of O and SO which were monitored by the air and SO_2 afterglows. Obtained $k_{O+OH}/k_{SO+OH}=0.4$ (298K). Using $k_{O+OH}=2.1\times10^{-11}$ [Baulch, et al., 1969] this gives $k_{SO+OH}=5.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} with an uncertainty of at least a factor of 2.
$S+OH \rightarrow SO+H$	−22.37	No information yet available.
$S_2+O \rightarrow SO+S$	−22.08	An approximate value has been obtained by Homann, et al. (1968) using a heated flow tube at a total pressure of a few torr. S_2/Ar vapor was reacted with atomic O (from N/NO titration) the SO being monitored by a TOF mass spectrometer. $k \sim 7\times10^{-12}$ at 1050 K.
$O+CS_2 \rightarrow OCS+S$	−53.94	Homann, et al. (1968) used a heated flow tube at 3–6 torr pressure to study the $O+CS_2$ reactions. These were monitored with a TOF mass spectrometer. In addition to the main $O+CS_2 \rightarrow CS+SO$ reaction (q.v.) they report finding a contribution from this reaction at higher temperatures and give $k_{1100\ K} \sim 2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. Hancock and Smith (1971) found in the room temperature flash photolysis of CS_2/NO_2, $\lambda>3000$ Å, that the reaction of $O+CS_2 \rightarrow CS+SO$ was dominant. No S_2 absorption could be detected and it was concluded that the alternate reaction path being discussed here must be at least two orders of magnitude slower, i.e. $<4\times10^{-14}$ at room temperature.
$CS+O_2 \rightarrow CO+SO$	−94.78*	This reaction is a four center interaction and consequently is not expected to be fast. Previous studies tend to confirm this. Kondratiev and Magaziner (1940), monitoring CS spectroscopically, reported that at 20–100° C practically no reaction between CS and O_2 occurred. Flash photolysis studies of CS_2/O_2 mixtures by Wright (1960), Callear (1963), and DeSorgo, et al. (1965) further support this. Wright found that at about 1 ms after the flash the rate of removal of CS was constant within a factor of 2 over a 25 fold range of O_2 pressure. Callear (1963) noted that in the presence of 50 torr O_2 that CS survived for 1 s with no significant change. DeSorgo, et al. (1965) found no effect even with 90 torr O_2/22 torr CS_2/280 torr N_2 mixtures. McGarvey and McGrath (1964) flash photolysed CS_2/inert gas mixtures. In the presence of O_2, CS absorption was weak and disappeared rapidly. However, in their case the CS_2 concentration was low and the [CS] decay probably occurred via the reactions $CS_2+h\nu \rightarrow CS+S, S+O_2 \rightarrow SO+O, O+CS \rightarrow CO+S.$ Flash photolysis of higher concentrations of CS_2 in O_2 incompletely dissociates the CS_2 which then removes the flash generated O atoms. Thereafter the CS concentration remains essentially steady for long periods. Callear and Dickson (1972) estimate $k<3\times10^{-18}$ and it could be considerably less. Recent interpretation by Heicklen, et al. (1969) and Wood and Heicklen (1971) of their photolysis data includes this reaction. 2–70 torr CS_2/1–745 torr O_2 were photolyzed at 3130Å in a 200 cm^3 quartz vessel at room temperature and the products analyzed gas chromatographically. Quantum yields were low and exposure times 10–520 min. Relative quantum yields of OCS and CO were considered formed from this and the alternative reaction path. They give $k_{CS+O_2 \rightarrow OCS+O} : k_{CS+O_2 \rightarrow CO+SO}=1.2,$ at room temperature. An additional study of the explosive limits of 0.0025–0.5 $CS_2:O_2$ mixtures at pressures of about 10–400 torr [Wood and Heicklen, 1971b] showed that the data could be reproduced by computer fit to an eight reaction kinetic scheme in which rate constant ratios were adjusted to give a best fit to the experimental data. Values for $k_{CS+O_2 \rightarrow OCS+O} : k_{CS+O_2 \rightarrow CO+SO}$ were taken as 1.08 (341 K) and 1.04 (415 K). However, because of the several supporting studies which contradict this interpretation these values all must be regarded with a certain skepticism until additional information Heicklen is obtained.

See footnote at end of table.

These are reactions for which only limited information, if any, is yet available—Continued

Reaction	$\Delta H^0_{298\ K}$	Comments
$CS+O_2 \rightarrow OCS+O$	−43.52*	This reaction corresponds closely to $CO+O_2 \rightarrow CO_2+O$ which is known to have a large activation energy of about 50 kcal mol^{-1}. Available information, discussed above under the alternate reaction path, $CS+O_2 \rightarrow CO+SO$, tends to confirm this although it is still somewhat controversial in the light of the recent interpretation by Heicklen, et al. (1969) and Wood and Heicklen (1971).
$O+CS \rightarrow CO+S$	−89.30*	At 3–6 torr pressure in a heated flow tube [Homann, et al., 1968], O_2/Ar subjected to a microwave discharge (or O atoms from N/NOtitration). Mixed with 0.03 percent CS_2/Ar so that O atoms in excess. Sampled with TOF mass spectrometer. At 900 K, k is at least 5 times greater than k_{O+CS_2} (q.v.) giving $k_{900K} \geq 5\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. Similarly, Westenberg, and DeHaas (1969) established a value of 2 for the O:CS_2 stoichiometry at 227–538 K. 0.03 percent O_2/He mixtures were discharged at about 2 torr and CS_2 added downstream in amounts 5–10 times [O]. The latter was monitored by ESR and the stable products mass analyzed. The value of two suggests a mechanism based on the reaction $O+CS_2 \rightarrow CS+SO$ being followed by the faster $O+CS \rightarrow CO+S$. More recently Hancock and Smith (1971) have monitored in a flow system the intensity of IR chemiluminescence identified with this reaction and measured the decrease in intensity caused by the presence of NO_2. The reactants are extensively diluted with argon. Typical experimental conditions were [O_2], [CS_2]$\sim$0.2 millitorr, [NO_2] 0.1–0.9 millitorr, total pressure 2.9 torr. An approximate value of $k_{O+CS}/k_{O+NO_2}=2.3$ was estimated and leads to $k_{O+CS} \sim 1.4\times10^{-11}$ (298 K). Callear and Dickson also have obtained a value$\sim10^{-11}$ by monitoring the decay of CS in flash photolysis experiments with CS_2/O_2 mixtures. These estimates all support a high value for k_{O+CS} in the 200–900 K range. For this reason it seems unlikely that its activation energy will exceed 1 kcal mol^{-1}. A large fraction of the available chemical exothermicity appears as vibrational energy in the CO. Hancock, Morley, and Smith (1971) and Hancock, Ridley, and Smith (1972) recently have measured the relative rates at which the vibrationally excited CO is formed in specific vibrational levels. The maximum rate is that populating the $v=13$ state which is close to the highest energetically accessible.
$S+OCS \rightarrow CO+S_2$	−29.18	Gunning and Strausz (1966) state that at room temperature $k_{S+OCS}<0.04\ k_{S+C_2H_4}$. Since the latter has a value in the range $(0.5–1.5)\times10^{-12}$ (300 K) [Donovan, et al., 1970; Connor, et al., 1971; Davis, et al., 1972] this gives a value $k_{S+OCS} \leq (2–6)\times10^{-14}$ (300 K). At 2570 K, from a shock tube-mass spectrometric study of the thermal decomposition of OCS in Ar, Hay and Belford (1967) assess its value at approximately 1×10^{-12} cm^3 molecule^{-1} s^{-1}. Based on these two estimates a very approximate expression for the upper limit value is tenatively $k=1.5\times10^{-12}\exp(-2500/RT)$.
$OH+H_2S \rightarrow H_2O+HS$	−27.75	The rate for this is not known [Fair and Thrush, 1969; Liuti, et al.,1966].
$HS+O_2 \rightarrow OH+SO$	−23.53	Four center interaction, not expected to be fast. Cupitt and Glass (1971) have observed HS co-existing with large O_2 concentrations in a flow system at room temperature.
$HS+OH \rightarrow SO+H_2$	−42.39	Four center interaction, not expected to be fast.
$HS+OH \rightarrow H_2O+S$	−35.15	No information yet available [Fair and Thrush, 1969].

See footnote at end of table.

These are reactions for which only limited information, if any, is yet available—Continued

Reaction	$\Delta H^0_{298\ \mathrm{K}}$	Comments
$HS+O\rightarrow H+SO$	—40. 42	Appears to be more important than the alternative reaction which gives $OH+S$ as products [Fair and Thrush, 1969; Liuti, et al., 1966]. Cupitt and Glass (1971) have obtained $k_{HS+O}/k_{H+HS}=6.5\pm0.7$ at 295 K from a flow system at <1 torr total pressure. 5 percent H_2/Ar was discharged and O_2 added after the discharge with H_2S addition further downstream. [O], [H], [SO], [HS], and [S] were monitored by ESR. For $[H]>[H_2S]$ and an exces of O_2 the system could be described by the reactions $H+H_2S\xrightarrow{k_1}H_2+HS,$ $H+HS\xrightarrow{k_2}H_2+S,$ $S+O_2\xrightarrow{k_3}SO+O,$ $HS+O\xrightarrow{k_4}H+SO,$ which give $k_4/k_2=[H]/[O]$ for steady state concentrations of O and S. k_2/k_1 was also measured as 37.8 ± 7. Based on a value of $k_{H+H_2S}=8.3\times10^{-13}$ this gives $k_{HS+O}=2.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (295 K).
$HS+O\rightarrow OH+S$	—18. 05	From a theoretical computation based on a modified Johnston-Parr method, Mayer and Schieler (1968) give $k=3.8\times10^{-13}T^{0.67}\exp(-1900/RT)$ cm^3 molecule^{-1} s^{-1}. The value at 295 K is 6.7×10^{-13}.

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*These values are based on $\Delta Hf^\circ_{298K}(CS)=70.0$ kcal mol^{-1} [Hildenbrand, Chem Phys. Letters 15, 379(1972)] rather than the JANAF value of 55.0 which is now recognized as being too low.

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5. Rate Constants—A Summary

Detailed rate constant evaluations

Reaction	k (cm^3 molecule s units)	T K	Comments	Suggested error limits
$O+H+Ar \rightarrow OH+Ar$	$\sim 2\times 10^{-32}$	1000–3000	Limited data	Factor of 10?
$CO+Ar \rightarrow C+O+Ar$	$\leq 5\times 10^{-16}$	8000	One measurement	±50%?
$CO+Ar/C+O+Ar$	$1.46\times 10^{6} T^{-3.52}$ exp $(-255{,}760/RT)$	7000–15, 000	Overall rate	±75% (<10,000 K). ±50% (>10,000 K).
$N_2O+Ar \rightarrow N_2+O+Ar$	7.8×10^{-10} exp $(-58{,}000/RT)$	1500–2500		±25%.
$N_2O+Ne \rightarrow N_2+O+Ne$	4.2×10^{-11} exp $(-43{,}600/RT)$	1500–2600		±50%.
$N_2O+Kr \rightarrow N_2+O+Kr$	1.2×10^{-11} exp $(-40{,}700/RT)$	1750–2800		Factor of 2.
$N_2O+N_2O \rightarrow N_2+O+N_2O$	4.7×10^{-9} exp $(-59{,}400/RT)$	850–1050		Factor of 2–3.
$N_2O \rightarrow N_2+O$	$k_\infty = 1.4\times 10^{11}$ exp $(-59{,}500/RT)$	800–2100	1st order	±50%.
$O+N_2+N_2 \rightarrow N_2O+N_2$	$\leq 5\times 10^{-38}$	300–568	Limited data	Not known.
$O(^1D)+N_2+N_2 \rightarrow N_2O+N_2$	$\sim 5\times 10^{-36}$	300	Very approximate	Factor of 50?
$N_2O_4+N_2 \rightarrow NO_2+NO_2+N_2$	3.3×10^{-7} exp $(-11{,}000/RT)$	250–350		±40%.
$NH_3+Ar \rightarrow NH_2+H+Ar$	7.2×10^{-9} exp $(-79{,}500/RT)$	1800–3200		Factor of 2.5.
$NH_2+H+NH_3 \rightarrow NH_3+NH_3$	3×10^{-30}	298	Very approximate	Factor of 10?
$SO+O+Ar \rightarrow SO_2+Ar$	8.8×10^{-31}	300	One measurement	Factor of 2?
$SO_2+Ar \rightarrow SO+O+Ar$	4.2×10^{-10} exp $(-110{,}000/RT)$	4500–7500	One set of data	Factor of 2?
$SO+O_2 \rightarrow SO_2+O$	3.0×10^{-13} exp $(-5600/RT)$	400–2500		Factor of 2.
$SO_2+O+Ar \rightarrow SO_3+Ar$	1×10^{-33} exp $(+1000/RT)$	250–1000		Factor of 2 (300 K), larger at other temperatures.
$SO_3+M \rightarrow SO_2+O+M$	(?)		Data too speculative	
$SO+SO \rightarrow SO_2+S$	$\leq 3\times 10^{-15}$ $\leq 2\times 10^{-13}$	300 1000	Upper limit estimates only	Not known.
$S+O_2 \rightarrow SO+O$	2.2×10^{-12} exp $(-\ 0/RT)$	250–450		±30%.
$H+SO_2+M \rightarrow HSO_2+M$	(?)		Limited data	
$O+CS_2 \rightarrow CS+SO$	2.0×10^{-11} exp $(-1030/RT)$	200–1000		±20%.
$O+OCS \rightarrow CO+SO$	6.8×10^{-11} exp $(-5080/RT)$	270–1500		±35%.
$O+H_2S \rightarrow OH+HS$	6.3×10^{-13} exp $(-1830/RT)$	200–350		Less than factor of 2.
$H+H_2S \rightarrow H_2+HS$	1.5×10^{-11} exp $(-1700/RT)$	190–500		±30%.
$H+HS+M \rightarrow H_2S+M$	(?)		No data	
$HS+HS \rightarrow H_2S+S$	$\sim 1.5\times 10^{-11}$	298		Factor of 4?
$HS+HS \rightarrow H_2+S_2$	$<5\times 10^{-14}$	295	Limited data	Not known.
$H+HS \rightarrow H_2+S$	3×10^{-11}	295	Limited data	Factor of 3?
$S+HS \rightarrow S_2+H$	4×10^{-11}	295	Limited data	Factor of 4?

Miscellaneous reactions

Reaction	k (cm^3 molecule s units)	T K	Comments	Suggested error limits
$O+H_2+M \rightarrow H_2O+M$			No evidence of it	
$O(^1D)+H_2+M \rightarrow H_2O+M$	No data		Generally unimportant	
$N+NO+M \rightarrow N_2O+M$	Negative results	673	No evidence of it	
$N(^2D)+NO+M \rightarrow N_2O+M$	Negative results	343	No evidence of it	
$SO+O_2+M \rightarrow SO_3+M$			No evidence of it	
$SO+O_3 \rightarrow SO_2+O_2$	$2.5 \times 10^{-12} \exp(-2100/RT)$	223–303	One set of good data	Factor of 2–3.
$O+SO_3 \rightarrow SO_2+O_2$	$5 \times 10^{-10} \exp(-12{,}000/RT)$?	1480–1550	One set of questionable data.	Uncertain.
$SO+OH \rightarrow SO_2+H$	5×10^{-11}	298	One set of good data	Factor of 2–3.
$S+OH \rightarrow SO+H$	No data			
$S_2+O \rightarrow SO+S$	$\sim 7 \times 10^{-12}$	1050	One value	Uncertain.
$O+CS_2 \rightarrow OCS+S$	$\sim 2 \times 10^{-12}$	1100	One value	Not known.
	$< 4 \times 10^{-14}$	298	Estimated value	Not known.
$CS+O_2 \rightarrow CO+SO$	$< 3 \times 10^{-18}$	298	Estimated value	Not known.
$CS+O_2 \rightarrow OCS+O$	$< 3 \times 10^{-18}$	298	Estimated value	Not known.
$O+CS \rightarrow CO+S$	$\sim 1.4 \times 10^{-11}$	298	One value	Factor of 2?
	$\sim 5 \times 10^{-11}$	900	One value	Factor of 2?
$S+OCS \rightarrow CO+S_2$	$1.5 \times 10^{-12} \exp(-2500/RT)$?	300–2570	Limited data	Uncertain.
$OH+H_2S \rightarrow H_2O+HS$	No data			
$HS+O_2 \rightarrow OH+SO$	No data			
$HS+OH \rightarrow SO+H_2$	No data			
$HS+OH \rightarrow H_2O+S$	No data			
$HS+O \rightarrow H+SO$	$\sim 2 \times 10^{-10}$	295	One value	Factor of 3?
$HS+O \rightarrow OH+S$	$3.8 \times 10^{-13} T^{0.67} \exp(-1900/RT)$	298–2500	Theoretical estimate	Uncertain.

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Appendix

Current Sources of Evaluated Rate Constants, Useful Compilations, and Reviews

For it to be of any general use, a compilation of data has to be readily available, presented in simple, easily usable form, and be at least partially evaluated or annotated. Fortunately, in recent years, efforts have been made by various individuals and groups to start condensing the mass of available gas phase kinetic rate data and a variety of publications have appeared, reviewing the available rate constants particularly for the light gas molecule reactions. The last decade has been such a tremendously productive era in the field of gas phase kinetics and has seen emerge such a variety of evaluations and reviews that it may be opportune to present as comprehensive a list as possible for the general user, with annotations on their usefulness and general character. Five groups will be discussed in more detail, those concerning evaluated data, tabulations of non-evaluated data, specialized reviews emphasizing either particular types of reactions or techniques, and certain miscellaneous reviews. The references are alphabetized by author at the end of this section for convenience.

Evaluated Data

Article by Schofield (1967) for which a reference addendum is available on request. (110 reactions of H_2, O_2, N_2, H_2O, H, O, N, OH, HO_2, O_3, oxides of nitrogen, and hydrocarbons.)

Leeds University Reports Nos. 1–5 by Baulch, et al. (1968–70), now being published by Butterworth. (47 reactions of hydrogen/oxygen, carbon and nitrogen oxides.)

NSRDS-NBS 20 by Johnston (1968). (6 reactions of O, O_2, and O_3.)

NBS Technical Note 484 by Bortner (1969). (7 reactions of high temperature air, O_2, N_2, N, O, NO, O_3.)

Article by Herron (1969). (The reactions $O+CH_4$ and C_2H_6.)

NSRDS-NBS 21 by Benson and O'Neal (1970). (About 516 unimolecular reactions, the majority concerning organic or organometallic molecules or radicals.)

Review by Drysdale and Lloyd (1970). (About 60 reactions of OH.)

Review by Lloyd (1971). (F_2 and Cl_2 dissociation and recombination reactions.)

Review by Cohen (1971). (Reactions in the H_2/F_2 laser system.)

Review by Waage and Rabinovitch (1971). (Critical examination of the C_2H_6–CH_3 radical system.)

Article by Schofield (1972). (14 reactions of H, O, N, S, I, H_2, O_2 O_3, H_2O, CH_4, NO, N_2O, OCS, Cl_2, Br_2, CH_3I comparing rates of ground state and electronically excited reactants.)

Review by Wilson (1972). (Abstraction reactions of OH.)

Review by Lloyd (1972). (20 reactions of the HO_2 radical.)

NBS evaluation project, Hampson et al. (1972). (Data sheets for 27 reactions of potential interest for stratospheric chemistry, reactions of $O(^3P,^1D)$, H, OH, O_2 $(^1\Delta_g, ^1\Sigma_g)$, O_3, HO_2, H_2O, H_2O_2, NO, NO_2, N_2O, N_2O_5, HNO, HNO_2, HNO_3.)

Book by Kerr and Parsonage (1972). (Reactions of atoms and radicals with alkenes, alkynes, and aromatic compounds.)

Current efforts in the compiling and evaluation of chemical kinetic data have been outlined by Gevantman and Garvin (1972).

Tabulations of Non-Evaluated Data

General review articles tend to date rapidly. They are most useful for their bibliographic content, for illustrating the development of the field, and for discussions of the limitations and difficulties of particular experimental techniques. Those containing more extensive lists of information on reactions have greater longevity. Several publications have appeared recently, of value for their extensive coverage of the available data but, generally, no evaluation has been made. The master reference source by Hochstim, et al. (1969) for 1900–1966 publications is a monumental work. However, it is of main value only for the evaluator and is not a ready reference of data for the general user.

Tabulations and reviews that are most useful for establishing quickly the availability of information on certain reactions are:

Trotman-Dickinson and Milne (1967). Extensive tables of bimolecular gas reaction rates.

Ratajczak and Trotman-Dickinson (1970). Supplementary tables of data.

Jensen and Kurzius (1967). 72 neutral reactions important in nozzle and rocket exhaust calculations.

Jensen and Jones (1971). 73 neutral reactions important in nozzle and rocket exhaust calculations.

Grewer, et al. (1968). Extensive tables of rate constants.

Kaufman (1969a). An excellent review of elementary gas phase reactions.

Carnicom (1966). Of limited use since mainly superseded by more recent evaluated data reports.

Carnicom (1968). 89 neutral reactions of air with carbon and sodium impurities.

Tunder, et al. (1967). Several hundred reactions are listed of importance for reentry and propellant performance programs.

Cherry, et al. (1967, 1968). 82 reactions important in propellant performance programs. Reaction rates are discussed and references listed in the original report.

Greene and Toennies (1964). Tables listing shock tube investigations.

Strehlow (1969). A continuation and updating to 1967 of Greene and Toennies' tables.

Benson and DeMore (1965). Review containing useful tables of referenced data.

Franklin (1967). Review containing useful tables of referenced data.

Heicklen (1967). Review of combustion reactions associated with reentry.

Kerr (1967). Review containing useful tables of referenced data.

Clyne (1968). Review containing useful tables of referenced data.

Kerr (1968). Useful tables of rate data for organic radicals and molecules.

Flowers (1969). Useful tables of rate data for organic radicals and molecules.

Specialized Reviews

The following reviews restrict themselves to specifically defined areas and discuss in some detail particular groups of reactions. Many of these articles, particularly the more recent ones, still are quite useful as an initial inroad to the available information.

Kaufman (1961). Reactions of oxygen atoms.

Avramenko and Kolesnikova (1964). Reactions of OH and O.

Thrush (1965). Reactions of H atoms.

Kaufman (1969b). 21 reactions involving H, OH, and O.

Brocklehurst and Jennings (1967). Reactions of N atoms.

Wright and Winkler (1968). Tables with references of data for reactions of N atoms.

Schiff (1969). 17 reactions involving O, N, NO.

Peterson and Wolfgang (1971). Reactions of atomic carbon.

Fettis and Knox (1964). Halogen atom reactions.

Husain and Donovan (1970). Reactions of electronically excited halogen atoms.

Gunning and Strausz (1966); Strausz (1967). Reactions of S atoms.

Wayne (1969). Reactions of singlet O_2.

Kearns (1971). Reactions of singlet O_2.

Peters and Wingard (1970). Reactions of O_3 with hydrocarbons.

Zafonte (1970). Reactions of O and O_3 with hydrocarbons.

Schuck and Stephens (1969). Reactions of oxides of nitrogen.

Thomas (1965). Oxidation reactions of NO_2.

Heicklen and Cohen (1968). Reactions of NO.

Stepukhovich and Umanskii (1969). Three-body recombination reactions.

Golden and Benson (1969). Reactions of hydrocarbons and organic iodides with iodine.

Kerr and Trotman-Dickenson (1961). Reactions of alkyl radicals.

Kerr and Lloyd (1968). Decomposition reactions of organic radicals.

Rabinovitch and Setser (1964). Unimolecular decomposition reactions of simple alkanes and alkyl radicals.

Stepukhovich and Ulitskii (1966). Reactions of alkyl radicals.

Gray, Herod, and Jones (1971). Methyl and trifluoromethyl abstraction of H and D atom reactions.

Cvetanovic (1963). Addition reactions of O, H, C, N, S, and halogens to olefins.

Frey (1964). Reactions of methylene and carbenes.

DeMore and Benson (1964). Reactions of methylene.

Gray, et al. (1967). Alkoxy radical reactions.

Tedder and Walton (1967). Halogenomethyl radical reactions.

Donovan and Husain (1970). Reactions of 14 electronically excited atoms.

Gilmore, et al. (1969). A table of rates for several excitation, deexcitation, and energy transfer processes.

Rabinovitch and Flowers (1964). Reactions producing chemically activated products.

Troe and Wagner (1967). Review of unimolecular decompositions of small molecules.

The following reviews emphasize particular research techniques used for rate constant measurements. They tend to be of interest mainly in illustrating the problems, limitations, and state of activity in the field of discussion.

Voevodsky and Kondratiev (1961). Measurements utilizing gaseous explosion limits.

Campbell and Thrush (1965). Discharge-flow system studies.

Cvetanovic (1964). Mercury photosensitized reaction measurements.

Belford and Strehlow (1969). Shock tube studies.

Strehlow (1968). Shock tube studies.

Bauer (1965). Shock tube studies.

Bradley (1965). Shock tube studies.

Wolfsberg (1969). Isotope effects in gas phase studies.

Miscellaneous Reviews

These reviews are of some bibliographic assistance and illustrate the development of gas kinetics over recent years. However, they are rather limited in their value as rate data reference sources. The latter ones, being more current, do discuss certain relevant problem areas.

Calvert (1960). Annual review of gas phase kinetic studies.

Walters (1961). Annual review of gas phase kinetic studies.

Boudart (1962). Annual review of gas phase kinetic studies.

Knox (1962). Oxidation reactions.

Kondratiev (1965). Several reactions reviewed.

Mahan (1966). Annual review of gas phase kinetic studies.

Thrush (1968). Review of several reactions producing electronically excited states.

Spicer and Rabinovitch (1970). Discussion of various problem areas in elementary gas phase kinetics.

Jonathan (1969). Annual review of gas phase kinetic studies.

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