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Evaluated kinetic data for high temperature reactions

Volume 4 Homogeneous gas phase reactions of halogen- and cyanide-containing species

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and the **American Institute of Physics** for
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Physical and Chemical Reference Data

David R. Lide, Jr., Editor

The Journal of Physical and Chemical Reference Data is published quarterly by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards. The objective of the Journal is to provide critically evaluated physical and chemical property data, fully documented as to the original sources and the criteria used for evaluation. Critical reviews of measurement techniques, whose aim is to assess the accuracy of available data in a given technical area, are also included. One of the principal sources for the Journal is the National Standard Reference Data System (NSRDS), which is described more fully below. The Journal is not intended as a publication outlet for original experimental measurements such as are normally reported in the primary research literature, nor for review articles of a descriptive or primarily theoretical nature.

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David R. Lide, Jr., Editor
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Foreword

The *Journal of Physical and Chemical Reference Data* is published jointly by the American Institute of Physics and the American Chemical Society for the National Bureau of Standards. Its objective is to provide critically evaluated physical and chemical property data, fully documented as to the original sources and the criteria used for evaluation. One of the principal sources of material for the journal is the National Standard Reference Data System (NSRDS), a program coordinated by NBS for the purpose of promoting the compilation and critical evaluation of property data.

The regular issues of the *Journal of Physical and Chemical Reference Data* are published quarterly and contain compilations and critical data reviews of moderate length. Longer monographs, volumes of collected tables, and other material unsuited to a periodical format are published separately as *Supplements* to the *Journal.* This monograph, "Evaluated Kinetic Data for High Temperature Reactions. Volume 4. Homogeneous Gas Phase Reactions of Halogen- and Cyanide-Containing Species," by D. L. Baulch, J. Duxbury, S. J. Grant, and D. C. Montague is presented as Supplement No. 1 to Volume 10 of the *Journal of Physical and Chemical Reference Data.*

David R. Lide, Jr., Editor
Journal of Physical and Chemical Reference Data

Evaluated kinetic data for high temperature reactions

Volume 4

Homogeneous gas phase reactions of halogen- and cyanide-containing species

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The available kinetic data for 300 homogeneous gas phase reactions involving halogens, the cyanide radical and their compounds have been compiled and critically evaluated. For each reaction, relevant thermodynamic data, a table of measured rate constants, a discussion of the data, and a comprehensive bibliography are presented. Wherever possible the preferred rate parameters are given with their associated error limits and temperature ranges. A table summarising the recommended values is provided.

Key words: Chemical kinetics; critical evaluation; cyanide; gas phase; halogens; high temperature; rate constant.

Preface

In 1966 a special working party of the United Kingdom Science Research Council concluded that the field of high temperature processes merited special stimulation and development. The working party recognised the need for reliable data in this area and, in particular, recommended that work on compilation of chemical reaction rate data be initiated. In response to this recommendation the Office for Scientific and Technical Information (Department of Education and Science) instituted a project on compilation and evaluation of kinetic data for reactions of interest in high temperature systems, in the Department of Physical Chemistry, University of Leeds, as part of the British data and information programme. Responsibility for continued support has since been transferred to the Science Research Council. The project is directed by Dr. D. L. Baulch and has an advisory panel, originally under the Chairmanship of the late Professor J. W. Linnett (University of Cambridge), and now Professor A. Maccoll (University College, London) consisting of representatives from university, government, and industrial research establishments having interests in the high temperature field. This volume is part of the output from that project.

Our aims in this work have been to (a) select specific homogeneous gas phase reactions of importance in high temperature systems, (b) prepare for each reaction a comprehensive tabulation of the available reaction rate data, (c) evaluate critically the existing data and, wherever possible, recommend reliable values for the rate parameters, (d) produce this material in a convenient format. We hope that these tables will be sufficiently comprehensive to serve as a primary data source to which later results may be added, will be sufficiently critical and authoritative for the non-specialist to use them with confidence, and will indicate areas in which more data are required and further research would be of significant value.

High temperature systems of greatest practical importance involve reactions of atoms, small radicals and molecules, composed of the elements hydrogen, carbon, nitrogen, oxygen, sulphur, fluorine and chlorine. Even restricting our interest to the homogeneous gas phase reactions of these species leaves a formidable number of possible reactions; selection is unavoidable. We have concentrated our attention on those reactions for which sufficient rate data exist to allow some critical assessment. However, we have included other reactions which are related to those critically assessed or which may be important in either high temperature processes or related low temperature systems. No doubt some reactions of interest will have been overlooked and we hope that users of these tables will not hesitate to inform us of such omissions.

This compilation is of potential interest to a wide spectrum of technologists, physicists, chemists and engineers. In drawing up the table, we have tried to keep in mind the various needs of this range of users. Particular attention has been given to the format and the introductory notes to assist the non-specialist in chemical kinetics in finding quickly the information he requires and in understanding the terms and symbols used. At the other extreme we have the kineticist capable of making his own evaluation. Here we have concentrated on providing as comprehensive a bibliography as possible and in the "Discussion" sections have indicated briefly our reasons for selecting or rejecting particular measurements. For rapid reference we have provided at the end of the volume a summary table in which all our recommendations for rate constants are listed.

The present volume, dealing with reactions of halogen- and cyanide-containing species, is the fourth in the series planned to cover all the major areas of high temperature gas phase kinetics. The previous three volumes, published by Butterworth and Co. (London), covered the H_2–O_2, H_2–N_2–O_2, O_2–O_3, and CO–O_2–H_2 systems and reactions of sulphur-containing species. A further volume is planned dealing with the reactions involving atoms, small radicals and hydrocarbons.

Many people have contributed to this work. The authors particularly acknowledge the contribution of Professor P. Gray F.R.S. (Department of Physical Chemistry, University of Leeds) who has generously given time and energy to the administration and guidance of the project and provided departmental facilities. The project's advisory panel, on which Professor A. Maccoll (University College, London), the late Professor J. W. Linnett F.R.S. (University of Cambridge), Dr. L. C. F. Blackman and Mr. P. G. Hawksley (B.C.U.R.A.), Dr. D. R. Jenkins (Shell), Dr. A. S. Kallend (Central Electricity Generating Board), Dr. J. D. Lewis (Rocket Propulsion Establishment), Mr. J. J. Macfarlane (National Gas Turbine Establishment), Dr. A. Melvin and Dr. C. T. Brooks (Gas Council), Professor P. Gray and representatives of the Office for Scientific and Technical Information and the Science Research Council have served, has throughout offered helpful criticism and assistance. Drs. D. Garvin and R. Hampson (Chemical Kinetics Information Centre, National Bureau of Standards, U.S.A.) have provided bibliographies for many of the reactions studied and have been most knowledgeable and constructive critics.

We are also grateful to those who assisted in collecting bibliography, preparing diagrams, and producing the text for photocomposition.

D. L. Baulch
J. Duxbury
S. J. Grant
D. C. Montague

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Introduction

This volume contains critical evaluations of elementary reactions of halogen and cyanide containing species. A separate section is devoted to each reaction and within each section the material is presented in the following order:

1. Thermodynamic data
2. Recommended values of the rate parameters and their range of validity
3. Graphical presentation of rate data
4. Table of rate data
5. Discussion
6. References

The reactions are presented in pairs comprising the forward and reverse of each elementary reaction. The order of presentation is given in the Contents and there is an index at the end of the volume which lists the reactions according to the participating species.

1. Thermodynamic Data

Thermodynamic data were calculated from the most recent JANAF Tables [1–3]. For most reactions values of ΔH°, ΔS° and log K_p are given at intervals over the temperature range 298–5000 K. For those reactions in which a change in the number of molecules occurs values of K_c are also tabulated. They have been calculated from each value of K_p assuming ideal gas behaviour. K_p and K_c are given in atmosphere and cm·mol units, respectively.

Although it is currently recognised that the JANAF value of $\Delta H^\circ_{f,298}$ for the ClO radical is inaccurate (see section B13), in the absence of improved values at room temperature and higher, we have continued to use the JANAF tabulation.

2. Recommended Values of the Rate Parameters and Their Range of Validity

Throughout this volume the rate constant for the elementary reaction,

$$aA + bB + \dots \rightarrow mM + nN + \dots,$$

is defined by the relation,

$$\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \dots = k[A]^a[B]^b \dots = \frac{1}{m}\frac{d[M]}{dt} = \frac{1}{n}\frac{d[N]}{dt} = \dots .$$

The recommended value of the rate constant is given in cm·mol·s and cm·molecule·s units.

The recommended value of the rate constant denotes the value which, in the opinion of the authors, is most consistent with the available experimental rate determinations and the thermodynamic data. In certain cases, where there is a paucity of reliable data, an expression for the rate constant has been obtained by using the relationship between the equilibrium constant (K_c) and the rate constants for the forward (k_f) and reverse (k_r) reactions: $K_c = k_f/k_r$. Where no reliable data are available for either forward or reverse reactions the authors have not felt justified in making recommendations.

The validity of the above relationship between the equilibrium constant and the forward and reverse rate constants has been the subject of controversy. However, while there seem to be no well-documented exceptions to it, the relationship has been shown to hold in many cases and we assume it to be valid for all reactions discussed in this volume. It has been used in the following way. Where no reliable data exist for a rate constant k_r, and an expression for k_f has been recommended, then values of k_r have been calculated from k_f/K_c at a series of temperatures and an expression for k_r has been derived from these values.

Whenever possible the recommended rate expression is given in the simple Arrhenius form,

$$k = A \exp(-C/T), \qquad 2.1$$

where A (the pre-exponential or "A" factor) and C are constants. We have chosen to use C rather than the ratio E/R, which is more commonly used, in order to avoid any confusion which might arise from the use of various units for E.

The available data are rarely sufficiently accurate to show any temperature dependence in the pre-exponential factor. However in a few cases the data cannot be fitted to a simple Arrhenius expression and expressions of the form,

$$k = A'T^n \exp(-C'/T), \qquad 2.2$$

have been used, where A', n, and C' are constants.

When the data fit equation 2.1 the recommended values of the pre-exponential factor (A) and the activation energy ($E = CR$) for each reaction were obtained from the best straight line which could be drawn through the data plotted on an Arrhenius diagram (log k vs T^{-1}), taking into account the differing reliabilities of the various experimental determinations. Where it has been necessary to use an expression for k involving a pre-exponential temperature dependence (expression 2.2) then values of A' and C' have been obtained from the best straight line drawn through the data on a plot of $\log(kT^{-n})$ vs T^{-1}. The energy of activation (E) is related to C' by the relationship $E = C'R + nRT$. Fitting of a straight line to the data has been purely visual; application of a least squares calculation involves the assignment of weighting factors, which is difficult to do on a rational basis, and in most cases any attempt to improve the accuracy of the fit is not justified by the quality of the data.

The error limits for A and E were obtained by examining the extreme lines that could reasonably be drawn through the experimental points. There is no simple means of relating the errors in A and E to the error in k when calculated from the recommended expression, and there is a danger of grossly overestimating errors in k by simple substitution of errors in A and E into the expression for k. To avoid this we have chosen to specify an error in k estimated from the scatter of data over the entire investigated temperature range. It is this error which should be used when values of k are calculated from the recommended expression. When an expression for k has been derived from the experimental data on the reverse reaction the error in k has been specified without making any allowance for possible errors in the thermodynamic data.

Each rate constant expression has been recommended for use in a limited temperature range dependent on the extent of the available data. The recommended expression can be used outside that range but the error is likely to be large and is difficult to specify.

3. Graphical Presentation of Rate Data

All the available data are presented on a graph, usually as log k vs T^{-1} (the Arrhenius form, equation 2.1). Wherever possible the original rate constant data have been recorded as points on the diagram rather than as the rate constant expressions derived from them by the original authors. In some cases, where the original data are only presented as points on a graph, they have been transferred to our own diagram by measuring the coordinates of each point in the original paper. Only when the experimental results are given solely in the form of a temperature dependent expression (e.g., equations 2.1 and 2.2) do we record it as a line on our diagram.

There have been previous evaluations for many of the reactions in this volume. All such recommendations for k are also presented, sometimes on a separate diagram, so that they may be conveniently compared with those derived here.

4. Table of Rate Data

For each entry in these tables the following features are recorded (a) measured values of the rate constant, (b) the temperature of each measurement, (c) a brief outline of the experimental method used and the reference, (d) any pertinent comments on special features of the work. Wherever necessary the rate constant recorded in the first column has been converted to the system of units used throughout this volume (cm·mol·s). In a few cases, which are noted in the text, a different definition of k has been used from that in the original paper (see section 2 for definition of k) and the appropriate changes to the values for k have been made. In the third column the intention has been to record sufficient details of the technique for the specialist to be able to understand how the determination was made. Comments on the technique and other aspects of the work are given in the fourth column. Also recorded in that column are references to all the work in which that particular determination of the rate constant has been subsequently discussed or used. By use of this feature of the tables, in conjunction with the references, it is possible to trace any quoted value of a rate constant to its source.

The entries in the tables are in chronological order but the tables themselves are divided into at least two sections. The first contains details of original experimental and theoretical determinations while the second comprises other work, i.e., recommended expressions from review articles, compilations, and evaluations. A third section has been added in a few cases to record the available data on isotopic reactions.

5. Discussion

The principal aim of this section is to present concisely the reasons leading to the recommended rate expression. In some cases it is possible to state specifically why some results are rejected in favour of others but often it is not possible to be so specific. The data are subjected to a variety of comparative tests; their relation to the work of others, to theory, and to the results on other reactions are considered, and as far as is reasonably possible the conclusions from each comparison are recorded. However, in all of this there is an element of personal judgment on the part of the evaluator, which is difficult to record, but which is an essential feature of the evaluation process.

6. References

The bibliographies have been based on those provided by the Chemical Kinetics Information Center, National Bureau of Standards, U.S.A. (Dr. R. Hampson) [e.g., 4–6] and on literature searches by the authors. Extensive use has also been made of the compilations of Bahn [7], Carnicom [8], Hochstim [9], Kondratiev [10], Prud'homme and LeQuoy [11], Engleman [12], and those of Trotman-Dickenson [13,14] and Kerr [15,16]. There are also a number of reviews which we have found useful in evaluating reactions in this volume [17–25]. Those of Watson [23,24] have been particularly valuable.

Our literature search was terminated in July 1978. Monitoring of the literature will continue for all the reactions evaluated here and any changes in our recommendations will be gladly supplied on request.

7. Miscellaneous Reactions

At several points in the volume, sections on miscellaneous reactions have been inserted. In each section of this kind we list relevant bibliography for a number of reactions which have been postulated as being of importance in the various systems covered but for which there are insufficient data to permit evaluation of either the forward or reverse reaction.

8. Symbols and Units

A list of the symbols used in this work is presented following the Introduction. Mainly, SI units have been used throughout but, for those more familiar with other units, some quantities (e.g., pressure, activation energy) have been quoted both in SI and the more familiar units. The conversion factors are shown in table 1.

Rate constants have been expressed in cm·mol·s units and, to assist conversion between these and other units, conversion factors are given in tables 2 and 3 [26].

TABLE 1. Conversion factors

1 cal	= 4.184 J
1 mm Hg	= 133.3 Pa
1 atm	= 101.3 kPa

TABLE 2. Conversion factors for second order reactions

A	$cm^3mol^{-1}s^{-1}$	$L\ mol^{-1}s^{-1}$	$m^3mol^{-1}s^{-1}$	$cm^3molecule^{-1}s^{-1}$	$(mm\ Hg)^{-1}s^{-1}$
B					
$cm^3mol^{-1}s^{-1}$		10^3	10^6	6.023×10^{23}	62.40×10^3T
$L\ mol^{-1}s^{-1}$	10^{-3}		10^3	6.023×10^{20}	$62.40\ T$
$m^3mol^{-1}s^{-1}$	10^{-6}	10^{-3}		6.023×10^{17}	$62.40\times10^{-3}T$
$cm^3molecule^{-1}s^{-1}$	0.1660×10^{-23}	0.1660×10^{-20}	0.1660×10^{-17}		$10.36\times10^{-20}T$
$(mm\ Hg)^{-1}s^{-1}$	$16.03\times10^{-6}T^{-1}$	$16.03\times10^{-3}T^{-1}$	$16.03\ T^{-1}$	$96.53\times10^{17}T^{-1}$	

TABLE 3. Conversion factors for third order reactions

A	$cm^6mol^{-2}s^{-1}$	$L^2mol^{-2}s^{-1}$	$m^6mol^{-2}s^{-1}$	$cm^6molecule^{-2}s^{-1}$	$(mm\ Hg)^{-2}s^{-1}$
B					
$cm^6mol^{-2}s^{-1}$		10^6	10^{12}	36.28×10^{46}	$38.94\times10^8T^2$
$L^2mol^{-2}s^{-1}$	10^{-6}		10^6	36.28×10^{40}	$38.94\times10^2T^2$
$m^6mol^{-2}s^{-1}$	10^{-12}	10^{-6}		36.28×10^{34}	$38.94\times10^{-4}T^2$
$cm^6molecule^{-2}s^{-1}$	2.76×10^{-48}	2.76×10^{-42}	2.76×10^{-36}		$1.07\times10^{-38}T^2$
$(mm\ Hg)^{-2}s^{-1}$	$2.57\times10^{-10}T^{-2}$	$2.57\times10^{-4}T^{-2}$	$2.57\times10^2T^{-2}$	$93.18\times10^{36}T^{-2}$	

To convert a rate constant from one set of units A to a new set B, the conversion factor is found vertically below A and in the horizontal row B of the appropriate table, e.g., a second order rate constant in units of $cm^3molecule^{-1}s^{-1}$ can be converted to units of $L\ mol^{-1}s^{-1}$ by multiplying by 6.023×10^{20}.

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List of Symbols

A	Pre-exponential factor in the Arrhenius equation (2.1).
A'	Temperature-independent part of the pre-exponential factor in non-Arrhenius equation (2.2).
C	Constant in the exponential term of the Arrhenius equation $C=E/R$.
C'	Constant in the exponential term of the non-Arrhenius expression $C'=(E-nRT)/R$.
E	Activation energy. $E=-2.303\mathrm{R}\{\partial \log k/\partial(1/\mathrm{T})\}$.
E'	$E'=E-nRT=C'R$.
T	Temperature in kelvins (K).
k	Rate constant, defined in section 2.
k^0, k^∞	Rate constants for unimolecular reaction at the limits $[M]=0$ and $[M]=\infty$, respectively.
K_p	Equilibrium constant (standard state 1 atm). $\log K_p=-2.303(\Delta H^\circ - T\Delta S^\circ)/RT$.
K_c	Equilibrium constant (standard state 1 mol cm^{-3}). $\log K_c=\log K_p-\Delta\nu\log(RT)$ where $\Delta\nu$ is the change in the number of molecules.
M	Third body or collision partner.
n	Constant in non-Arrhenius equation (2.2).
[X]	Concentration of X.
R	Ideal gas constant, $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $= 1.987\ \mathrm{cal\ K^{-1}\ mol^{-1}}$ $= 82.05\ \mathrm{cm^3\ atm\ K^{-1}\ mol^{-1}}$.
ΔH°	Standard enthalpy change (standard state 1 atm).
ΔS°	Standard entropy change (standard state 1 atm).

Throughout this work the symbol log refers to logarithm to the base 10.

A1 $F_2 + M \rightarrow F + F + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	157.820	114.587	-21.664	-26.052
300	157.846	114.679	-21.492	-25.883
500	160.222	120.838	-10.426	-15.039
1000	163.778	125.943	- 1.976	- 6.890
1500	166.029	127.788	0.894	- 4.196
2000	167.728	128.771	2.346	- 2.869
2500	169.059	129.373	3.226	- 2.086
3000	170.096	129.754	3.816	- 1.575
3500	170.883	129.993	4.240	- 1.218
4000	171.418	130.139	4.560	- 0.956
4500	171.711	130.210	4.808	- 0.759
5000	171.787	130.223	5.008	- 0.605

SI Units: log (K_p/Pa) = log(K_p/atm) + 5.0056
log(K_c/mol m^{-3}) = log(K_c/mol cm^{-3}) + 6.000

RECOMMENDED RATE CONSTANT

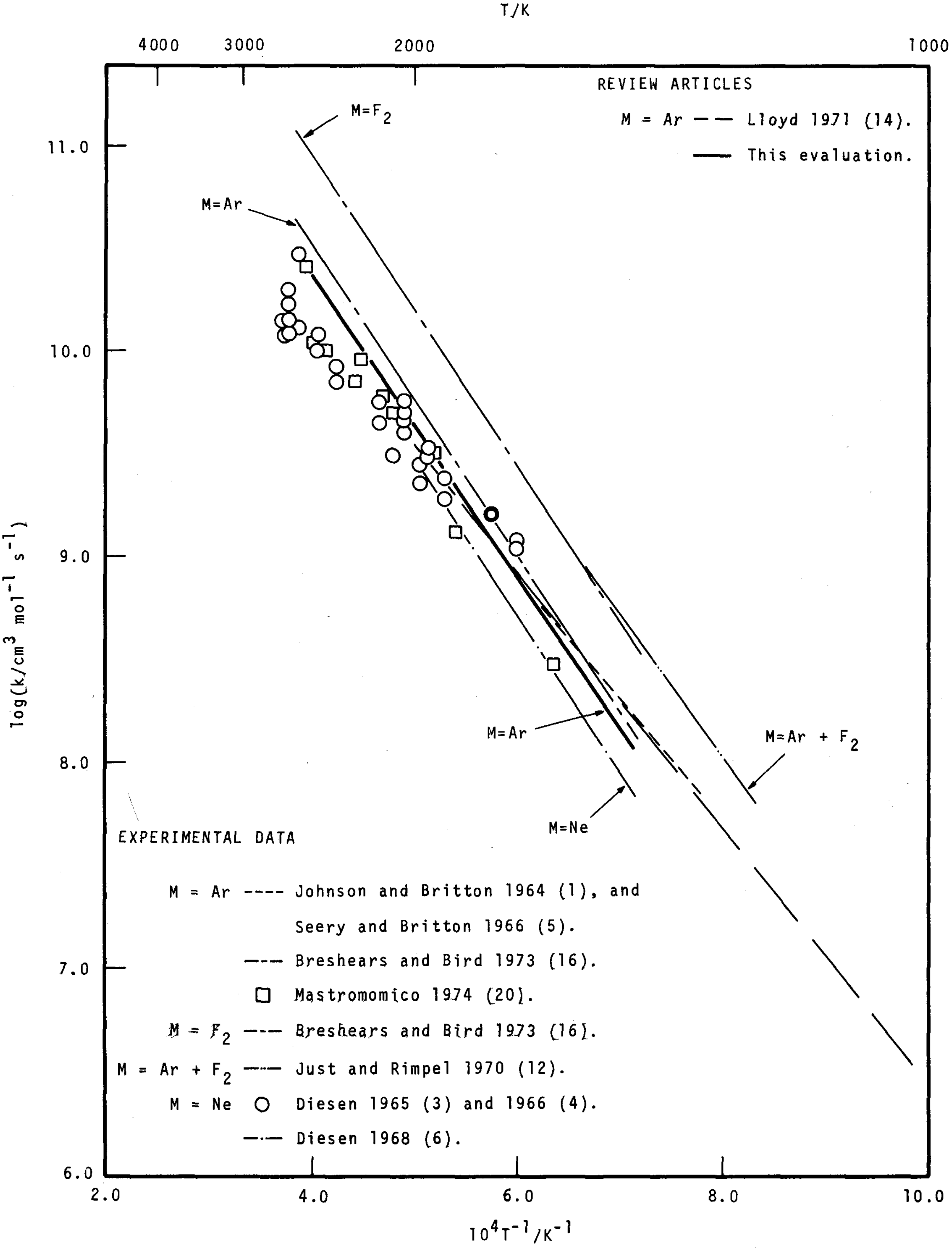
$k = 2.12 \times 10^{13} \exp(-16\ 970/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)
$= 3.52 \times 10^{-11} \exp(-16\ 970/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar)
(k is defined by $-d[F_2]/dt = k[F_2][M]$)
Temperature Range: 1400-2600 K

Suggested Error Limits for Calculated Rate Constant: ±30% at 1400 K rising to ±50% at 2600 K.

Note: expressions for k_1(M=Ne) and k_1(M=F_2) are given in the Discussion

Rate Parameters:			
	log(A/cm^3 mol^{-1} s^{-1}) =	13.33	±0.11
	log(A/cm^3 $molecule^{-1}$ s^{-1}) =	-10.45	±0.11
	E/J mol^{-1} =	141 100	±9290
	E/cal mol^{-1} =	33 720	±2220

$F_2 + M \rightarrow F + F + M$



$F_2 + M \rightarrow F + F + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$7.08\times10^{12}\exp(-15\ 020/T)$ $3.47\times10^{11}\exp(-10\ 410/T)$ $4.07\times10^{9}\ \exp(-5550/T)$	M=F_2 +Ar	1300-1600 1300-1600 1300-1600	Shock tube study. F_2(5%,10% and 20%)/ Ar mixtures behind incident shocks, and F_2(5%)/CO_2(1%) or O_2(2.5%)/Ar mixtures behind reflected shocks. F_2 monitored by absorption at 313 nm. JOHNSON and BRITTON 1964 (1)	No emission detected, and vibrational relaxation assumed complete. Values of k_1 determined from initial slopes of absorption profiles. $F_2 + M \rightarrow F + F + M$ 1 Expressions are least-squares fits to incident shock data in 5%, 10% and 20% mixtures, respectively. Authors consider 5% data to be most reliable. Reflected shock data poor, and showed large scatter. Authors could only give $k_1(M = F_2)/k_1(M = Ar)$ as within range 1-20. LLOYD (14) presents individual data points for this study from enlarged graph. 5% data given by (19) as relevant to range 1100-1600 K, with corresponding empirical expression $k_1 = 1.22 \times 10^{22}\ T^{-2.6}\ \exp(-18\ 470/T)\ cm^3\ mol^{-1}\ s^{-1}$.
(a) 1.2×10^{9} 1.6×10^{9} 1.9×10^{9} 3.4×10^{9} 2.8×10^{9} 4.6×10^{9} 5.0×10^{9} 3.1×10^{9} 5.7×10^{9} 8.5×10^{10} 1.2×10^{10} 1.3×10^{10} 1.4×10^{10} 1.7×10^{10} 1.4×10^{10} (b) 1.1×10^{9} 1.6×10^{9} 2.4×10^{9} 3.1×10^{9} 2.3×10^{9} 4.0×10^{9} 5.7×10^{9} 4.5×10^{9} 7.2×10^{9} 1.0×10^{10} 3.0×10^{10} 1.2×10^{10} 2.0×10^{10} 1.2×10^{10}	M=Ne	1665 1735 1885 1945 1975 2040 2040 2090 2145 2355 2460 2575 2645 2645 2670 1665 1735 1885 1945 1975 2040 2040 2145 2355 2460 2575 2645 2645 2670	Shock tube study. F_2(0.5 and 1%)/Ar, Ne or Kr mixtures behind reflected shocks, at pressures of 214-512 mm Hg (28.5-68.3 kPa). Reaction monitored by t.o.f. mass spectrometry. DIESEN 1965 (3) and 1966 (4)	Boundary layer effects considered negligibly small. For each experiment, values of k_1 obtained from profiles of both (a)F_2 and (b)F, according to $k_1[F_2][M] = -d[F_2]/dt = \frac{1}{2}d[F]/dt$. Data from mixtures in Ar and Kr approximately 50% higher than from mixtures in Ne, but with larger scatter. Least-squares fit to data ("only for reference") not quoted in (3) but given as $k_1(M{=}Ne) = 1.51 \times 10^{12}\ \exp(-12\ 040/T)\ cm^3\ mol^{-1}\ s^{-1}$ in (4). Used by (8 and 13). Data considered unreliable by LLOYD (14).
$1.41\times10^{13}\exp(-15\ 660/T)$ $3.72\times10^{11}\exp(-9860/T)$	M=F_2+ Ar+Kr	Unspecified	Shock tube study. F_2 (5%)/Ar and F_2 (5% and 10%)/Kr or Xe (20%)/Ar mixtures. Incident shock conditions. Absorption at 313 nm used to follow $[F_2]$. SEERY and BRITTON 1966 (5)	Results from 5% F_2 mixtures combined with those of (1) to give expression $k_1(M{=}Ar) = 3.09\times10^{12}\exp(-13\ 750/T)\ cm^3\ mol^{-1}\ s^{-1}$. Expressions for F_2/Kr/Ar mixtures are for 5% and 10% F_2 respectively. Abnormal behaviour of F_2/Xe/Ar mixtures postulated to be result of formation of stable XeF_2 or XeF species. Used by (9,10,11, and 15).

$F_2 + M \rightarrow F + F + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2.0 \times 10^{13} \exp(-17\ 610/T)$ M=Ne	1400-2000	Shock tube study. F_2(0.5%)/Ar(0.25%)/Ne mixtures. Reflected shocks. T.o.f. mass spectrometry used to follow reaction. DIESEN 1968 (6)	Values of k_1 obtained from $[F_2]$ profiles. Result reported by (2). LLOYD (14) presents individual data points taken from enlargement of graph in original.
$3.69 \times 10^{13} \exp(-15\ 950/T)$ M=F_2 +Ar	1200-1500	Shock tube study. F_2(10%)/Ar mixtures behind incident shocks. Absorption by F_2 at 313 nm used to follow reaction. JUST and RIMPEL 1970 (12)	Shock speeds measured by magnitude of equilibrium absorption, thereby limiting temperature range. Uncertainties given as a factor 1.59 on pre-exponential and ± 5.02 kJ mol^{-1} (±1.2 kcal mol^{-1}) on activation energy. Effects of uncertainties in F_2 absorption coefficient and in shock speed attenuation considered. Setting activation energy equal to $D(F_2)$ (153.6 kJ mol^{-1}; 36.7 kcal mol^{-1}) alternative expression given as $k_1(M=F_2+Ar) = 2.08 \times 10^{20}\ T^{-1.9} \exp(-18\ 470/T)\ cm^3\ mol^{-1}\ s^{-1}$. $F_2 + M \rightarrow F + F + M$ 1
$3.59 \times 10^{13} \exp(-17\ 460/T)$ M=Ar $9.85 \times 10^{13} \exp(-17\ 510/T)$ M=F_2	1400-2600 1400-2600	Shock tube study. F_2(10% and 20%)/Ar mixtures behind incident shocks. Laser-beam deflection technique used to monitor density gradient during reaction. BRESHEARS and BIRD 1973 (16)	Deflection of laser beam directly proportional to density gradient behind shock. Initial dissociation rate taken at point where vibrational equilibrium clearly complete. Authors obtained $k_1(M=F) \leqslant 5k_1(M=F_2)$ by numerical integration of density gradient profiles. Pre-exponential value $4.6 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ attributed to this work and used by (22).
3.0×10^{8} M=Ar	1575	Shock tube study. F_2(0.5%)/Ar mixtures under reflected shock conditions. Pressures 120-320 mm Hg (16-42.7 kPa). Reaction followed by t.o.f. mass spectrometry. MASTRONOMICO 1974 (20)	Boundary layer and shock wave attenuation effects considered negligible. Least-squares fit given to these data by author as $k_1 = 1.25 \times 10^{13} \exp(-16\ 460/T)\ cm^3\ mol^{-1}\ s^{-1}$.
1.3×10^{9}	1850		
3.2×10^{9}	1924		
5.0×10^{9}	2089		
6.0×10^{9}	2129		
9.1×10^{9}	2234		
7.1×10^{9}	2263		
9.9×10^{9}	2417		
1.1×10^{10}	2489		
2.6×10^{10}	2540		

$F_2 + M \rightarrow F + F + M$

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.52 \times 10^{12} \exp(-12\,040/T)$	1600-2700	Review. Expression of DIESEN (4) MODICA 1968 (7)	Used by (17,21 and 23). Not shown on Arrhenius plot.
$4.57 \times 10^{12} \exp(-14\,340/T)$ M=Ar	1000-2000	Evaluation. Derived from least-squares treatment of data of BRITTON et al. (1,5). LLOYD 1971 (14).	Third-body efficiency of Ar relative to Ne found to lie in range 1.6-2, by comparing DIESEN's (6) data for k_1(M=Ne) with those of BRITTON et al. (1,5) for k_1(M=Ar). Used by (18).

Discussion

Of the data available for the rate of dissociation of molecular fluorine, all of which have been produced in shock tube studies,

$$F_2 + M \rightarrow F + F + M, \quad (1)$$

only three groups of investigators have separated the effects of F_2 and the diluent as third bodies. Diesen [3,4,6] and Mastronomico [20] used very low percentages of F_2 in Ne and in Ar, respectively, and Breshears and Bird [16] were able to separate the effects by considering two mixtures of F_2 in Ar, using a sensitive laser-deflection method.

As there is good agreement between the results of Mastronomico [20] and of Breshears and Bird [16] for $k_1(M=Ar)$ we recommend the expression

$$k_1(M=Ar) = 2.12\times10^{13} \exp(-16\,970/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for the temperature range 1400–2600 K, with uncertainty limits of ±30% at 1400 K rising to ±50% at the higher limit.

The later data of Diesen [6] seem to be the more reliable [14] for $k_1(M=Ne)$ and we tentatively recommend his expression,

$$k_1(M=Ne) = 2.0\times10^{13} \exp(-17\,610/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

(1400–2000 K). Similarly, although the only data for $k_1(M=F_2)$ are those of Breshears and Bird [16], the apparently good results obtained by them for $k_1(M=Ar)$ with the same method and equipment leads us tentatively to recommend their expression,

$$k_1(M=F_2) = 9.85\times10^{13} \exp(-17\,510/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for 1400 to 2600 K.

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A2 $F + F + M \rightarrow F_2 + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-157.820	-114.587	21.664	26.052
300	-157.846	-114.679	21.492	25.883
500	-160.222	-120.838	10.426	15.039
1000	-163.778	-125.943	1.976	6.890
1500	-166.029	-127.788	- 0.894	4.196
2000	-167.728	-128.771	- 2.346	2.869
2500	-169.059	-129.373	- 3.226	2.086
3000	-170.096	-129.754	- 3.816	1.575
3500	-170.883	-129.993	- 4.240	1.218
4000	-171.418	-130.139	- 4.560	0.956
4500	-171.711	-130.210	- 4.808	0.759
5000	-171.787	-130.223	- 5.008	0.605

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.0056$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 3.25 \times 10^8\ T \exp(3190/T)\ cm^6\ mol^{-2}\ s^{-1}$ (M=Ar)

$= 8.96 \times 10^{-40} T \exp(3190/T)\ cm^6\ molecule^{-2}\ s^{-1}$ (M=Ar)

Temperature Range: 1400-2600 K

Suggested Error Limits for Calculated Rate Constant: ±30% at 1400 K rising to ±50% at 2600 K.

Note: Expression based on the rate constant for the reverse reaction and equilibrium data.

Rate Parameters:

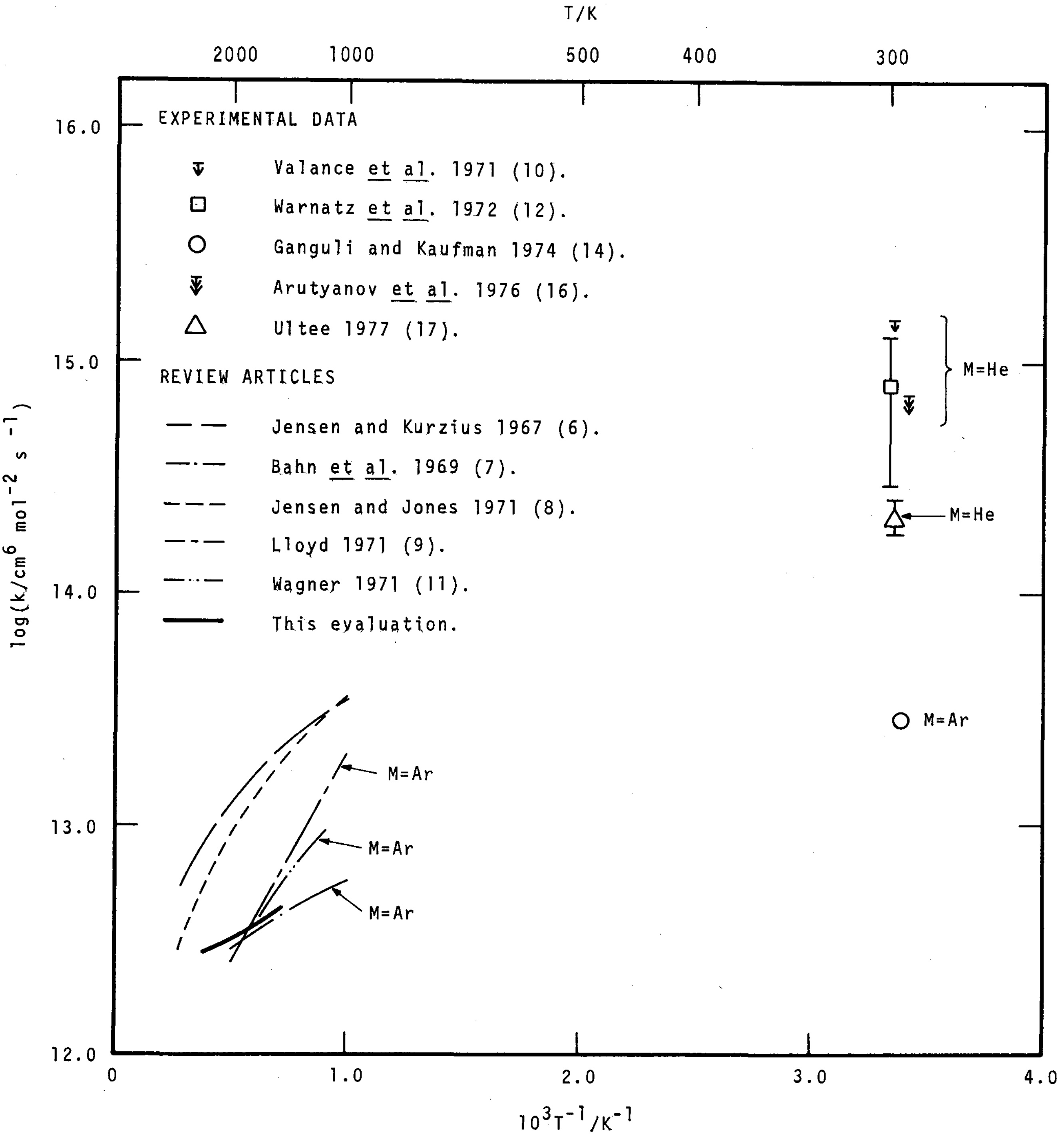
$\log(A'T/cm^6\ mol^{-2}\ s^{-1}) = 8.512 \pm 0.11 + \log T$

$\log(A'T/cm^6\ molecule^{-2}\ s^{-1}) = -39.0 \pm 0.11 + \log T$

$E'/J\ mol^{-1} = -26\,490 \pm 9290$

$E'/cal\ mol^{-1} = -6330 \pm 2220$

$F + F + M \rightarrow F_2 + M$



$F + F + M \rightarrow F_2 + M$

EXPERIMENTAL DATA

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
$\leq 1.5\times10^{15}$ M=He	298	Discharge flow system. F_2/He mixture passed through microwave discharge, total pressures 10-40 mm Hg (1.3-5.3 kPa). [F] monitored by esr spectrometry. VALANCE, BIRANG and MACLEAN 1971 (10)	Upper limit to k_1 $F + F + M \rightarrow F_2 + M$ 1 obtained by comparison with principal F-removing process $F + wall \rightarrow \frac{1}{2}F_2$ Value halved to correspond to our definition of k_1.
$(8\pm5)\times10^{14}$ M=He	300	F_2-discharge flow system. F atom decay followed by mass spectroscopy. WARNATZ, WAGNER and ZETZSCH 1972 (12)	Preliminary measurements, all F removal attributed to reaction 1. Data also reported by FOON and KAUFMAN (15).
$(2.9\pm0.2)\times10^{13}$ M=Ar	295	Discharge flow system. F_2/Ar mixture subjected to microwave discharge, Cl_2 added downstream. Total pressures 10-81 mm Hg (1.3-10.8 kPa). Chemiluminescence from reaction $F+Cl_2$ monitored simultaneously at two stations, at 516-620 nm. Teflon coated flow tube. GANGULI and KAUFMAN 1974 (14)	Contribution to F removal at wall negligible in most experiments; allowance made for few cases where necessary. Preliminary measurements with $M=N_2$ also reported, in which $k_1(M=N_2)\approx10k_1(M=Ar)$. $F + F + M \rightarrow F_2 + M$
$<7.25\times10^{14}$ M=He	293±2	F_2-discharge flow system. F_2(5%)/He mixture passed through discharge. Total pressures 0.5-5 mm Hg (66.7-666.5 Pa). Esr Spectrometry used to monitor [F]. ARUTYANOV, POPOV and CHAIKIN 1976 (16).	Esr signal calibrated by reference to signal for O_2. Predominant removal route for F atoms found to be reaction at wall, so that value of k_1 only estimated as upper limit.
$(2.18\pm0.4)\times10^{14}$ M=He	298	Discharge flow system. F_2/He mixtures passed through discharge. Total pressures 1-35 mm Hg (0.13-4.7 kPa). [F] monitored by esr spectrometry. KF and LiF coated flow tubes. ULTEE 1977 (17)	Wall recombination rate constant determined at low pressures, so that correction could be made to F atom decay measured at higher pressures. Author presented preliminary estimate that $k_1(M=F_2)>k_1(M=He)>k_1(M=Ar)$.

$F + F + M \rightarrow F_2 + M$

REVIEW ARTICLES

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.1x10^{18}T^{-1.5}$ M=rocket exhaust products	1000-3500	Review. Based on data for reverse reaction of (2 and 3), for use in calculations on conditions in rocket exhaust flames. JENSEN and KURZIUS 1967 (6)	Allowance made for rocket exhaust products being more efficient as collision partners. Error factor given as 10 in either direction. Used by (5 and 7).
$5.7x10^{15}T^{-1}$ M=Ar	Unspecified	Evaluation. For use in calculating rocket performance parameters. BAHN, CHERRY, GOLD, MITCHELL and WEBER 1969 (7)	Expression of (6) also quoted, for "representative" third body. Temperature range used in Arrhenius plot is 1000-2000 K.
$3.63x10^{19}T^{-2}$ M="average" third body	1000-3500	Evaluation. Based on reverse rate constant data of (2, 3 and 4) at 1600 K, and "arbitrary but reasonable" T^{-2} dependence. JENSEN and JONES 1971 (8)	Updating of previous report (6). Error factors in each direction increased to 30.
$3.09x10^{11}exp(4190/T)$ M=Ar	1000-2000	Evaluation. Derived from author's expression for k_{-1}(M=Ar) and K_1. LLOYD 1971 (9)	Expression compared with theoretical values obtained using method of BENSON and FUENO (1).
$9.38x10^{19}T^{-2.3}$ M=Ar	1100-1600	Review. Expression derived from reverse rate constant data of (2). WAGNER 1971 (11)	Author originally presented expression in empirical form, $k_1=A(T/\bar{T})^n$, where $\bar{T}$ is the mean temperature over the temperature range covered experimentally. Expression misquoted in (13).

Discussion

There are only three absolute and direct determinations [12,14,17] of the rate constant for the recombination of fluorine atoms,

$$F + F + M \rightarrow F_2 + M, \qquad (1)$$

which provide room temperature values of k_1. All these values fall below the upper limit determined by Valance et al. [10], from a comparison of homogeneous and heterogeneous F-removing processes in their discharge-flow study.

The values found by Ganguli and Kaufman [14] at 295 K and Ultee [17] at 298 K are extremely low compared with the room temperature recombination rate constants for bromine and chlorine atoms, and also compared with all but one [7] of the high temperature expressions for k_1 derived from the reverse reaction rate constant k_{-1},

$$F_2 + M \rightarrow F + F + M. \qquad (-1)$$

The other room temperature value is that of Warnatz et al. [12], which is reported as only a preliminary measurement by Foon and Kaufman [15]. The large error margin is due to the possible contributions to F-atom removal by reaction with O_2 or N_2, and on the flow tube wall.

The scarcity and wide variation of these data for k_1 do not permit us to make any recommendation for temperatures below 1400 K. For the temperature range 1400–2600 K we are able to use our suggested expression for k_{-1} (see this volume, section A1) together with the equilibrium constant K_1 to derive the expression

$$k_1 = 3.25\times10^8\ T\ \exp(3190/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}.$$

Error limits are those of the expression for k_{-1}: ±30% at the lower end of the temperature range, rising to ±50% at 2600 K.

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A3 $HF + M \rightarrow H + F + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	569.455	99.579	-94.571	-98.959
300	569.485	99.671	-93.949	-98.340
500	572.296	106.872	-54.205	-58.818
1000	578.723	115.851	-24.178	-29.092
1500	584.041	120.232	-14.059	-19.149
2000	588.370	122.713	- 8.957	-14.172
2500	591.861	124.274	- 5.875	-11.187
3000	594.777	125.340	- 3.809	- 9.200
3500	597.287	126.118	- 2.326	- 7.784
4000	599.483	126.704	- 1.210	- 6.726
4500	601.429	127.169	- 0.339	- 5.906
5000	603.178	127.533	0.360	- 5.253

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.0056$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k = 3.12 \times 10^{13} \exp(-49\ 980/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)

$= 5.18 \times 10^{-11} \exp(-49\ 980/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar)

Temperature Range: 3500-6500 K

Suggested Error Limits for Calculated Rate Constant: factor 2 over given temperature range.

Rate Parameters:

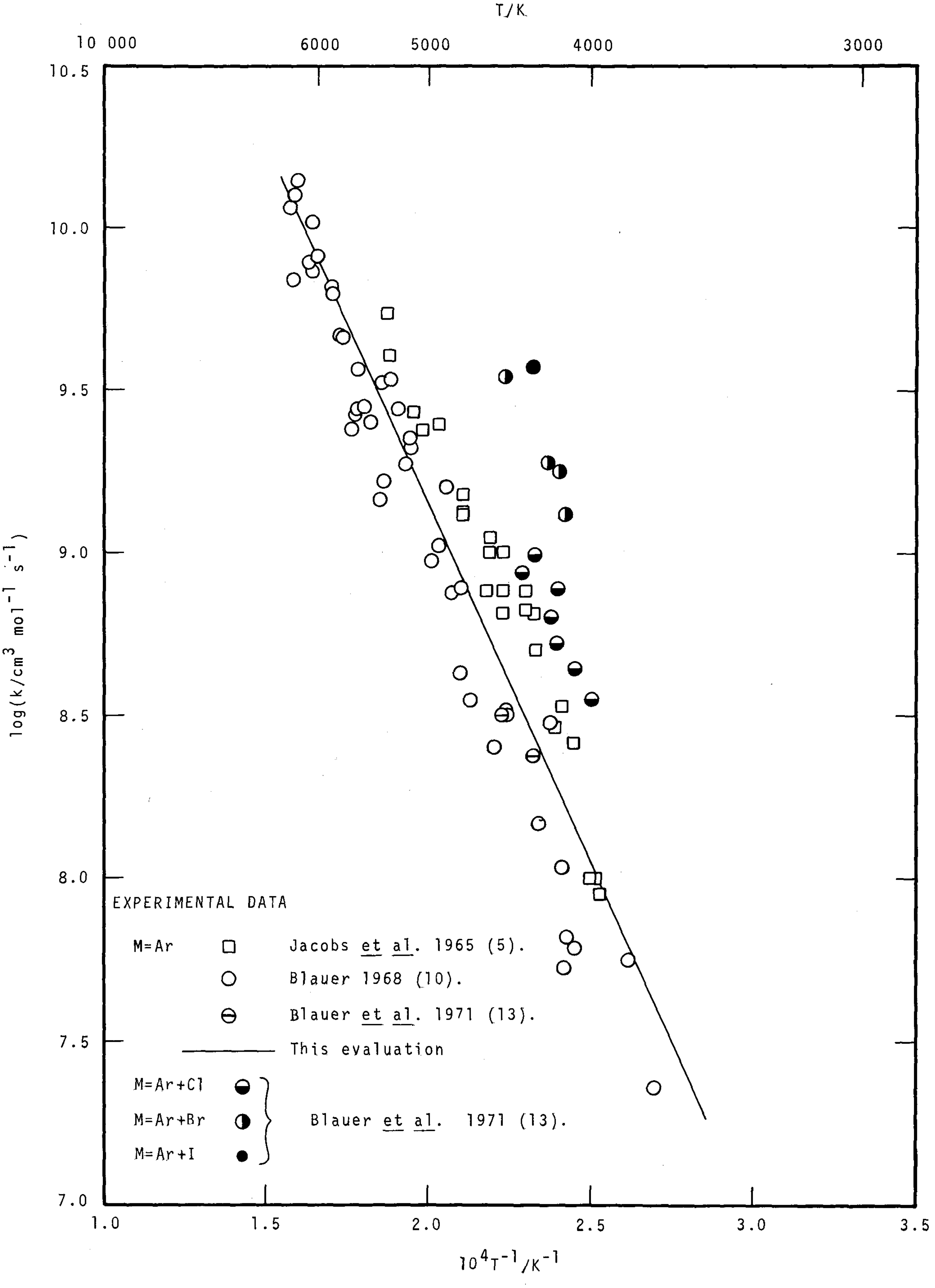
$\log(A/cm^3\ mol^{-1}\ s^{-1})$ = 13.49 ±0.3

$\log(A/cm^3\ molecule^{-1}\ s^{-1})$ = -10.29 ±0.3

$E/J\ mol^{-1}$ = 415 560 ±87 030

$E/cal\ mol^{-1}$ = 99 320 ±20 800

$HF + M \rightarrow H + F + M$



$HF + M \rightarrow H + F + M$

EXPERIMENTAL DATA

	Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
	9.13×10^7	M=Ar	3960	Shock tube study. HF(0.2%, 1% and 2%)/Ar and HF(1%)/H_2(1%)/Ar mixtures behind incident shocks. Shocked pressures in region of 1.3-1.82 atm (132-184 kPa). Reaction followed by ir HF emission, monitored by InSb cell. JACOBS, GIEDT and COHEN 1965 (5)	Authors demonstrated that emission monitored under optically thin conditions. Values of k_1 derived from initial slopes of emission decay curves. $HF + M \rightarrow H + F + M$ 1 Computer matching of HF profiles showed theoretical curves largely independent of k_2 $H + HF \rightarrow H_2 + F$ 2 in HF/Ar mixtures, but sensitivity to both k_2 and k_3 $H + H + M \rightarrow H_2 + M$ 3 greater in HF/H_2/Ar mixtures. Authors arbitrarily chose T^{-1} and T^{-2} dependences to fit these data (which we have taken from authors' graph), giving expressions $k_1(M=Ar) = 1.13\times10^{19}T^{-1}\exp(-67\ 480/T)$ cm^3 mol^{-1} s^{-1}, and $5.13\times10^{22}T^{-2}\exp(-67\ 480/T)$ cm^3 mol^{-1} s^{-1} (3800-5300 K) Latter expression quoted by (7). Data fitted to simple Arrhenius expression by (11), giving E_1=452 kJ mol^{-1} (108 kcal mol^{-1}), and by (16), giving k_1 (M=Ar) = $3.4\times10^{14}\exp(-58\ 470/T)$ cm^3 mol^{-1} s^{-1}.
	1.01×10^8		3980		
	1.01×10^8		4010		
	2.61×10^8		4100		
	3.38×10^8		4150		
	2.94×10^8		4190		
	5.11×10^8		4300		
	6.56×10^8		4300		
	6.72×10^8		4360		
	7.87×10^8		4360		
	1.01×10^9		4490		
	6.56×10^8		4550		
	7.87×10^8		4550		
	1.00×10^9		4580		
	1.10×10^9		4580		
	7.36×10^8		4590		
	1.30×10^9		4740		
	1.34×10^9		4740		
	1.51×10^9		4760		
	2.49×10^9		4930		
	2.39×10^9		5070		
	2.70×10^9		5140		
	3.96×10^9		5330		
	5.46×10^9		5370		
(a)	2.33×10^7	M=Ar	3696	Shock tube study. Mixtures of (a) HF(0.852-3.57%)/Ar, (b) HF(1%-2.02%)/H_2(0.232 and 0.323%)/Ar, and (c) HF (1.34-3.12%)/F_2(0.375-5.84%)/Ar behind incident shocks. Initial post-shock values of [HF] 4×10^{-8}-4.26×10^{-7} mol cm^{-3}. I.r. HF emission intensity followed using InSb detector. BLAUER 1968 (10)	Values of k_1 determined from initial slopes of emission profiles. Author gave best fit to all data as $k_1(M=Ar) = 4.7\times10^{18}T^{-1}\exp(-67\ 480/T)$ cm^3 mol^{-1} s^{-1} (3700-6100 K) but for mixtures (a) and (b) better fit appeared to $k_1(M=Ar) = 2.5\times10^{22}T^{-2}\exp(-67\ 480/T)$ cm^3 mol^{-1} s^{-1}. No great difference observed between third-body efficiencies of F and Ar.
	5.74×10^7		3822		
	3.20×10^8		4425		
	3.33×10^8		4426		
	7.84×10^8		4768		
	9.53×10^8		4970		
	2.13×10^9		5150		
	2.01×10^9		5174		
	2.78×10^9		5216		
	3.41×10^9		5320		
	5.39×10^7		5370		
	3.37×10^9		5379		
	2.82×10^9		5563		
	2.78×10^9		5613		
	4.69×10^9		5784		
	6.79×10^9		5905		
	6.93×10^9		6314		
(b)	1.49×10^8	M=Ar	4274		
	1.83×10^9		5124		
	1.85×10^9		5206		
	3.33×10^9		5390		
	9.30×10^9		5977		
	7.75×10^9		6153		
(c)	6.14×10^7		4089		
	6.66×10^7		4110		
	5.39×10^7		4138		
	1.09×10^8		4145		
	3.05×10^8		4218		
	2.56×10^8		4522		
	3.55×10^8		4700		
	4.30×10^8		4784		
	6.94×10^8		4824		
	1.61×10^9		4871		
	1.05×10^9		4914		
	2.29×10^9		5155		

$HF + M \rightarrow H + F + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1.66×10^{9} M=Ar	5367		
1.46×10^{9}	5413		
2.56×10^{9}	5513		
3.71×10^{9}	5613		
2.66×10^{9}	5635		
2.44×10^{9}	5672		
4.66×10^{9}	5756		
6.35×10^{9}	5862		
8.22×10^{9}	6022		
7.41×10^{9}	6102		
1.04×10^{10}	6109		
1.40×10^{10}	6276		
1.27×10^{10}	6320		
1.16×10^{10}	6365		
(a) 2.39×10^{8} M=Ar	4310	Shock tube study. (a) HF (1.6%)/Ar, and HF(1.6%)/ (b) Cl_2 or (c) Br_2 or (d) I_2 (1%)/Ar mixtures. Incident shocks. Initial [HF] values 7.1×10^{-8} to 2.85×20^{-7} mol cm^{-3}. Ir emission from HF monitored at 2.5μ. BLAUER, ENGLEMAN and SOLOMON 1971 (13)	Values of k_1 derived from initial slopes of emission profiles. Authors tabulated results as $k_1T^2\exp(67\ 480/T)$ $cm^3\ K^2\ mol^{-1}\ s^{-1}$. For mixtures in which [X]/[M]=0.019, authors give $k_1(M{=}I):k_1(M{=}Br):k_1(M{=}Cl):k_1(M{=}F):k_1(M{=}Ar)=850:500:150:1:1$. $HF + M \rightarrow H + F + M$ 1
3.20×10^{8}	4485		
(b) 3.50×10^{8} M=Ar+Cl	3991		
4.41×10^{8}	4075		
5.30×10^{8}	4183		
7.71×10^{8}	4185		
6.43×10^{8}	4208		
9.84×10^{8}	4300		
8.68×10^{8}	4371		
(c) 1.32×10^{9} M+Ar+Br	4143		
1.77×10^{9}	4166		
1.91×10^{9}	4219		
3.47×10^{9}	4471		
(d) 3.71×10^{9} M=Ar+I	4299		

Discussion

There are only three studies of the rate of dissociation of HF,

$$HF + M \rightarrow H + F + M, \qquad (1)$$

all of which have been made using shock tube methods, the i.r. emission from HF being monitored in all cases.

The data for $k_1(M{=}Ar)$ of Blauer [10 and 13] are only a factor of 2 lower than the earlier results of Jacobs et al. [5]. As all the available data were obtained by essentially identical methods, we have chosen to fit a single expression to all the data, rather than to compromise between two separate expressions [5 and 10, 13]. Neither Blauer [10] nor Jacobs et al. [5] gave any a priori reason for choosing the T^{-2} temperature dependence, and so we feel justified in recommending a simple Arrhenius expression

$$k_1(M{=}Ar) = 3.12\times10^{13} \exp(-49\ 980/T)\ cm^3\ mol^{-1}\ s^{-1}$$

(3500–6500 K), which, as a least-squares fit, has a standard deviation of only 20%, but in order to encompass all of the available data, error limits of a factor 2 should be taken into account.

Although Jacobs et al. [5] used their expression for $k_1(M{=}Ar)$ to model $HF/H_2/Ar$ mixtures, and Blauer [10] could detect no great increase in collision efficiency for F over Ar, in $HF/F_2/Ar$ mixtures, there are insufficient data to make any recommendations for $k_1(M{=}H)$, $k_1(M{=}F)$, and $k_1(M{=}HF)$.

Rate of the Reverse Reaction

There have been no experimental studies on the rate of the reverse reaction

$$H + F + M \rightarrow HF + M. \qquad (-1)$$

Prior to any data on k_1, estimates for k_{-1} were made by comparison with k_3

$$H + H + M \rightarrow H_2 + M \qquad (3)$$

e.g., Sarli [2], $k_{-1}=1.09\times10^{15}\ T^{1/2}\ cm^6\ mol^{-2}\ s^{-1}$; Wilde [3], $k_{-1}(M{=}H_2,HF)=7.5\times10^{18}\ T^{-1}\ cm^6\ mol^{-2}\ s^{-1}$, the expression for k_3 $(M{=}H_2)$ determined by Patch [1], and used by [6,8 and 12]; and Mayer, Cook and Schieler [4], $k_{-1}(M{=}HF)=10^{19}\ T^{-0.5}\ cm^6\ mol^{-2}\ s^{-1}$, being similar to the expression of Wilde [3], plus other expressions for $M{=}H_2$, H, H_2O and OH.

Using the data for k_1 of Jacobs et al. [5], Bittker [6] quoted $k_{-1}(M{=}Ar)=3\times10^{18}\ T^{-1}\ cm^6\ mol^{-2}\ s^{-1}$, and taking $k_3(M{=}H_2O)=15k_3(M{=}Ar)$ he used the similarity between

HF and H_2O to suggest $k_{-1}(M=HF)=10k_{-1}(M=Ar)$. The k_1 data of [5] were also used by Jensen and Kurzius [9] to give $k_{-1}(M=Ar)=1.8\times10^{19}\ T^{-1}$ cm^6 mol^{-2} s^{-1}, a factor of 6 higher than the expression derived by Bittker [6]. The higher efficiency of molecular third bodies typically found in rocket exhausts suggested [9] the expression $k_{-1}=3.6\times10^{19}\ T^{-1}$ cm^6 mol^{-2} s^{-1}. With the publication of the results of Blauer [10], Jensen and Jones [14] updated the expression for $k_{-1}(M=Ar)$, giving $k_{-1}(M=Ar)=3.6\times10^{18}\ T^{-1}$ cm^6 mol^{-2} s^{-1}, and increased their estimate of the relative efficiency of rocket nozzle collision partners to threefold, giving $k_{-1}=10^{19}\ T^{-1}$ cm^6 mol^{-2} s^{-1}. Wagner [15] used the data of [5] to give $k_{-1}(M=Ar)=1.13\times10^{21}\ T^{-2}$ cm^6 mol^{-2} s^{-1}.

Using our own expression for $k_1(M=Ar)$, and the equilibrium constant, we obtain for $k_{-1}(M=Ar)$ the expression,

$$k_{-1}(M=Ar) = 7.5\times10^{12}\exp(17\,680/T)\ \text{cm}^6\ \text{mol}^{-2}\ \text{s}^{-1},$$

over the temperature range 3500–6000 K. The factor 2 error limits for k_1 apply also to k_{-1}.

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A4 $F + H_2 \rightarrow HF + H$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-133.457	-0.945	23.332
300	-133.469	-0.958	23.187
500	-133.787	-1.795	13.883
1000	-134.231	-2.447	6.884
1500	-134.649	-2.577	4.545
2000	-134.558	-2.673	3.375
2500	-134.816	-2.790	2.671
3000	-135.197	-2.929	2.202
3500	-135.725	-3.092	1.864
4000	-136.441	-3.284	1.610
4500	-137.374	-3.498	1.411
5000	-138.528	-3.740	1.252

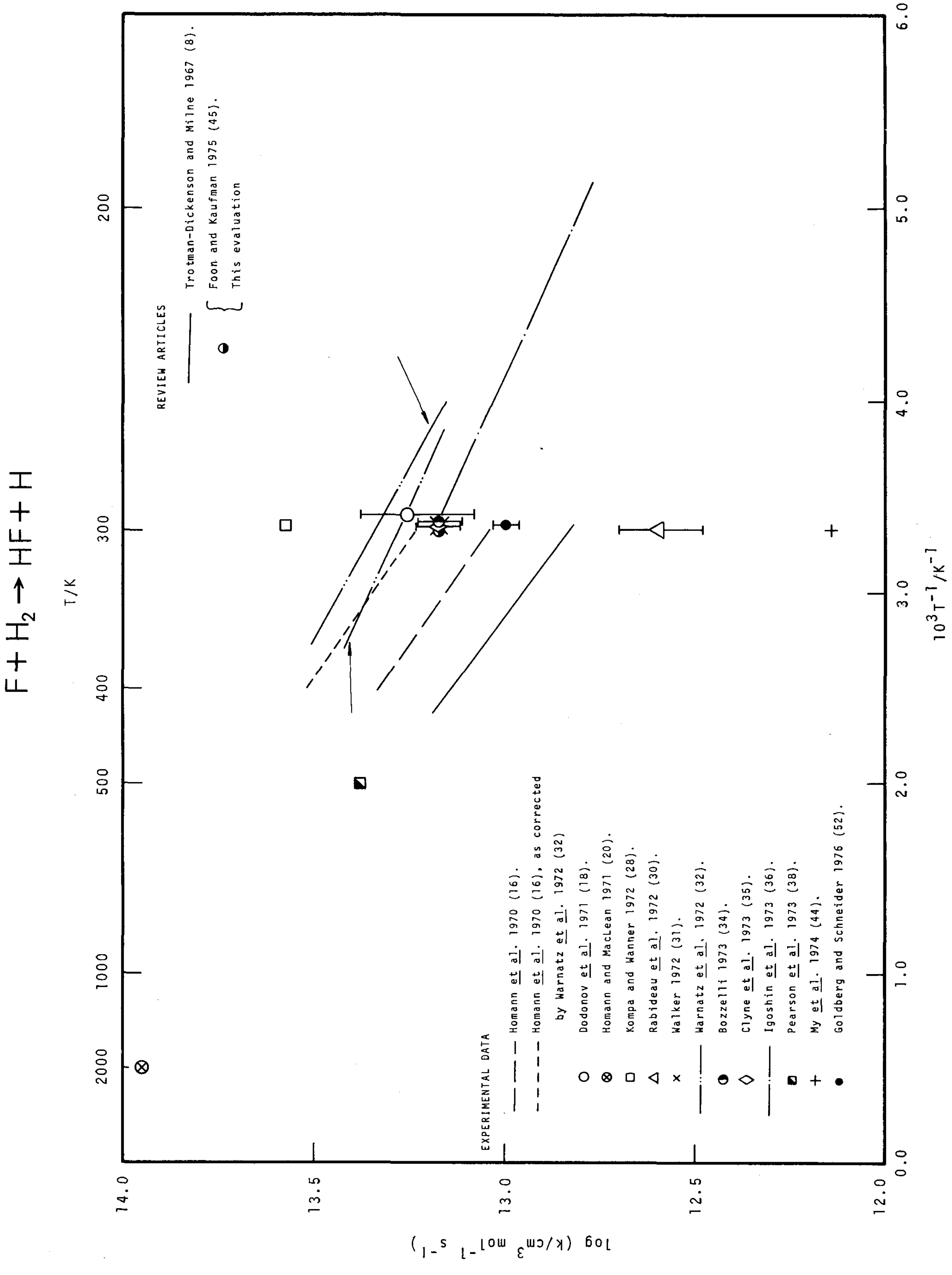
RECOMMENDED RATE CONSTANT

$$k = 1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$= 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature: 300±3 K

Suggested Error Limits for Rate Constant: ±30%

(Note: this value is the same as that given by FOON and KAUFMAN (45)).



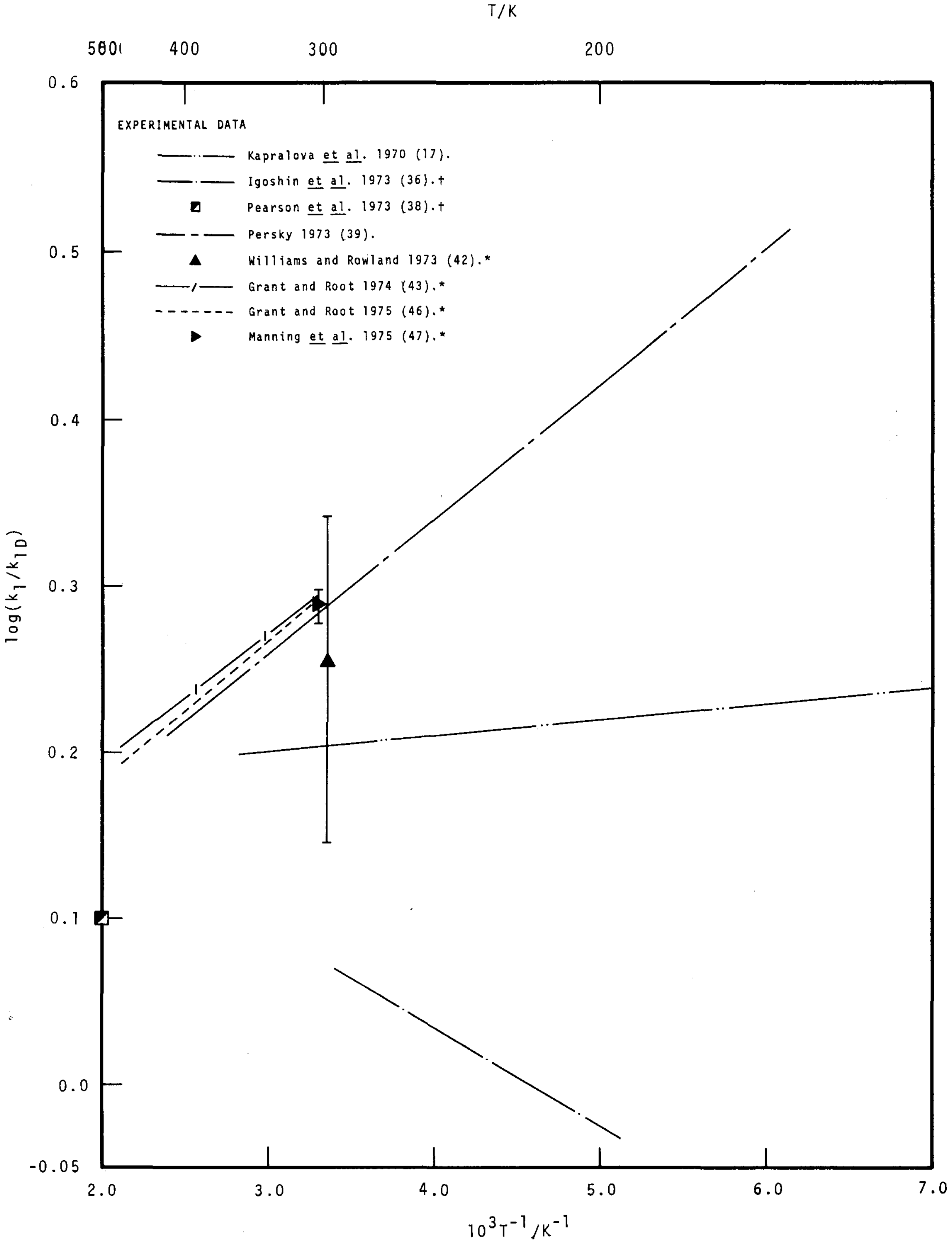
$F + H_2 \rightarrow HF + H$

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	298-423	Static system. F_2(∿1mm Hg; 133.3 Pa)/H_2(∿3mm Hg; 400 Pa)/CH_4(∿3mm Hg; 400 Pa)/N_2 or CO_2(350 mm Hg; 46.7 kPa) mixtures photolysed using medium pressure Hg lamp. Ratio $[H_2]/[CH_4]$ varied 2:1 to 1:2. Mass spectrometry used to analyse reaction products. MERCER and PRITCHARD 1959 (1)	H_2 and CH_4 remaining in products gave ratio k_2/k_1 at several temperatures $F + H_2 \rightarrow HF + H$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 Authors quote $k_2/k_1 = 2.45\pm0.2$ (298 K) and 2.37 ± 0.07 (309 K), and expression $k_2/k_1 = 1.05\exp(252\pm100/T)$ (298-423 K). Used by FETTIS *et al.* (3) together with their expression for k_2 to give $k_1 = 4.68\times10^{13}$ $\exp(-860/T)$ cm^3 mol^{-1} s^{-1}. FETTIS and KNOX (4) quote $k_1 = 5.9\times10^{13}$ $\exp\{-(860\pm110)/T\}$ cm^3 mol^{-1} s^{-1} on the basis of this work and (3). We have used these data solely for the evaluation of k_2 (see this Volume, section A6).
	395-435	Static system. F_2(20.5-241 mm Hg; 2.7-32.1 kPa)/H_2(20.5-340 mm Hg: 2.7-45.3 kPa)/O_2(255-512 mm Hg: 34-68.3 kPa)/N_2 mixtures at total pressures of 645 mm Hg(86 kPa). Decay of F_2 monitored by absorption at 284.9 nm. LEVY and COPELAND 1965 (6)	Most experiments performed at 405 K. Removal of F_2 inhibited by O_2 such that limiting rate is reached. In region of this limit, kinetics obeyed expression $-d[F_2]/dt = k[F_2][H_2]^{0.5}$, where k is overall rate constant. Authors assumed inhibition due to competition between reactions 1 and 3 $F + H_2 \rightarrow HF + H$ 1 $F + O_2 + M \rightarrow FO_2 + M$ 3 For $[O_2]/[H_2] = 5$, authors took removal of F by reaction 3 to be ∿100 times faster than that by reaction 1. Taking $k_3 = 1.3\times10^{14}$ cm^6 mol^{-2} s^{-1} (2), authors obtain $k_1 = 2\times10^8$ cm^3 mol^{-1} s^{-1} (405 K). "Reasonable" pre-exponential factor for k_1 taken as 10^{12} cm^3 mol^{-1} s^{-1}, giving E_1 = 29.3 kJ mol^{-1} (7 kcal mol^{-1}). For ratio of F atom removal rates of ∿10, authors give E_1 = 20.9 kJ mol^{-1}(5 kcal mol^{-1}). In a re-evaluation of these data by the authors (11), this interpretation of the data was rejected.

$F + H_2 / F + D_2$



* Refer to those studies using ^{18}F

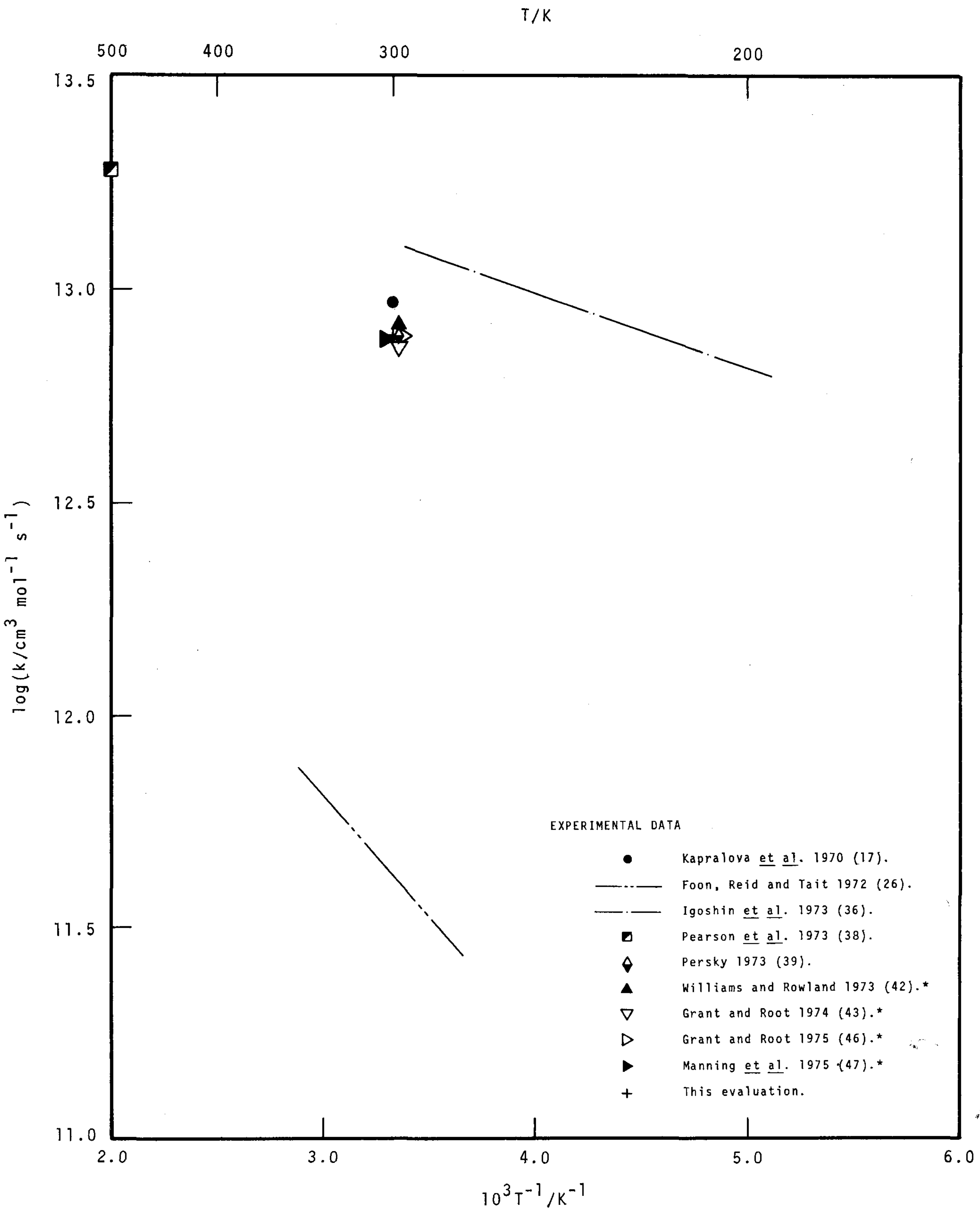
† Refer to k_1/k_{1D} from absolute values of both k_1 and k_{1D}

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.6x10^{14}exp(-805/T)$	300-400	Discharge flow system. N_2/He mixtures passed through discharge, and added to NF_2 (from thermally dissociated N_2F_4). H_2 added downstream through moveable inlet. Total pressures 3.5 mm Hg (466.6 Pa). Reaction followed by mass spectrometry, [F] determined by titration with NOCl. HOMANN, SOLOMON, WARNATZ, WAGNER and ZETZSCH 1970 (16)	Good agreement obtained for k_1 derived from decay of F and rise of HF. Values believed low, due to neglect of diffusion effects, by FOON and KAUFMAN (45). Used by (27, 49, 50 and 51). These data corrected for background interference by H_2 by WARNATZ et al. (32) to give $k_1 = 2.3x10^{14}exp(-780/T)$ cm^3 mol^{-1} s^{-1}.
	77-353	Static system. F_2/He mixtures ($[He]/[F_2]$ ratios 50 to 150:1) added to 200-400 mm Hg (26.7-53.3 kPa) H_2/D_2 and CH_4/D_2 mixtures. $[F_2] \not> 10\%$ smallest reactant concentration. Products analysed by epr spectroscopy. KAPRALOVA, MARGOLIN and CHAIKIN 1970 (17)	Relative HF and DF yields gave ratios k_1/k_{1D} and k_2/k_{1D} $F + H_2 \rightarrow HF + H$ 1 $F + D_2 \rightarrow DF + D$ 1D $F + CH_4 \rightarrow HF + CH_3$ 2 Authors quote statistical treatment of data as giving $k_1/k_{1D} = (1.48 \pm 0.22)exp(23 \pm 15/T)$ and $k_2/k_{1D} = (3.58 \pm 0.75)exp(493 \pm 76/T)$. Authors use these ratios to get k_1/k_2, and using $E_2 = 5.06$ kJ mol^{-1}(1.21 kcal mol^{-1}) quoted by FETTIS et al. (3), obtain $E_1 = (8.98 \pm 0.96)$ kJ mol^{-1} ((2.15±0.23) kcal mol^{-1}). These data only used to evaluate k_2 (this volume, section A6).
$(1.81 \pm 0.6)x10^{13}$	293	F_2-discharge flow system. F_2/He mixtures passed through discharge and 30% H_2/He mixture added through capillary, forming diffusion cloud. Total pressure 3 mm Hg (400 Pa). Mass spectrometry used to monitor reaction. Reaction vessel coated with H_3BO_3. DODONOV, LAVROSKAYA, MOROZOV and TAL'ROZE 1971 (18)	Authors considered further reactions of H and HF to be negligible. They derived $k_1 = 1.99x10^{13}$ cm^3 mol^{-1} s^{-1} from the variation of $[H_2]$, and $k_1 = 1.63x10^{13}$ cm^3 mol^{-1} s^{-1} from that of [H]. Both values dependent upon diffusion coefficients, for H_2 and H respectively. Quoted value takes into account 10%-20% reliability in [F]. Ascribed to other authors by (15).

$F + D_2 \rightarrow DF + D$



* Refer to those studies using ^{18}F.

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	(a) 253-348 (b) 273,298, 343	Static system. (a) $F_2/H_2/CH_4/Ar$ mixtures, $[H_2]/[CH_4]$ ratios 3.2:1 to 1.49:1, and $[Ar]/[F_2]$ and $[H_2+CH_4]/[F_2]$ ratios 10-18 and 11-30 respectively. (b) $F_2/H_2/C_2H_6/N_2$ mixtures with $[H_2]/[C_2H_6]$ 4.2:1 to 8.0:1. Remaining concentrations of hydrogen donors measured by gas chromatography. FOON and REID 1971 (19)	Self-heating avoided by packing reaction vessel. Cold flames detected in absence of packing, thought by authors to be due to presence of O_2 impurities. Consumption of H_2, CH_4 and C_2H_6 gave ratios k_1/k_2 and k_1/k_4 $F + H_2 \rightarrow HF + H$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 $F + C_2H_6 \rightarrow HF + C_2H_5$ 4 Authors give least squares fit to k_1/k_2 as $(1.22\pm0.05)\exp\{-(320\pm15)/T\}$ and to k_1/k_4 as $(4.6\pm2.1)\exp\{-(980\pm140)/T\}$. From further experiments with $F_2/CH_4/C_2H_6/N_2$ mixtures, giving k_2/k_4, good agreement obtained between k_1/k_2 and product $(k_1/k_4)(k_4/k_2)$. Assuming $A_4=10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$, average k_1 derived from two competitive routes given as $(4.85\pm0.25)\times10^{13}\exp\{-(1240\pm140)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ (273-343 K). We have used these results solely in the evaluation of k_2 (this volume, section A6).
$\sim9\times10^{13}$	$\sim$2000	Flame study. $F_2/H_2/Ar$ flames at 6-8 mm Hg (800-1070 Pa), analysed by mass spectrometric probe. HOMANN and MACLEAN 1971 (20)	Rate constant k_1 derived from H_2 profile.
3.8×10^{13}	298	Flash photolysis study. WF_6(0.25 mm Hg; 33.3 Pa)/H_2 mixtures at total pressures of 0.5 mm Hg (66.7 Pa). Intensity of laser emission signals monitored. KOMPA and WANNER 1972 (28)	Assuming negligible vibrational deactivation of HF* formed in reaction 1, decay of emission intensity gave k_1, independent of [F], which was only estimated by extent of light absorption and N_2O actinometry.

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(4 \pm 1) \times 10^{12}$	300	Discharge flow system. H_2/He mixtures passed through moveable discharge. F_2 added downstream. Total pressures ∿2.5 mm Hg (333.3 Pa). [H] and [F] determined by epr spectrometry. Flow tube coated with teflon or H_3BO_3. RABIDEAU, HECHT and LEWIS 1972 (30)	k_1 obtained by computer matching of [H] vs. [F_2] profiles, assuming reaction mechanism to be $H + F_2 \rightarrow HF + F$ 5 $\rightarrow HF^* + F$ 5* $F + H_2 \rightarrow HF + H$ 1 Deactivation of HF* apparently unimportant $HF^* + F_2 \rightarrow HF + 2F$ Used by (49 and 50).
$(1.5 \pm 0.2) \times 10^{13}$	298	Discharge flow system. CF_4(3%)/Ar mixtures passed through discharge. H_2 added downstream with $2 \times 10^{-12} < [H_2] < 5 \times 10^{-12}$ mol cm^{-3}, with $[F]/[H_2]$ in range 6-40. Mass spectrometry used to follow reaction, with F atoms calibrated against NOCl. WALKER 1972 (31)	Value of k_1 obtained from decay of H_2. HF only reaction product detected.
(a) $1.6 \times 10^{14} \exp(-600/T)$ (b) $1.1 \times 10^{14} \exp(-530/T)$	250-375 260-370	F_2- discharge flow system. Mixtures with both (a) F and (b) H_2 in excess studied, using mass spectrometry. WARNATZ, WAGNER and ZETZSCH 1972 (32)	Mass spectra confused by large H_2 background signal. Expressions (a) and (b) obtained from first order decay of H_2 and F respectively.
$(1.5 \pm 0.2) \times 10^{13}$	296	Molecular beam study. Few details available. Mass spectrometry used to follow H and HF. BOZZELLI 1973 (34)	Reported by (45).
1.5×10^{13}	298	Discharge flow system. CF_4 (1%)/Ar mixtures passed through discharge. H_2 added downstream, such that $[F] \gg [H_2]$. Range of [F] 3.5×10^{-11} to 8.0×10^{-11} mol cm^{-3}. Reaction monitored by mass spectrometry, and NOCl titration used to calibrate F. CLYNE, McKENNY and WALKER 1973 (35)	Values of k_1 determined by consumption of H_2. Error margin of ±50% given by authors. Used by (48).

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$9.3\times10^{13}\exp\{-(540\pm90)/T\}$	195-295	Static system. Electric discharge through 4:1 NF_3/H_2 mixtures at pressures below 10 mm Hg (1.33 kPa). HF laser emission monitored. IGOSHIN, KULAKOV and NIKITIN 1973 (36 and 37)	k_1 determined from duration of laser pulse.
2.4×10^{13}	∿500	Static system. Electric discharge (6J) through H_2 (10, 20 and 40 mm Hg; 1.3, 2.7 and 5.3 kPa)/NF_3 mixtures, with $[NF_3]/[H_2]$ = 5, 10 and 15, in laser cavity. Laser pulse followed by Cd-Hg-Te detector. PEARSON, COWLES, HERMANN, GREGG and CREIGHTON 1973 (38)	Laser pulses showed exponential decay characteristics, hence production of HF shown to be via chain reaction. $F + H_2 \rightarrow HF + H$ 1 $H + F_2 \rightarrow HF + F$ 5 Laser pulse width at 10% maximum laser output, corrected for delay between discharge maximum and onset of lasing, plotted vs. p^{-1} gave k_1.
	298	Static system. Nuclear recoil studies in SF_6 (2680-2900 mm Hg; 357-387 kPa)/C_2H_2(10-57 mm Hg; 1.3-7.6 kPa)/HI(3-72 mm Hg; 0.4-9.6 kPa)/H_2(49-133 mm Hg; 6.5-17.7 kPa) mixtures. Product analysis by radio gass chromatography. WILLIAMS and ROWLAND 1973 (42)	Neutron bombardment of SF_6 generated near-thermal ^{18}F atoms. Yields of $CH_2{=}CH^{18}F$ (from sequence 6+7) measured $^{18}F + C_2H_2 \rightarrow CH^{18}F{=}CH$ 6 $CH^{18}F{=}CH + HI \rightarrow CH_2{=}CH^{18}F + I$ 7 and compared with total available ^{18}F atoms, to give ratio k_8/k_6 $^{18}F + HI \rightarrow H^{18}F + I$ 8 in simple $SF_6/C_2H_2/HI$ mixtures. Addition of H_2 alters $CH_2{=}CH^{18}F$ yield, giving ratio $k_{1'}/k_6$, with $^{18}F + H_2 \rightarrow H^{18}F + H$ 1' value (0.14±0.02). Less comprehensive report by these authors (25) gives same value. Authors point out that the rate constants are averaged over energy distributions that are not necessarily Maxwell-Boltzmann.

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	303-475	Static system. Nuclear recoil studies in H_2/C_3F_6 mixtures (mole fraction C_3F_6 10.4%-80.5%) at total pressures 1000 mm Hg (133.3 kPa). $H^{18}F$ determined by absorption on K_2CO_3 and radio assay. GRANT and ROOT 1974 (43)	Variation of $[H^{18}F]$ with $[C_3F_6]$ gave ratio $k_{1'}/k_9$ $^{18}F + H_2 \rightarrow H^{18}F + H$ 1' $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9 Ratios $k_9/k_{1'}$ given as (0.702±0.004) (303 K), (0.463±0.006) (353.5 K), (0.339±0.004) (405 K), and (0.276±0.003) (475 K). Authors quote Arrhenius equation to these data as $k_9/k_{1'}$ = (0.05±0.002)exp(800±6/T).
1.4×10^{12}	300	Discharge flow system. SF_6/He mixtures passed through discharge, and added to H_2 in reaction chamber. HF* laser emission monitored by spectrophotometry, using PbS or PbTe detectors. MY, PEYRON and PUGET 1974 (44)	Laser power expressed as function of $[H_2]$, giving k_1 to within ±10%.
	273-475	Static system. Nuclear recoil study in H_2/C_3F_6 mixtures (C_3F_6 mole fraction varied 0-1.0) with C_2F_6 moderator (95% of overall mixture), at <1600 mm Hg (214 kPa). $[H^{18}F]$ measured by absorption on K_2CO_3 and radio assay. GRANT and ROOT 1975 (46)	Variation of $H^{18}F$ yield with $[C_3F_6]$ gave $k_9/k_{1'}$ = (0.824±0.01) at 273 K, and values of this ratio at 303 K, 353 K, 405 K and 475 K as given in (43). Regression analysis used to give $k_9/k_{1'}$ = (0.056±0.002)exp (760±9/T). $^{18}F + H_2 \rightarrow H^{18}F + H$ 1' $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9 Hot ^{18}F atom reaction effects considered negligible.
	303	Static system. Nuclear recoil studies in H_2/C_3F_6 mixtures (variation in C_3F_6 mole fraction 0-1.0) with SF_6(90% of overall mixture), at 1000 mm Hg (133 kPa) total pressures. $[H^{18}F]$ measured by absorption on K_2CO_3 and radio assay. MANNING, GRANT, MERRILL, PARKS and ROOT 1975 (47)	Total pressures assumed same as for GRANT and ROOT (43). Variation in $H^{18}F$ yields with $[C_3F_6]$ gave $k_9/k_{1'}$ = (0.702±0.004) (as for (43)) at 303 K. $^{18}F + H_2 \rightarrow H^{18}F + H$ 1' $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9

$F + H_2 \rightarrow HF + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(1.00 \pm 0.08) \times 10^{13}$	298	Discharge flow study. CF_4 or F_2/He mixtures passed through discharge. H_2 (16.85%)/He mixtures added, such that $4.6 \times 10^{-11} < [F] < 1.09 \times 10^{-10}$ mol cm^{-3}, and $1.94 \times 10^{-10} < [H_2] < 5.80 \times 10^{-10}$ mol cm^{-3}, at total pressures of ∿2 mm Hg (267 Pa). [F] monitored by esr spectrometry. GOLDBERG and SCHNEIDER 1976 (52)	Relative esr signal, plotted vs. H_2 flow rate, showed absence of significant undissociated F_2 concentrations. k_1 given by finite difference solutions to rate equations, assuming negligible wall reactions.
	298	CF_4 - discharge flow system. CF_4(0.3%)/Ar mixtures passed through discharge, and into flow tube. H_2 or CH_4 added downstream, such that $[H_2]:[Ar]$ and $[CH_4]:[Ar]$ ratios varied ∿2×10^{-3} - 1×10^{-2}. Ar pressure ∿1 mm Hg (133.3 Pa). HF emission intensities monitored between 2.4 and 3.1μ. SMITH, SETSER, KIM and BOGAN 1977 (53)	Relative rate constants for the formation of HF(v≥1) obtained for CH_4 and H_2 from gradients of HF intensity vs. $[CH_4]$ or $[H_2]$. Rate constants for formation of HF(v=0) assumed negligible. Diffusion and quenching also ignored. Relative HF* populations obtained by computer simulation of observed spectra. Values k_1/k_2 $F + H_2 \rightarrow HF + H$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 obtained as 0.37, and with [F] reduced by factor 10, 0.36. These data have been used solely for the evaluation of k_2 (see this volume, section A6).
		REVIEW ARTICLES	
$1.18 \times 10^{14} \exp\{-(860 \pm 110)/T\}$	298-423	Review. Expression derived from work of MERCER and PRITCHARD (1) and of FETTIS and KNOX (4). TROTMAN-DICKENSON and MILNE 1967 (8)	Authors used ratios k_1/k_2 from (1) and k_2/k_4 from (3) $F + H_2 \rightarrow HF + H$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 $F + C_2H_6 \rightarrow HF + C_2H_5$ 4 and took $k_4 = 6.03 \times 10^{13} \exp(-140/T)$ cm^3 mol^{-1} s^{-1} (cf. those values used by (3 and 19)).
1.5×10^{13}	293-300	Review. Value chosen for good agreement between data of (16, 18, 34 and 35). FOON and KAUFMAN 1975 (45)	

$F + H_2 \rightarrow HF + H$

ISOTOPIC REACTION $F + D_2 \rightarrow DF + D$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature	Method and Reference	Comments
	77-353	Static system. F_2/He mixtures ($50<[He]/[F_2]<$ 150) added to 200-400 mm Hg(26.7-53.3 kPa) H_2/D_2 or D_2/CH_4 mixtures. $[F_2]$ $\leq$ 10% smallest reactant concentration. Epr spectroscopy used to follow reaction. KAPRALOVA, MARGOLIN and CHAIKIN 1970 (17)	Method of analysis as described under reaction 1. Authors give $k_1/k_{1D}=(1.48\pm0.22)\exp(23\pm15/T)$. $F + H_2 \rightarrow HF + H$ 1 $F + D_2 \rightarrow DF + D$ 1D $k_2/k_{1D}=(3.58\pm0.75)\exp(493\pm76/T)$. $F + CH_4 \rightarrow HF + CH_3$ 2 FOON <u>et al</u>. (26) used these ratios and their own values for k_1 and k_2 (19) to give $k_{1D}=(3.3\pm0.3)\times10^{13}$ $\exp\{-(1270\pm150)/T\}$ and $(1.1\pm0.8)\times10^{13}\exp\{-(1420\pm150)/T\}$ cm^3 mol^{-1} s^{-1} respectively.
	(a) 183-348 (b) 273,293, 346	Static system (a) $F_2/CH_4/D_2$/Ar mixtures, ratio $[CH_4]/[D_2]$ varied 0.82 to 9.20. (b) $F_2/C_2H_6/D_2$/Ar mixtures, $3.85\leq[C_2H_6]/[D_2]\leq8.21$. Remaining CH_4, C_2H_6 and D_2 concentrations measured by gas chromatography. FOON, REID and TAIT 1972 (26)	Method of analysis same as that of FOON and REID (19) for reaction 1. Ratios k_2/k_{1D} and k_4/k_{1D} given as $(1.26\pm0.07)\exp(360\pm12/T)$ and $(0.27\pm0.1)\exp(1070\pm110/T)$ respectively. $F + D_2 \rightarrow DF + D$ 1D $F + CH_4 \rightarrow HF + CH_3$ 2 $F + C_2H_6 \rightarrow HF + C_2H_5$ 4 Using results from (19) for k_2 and k_4 authors give average k_{1D} = $(3.3\pm0.3)\times10^{13}\exp\{-(1310\pm150)/T\}$ cm^3 mol^{-1} s^{-1}.
$4.9\times10^{13}\exp\{-(400\pm90)/T\}$	195-295	Static system. Electric discharge through NF_3/D_2 mixtures. HF laser emission monitored. IGOSHIN, KULAKOV and NIKITIN 1973 (36 and 37)	k_1 determined from duration of laser pulse.
1.9×10^{13}	~500	Static system. 6J discharge through D_2(10, 20 and 40 mm Hg: 1.3, 2.7 and 5.3 kPa)/NF_3 mixtures, with $[NF_3]/[D_2]$ = 5,10 and 15, in laser cavity. Cd-Hg-Te detector used to follow laser pulse. PEARSON, COWLES, HERMANN, GREGG and CREIGHTON 1973 (38)	Data analysed as for reaction 1.

$F + H_2 \rightarrow HF + H$

ISOTOPIC REACTION $F + D_2$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	163-147	Discharge flow system. SF_6 or CF_4/He mixtures passed through discharge, and added to H_2/D_2 mixtures. Total pressures ∿0.5 mm Hg (66.7 Pa). Reaction products monitored by mass spectrometry. PERSKY 1973 (39)	Ratio of products [HF]/[DF] gives directly k_1/k_{1D} $F + H_2 \rightarrow HF + H$ 1 $F + D_2 \rightarrow DF + D$ 1D Author gave as least squares fit to data k_1/k_{1D} = (1.04±0.02)exp(190±5/T). Average of 29 experiments at 298 K gives ratio (1.91±0.08). Used by (33).
	298	Static system. Nuclear recoil studies in SF_6 (2840 and 3060 mm Hg; 379 and 408 kPa)/C_2H_2 (14, 24 and 57 mm Hg; 1.9, 3.2 and 7.6 kPa)/ HI (14 mm Hg; 1.9 kPa)/ D_2(86,119 and 129 mm Hg; 11.5, 15.9 and 17.2 kPa) mixtures. Product analysis by radio gas chromatography WILLIAMS and ROWLAND 1973 (42)	Data analysed as for reaction 1. Authors give $k_{1D'}/k_6$ as (0.08±0.02) $^{18}F + D_2 \rightarrow D^{18}F + D$ 1D′ $^{18}F + C_2H_2 \rightarrow CH^{18}F{=}CH$ 6 Combined with their value for $k_{1'}/k_6$, this gave $k_{1'}/k_{1D'}$ = (1.8±0.4). Lower error limits (±0.01) given for $k_{1D'}/k_6$ in shorter communication by these authors (25).
	303-457	Static system. Nuclear recoil studies in D_2/C_3F_6 mixtures (C_3F_6 mole fraction 10.2%-80.8%) at 1000 mm Hg (133.3 kPa). $D^{18}F$ measured by absorption on K_2CO_3 and radio assay. GRANT and ROOT 1974 (43)	Variation in yield of $D^{18}F$ with $[C_3F_6]$ gives ratio $k_9/k_{1D'}$ $^{18}F + D_2 \rightarrow D^{18}F + D$ 1D′ $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9 Authors give ratios $k_9/k_{1D'}$ as (1.361±0.028) (303 K), (0.903±0.01) (345 K), (0.656±0.002) (405 K), and (0.443±0.004) (457 K), with Arrhenius fit as $k_9/k_{1D'}$ = (0.055±0.002) exp(976±10/T). Using their expression for $k_9/k_{1'}$ $^{18}F + H_2 \rightarrow H^{18}F + H$ 1′ authors quote $k_{1'}/k_{1D'}$ = (1.11±0.05) exp(180±13/T) (303-475 K). BERRY (33) quotes ROOT (private communication) as giving k_1/k_{1D} = (1.89±0.08) (297 K).

$F + H_2 \rightarrow HF + H$

ISOTOPIC REACTION $F + D_2$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	273-457	Static system. Nuclear recoil studies in D_2/C_3F_6 (0-100%) mixtures with C_2F_6 moderator (95% of total mixture), at <1600 mm Hg (214 kPa). $[D^{18}F]$ determined by absorption on K_2CO_3 and radio assay. GRANT and ROOT 1975 (46)	$D^{18}F$ yields analysed as for $H^{18}F$ yields in study of reaction 1′ (see Comments column for reaction 1 under this reference). $^{18}F + H_2 \rightarrow H^{18}F + H$ 1′ Authors give $k_9/k_{1D'}$ = (1.77±0.07) at 273 K, and values for this ratio at 303 K, 345 K, 405 K and 457 K, as given in (43). Arrhenius fit to these data given as $k_9/k_{1D'}$ = (0.058±0.002) exp(950±10/T) $^{18}F + D_2 \rightarrow D^{18}F + D$ 1D′ $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9 Using their expression for $k_{1'}/k_9$ obtained in same work authors derive $k_{1'}/k_{1D'}$ = (1.04±0.06) exp (190±18/T). Contributions from hot ^{18}F atoms considered negligible. Authors quote k_1/k_{1D} = (1.94±0.04) at 298 K for this work.
	303	Static system. Nuclear recoil studies in D_2(0-100%)/C_3F_6 mixtures with 90% SF_6 moderator at 1000 mm Hg (133 kPa) total pressures. $D^{18}F$ absorbed on K_2CO_3 and measured by radio assay. MANNING, GRANT, MERRILL, PARKS and ROOT 1975 (47)	$D^{18}F$ yields analysed as for $H^{18}F$ yields in study of reaction 1′ $^{18}F + H_2 \rightarrow H^{18}F + H$ 1′ $^{18}F + D_2 \rightarrow D^{18}F + D$ 1D′ Authors obtained $k_9/k_{1D'}$ = (1.36± 0.03) at 303 K. $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 9 Using their value of $k_9/k_{1'}$ they quote $k_{1D'}/k_{1'}$ = (0.516±0.012).

$F + H_2 \rightarrow HF + H$

ISOTOPIC REACTIONS $F + HD \rightarrow HF + D$ AND $F + DH \rightarrow DF + H$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	300	Flash photolysis laser study. Equimolar UF_6/HD or D_2 mixtures at 2 mm Hg (267 Pa). Laser pulse intensity followed. KOMPA, PARKER and PIMENTEL 1968 (10)	Intensity of DF emission from UF_6/HD mixture ∿0.7 times that from UF_6/D_2 mixture. If the mechanism for the laser is $UF_6 + h\nu \rightarrow UF_5 + F$ $F + D_2 \rightarrow DF + D$ 1D $D + UF_6 \rightarrow DF + UF_5$ 10 reaction 1D solely responsible for DF pumping, rather than reactions 1 and 10. Hence by replacing reaction 1D by 1HD/1DH $F + HD \rightarrow HF + D$ 1HD $F + DH \rightarrow DF + H$ 1DH $k_{1DH}/(k_{1DH} + k_{1HD}) = 0.3$, or $k_{1HD}/k_{1DH} = 2.3$ (Authors quote this value as 2.5, as reported by FOON and KAUFMAN (45)).
	297	Flash photolysis laser study. CF_3I/HD/Ar mixtures (ratios 0.5:1:50, 0.1:1:50 and 0.02:1:50), CF_3I/H_2/Ar and CF_3I/D_2/Ar mixtures, at total pressures of 50 mm Hg (6.7 kPa). Laser pulse intensity monitored by InSb detectors. BERRY 1973 (33)	$[H_2]$ and $[D_2]$ in respective mixtures with CF_3I and Ar varied, and extrapolated to give same threshold times as in CF_3I/HD/Ar mixtures. From extrapolated values, and gain coefficients for particular transitions of HF or DF, author derived ratios $k_{1HD}/k_1 = 0.38\pm0.03$ and $k_{1DH}/k_{1D} = 0.505\pm0.055$. Quoting k_1/k_{1D} of (39) and ROOT (private communication), author gives $k_{1HD}/k_{1DH} = 1.42\pm0.01$ $F + H_2 \rightarrow HF + H$ 1 $F + D_2 \rightarrow DF + D$ 1D $F + HD \rightarrow HF + D$ 1HD $F + DH \rightarrow DF + H$ 1DH Using our values for k_1 and k_{1D} we obtain $k_{1HD}/k_{1DH} = 1.44\pm0.3$.
	159-413	Discharge flow system. Discharge in SF_6/He mixtures, added to HD at total pressures ∿0.5 mm Hg (66.7 Pa). Products measured by mass spectrometry. PERSKY 1973 (40)	Method as for reaction 1D. Ratio k_{1HD}/k_{1DH} given as $(1.26\pm0.02)\exp(35\pm3/T)$ (159-413 K) $F + HD \rightarrow HF + D$ 1HD $F + DH \rightarrow DF + H$ 1DH with average value (over 15 results) at 298 K of (1.45 ± 0.03).

Discussion

The development of the HF laser has led to a large number of studies, both experimental and theoretical, of the reaction

$$F + H_2 \rightarrow HF + H. \qquad (1)$$

Several of these investigations have been primarily concerned with the rate constants for the population of particular vibrational levels of excited HF [13,14,22,23,29] and, although in one study [22] an assessment has been made of the overall rate constant, we do not consider these papers in our evaluation.

The experimentally determined absolute room temperature values of k_1 cover a wide range, 1.4×10^{12} [44] to 3.8×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ [28]. However, within this range there are seven studies [16,18,32,34,35,36,52] that are in agreement over k_1 to within 30%. The values of k_1 reported in these studies were derived from the rates of change of different reactants and products (in some cases more than one [18,20,32,36]), with F atoms being produced by a variety of discharge methods. There is excellent agreement between the data of [32,35 and 36], and the low value of 1.09×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ derived by Homann et al. [16] has been corrected by Warnatz et al. [32] to give $k_1=1.7\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ at 298 K. Because of this good agreement at room temperature we follow Foon and Kaufman [45] in recommending $k_1=1.5\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ (300±3 K). The only theoretically derived expression to agree with this value is that of Wilkins [24], $k_1=1.35\times10^{14}\exp(-805/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the range 250–500 K, obtained from classical trajectory calculations, using a London-Eyring-Polanyi-Sato (LEPS) potential energy surface.

The experimental studies that have investigated the temperature dependence of k_1 [16,32,36] give activation energies of 6.5 kJ mol^{-1} (1.55 kcal mol^{-1}—the corrected value [32]), 4.5 kJ mol^{-1} (1.08 kcal mol^{-1}), and 4.4–5.0 kJ mol^{-1} (1.05–1.2 kcal mol^{-1}), respectively. If the low values of E_1 given by Igoshin et al. [36] and Warnatz et al. [32] are correct, then together with our recommended room temperature value of k_1 these give an Arrhenius expression in agreement to within ~30% with both the value of Pearson et al. [38] at 500 K and the value at 2000 K given by Homann and MacLean [20]. Alternatively if we take the higher value for E_1 as determined by Homann et al. [16] as more accurate, there is only agreement to within ~60% with the value from the same authors [20] at 2000 K. Therefore, it would seem that, unless the point values of Pearson et al. [38] and Homann and MacLean [20] are widely inaccurate, an activation energy for k_1 of (4.6±2.1) kJ mol^{-1} ((1.1±0.5) kcal mol^{-1}) is indicated. But because of the discrepancies between the absolute and derived values of E_{1D} (see below), and in the absence of substantiating data above 300 K, we do not make any recommendation.

Rate of the Reverse Reaction

Only two measurements of k_{-1} have been recorded,

$$H + HF \rightarrow F + H_2, \qquad (-1)$$

both of which have used shock tube methods.

Jacobs, Giedt and Cohen [5] studied (a) HF(0.2, 1 and 2%)/Ar and (b) HF(1%)/H_2(1%)/Ar mixtures behind incident shocks, at temperatures 3800–5300 K, and at shocked pressures in the range 1.3–1.82 atm (132–184 kPa). They followed the i.r. emission from HF using an InSb cell. Assuming the activation energy E_{-1} to be 146.4 kJ mol^{-1} (35 kcal mol^{-1}) they computed [HF] profiles to match their experimental data, varying A_{-1}. The sensitivity of the computed profiles to k_{-1} was small for mixtures (a), but greater for the hydrogen-containing mixtures (b). The authors believed their expression $k_{-1} = 10^{13}\exp(-17\,610/T)$ $cm^3\ mol^{-1}\ s^{-1}$ to be accurate to within a factor of 2. This expression was used by Bittker [7] to obtain an expression for k_1.

In a similar study, principally of the HF dissociation rate, Blauer [9] used HF(0.852–3.57%)/Ar, HF(1.96–2.02%)/H_2(0.232 and 0.323%)/Ar, and HF(1.34–3.12%)/F_2(0.375–5.84%)/Ar mixtures in the incident shock region, at temperatures of 3700–6100 K. The initial post-shock [HF] range was 4×10^{-8}–4.26×10^{-7} mol cm^{-3}. Again the i.r. HF emission was followed. Taking the HF dissociation mechanism as

$$HF + M \rightarrow H + F + M$$

$$H + HF \rightarrow F + H_2$$

$$F + HF \rightarrow H + F_2$$

the integrated rate equations yielded [HF] profiles which best matched the experimental data with $k_{-1}=2\times10^{12}\exp(-17\,610/T)$ $cm^3\ mol^{-1}\ s^{-1}$.

The results of Jacobs et al. [5] and Blauer [9] were used by Jensen and Jones [21], who recommended the expression $k_{-1}=1.2\times10^{13}\exp(-17\,500/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (1000–3500 K) for use in calculating rocket exhaust compositions.

Theoretical expressions for k_{-1} have also been given by Mayer and Schieler [12], using the Johnson-Parr method, and by Wilkins [24] using the London-Eyring-Polanyi-Sato technique to construct a potential energy surface for reaction -1.

All of the above expressions for k_{-1}, when converted to rate constants for the forward reaction using the equilibrium constant, give values of k_1 at 300 K that are at least 2 orders of magnitude below our recommended value, and so we make no recommendation for the rate constant k_{-1}.

$F + D_2 \rightarrow DF + D$

Most of the studies of the isotopic reaction,

$$F + D_2 \rightarrow DF + D, \qquad (1D)$$

have produced a value of k_{1D} relative to k_1, principally in static systems [17,26,42,43,46,47]. In four of these studies [42,43,46,47] the nuclear recoil method was used, in which the fluorine was the isotope ^{18}F. Consequently the possibility that these atoms were "hot," i.e., that their thermal energy distribution was non-Maxwellian, must be considered.

However the good agreement between the room temperature values of $k_{1'}/k_{1D'}$

$$^{18}F + H_2 \rightarrow H^{18}F + H \qquad (1')$$

$$^{18}F + D_2 \rightarrow D^{18}F + D \qquad (1D')$$

obtained using SF_6 [42] or C_3F_6 [43,46,47] as the source of ^{18}F, and the values of k_1/k_{1D} determined by Persky [39] (discharge flow system) and by Kapralova et al. [17] (static system) indicates that the moderators used in the nuclear recoil studies effectively thermalised the reacting ^{18}F atoms.

The good agreement between the values of k_{1D} at ~300 K, whether absolute [36] or derived from the ratio k_1/k_{1D} [17,39,42,43,46,47] leads us to recommend the value $k_{1D} = 7.85\times10^{12}$ cm^3 mol^{-1} s^{-1} at 300±3 K, with confidence limits of ±60%.

There is considerable disagreement over the temperature variation of k_{1D}. From the good agreement between the values for E_{1D}–E_1 of Persky [39] (1.55±0.04 kJ mol^{-1}; 370±10 cal mol^{-1}) and Grant and Root [43] (1.49±0.1 kJ mol^{-1}; 356±26 cal mol^{-1}) and [46] (1.60±0.15 kJ mol^{-1}; 382±35 cal mol^{-1}), obtained using entirely different methods, it would appear that E_{1D}–E_1 is in the region 1.55±0.2 kJ mol^{-1} (370±50 cal mol^{-1}). The negative value of E_{1D}–E_1 obtained by Igoshin et al. [36] may arise solely as a result of taking the small difference between two large numbers: the minimum and maximum values of E_{1D}–E_1, using the authors' expressions, are –2.68 kJ mol^{-1} (–640 cal mol^{-1}) and 251 J mol^{-1} (60 cal mol^{-1}). The low value for E_{1D}–E_1 of Kapralova et al. [17] (188 J mol^{-1}; 45 cal mol^{-1}) was also possibly as high as 314 J mol^{-1} (75 cal mol^{-1}) according to the authors.

Therefore if we accept the value of E_1 as ~4.6 kJ mol^{-1} (1.1 kcal mol^{-1}), and that E_{1D}–E_1~1.55 kJ mol^{-1} (370 cal mol^{-1}), we obtain E_{1D}~6.15 kJ mol^{-1} (1.47 kcal mol^{-1}). But the above E_1 value was based largely on the results of Igoshin et al. [36], so it should also be reasonable to accept their value of E_{1D}, (3.3±0.8)kJ mol^{-1} ((790±180) cal mol^{-1}), and this is nearly half the value for E_{1D} estimated above.

Consequently we do not make any recommendation for k_{1D} other than the above room temperature value.

F + HD → HF + D and F + DH → DF + H

There have been no absolute determinations of k_{1HD} or k_{1DH}

$$F + HD \rightarrow HF + D \qquad (1HD)$$

$$F + DH \rightarrow DF + H \qquad (1DH)$$

and only one investigation (Berry [33]) has linked these rate constants to known values, i.e., k_1 and k_{1D}. But in terms of the intramolecular kinetic isotope effect, there is excellent agreement between the value (1.45±0.03) for k_{1HD}/k_{1DH} determined by Persky [40] and that of (1.44±0.3) derived from the ratios k_{1HD}/k_1 and k_{1DH}/k_{1D} of Berry [33] and our value for k_1/k_{1D}. These both compare favourably with the value of 1.5 at 300 K derived from classical trajectory calculations, using a LEPS potential energy surface, by Wilkins [41].

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Note Added in Proof

Bulatov, Balakhnin, and Sarkisov (Izv. Akad. Nauk SSSR, Ser. Khim., 1734 (1977)) have reported measurements of both k_1 and k_{1D} over the temperature range 150–300 K, using a jet-stirred discharge flow system.

H_2 (or D_2)/He mixtures were added downstream to a flow of F atoms in He diluent (the F atoms being generated by passing CF_4(~3%)/He mixtures through a discharge), giving initial reactant ratios $[F]/[H_2]$ of 0.5 to 5. Total pressures were 0.5 to 1 mm Hg (66.7–133.3 Pa), and the decay of F atoms was measured by esr spectrometry.

The low concentrations of F enabled these authors to neglect other F atom removal processes such as

$$F + F + M \rightarrow F_2 + M$$

$$F + \text{wall} \rightarrow 1/2F_2$$

$$F + O_2 + M \rightarrow FO_2 + M$$

(the O_2 was present as a small impurity in the CF_4). From the initial slopes of F atom decay vs. $[H_2]$ they obtained $k_1 = 5.55 \times 10^{13} \exp\{-(257 \pm 100)/T\}$ cm^3 mol^{-1} s^{-1} (150–300 K), and in similar experiments with D_2, $k_{1D} = 5.66 \times 10^{13} \exp\{-(418 \pm 55)/T\}$ cm^3 mol^{-1} s^{-1} over the same temperatures. Hence $k_1/k_{1D} = 0.98 \exp\{(161 \pm 115)/T\}$.

Their values of k_1 and k_{1D} at 300 K are ~60% and 80% respectively, above our recommended values, but we see no reason to alter these recommendations.

At 2.1 kJ mol^{-1} (510 cal mol^{-1}), their activation energy E_1 is the lowest yet measured. However they emphasize that these measurements were made at low temperatures, and the disagreement with previous values (e.g., [16]), obtained at higher temperatures, may merely be an indication of non-Arrhenius behaviour. Their temperature dependence for the ratio k_1/k_{1D} is only slightly smaller than those of Persky [39] and Grant and Root [43,46] and tends to confirm our suggestion that $E_{1D} - E_1 \sim 1.55$ kJ mol^{-1}.

A5 $H + F_2 \rightarrow HF + F$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-411.635	15.008	72.900
300	-411.639	15.008	72.457
500	-412.074	13.966	43.779
1000	-414.944	10.092	22.202
1500	-418.053	7.556	14.953
2000	-420.642	6.058	11.303
2500	-422.802	5.100	9.101
3000	-424.681	4.414	7.625
3500	-426.404	3.874	6.566
4000	-428.065	3.435	5.770
4500	-429.717	3.042	5.147
5000	-431.341	2.690	4.648

RECOMMENDED RATE CONSTANT

$$k = 8.8 \times 10^{13} \exp(-1210/T) \ cm^3 \ mol^{-1} \ s^{-1}$$
$$= 1.46 \times 10^{-10} \exp(-1210/T) \ cm^3 \ molecule^{-1} \ s^{-1}$$

Temperature Range: 290-570 K.

Suggested Error Limits for Calculated Rate Constant: ±70% in the temperature range quoted.

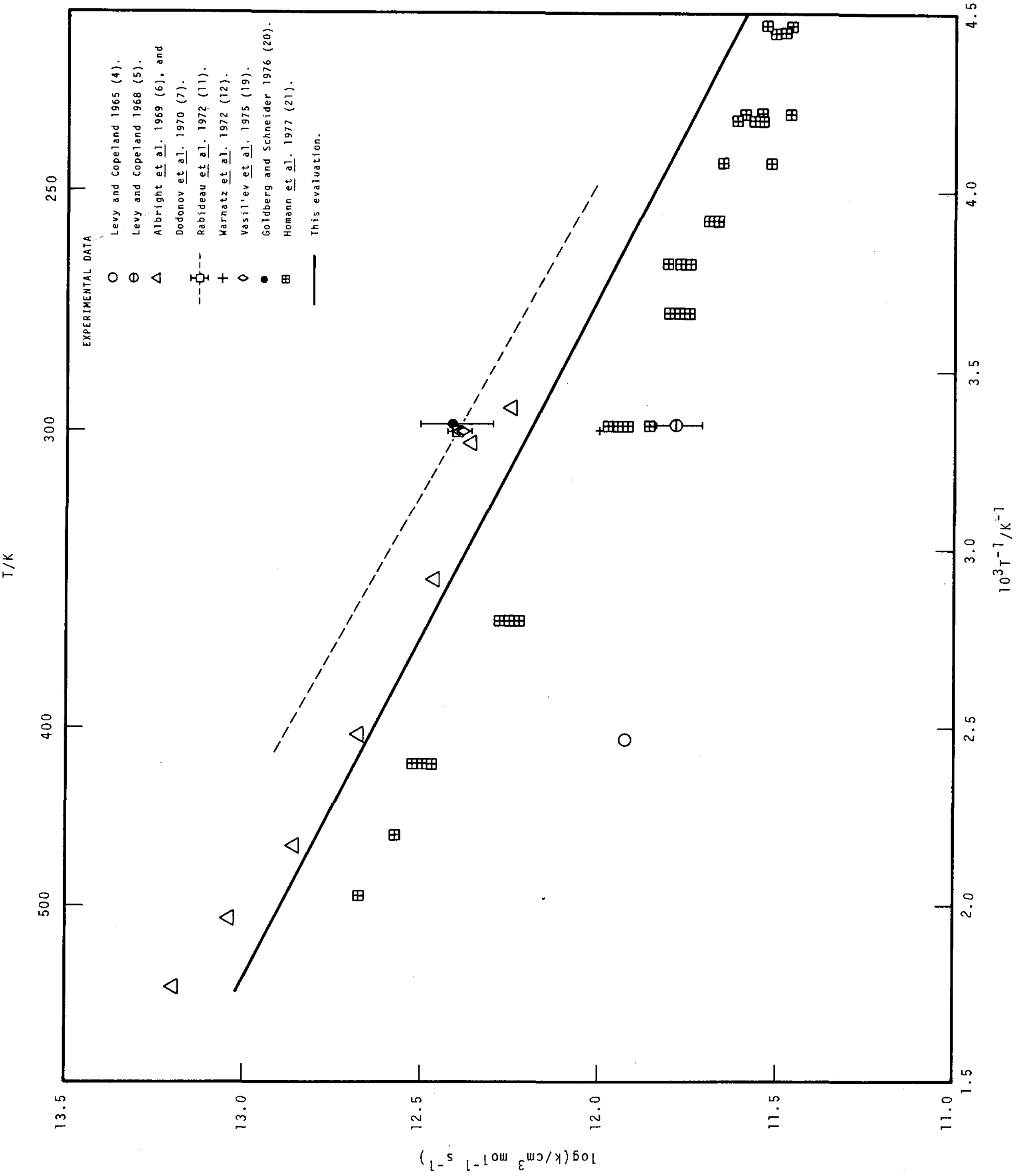
Rate Parameters: $\log(A/cm^3 \ mol^{-1} \ s^{-1}) = 13.95 \pm 0.23$

$\log(A/cm^3 \ molecule^{-1} \ s^{-1}) = -9.84 \pm 0.23$

$E/J \ mol^{-1} = 10\,040 \pm 5190$

$E/cal \ mol^{-1} = 2\,400 \pm 1240$

$H + F_2 \rightarrow HF + F$



$H + F_2 \rightarrow HF + F$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	405	Static system. F_2(20.5-241 mm Hg; 2.7-32.1 kPa)/ H_2(20.5-340 mm Hg; 2.7-45.3 kPa)/O_2(255-512 mm Hg; 34-68.3 kPa)/N_2 mixtures at total pressures of 645 mm Hg (86 kPa). Decay of F_2 monitored by absorption at 284.9 nm. LEVY and COPELAND 1965 (4)	Removal of F_2 inhibited by O_2 such that limiting F_2 removal rate reached. Assuming initiation at wall, authors described inhibition in terms of competition between reactions 1 and 2 $H + F_2 \rightarrow HF + F$ 1 $H + O_2 + M \rightarrow HO_2 + M$ 2 or between reactions 3 and 4 $F + H_2 \rightarrow HF + H$ 3 $F + O_2 + M \rightarrow FO_2 + M$ 4 If step 2 ∿100 times faster than step 1, then for $[O_2]/[H_2]=5$, and taking $k_2=1.3\times10^{14}\ cm^6\ mol^{-2}\ s^{-1}$ (2), authors obtain $k_1 \approx 2\times10^{8}\ cm^3\ mol^{-1}\ s^{-1}$ (405 K). Using a "reasonable" pre-exponential factor $A_1=10^{12}\ cm^3\ mol^{-1}\ s^{-1}$, authors give $E_1=29.3$ kJ mol^{-1} (7 kcal mol^{-1}). If the F atom removal rate ratio is ∿10, then E_1 given as 20.9 kJ mol^{-1} (5 kcal mol^{-1}). Authors re-examined these data in light of later work (5) to give $k_1/k_2[M]=13.6$ (405 K, 1 atm (101.3 kPa)), using $E_2=0$ and $E_1=6.3$ kJ mol^{-1} (1.5 kcal mol^{-1}). Using our expression for $k_2(M=N_2)$ (Volume 1, p.377) we obtain from this re-evaluated ratio $k_1=8.44\times10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ (405 K).
	298	Static system. F_2(10-100 mm Hg; 1.3-13.3 kPa)/H_2 (2.2-400 mm Hg; 0.29-53.3 kPa)/O_2 (2.2-100 mm Hg; 0.29-13.3 kPa)/N_2 mixtures at total pressures 95-760 mm Hg (12.7-101.3 kPa), irradiated at 313 nm. F_2 decay followed by absorption at 285 nm. LEVY and COPELAND 1968 (5)	Rate of F_2 removal found to be independent of $[H_2]$, directly proportional to incident light intensity I, and inversely proportional to $[O_2]$, consistent with mechanism $F_2 + h\nu \rightarrow 2F$ $F + H_2 \rightarrow HF + H$ 3 $H + F_2 \rightarrow HF + F$ 1 $H + O_2 + M \rightarrow HO_2 + M$ 2 $HO_2 + F_2 \rightarrow HF + F + O_2$ 5 $F + HO_2 \rightarrow HF + O_2$ 6 in the limit that $k_6[F][HO_2] >> k_5\ [F_2][HO_2]$. For $p_{F_2} \leqslant 30$ mm Hg (4 kPa) data analysed by Taylor expansion of integrated

$H + F_2 \rightarrow HF + F$

EXPERIMENTAL DATA - CONTINUED

Rate Constant K (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		LEVY and COPELAND 1968 (5) continued.	expression, giving $k_1/k_2[M]$=(4.6 ±0.7) at 298 K. Graphical analysis of F_2 decay for p_{F_2}>30 mm Hg (4 kPa) gave average (over 6 measurements) for $k_1/k_2[M]$ as 4.2 (298 K and 1 atm (101.3 kPa)) Authors used $k_2(M=N_2)=9.2\times10^{15}$ cm^6 mol^{-2} s^{-1} (1, together with $k_2(M=N_2)/k_2(M=H_2)$ of 3), to give $k_1=1.8\times10^{12}$ cm^3 mol^{-1} s^{-1}. Using BENSON's data (2) authors took $E_1=6.3\pm1.3$ kJ mol^{-1} (1.5±0.3 kcal mol^{-1}). Using our expression for $k_2(M=N_2)$ (Volume 1, p.377) we obtain $k_1=(6.04\pm0.9)\times10^{11}$ cm^3 mol^{-1} s^{-1} (298 K).
1.75×10^{12}	294	Discharge flow system. 1% H_2/He mixture passed through discharge; F_2/He mixture added downstream such that $[H]>[F_2]$. Total pressures 3 mm Hg (400 Pa), and $3\times10^{13}<[H]<2\times10^{14}$ mol cm^{-3}. Reaction followed by mass spectrometry. ALBRIGHT, DODONOV, LAVROVSKAYA, MOROZOV and TAL'ROZE 1969 (6) and DODONOV, LAVROVSKAYA, MOROZOV, ALBRIGHT, TAL'ROZE and LYUBIMOVA 1970 (7)	Authors gave accuracy of k_1 as 25-30%, $H + F_2 \rightarrow HF + F$ 1 and fitted these data to expression $k_1=(1.21\pm0.1)\times10^{14}\exp\{-(1210\pm100)/T\}$ cm^3 mol^{-1} s^{-1} (294-565 K). Used by (10,13,14 and 15). Mean of A_1 values from this work and (11) used by (17 and 18).
2.29×10^{12}	303		
2.89×10^{12}	343		
4.70×10^{12}	403		
7.17×10^{12}	461		
1.09×10^{13}	509		
1.57×10^{13}	565		
$(2.5\pm0.2)\times10^{12}$	300	Discharge flow system. H_2/He mixture passed through moveable discharge, and F_2 added downstream. Initial $[H]= 2.5\times10^{-9}$ mol cm^{-2}. Flow tube coated with H_3BO_3. [F] and [H] followed by esr spectrometry, and temperature profile measured. RABIDEAU, HECHT and LEWIS 1972 (11)	Rate expressions from simple reaction mechanism integrated by computer, and values of k_1 and k_3 adjusted to obtain optimum fit $H + F_2 \rightarrow HF + F$ 1 $F + H_2 \rightarrow HF + H$ 3 Temperature profiles matched by varying E_1, assuming $A_1=1.2\times10^{14}$ cm^3 mol^{-1} s^{-1} (6), and using expression for k_3 of HOMANN *et al.* (8). Value determined for E_1 as 10.9 kJ mol^{-1} (2.6 kcal mol^{-1}), for T< 425 K. E_1 used by (17 and 18).

$H + F_2 \rightarrow HF + F$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	$\sim 10^{12}$	300	F_2-discharge flow system. H atoms produced in excess by reaction 3, and F_2 decay followed by mass spectrometry. WARNATZ, WAGNER and ZETZSCH 1972 (12)	k_1 obtained from pseudo-first order kinetics of F_2. Value only preliminary, and reported by FOON and KAUFMAN (16).
		300	Flash photolysis study. $F_2/H_2/O_2/He$, or Ar or CO_2 (in excess by about 100-fold) mixtures at total pressures 70-760 mm Hg (9.3-101.3 kPa). Reaction followed manometrically. VASIL'EV, MAKAROV and CHERNYSHEV 1975 (17)	Analysis of reaction mechanism $F + H_2 \rightarrow HF + H$ 3 $H + F_2 \rightarrow HF + F$ 1 $H + O_2 + M \rightarrow HO_2 + M$ 2 $H + HO_2 \rightarrow$ stable products gave pressure rise (neglecting reactant comsumption, flash heating of gas mixture, and heat losses) in terms of ratio k_1/k_2, and at long reaction times as function of k_2. Values of k_1/k_2 given as $3.14x10^{-4}$, $3.09x10^{-4}$, and $7.64x10^{-5}$ mol cm^{-3} for M=He, Ar and CO_2 respectively. Using their value of k_2, authors derived k_1=$1.39x10^{12}$ cm^3 mol^{-1} s^{-1}. Taking k_2(M=He,Ar) from Volume 1, (p.377) we derive k_1= $2.49x10^{12}$ and $2.45x10^{12}$ cm^3 mol^{-1} s^{-1} at 300 K.
	$(2.6 \pm 0.6)x10^{12}$	298	Discharge flow study. CF_4 or F_2/He mixtures passed through discharge. H_2/He mixtures added to give [F] = $5.67x10^{-11}$-$6.69x10^{-11}$ mol cm^{-3}, $[F_2]$ = $1.21x10^{-11}$-$1.93x10^{-11}$ mol cm^{-3}, and $[H_2]$ = $4.25x10^{-10}$-$6.16x10^{-10}$ mol cm^{-3}. Total pressures $\sim$2 mm Hg (267 Pa). [F] followed using esr spectrometry. GOLDBERG and SCHNEIDER 1976 (20)	Log of relative esr signal showed decay of [F] to be initially linear with probe distance from esr cavity, due to reaction 3, followed by decrease in observed removal rate due to reaction 1 $F + H_2 \rightarrow HF + H$ 3 $H + F_2 \rightarrow HF + F$ 1 One-dimensional finite difference technique used to obtain k_1 from rate equations.
(a)	$2.9x10^{11}$	224	Discharge flow system. (a) H_2/He mixtures passed through discharge, or (b) discharge in mixtures of F_2/He, with H_2 added downstream. F_2 added through	Under system (a), below $\sim$300 K, steady state [H] set up by reaction sequence $H + F_2 \rightarrow HF + F$ 1 $F + H_2 \rightarrow HF + H$ 3 and [H] given by decrease in
	$3.4x10^{11}$	224		
	$3.5x10^{11}$	238		
	$3.7x10^{11}$	238		
	$4.1x10^{11}$	238		
	$5.5x10^{11}$	263		
	$5.9x10^{11}$	263		
	$6.4x10^{11}$	263		
	$9.5x10^{11}$	298		

$H + F_2 \rightarrow HF + F$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	1.68×10^{12}	357	moveable inlet, giving total pressures 270 Pa. Initial $[H]/[F_2]$ ratios (a) 4-20, (b) 4-10. Reaction monitored by mass spectrometry. HOMANN, SCHWEINFURTH and WARNATZ 1977 (21)	$[H_2]$ observed in absence of F_2. At higher temperatures wall recombination allowed for, using k_w found in this study. $F + \text{wall} \rightarrow \frac{1}{2}F_2$ w Reaction 3 used as titration for [H] in system (b), with $\Delta[H] = -\Delta[H_2]$. Pseudo first order decay of F_2 (for T<360 K) used to derive k_1, with allowance for axial F_2 diffusion. Wall recombination of F for T>360 K gave F_2 decay no longer pseudo first order, k_1 derived from computer matching of $[F_2]$ profiles, using reaction sequence 1, 3 and w. These data fitted by expression $k_1 = 4 \times 10^{13} \exp\{-(1110 \pm 50)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
	1.71×10^{12}	357		
	1.82×10^{12}	357		
	1.85×10^{12}	357		
	1.89×10^{12}	357		
	3.0×10^{12}	417		
	3.2×10^{12}	417		
	3.3×10^{12}	417		
	3.7×10^{12}	455		
	4.7×10^{12}	493		
(b)	3.0×10^{11}	225		
	3.2×10^{11}	225		
	2.9×10^{11}	237		
	3.5×10^{11}	237		
	3.9×10^{11}	237		
	3.3×10^{11}	245		
	4.5×10^{11}	245		
	4.6×10^{11}	255		
	4.9×10^{11}	255		
	5.6×10^{11}	273		
	5.9×10^{11}	273		
	6.4×10^{11}	273		
	7.2×10^{11}	298		
	7.3×10^{11} (2 pts)	298		
	8.5×10^{11}	298		
	8.7×10^{11}	298		

Discussion

The strongly exothermic reaction of hydrogen atoms with fluorine,

$$H + F_2 \rightarrow HF + F, \qquad (1)$$

leads to vibrationally excited HF, and is therefore of interest in connection with the HF laser. To date there have been few studies of reaction 1, particularly at high temperatures. However those studies in which the temperature dependence of k_1 has been investigated have produced very similar values of E_1, namely 10.04 kJ mol^{-1} (2.4 kcal mol^{-1}) [6,7], 10.9 kJ mol^{-1} (2.6 kcal mol^{-1}) [11], and 9.2 kJ mol^{-1} (2.2 kcal mol^{-1}) [21]. On the other hand, the absolute values of k_1 from these studies vary by more than a factor of 3.

There is good agreement at 300 K between the H_2-discharge flow data of Rabideau et al. [11], the F_2-discharge flow data of Goldberg and Schneider [20], and the values derived from the flash photolysis data of Vasil'ev et al. [19], using our recommended expression for $k_2(M=He,Ar)$ (Volume 1, p. 377)

$$H + O_2 + M \rightarrow HO_2 + M. \qquad (2)$$

Our conversion of the ratio $k_1/k_2(M=N_2)$ determined by Levy and Copeland at 298 K [5] gives a value for k_1 a factor of 4 below the data of [11,19 and 20]. We attribute this discrepancy to hetero- or homogeneous F atom recombination, thereby reducing the apparent rate of F_2 decay. Homann et al. [21] on the other hand, accepted Levy and Copeland's original value of k_1 [5], i.e., without correcting for improved values of k_2. They attributed the difference between this value [5] and their own data [21] to uncertainties in the "comparatively complicated" reaction mechanism, whereas, according to our interpretation this difference is small.

The overall picture, then, is one of general agreement over the value of the activation energy, E_1, but with an uncertainty in the absolute values of more than a factor of 3. In view of this difference, we have adopted a compromise expression, taking E_1 as 10.04 kJ mol^{-1} (2.4 kcal mol^{-1}), and k_1 at room temperature as $1.52 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$, giving

$$k_1 = 8.8 \times 10^{13} \exp(-1210/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the temperature range 220–570 K. To encompass the lower values of Homann et al. [21] and the higher values of [11,19 and 20], we recommend uncertainty limits of ±70% over the whole of this range.

Rate of the Reverse Reaction

No experimental data are available on the reverse reaction -1

$$HF + F \rightarrow H + F_2. \qquad (-1)$$

Wilkins [9] has calculated both low- and high-temperature expressions for k_{-1} using a potential energy surface constructed by the London-Eyring-Polanyi-Sato technique. For the range 250–500 K he gives $k_{-1} = 2.4 \times 10^{14} \exp(48\,140/T)\ cm^3\ mol^{-1}\ s^{-1}$. It appears obvious that this expression has a minus sign missing from the activation energy. Using our recommended expression for k_1, together with the equilibrium constant K_1, we obtain $k_{-1} = 1.33\times10^{13}$ exp$(-50\ 680/T)$ cm^3 mol^{-1} s^{-1} over the range 298–500 K.

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A6 $F + CH_4 \rightarrow HF + CH_3$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-130.896	22.937	24.131
300	-130.880	22.991	23.989
500	-129.265	27.196	14.925
1000	-129.068	27.870	8.198
1500	-132.030	25.514	5.930
2000	-135.855	23.317	4.766
2500	-139.804	21.556	4.047
3000	-143.691	20.138	3.554
3500	-147.482	18.966	3.191
4000	-151.151	17.987	2.913
4500	-154.703	17.150	2.691
5000	-158.151	16.426	2.510

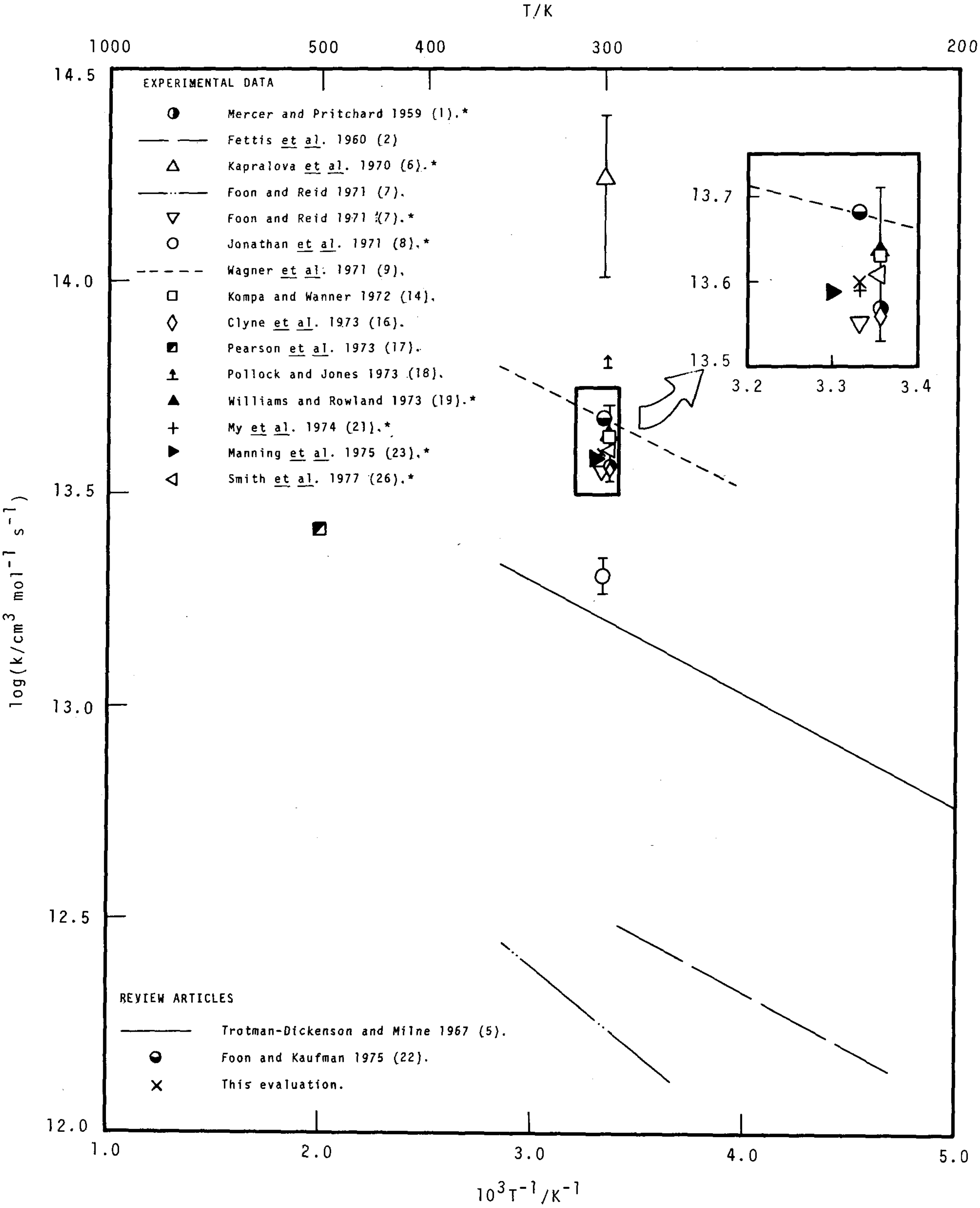
RECOMMENDED RATE CONSTANT

$$k = 4.0 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$$
$$= 6.65 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

Temperature: 300 ± 3 K

Suggested Error Limits for Rate Constant: ±20%

$F + CH_4 \rightarrow HF + CH_3$



Filled symbols refer to those studies using ^{18}F.

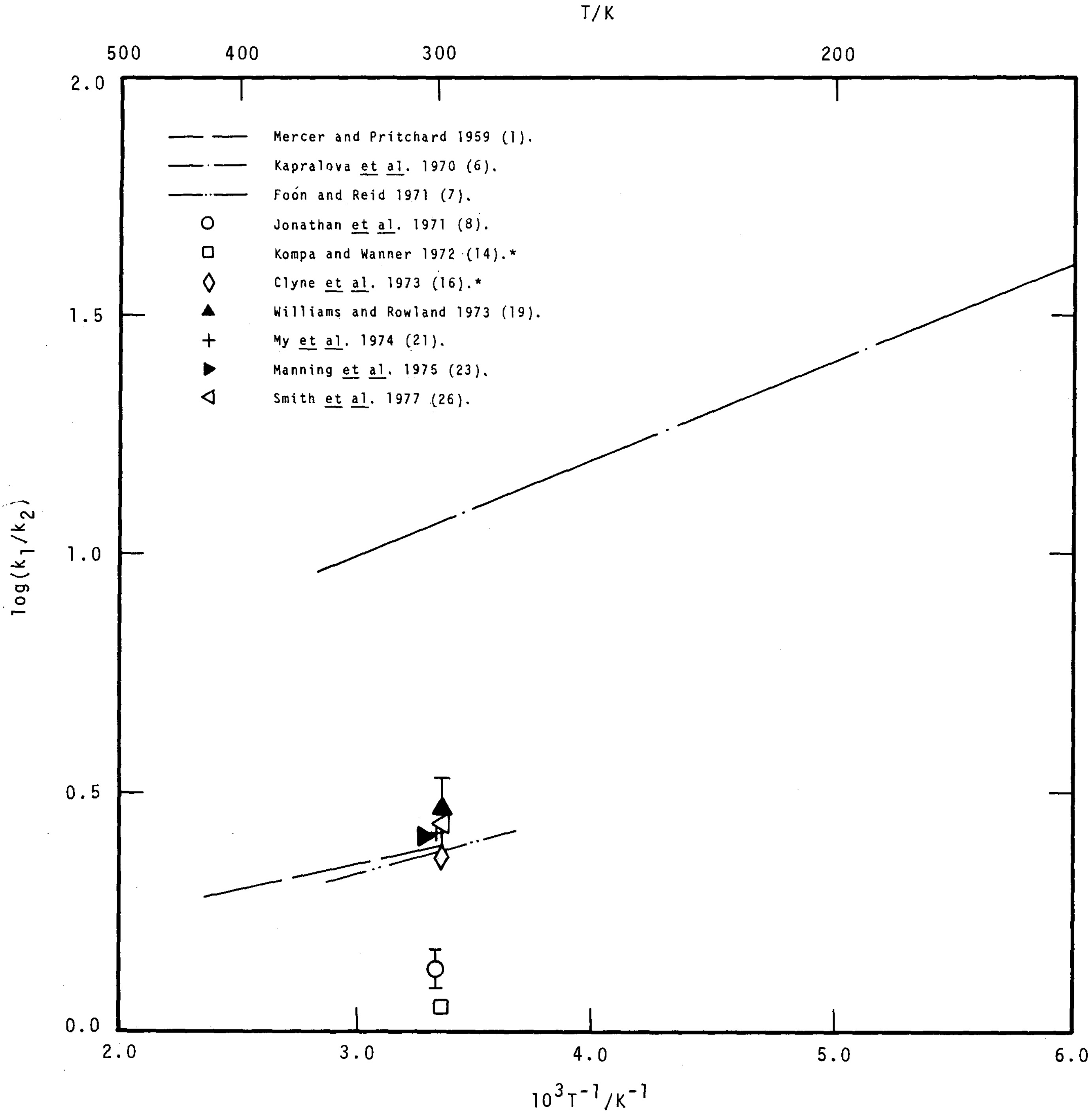
* Refer to values obtained from ratio k_1/k_2 and our value for k_2 (section A4)

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298-423	Static systems. F_2(∿1 mm Hg; 133.3 Pa)/H_2(∿3 mm Hg; 400 Pa)/CH_4(∿3 mm Hg: 400 Pa)/N_2 or CO_2(350 mm Hg; 46.7 kPa) mixtures photolysed by medium pressure Hg lamp. $[H_2]/[CH_4]$ ratios varied 2:1 to 1:2. Reaction products analysed by mass spectrometry. MERCER and PRITCHARD 1959 (1)	This study reported by FETTIS *et al*. (2) as a private communication. Relative concentrations of remaining H_2 and CH_4 gave ratios k_1/k_2 $F + CH_4 \rightarrow HF + CH_3$ 1 $F + H_2 \rightarrow HF + H$ 2 Authors quote values k_1/k_2=2.45±0.2 (298 K) and 2.37±0.07 (309 K) and expression k_1/k_2=1.05exp(252±100/T) for 298-423 K. Using our value of k_2 at ∿300 K (this Volume, section A4) we obtain $k_1=(3.68\pm0.3)\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$.
	(a) 198-351 (b) 213-293	Static system. (a) $F_2/CH_4/C_2H_6/N_2$ and (b) $F_2/C_2H_6/C_3H_8/CO_2$ mixtures at total pressures of ∿160 mm Hg (21.3 kPa). Hydrocarbon ratios varied between 1.5:1 and 1:1.5, and F_2/hydrocarbon ratio 1:10 to 1:20. F_2/diluent ratio 1:120. Products analysed by gas chromatography. FETTIS, KNOX and TROTMAN-DICKENSON 1960 (2)	Ratios k_1/k_3 and k_3/k_4 $F + CH_4 \rightarrow HF + CH_3$ 1 $F + C_2H_6 \rightarrow HF + C_2H_5$ 3 $F + C_3H_8 \rightarrow HF + C_3H_7$ 4 obtained as equal to $[CH_3F][C_2H_6]/[C_2H_5F][CH_4]$ and $[C_2H_5F][C_3H_8]/[C_3H_7F][C_2H_5]$ respectively. Fluorinated products in these expressions formed by reactions $R + F_2 \rightarrow RF + F$ Authors quote $k_3/k_1=(0.38\pm0.04)\exp\{-(467\pm21)/T\}$ and $k_3/k_4=(1.84\pm0.05)\exp\{-(140\pm6)/T\}$. Assuming zero activation energy for k_4, and that pre-exponential factor $A_3=7.94\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$, authors quote $k_1=2.46\times10^{13}\exp(-610/T)\ cm^3\ mol^{-1}\ s^{-1}$. FETTIS and KNOX (3) also assumed $E_4=0$, but took $A_3=10^{13}\ cm^3\ mol^{-1}\ s^{-1}$, the value calculated from transition state theory, giving $k_1=(3.05\pm0.5)\times10^{13}\exp\{-(610\pm40)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
$9\times10^{10}T^{0.685}\exp(-705/T)$	298-2500	Theoretical expression, derived from the Johnston-Parr transition state theory, using the rigid-sphere collision model. MAYER and SCHIELER 1966 (4)	For use in propellant combustion problems. Not plotted on Arrhenius diagram.

$F + CH_4 / F + H_2$



Filled symbols refer to those studies using ^{18}F.

* Refer to k_1/k_2 from absolute values of both k_1 and k_2.

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	77-353	Static system. F_2/He mixtures (F_2:He ratios 50 to 150) added to 200-400 mm Hg (26.7-53.3 kPa) H_2/D_2 or D_2/CH_4 mixtures. $\|F_2\| \not> 10\%$ smallest reactant concentration. Product analysis by epr spectroscopy. KAPRALOVA, MARGOLIN and CHAIKIN 1970 (6)	Ratios k_1/k_{2D} and k_2/k_{2D} $F + CH_4 \rightarrow HF + CH_3$ 1 $F + H_2 \rightarrow HF + H$ 2 $F + D_2 \rightarrow DF + D$ 2D given by relative HF and DF yields. Authors quote values of these ratios at several temperatures, and give using statistical treatment $k_1/k_{2D}=(3.58\pm0.75)\exp(493\pm76/T)$, and $k_2/k_{2D}=(1.48\pm0.22)\exp(23\pm15/T)$. Therefore the ratio $k_1/k_2=(2.42\pm1.0)\exp(470\pm90/T)$. Using our room temperature value of k_2 (this Volume, section A4) we obtain $k_1=(1.74\pm0.7)\times10^{14}$ cm^3 mol^{-1} s^{-1} (300 K).
	(a) 253-348 (b) 273,294, and 358	Static system. (a) $F_2/H_2/CH_4$/Ar mixtures, H_2/CH_4 ratios 3.2:1 to 1.49:1, and $(H_2+CH_4)/F_2$ and Ar/F_2 ratios 11 to 30 and 10 to 18 respectively. (b) $F_2/CH_4/C_2H_6$/He mixtures, with CH_4/C_2H_6 ratios 1.6:1 to 3.3:1. Concentrations of remaining hydrogen donors measured by gas chromatography. FOON and REID 1971 (7)	Reaction vessel packed to prevent self-heating. Absence of packing produced cold flames, suggested by authors as due to presence of small amounts O_2. Ratios k_2/k_1 and k_1/k_3 given by consumption of CH_4, H_2 and C_2H_6. Authors give $k_2/k_1=(1.22\pm0.05)\exp\{-(320\pm15)/T\}$ and $k_1/k_3=(4.2\pm1.8)\exp\{-(690\pm110)/T\}$ as least squares fit to data. $F + CH_4 \rightarrow HF + CH_3$ 1 $F + H_2 \rightarrow HF + H$ 2 $F + C_2H_6 \rightarrow HF + C_2H_5$ 3 Experiments also performed in $F_2/H_2/C_2H_6/N_2$ and $F_2/C_2H_6/C_3H_8/N_2$ mixtures. From latter, assuming $A_3=10^{13}$ cm^3 mol^{-1} s^{-1} and $E_4=0$, authors obtained k_3. $F + C_3H_8 \rightarrow HF + C_3H_7$ 4 Average k_1 derived from available competitive routes given as $(4.0\pm0.2)\times10^{13}\exp\{-(930\pm120)/T\}$ cm^3 mol^{-1} s^{-1}. At 300 K we obtain $k_1=(3.6\pm0.2)\times10^{13}$ using authors' k_1/k_2 and our value of k_2(this Volume, section A4).
	300	Discharge flow system. CF_4 (∿1%)/Ar passed through discharge and CH_4 or H_2 added downstream. Total pressures 80-100 μ Hg(10.7-13.3 Pa). Emission	Ratios of intensity peaks of emission spectrum gave relative rate constants for population of various vibrational levels of HF. Corrections made for collisional de-activation, by extrapolating

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		spectrum of vibrationally excited HF product recorded. JONATHAN, MELLIAR-SMITH, OKUDA, SLATER and TIMLIN 1971 (8)	to zero time, and for production of HF(v=o). Authors give k_2/k_1 as (0.74±0.07) and assuming A_1= A_2= $1.26x10^{14}\ cm^3\ mol^{-1}\ s^{-1}$, and using E_2=7.2kJ mol^{-1}(1.71 kcal mol^{-1}) (5), quote E_1=6.4 kJ mol^{-1} (1.53 kcal mol^{-1}) Also reported by JONATHAN (12). Using our value for k_2 (this Volume, section A4) we obtain k_1=$(2.03±0.2)x10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ (300 K).
$3.3x10^{14}exp\{-(580±150)/T\}$	253-352	Discharge flow system. N_2/He mixture passed through discharge and added to thermally dissociated N_2F_4, forming F atoms via $N + NF_2 \rightarrow N_2 + 2F$ CH_4 added downstream, ratio $[CH_4]/[F]\approx9$. Total pressure 3.5 mm Hg (467 Pa). Reaction followed by mass spectrometry. WAGNER, WARNATZ and ZETZSCH 1971 (9)	Reaction performed in presence of excess of N atoms, such that CH_3 removed by reactions such as $N + CH_3 \rightarrow HCN + 2H$
$4.3x10^{13}$	298	Flash photolysis study. WF_6(0.25 mm Hg; 33.3 Pa)/CH_4 mixtures at total pressures 0.5 mm Hg(66.7 Pa). Intensity of laser emission signals monitored. KOMPA and WANNER 1972 (14)	F atom concentration estimated by extent of light absorption and N_2O actinometry. Assuming negligible vibrational deactivation of HF*, decay of emission intensity gives k_1, independent of [F]. Authors also measured k_2 $F + H_2 \rightarrow HF + H$ 2
$3.6x10^{13}$	298	Discharge flow system. CF_4 (1%)/Ar mixtures passed through discharge. CH_4 added downstream, such that $[F]>>[CH_4]$. [F] range $2.5x10^{-11}$ to $4.0x10^{-11}\ mol\ cm^{-3}$. Reaction monitored by mass spectrometry, with F calibrated by titrating with NOCl. CLYNE, McKENNEY and WALKER 1973 (16)	Wide error margin of ±100% given by authors, owing to fact that later, improved technique, as used to remeasure k_5 $F + Cl_2 \rightarrow FCl + Cl$ 5 (see this Volume, section E1), showed this work to be imprecise. k_2 also determined in this work. k_1 used by (24). WALKER (15) reports k_1 as $(3.6±1)x10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ (298 K).

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.6×10^{13}	∿500	Static system. 6J discharge through CH_4(10,20, and 40 mm Hg; 1.3,2.7 and 5.3 kPa)/NF_3 mixtures, with $[NF_3]/[CH_4]$ = 5,10 and 15, in laser cavity. Cd-Hg-Te detection used to monitor laser output. PEARSON, COWLES, HERMANN, GREGG and CREIGHTON 1973 (17)	Exponential decay of laser pulses showed HF production to be via chain reaction $F + CH_4 \rightarrow HF + CH_3$ 1 $CH_3 + F_2 \rightarrow CH_3F + F$ 11 From laser pulse width at 10% maximum laser output, corrected for delay between discharge maximum and onset of laser activity, plotted vs. p^{-1}, authors derived k_1.
	298	Flow system. F_2/Ar mixtures added to NO/CH_4 mixtures at total pressure 3.7 mm Hg (493 Pa). Emission intensity monitored downstream from mixing region. POLLOCK and JONES 1973 (18)	Reaction sequence causing emission given as $F_2 + NO \rightarrow FNO + F$ $F + NO + M \rightarrow FNO^* + M$ 6 $FNO^* \rightarrow FNO + h\nu$ Addition of CH_4 promotes competition between reactions 6 and 1 $F + CH_4 \rightarrow HF + CH_3$ 1 and changes emission intensity to give ratio $k_6[M]/k_1$ as $\leqslant 0.9\times10^{-4}$. Using k_6 from (13) authors gave $k_1 \geqslant 6\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$. We have used our value of k_6 (this Volume, section A22) to give $k_1 \geqslant 6.3\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$.
	298	Static system. Nuclear recoil studies in SF_6(2840 and 2860 mm Hg; 379 and 381 kPa)/C_2H_2 (14-47 mm Hg; 1.9 -6.3 kPa)/HI (7-24 mm Hg; 0.9-3.2 kPa)/CH_4 (92-125 mm Hg; 12.3-16.7 kPa) mixtures. Product analysis by radio-gas-chromatography. WILLIAMS and ROWLAND 1973 (19)	^{18}F atoms generated by neutron bombardment of SF_6. Authors measured yields of $CH_2{=}CH^{18}F$ from reaction sequence 7 and 8 $^{18}F + C_2H_2 \rightarrow CH^{18}F{=}CH$ 7 $CH^{18}F{=}CH + HI \rightarrow CH_2{=}CH^{18}F + I$ 8 and compared with total available ^{18}F atoms, gave ratio k_9/k_7 $^{18}F + HI \rightarrow H^{18}F + I$ 9 determined from $SF_6/C_2H_2/HI$ mixtures. Addition of CH_4 alters $CH_2{=}CH^{18}F$ yield, to give $k_{1'}/k_7$ $^{18}F + CH_4 \rightarrow H^{18}F + CH_3$ 1' Experiments also performed with $SF_6/C_2H_2/HI/C_2H_6$ and $SF_6/C_2H_2/HI/H_2$ mixtures. Authors quote $k_{1'}/k_7 = 0.41 \pm 0.04$, and combining their results for $k_{2'}/k_7$ and $k_{3'}/k_7$ $^{18}F + H_2 \rightarrow H^{18}F + H$ 2' $^{18}F + C_2H_6 \rightarrow H^{18}F + C_2H_5$ 3'

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		WILLIAMS and ROWLAND 1973 (19) continued	they give $k_{1'}/k_{2'}$=2.9±0.5 and $k_{3'}/k_{1'}$=3.4±0.5. Authors remark that various rate constants are averaged over energy distributions that are not necessarily Maxwell-Boltzmann. Earlier, less complete report by these authors (10) gives $k_{1'}/k_7$=0.43±0.04. We have used our value of k_2 (this Volume, section A4) to give k_1= (4.35±0.8)x10^{13} cm^3 mol^{-1} s^{-1} (298 K).
	300	Discharge flow system. SF_6 /He mixtures passed through discharge, and added to CH_4 or H_2 in reaction chamber. Intensity of laser emission from HF* monitored spectrophotometrically. MY, PEYRON and PUGET 1974 (21)	Variation in laser power with $[CH_4]$ and $[H_2]$ gave ratio k_1/k_2 $F + CH_4 \rightarrow HF + CH_3$ 1 $F + H_2 \rightarrow HF + H$ 2 where rate constants are summation of rate constants for excitation into available vibrational levels of HF. Authors obtained k_1/k_2=2.6 at 300 K. Using their own value of k_2 (this Volume, section A4) this gives k_1=3.64x10^{12} cm^3 mol^{-1} s^{-1}, but using our value for k_2 (see section A4 of this Volume) we obtain k_1=3.9x10^{13} cm^3 mol^{-1} s^{-1}.
	303	Static system. Nuclear recoil studies in CH_4/C_3F_6 mixtures (mole fraction C_3F_6 0-1.0) with 95% C_2F_6 or 90% SF_6 moderators at 1000 mm Hg (133 kPa) total pressures. $H^{18}F$ determined by absorption on K_2CO_3 and radio assay. MANNING, GRANT, MERRILL, PARKS and ROOT 1975 (23)	Pressure assumed to be same as in (20). Variation in $H^{18}F$ yields with $[C_3F_6]$ gives ratio $k_{1'}/k_{10}$ $^{18}F + CH_4 \rightarrow H^{18}F + CH_3$ 1' $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 10 Authors quote $k_{10}/k_{1'}$=(0.272± 0.006). Experiments also performed with H_2/C_3F_6 and C_2H_6/C_3F_6 mixtures giving $k_{10}/K_{2'}$, and $k_{10}/k_{3'}$: $^{18}F + H_2 \rightarrow H^{18}F + H$ 2' $^{18}F + C_2H_6 \rightarrow H^{18}F + C_2H_5$ 3' Authors quote $k_{1'}/k_{2'}$ as (2.58± 0.06) and $k_{3'}/k_{2'}$ as (7.39±0.39). With our value for k_2(this Volume section A4) the former gives k_1= (3.87±0.1)x10^{13} cm^3 mol^{-1} s^{-1} (303 K).

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(4.52\pm1.0)x.0^{13}$	298	Discharge flow system. (F_2 +He)(4%)/Ar mixtures passed through discharge, giving typically $[F]=5.0x10^{-12}$ mol cm^{-3}. CH_4 added in excess downstream. Total pressures 150 Pa. [F] decay monitored by resonance fluorescence at 94.58 nm. CLYNE and NIP 1977 (25)	Although CH_4 in excess by factor 2.5-20, correction (from 2-14%) to pseudo first order F atom removal necessary to allow for CH_4 consumption. Absence of deviation of first order rate constants from linear variation with $[CH_4]$ indicated valid assumption of 1:1 stoichiometry. Authors recommend $k_1=(4.34\pm0.7)x10^{13}$ cm^3 mol^{-1} s^{-1}, as mean of results of this work and of (9 and 16).
	298	Discharge flow system. CF_4 /Ar mixture passed through discharge. CH_4/Ar and H_2/Ar mixtures (typically 1:100 and 1:500 in Ar) added downstream. Typical values: $[F]\approx8.3x10^{-12}$, $1.7x10^{-13}\leqslant [H_2]$ or $[CH_4]\leqslant6.6x10^{-11}$ mol cm^{-3}. Several experiments also performed at $[F]\approx8.3x10^{-13}$ mol cm^{-3}. HF emission intensity monitored 2.4-3.1 μ. SMITH, SETSER, KIM and BOGAN 1977 (26)	Intensity of emission at given wavelength plotted vs. $[H_2]$ and $[CH_4]$, and compared. Authors took reaction 1 as their reference reaction, and quoted $k_2/k_1=0.37$ $F + H_2 \rightarrow HF + H$ 2 At the lower [F] value, k_2/k_1 quoted as 0.36. Using our recommended value for k_2 (this Volume, section A4) we obtain $k_1=4.05x10^{13}$ cm^3 mol^{-1} s^{-1}.

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.23x10^{14}exp\{-(610\pm40)/T\}$	198-351	Review. TROTMAN-DICKENSON and MILNE 1967 (5)	Based on ratio k_3/k_1 of (2) $F + CH_4 \rightarrow HF + CH_3$ 1 $F + C_2H_6 \rightarrow HF + C_2H_5$ 3 and on assumed expression $k_3=6.03x10^{13}exp(-140/T)$ cm^3 mol^{-1} s^{-1}. Used by (8).
$4.8x10^{13}$	293-300	Review. FOON and KAUFMAN 1975 (22)	Derived from expression of WAGNER <u>et al</u>. (9), as being in agreement with average of other less accurate measurements.

$F + CH_4 \rightarrow HF + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		ISOTOPIC REACTION $F + CD_4 \rightarrow DF + CD_3$	
	238-352	Static system. $F_2/C_2H_6/CD_4/Ar$ mixtures. Ratio C_2H_6/CD_4 varied 2.88 to 11.75. Concentrations of C_2H_6 and CD_4 measured by gas chromatography. FOON, REID and TAIT 1972 (11)	Data analysed as by FOON and REID (7). Ratio k_3/k_{1D} $F + CD_4 \rightarrow DF + CD_3$ 1D $F + C_2H_6 \rightarrow HF + C_2H_5$ 3 given as $(0.24\pm0.04)\exp(805\pm100/T)$. Using value for k_3 derived previously (7) authors quote $k_{1D} = (3.7\pm0.3)\times10^{13}\exp\{-(1050\pm25)/T\}$ cm^3 mol^{-1} s^{-1}.
	298	Static system. Nuclear recoil studies in SF_6(2730-2850 mm Hg: 364-380 kPa)/C_2H_2(14-70 mm Hg; 1.9-9.3 kPa)/HI (7-35 mm Hg; 0.9-4.7 kPa)/CD_4(70-126 mm Hg; 9.3-170 kPa) mixtures. Product analysis by radio gas chromatography. WILLIAMS and ROWLAND 1973 (19)	Analysis as for reaction 1 (see previous entry in "Comments" column for (19)). Authors quote $k_{1D'}/k_7$ $^{18}F + CD_4 \rightarrow D^{18}F + CD_3$ 1D' $^{18}F + C_2H_2 \rightarrow CH^{18}F{=}CH$ 7 as (0.24±0.04). Combining this with their ratios $k_{1'}/k_7$ and $k_{2'}/k_7$ $^{18}F + CH_4 \rightarrow H^{18}F + CH_3$ 1' $^{18}F + H_2 \rightarrow H^{18}F + H$ 2' we obtain $k_{1D'}/k_{1'} = (0.59\pm0.2)$ and $k_{1D'}/k_{2'} = (1.7\pm0.6)$. Earlier, less complete report by these authors (10) gives $k_{1D'}/k_7$ as (0.27±0.04).
	303	Static system. Nuclear recoil method. CD_4/C_3F_6 mixtures with 90% SF_6 moderator. $D^{18}F$ measured by absorbing on K_2CO_3. MANNING, GRANT, MERRILL, PARKS and ROOT 1975 (23)	Consumption of CD_4 analysed as for reaction 1 (see "Comments" column for (23)), to give ratio $k_{1D'}/k_{10}$ $^{18}F + CD_4 \rightarrow D^{18}F + CD_3$ 1D' $^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$ 10 Authors give $k_{10}/k_{1D'} = (0.424\pm0.003)$. Experiments with H_2/C_3F_6 gave ratio $k_{10}/k_{2'}$ $^{18}F + H_2 \rightarrow H^{18}F + H$ 2' and authors quote $k_{1D'}/k_{2'} = (1.66\pm0.06)$.

Discussion

The rate constant for the reaction between fluorine atoms and methane,

$$F + CH_4 \rightarrow HF + CH_3, \quad (1)$$

has been principally obtained relative to that between F atoms and hydrogen,

$$F + H_2 \rightarrow HF + H. \quad (2)$$

At room temperature the values of k_1/k_2 given by Mercer and Pritchard [1] and Foon and Reid [7], using static systems, are in agreement with the results of My et al. [21], Clyne et al. [16], and Smith et al. [26], using discharge flow methods. The ratio k_1/k_2 for [16] shown on the Arrhenius plot is derived from absolute values of both k_1 and k_2. All these results also compare favourably with k_1/k_2 as found in nuclear recoil investigations by Williams and Rowland [19] and Manning et al. [23], using SF_6 [19] or C_3F_6 [23] as precursors of ^{18}F, indicating that the moderators used in these studies effectively thermalised any "hot" ^{18}F atoms. Moreover when all these k_1/k_2 ratios are converted to values of k_1, using our recommended value for k_2 (this volume, section A4), we find close agreement with the absolute values of k_1 determined by flash photolysis (Kompa and Wanner [14]) and discharge flow methods (Wagner et al. [9], and Clyne et al. [16,25]). The low value of k_1/k_2 obtained by Kompa and Wanner [14] is a result of their high value for k_2 (see the Arrhenius plot for k_2, this volume, section A4). The low values of k_1 reported by Fettis et al. [2] and Foon and Reid [7] were both derived from assumed values for the pre-exponential, A_3 for the reaction

$$F + C_2H_6 \rightarrow HF + C_2H_5. \quad (3)$$

On this basis these values of A_3 must be presumed low.

The close agreement of the room temperature data for k_1 [1,7,9,14,16,19,21,23,25,26] allows us to recommend $k_1 = (4.0 \pm 0.8) \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 300±3 K.

The temperature variation of k_1 is less clear. The similarity between the activation energy differences E_1-E_2 of Mercer and Pritchard [1] (E_1-E_2=-(2.1±0.8) kJ mol^{-1}; -(500±200) cal mol^{-1}) and Foon and Reid [7] (E_1-E_2= -(2.6±0.1) kJ mol^{-1}; -(630±30) cal mol^{-1}) suggests that $E_1 \sim 2.3$ kJ mol^{-1} (540 cal mol^{-1}) using the available data for E_2 (see Discussion of k_2 in section A4 of this volume). However, the only study on the absolute value of E_1 [9] gives E_1 as 4.8 kJ mol^{-1} (1.2 kcal mol^{-1}). Until further data are available on the activation energy of reaction 1 we feel any recommendation for E_1 would be unjustified.

Rate of the Reverse Reaction

There are no available data for the rate constant k_{-1}

$$HF + CH_3 \rightarrow F + CH_4. \quad (-1)$$

However, using our recommended room temperature value for k_1 and the equilibrium constant at 300 K, we derive $k_{-1} = 4.1 \times 10^{-11}$ cm^3 mol^{-1} s^{-1}.

$F + CD_4 \rightarrow DF + CD_3$

All the investigations of reaction 1D have been made in static systems,

$$F + CD_4 \rightarrow DF + CD_3, \quad (1D)$$

and have produced relative values of k_{1D}. Foon et al. [11] measured the ratio k_3/k_{1D},

$$F + C_2H_6 \rightarrow HF + C_2H_5, \quad (3)$$

but their final expression for k_{1D} was derived from their own expression for k_3, which has been shown, in the Discussion of reaction 1, to be too low.

The nuclear recoil studies of Williams and Rowland [19] and of Manning et al. [23] gave ratios $k_{1D'}/k_{2'}$

$$^{18}F + CD_4 \rightarrow D^{18}F + CD_3 \quad (1D')$$

$$^{18}F + H_2 \rightarrow H^{18}F + H \quad (2')$$

of (1.7±0.6) and (1.66±0.06), respectively, at room temperature. The excellent agreement between these values was obtained despite considerable differences in the methods used in these investigations. Williams and Rowland [19] also reported $k_{1D'}/k_{1'} = (0.59 \pm 0.2)$

$$^{18}F + CH_4 \rightarrow H^{18}F + CH_3 \quad (1')$$

As the ^{18}F atoms used in these studies have been shown to be essentially thermalised (see above), using our recommended values for k_2 and k_1 we obtain $k_{1D} = (2.55 \pm 0.9) \times 10^{13}$ and $(2.36 \pm 0.8) \times 10^{13}$ cm^3 mol^{-1} s^{-1} (300±3 K) respectively, from the above ratios.

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A7 $F_2O + M \rightarrow F + FO + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	163.176	127.880	-21.908	-26.297
300	163.193	127.943	-21.731	-26.122
500	164.636	131.733	-10.319	-14.932
1000	166.188	134.005	- 1.681	- 6.595
1500	167.055	134.704	1.220	- 3.870
2000	167.816	135.160	2.677	- 2.538
2500	168.678	135.536	3.556	- 1.756
3000	169.624	135.880	4.144	- 1.247
3500	170.703	136.377	4.568	- 0.890
4000	171.916	136.532	4.887	- 0.629
4500	173.285	136.859	5.137	- 0.430
5000	174.828	137.181	5.339	- 0.274

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 1.8 \times 10^{15} \exp(-17\ 500/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)

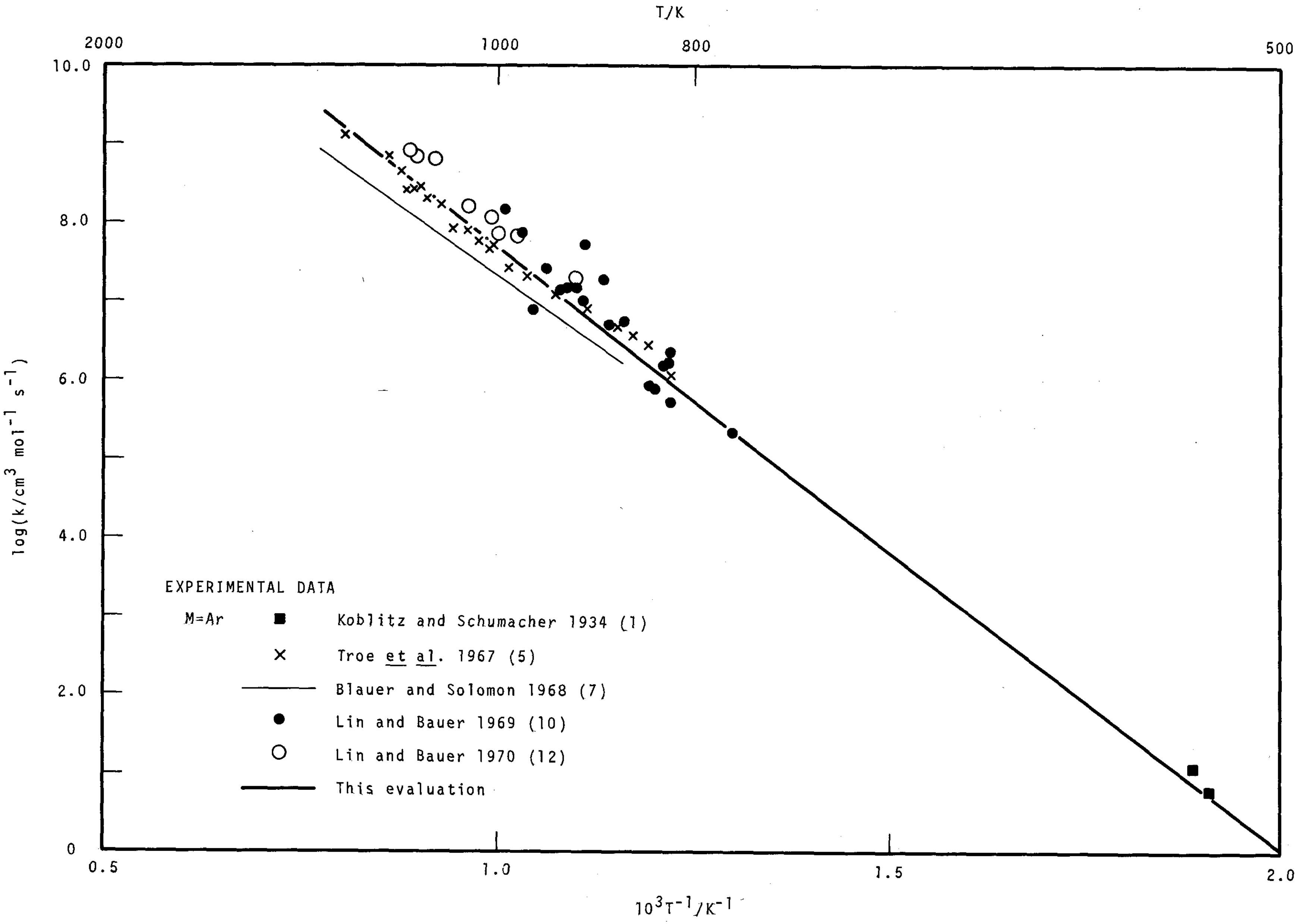
$= 3.0 \times 10^{-9} \exp(-17\ 500/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar)

Temperature Range: 800-1300 K.

Suggested Error Limits for Calculated Rate Constant: A factor of 3 over the quoted temperature range.

Note: Expression for $k^o(M=F_2O)$ given in the Discussion.

Rate Parameters:
$\log(A/cm^3\ mol^{-1}\ s^{-1}) = 15.25 \pm 0.50$
$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -8.52 \pm 0.50$
$E/J\ mol^{-1} = 145\ 500 \pm 16\ 500$
$E/cal\ mol^{-1} = 34\ 800 \pm 4000$



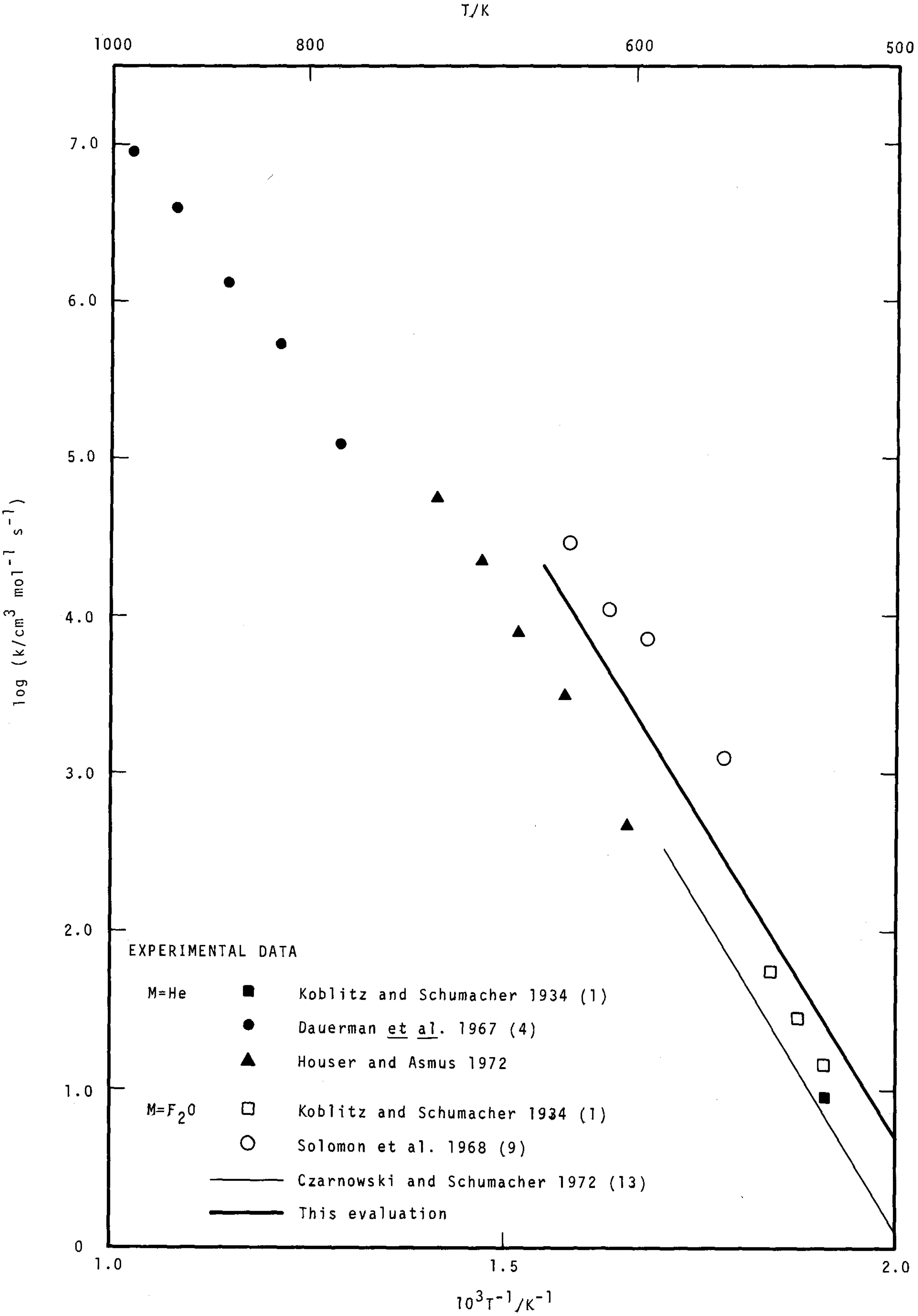
$F_2O + M \rightarrow F + FO + M$
SECOND ORDER PLOT

$F_2O + M \rightarrow F + FO + M$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k^o				
$1.4x10^{1}$	$M=F_2O$	523	Static system. F_2O(11.0-100%)/M mixtures, where M=O_2(0.77-47.1 kPa), N_2(39.3 kPa), He(37.0-71.1 kPa), Ar(49.3-66.7 kPa) or SiF_4 (1.23-54.2 kPa), total pressure 14.0-90.1 kPa. Reaction followed manometrically. KOBLITZ and SCHUMACHER 1934 (1)	Reaction 1 found to be a homogeneous second-order reaction under all conditions of pressure and for all surfaces except glass, which induced a heterogeneous reaction. $F_2O + M \rightarrow F + FO + M$ 1 Authors unable to identify reaction products other than the final F_2 and O_2. No attempt made to propose reaction mechanism. An expression $k_1=3.9x10^{17}exp(-19\ 500/T)$ cm^3 mol^{-1} s^{-1} is derived to fit these data in (4). This is given as $k_1=2.5x10^{17}exp(-19\ 500/T)$ cm^3 mol^{-1} s^{-1} in (5, 15) and $k_1=5.0x10^{17}$ $exp(-19\ 500/T)$ cm^3 mol^{-1} s^{-1} in (7, 9).
$2.9x10^{1}$		533		
$5.7x10^{1}$		543		
$1.3x10^{1}$	$M=O_2$	523		
$2.8x10^{1}$		533		
$5.6x10^{1}$		543		
$1.3x10^{1}$	$M=N_2$	523		
$2.8x10^{1}$	$M=F_2$	533		
$9.5x10^{0}$	M=He	523		
$6.0x10^{0}$	M=Ar	523		
$1.2x10^{1}$		533		
$1.2x10^{1}$	$M=SiF_4$	523		
$2.5x10^{1}$		533		
$5.0x10^{1}$		543		
$1.2x10^{5}$	M=He	773	Flow system. F_2O(0.1-1%)/He mixtures at total pressures of 8.0-13.3 kPa. Reaction followed mass spectrometrically. DAUERMAN, SALSER and TAJIMA 1967 (4)	Flow tube constructed of nickel to avoid surface effects. No evidence found for the FO radical, which the authors considered to be too reactive to be detected in this system. Authors derive expression $k_1=1.7x10^{14}exp(-16\ 300/T)cm^3$ mol^{-1} s^{-1} to fit their data. No explanation is given for the discrepancy between these results and those of (1). k_1 quoted by (7, 9), recalculated in (10) as $5x10^{12}exp(-10\ 000/T)$ cm^3 mol^{-1} s^{-1}. E_1 quoted by (15).
$5.3x10^{5}$		823		
$1.4x10^{6}$		873		
$4.0x10^{6}$		923		
$8.9x10^{6}$		973		
$1.1x10^{6}$	M=Ar	820	Shock tube study. F_2O(0.1-1%)/Ar mixtures at 409-3090 kPa pressure. Reflected shocks, [F_2O] decay monitored by u.v. absorption spectrometry at 225 nm. TROE, WAGNER and WEDEN 1967 (5).	Authors obtain expression $k_1=1.3x10^{15}exp(-17\ 200/T)$ cm^3 mol^{-1} s^{-1}. No evidence was found for a transition to first-order kinetics at the higher pressures. Extrapolating their results to lower temperatures, they find them to be a factor of two higher than those of (1) for M=Ar. They suspect this apparent doubling of k_1 could be due to reaction 2, but this claim could not be substatiated. $F_2O + F \rightarrow F_2 + FO$ 2 Quoted by (7, 9, 10). Used by (12).
$8.9x10^{5}$		833		
$2.8x10^{6}$		843		
$3.7x10^{6}$		852		
$4.6x10^{6}$		872		
$7.9x10^{6}$		898		
$1.2x10^{7}$		927		
$2.0x10^{7}$		966		
$2.6x10^{7}$		984		
$5.0x10^{7}$		1005		
$4.9x10^{7}$		1014		
$5.5x10^{7}$		1029		
$8.0x10^{7}$		1042		
$8.5x10^{7}$		1059		
$1.6x10^{8}$		1075		
$1.8x10^{8}$		1101		
$2.8x10^{8}$		1110		
$2.5x10^{8}$		1117		
$2.6x10^{8}$		1134		
$4.5x10^{8}$		1144		
$5.8x10^{8}$		1160		
$1.2x10^{9}$		1240		

$F_2O + M \rightarrow F + FO + M$
SECOND ORDER PLOT



$F_2O + M \rightarrow F + FO + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$<10^2$	594	Estimated value. BLAUER, JAYE and ROSE 1968 (6)	Value for use in analogue computer study of F_2O dissociation. Estimates of k_1, k_3 and k_4 put in to obtain computer estimate of k_2. $F_2O + M \rightarrow F + FO + M$ 1 $F_2O + F \rightarrow F_2 + FO$ 2 $FO + FO + M \rightarrow O_2 + 2F + M$ 3 $F + F + M \rightarrow F_2 + M$ 4
$1.7\times10^{14}\exp(-15\ 800/T)$ M=Ar	856-1290	Shock tube study. F_2O(2.5-10%)/Ar mixtures at 1.03-1.92 MPa pressure. Incident shocks. [F_2O] decay followed by u.v. absorption spectroscopy at 220 nm. BLAUER and SOLOMON 1968 (7)	Expression derived by computer analysis of results. No details of individual rate constants given. Authors neglected reaction 2 in their mechanism, but conceded that it might become important at the high [F_2O] used, leading to a chain mechanism. k_3 was assumed to be very fast, and k_4 was taken from (8). Quoted by (9, 10).
1.3×10^3 M=F_2O 7.1×10^3 1.1×10^4 3.0×10^4 1.5×10^3 M=N_2	563 593 611 633 563	Static system. F_2O(13-90%)/Ar(∿10%)/N_2 (83.5%) mixtures at 1.33-16.0 kPa total pressure. Reaction followed by mass spectrometry. SOLOMON, BLAUER and JAYE 1968 (9)	Above the pressures used, transition to first-order kinetics observed. Authors believe that the decomposition proceeds by a chain reaction, with reaction 2 chain-carrying. Quoted by (10).
2.2×10^5 M=Ar 2.2×10^6 1.6×10^6 5.0×10^5 1.5×10^6 7.0×10^5 8.0×10^5 5.6×10^6 5.0×10^6 1.8×10^7 5.3×10^7 1.0×10^7 1.5×10^7 1.4×10^7 1.3×10^7 2.8×10^7 7.9×10^6 7.1×10^7 1.4×10^8	770 810 815 818 823 835 840 865 877 882 898 900 910 917 925 945 960 965 990	Shock tube study. F_2O(0.3-7.4%)/Ar mixtures at 208-314 kPa pressure. Reflected shocks. Reaction followed mass spectrometrically. LIN and BAUER 1969 (10)	Results obtained for $k_{overall}$ in good agreement with previous values of k_1. For T<1000 K, authors give $k_{overall}=6.3\times10^{15}\exp(-19\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$; above this temperature, $k_{overall}$ began to level off to a constant value. The authors attributed this to attainment of equilibrium in reaction 1. Assuming $k_1=k_{overall}$ and $k_3=7.9\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ gave too low a value for O_2 production. If O_2 production was taken into consideration, k_1 was calculated as $2.0\times10^{17}\exp(-21\ 300/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Reaction 2 was found to be unimportant in the mechanism, but reactions -1 and -4 are important even in the early stages of the reaction. Values of k_1 thus obtained are somewhat lower than in earlier studies. $F_2O + M \rightarrow F + FO + M$ 1

$F_2O + M \rightarrow F + FO + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		LIN and BAUER - continued.	$FO + FO \rightarrow 2F + O_2$ 3 Used by (12).
1.8×10^{7} M=Ar	909	Shock tube study. F_2O(1.2-3.2%)/CO_2(0.8-2.9%)/Ar mixtures at total pressures of 13.3-133 kPa. Incident shocks. [F_2O] followed by u.v. absorption spectroscopy at 220 nm. HENRICI, LIN and BAUER 1970 (12)	Results obtained from the half-life of F_2O during its decay in the F_2O/CO system. These results were adjusted to fit the data for reaction 5, which is temperature-independent. $CO + FO \rightarrow CO_2 + F$ 5 The results thus obtained were combined with the data from (5 and 10) to give $k_1=5.0\times10^{16}\exp(-20\ 300/T)\ cm^3\ mol^{-1}\ s^{-1}$. If the results from (5) are excluded, this gives $k_1=1.3\times10^{17}\exp(-21\ 200/T)\ cm^3\ mol^{-1}\ s^{-1}$, in good agreement with the authors' earlier work (10).
6.8×10^{7}	975		
7.8×10^{7}	1000		
1.1×10^{8}	1010		
1.6×10^{8}	1036		
6.3×10^{8}	1086		
6.9×10^{8}	1115		
7.4×10^{8}	1125		
$7.8\times10^{16}\exp(-19\ 300/T)$ M=F_2O	501-583	Static system. F_2O(5.6-100%)/M mixtures, where M=O_2(13.3-80.0 kPa), N_2 (26.7-53.3 kPa), F_2(13.3-66.7 kPa), He(13.3-80.0 kPa) or SiF_4(13.3-66.7 kPa). Total pressure 1.33-99.8 kPa. Reaction followed manometrically. CZARNOWSKI and SCHUMACHER 1972 (13) and 1973 (15)	Using the mechanism developed by previous workers, authors obtained results in good agreement with those of (5). No details of individual results given. Relative third body efficiences given as $F_2O:O_2:N_2:F_2$:He:SiF_4=1:1.3:0.71:0.64:0.65:1.06.
4.9×10^{2} M=He	603	Stirred-flow system. F_2O (1.0-10%)/He mixtures at total pressures of 101 kPa. Reaction followed mass spectrometrically. HOUSER and ASMUS 1972 (14)	Authors obtained expression $k_1=7.9\times10^{16}\exp(-19\ 700/T)cm^3\ mol^{-1}\ s^{-1}$ in good agreement with the results of (15). Unlike previous investigations, a slightly different reaction mechanism was adopted. Reactions 3 and 4 were considered unimportant in a system where the overall kinetics were less than first order. $F_2O + M \rightarrow F + FO + M$ 1 $F_2O + F \rightarrow F_2 + FO$ 2 $FO + M \rightarrow F + O + M$ 6 $FO + FO + M \rightarrow F_2 + O_2 + M$ 7 $O + O + M \rightarrow O_2 + M$ 8
3.2×10^{3}	633		
8.4×10^{3}	658		
2.3×10^{4}	680		
5.5×10^{4}	704		

$F_2O + M \rightarrow F + FO + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^{∞} *			
1.3×10^{-3} M=N_2	563	Static system. F_2O(0.2-87%)/Ar(0-23%)/M mixtures, where M=N_2, F_2, He, Kr, CF_4 or O_2. Total pressures 90.6-745 kPa. Reaction followed by mass spectrometry. SOLOMON, BLAUER and JAYE 1968 (9)	Above 90 kPa pressure, reaction considered by authors to be almost in its first order region, although no limiting rate constant was found. Variation of k_1 with pressure over the pressure range studied is slight in contrast to findings of (5). Expression for M=N_2 given as k_1^{∞} = $1.0 \times 10^9 \exp(-15\,100/T)$ s^{-1}.
5.5×10^{-3}	594		
1.1×10^{-2}	614		
2.1×10^{-2}	634		
1.1×10^{-3} M=F_2O	563.5		
2.8×10^{-3}	574		
5.4×10^{-4} M=F_2	563		
1.8×10^{-3}	574		
9.0×10^{-4} M=He	563		
6.2×10^{-4} M=Kr	563		
1.1×10^{-3} M=CF_4	563		
1.2×10^{-3} M=O_2	563		

* s^{-1}

REVIEW ARTICLE

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1 \times 10^8 \exp(-11\,000/T)$ s^{-1} M=Ar	860-1680	General review of shock tube work. STREHLOW 1969 (11)	Expression derived from preliminary work of BLAUER and SOLOMON (3). Mixtures given as <20%F_2O in Ar at 2.3-17.5 atm. (233-1770 kPa). Results evaluated differently by original authors in (7). If expression extrapolated to 600 K, the value of k_1^{∞} given is two to three orders of magnitude higher than any in (9).

Discussion

Fluorine monoxide is believed to decompose via a chain mechanism. Most investigations have assumed the essential steps in the chain to be:

$$F_2O + M \rightarrow F + FO + M \qquad (1)$$

$$F_2O + F \rightarrow F_2 + FO \qquad (2)$$

$$FO + FO(+M) \rightarrow 2F + O_2(+M) \qquad (3)$$

$$F + F + M \rightarrow F_2 + M \qquad (4)$$

Lin and Bauer [10], and Houser and Asmus [14] have considered alternative paths, but in the temperature range studied, a reasonable agreement is given for k_1 whatever mechanism is assumed.

2nd Order Rate Constant k_1°

Rate constants have been obtained at low temperature using both static pyrolysis systems and flow systems. A variety of third bodies has been considered. The earliest work was in a static pyrolysis system by Koblitz and Schumacher [1]. Like Solomon et al. [9], in a similar study, they made no attempt to elucidate a mechanism, although both assumed that reaction 2 must be the chain-carrying reaction. Czarnowski and Schumacher [15] repeated the work of [1] using the above reaction mechanism as quantitatively predicting the overall stoichiometry. In this second work, the rate constants obtained are generally lower than in [1]. Dauerman et al. [4] consider surface effects responsible for the high values in [1], but it is hard to see any real reason for the discrepancy.

On the basis of these results, we recommend the expression $k_1(M=F_2O) = 3.0 \times 10^{17} \exp(-19\,400/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 500-650 K, with error limits of a factor of 4. As the activation energies of [1,9 and 15] agree well, we recommend a similar value, with large error limits due to discrepancies in the *A* factor.

The two flow studies show less agreement, the values of k_1 obtained by Dauerman et al. [4] being at least 100% lower than the extrapolation of the values of Houser and Asmus [14] to higher temperatures. The former authors obtained a lower activation energy than anybody else, although both expressions extrapolated back to $T = 523$ K agree reasonably with the single point determination for M = He by Koblitz and Schumacher. It should be noted that Dauerman et al. arbitrarily introduced a $T^{1/2}$ term in their rate expression. This has been removed to allow their expression to agree with their experimental data. Even allowing for this, we must reject the data of Dauerman et al. on the grounds of the low activation energy, and thus make no recommendation for k_1(M=He).

Of the high temperature shock tube studies, the main disagreement lies between the results of Troe et al. [5] and Blauer and Solomon [7] on the one hand, and Lin and Bauer [10,12] on the other. The former authors give a low A factor and activation energy, but the latter use a slightly different mechanism, considering the effects of the reverse reactions -1 and -4 to modify their apparent rate constants, giving higher A factors and activation energies. At temperatures around 1000 K, where the data were obtained, the agreement is quite good, but the opposing trends can be clearly seen as the temperature increases. Lin and Bauer claim that unless reactions -1 and -4 are taken into account, the calculated O_2 yield is less than that observed experimentally. However, the scatter on their results is large, with a correspondingly large error in their activation energy, which is sufficient for it to overlap with the values determined by other investigators. At this stage, it is not clear how important the modification of Lin and Bauer in the mechanism is to the determination of k_1. Certainly their expressions, extrapolated to 500 K are considerably below the experimental values at that temperature. They claim that surface effects are important at these temperatures, yet the work of Schumacher et al. [1,15] conclusively shows the reaction to be homogeneous on a variety of surfaces.

We thus recommend a compromise expression, based on all the high temperature studies [5,7,10,12] but only over the region where agreement is reasonable, viz., $k_1(\mathrm{M=Ar}) = 1.8\times10^{15}\exp(-17\,500/T)$ cm^3 mol^{-1} s^{-1}, temperature range 800–1300 K, with error limits of a factor of 3. Extrapolated to 500 K, this expression agrees well with the results of Koblitz and Schumacher for M=Ar.

1st Order Rate Constant k_1^∞

Evidence regarding the high-pressure first-order region of k_1 is conflicting. Troe et al. and Blauer and Solomon both found no evidence of first order kinetics in shock tubes in the region 10–30 atm, although some preliminary work of the latter is presented as such in [12]. However, Solomon et al. [9] claim that in their static pyrolysis system, fall-off began at about 0.2 atm, and that at 1 atm the reaction was almost entirely first order. In fact, their data suggest that the reaction remains in the fall-off region up to the maximum pressure considered by them, 745 kPa. On this information, it is impossible to make any firm decision as to the position of transition from first to second order kinetics, although the bulk of the evidence seems to indicate a high pressure transition.

Relative Efficiencies of Third Bodies

Most work on relative third body efficiencies comes from Schumacher et al [1,15]. The results are much as expected, with F_2O itself and SiF_4 showing an accelerating effect compared with He and Ar. Solomon et al. [9] have obtained similar results from their first order decomposition studies.

M=He	Ar	F_2O	N_2	O_2	F_2	SiF_4	Kr	CF_4	T/K	Ref.
1	0.63	1.47	1.37	1.37	1.37	1.26			523	[1]
1		1.54	1.09	2.00	0.99	1.63			501-583	[15]
1		1.22	1.44	1.33	0.87		0.69	1.22	563	[9]

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Miscellaneous Reactions Involving F/O Species

A8 F + O_3 → FO + O_2

The removal of ozone by fluorine atoms has received little attention.

$$F + O_3 \rightarrow FO + O_2 \qquad (1)$$

$$(\Delta H^\circ_{298} = -112.8 \text{ kJ mol}^{-1};\ -27.0 \text{ kcal mol}^{-1})$$

In an early study, Staricco et al. [1] photolysed mixtures of F_2(32.9–134.7 mm Hg; 4.4–18.0 kPa), O_2(1.7–395.4 mm Hg; 0.2–52.7 kPa), and O_3(29.5–156.6 mm Hg; 3.9–20.9 kPa) at 365 nm, over the small temperature range 273–293 K. The authors merely determined the activation energy of reaction 1 to be 11.72 kJ mol^{-1} (2.8 kcal mol^{-1}). The reaction was followed by monitoring the pressure and the absorbed light intensity.

On the other hand Wagner et al. [2,3] measured the activation energy as only 1.88 kJ mol^{-1} (450 cal mol^{-1}), over the range 253–365 K. These authors used a discharge flow system, generating F atoms by discharges in F_2/He mixtures at total pressures of 3.5–6.2 mm Hg(467–827 Pa), in CF_4/He mixtures at 3.5 mm Hg(467 Pa), and in N_2/He mixtures, followed by the addition of thermally dissociated N_2F_4

$$N + NF_2 \rightarrow N_2 + 2F$$

at 2.8 mm Hg(373 Pa). O_3 was added downstream through a moveable inlet. Reactant concentration ranges were [F], 1.3×10^{-11} to 7.6×10^{-11} mol cm^{-3}, and [O_3] 1.7×10^{-11} to 3×10^{-10} mol cm^{-3}. The reaction was followed by mass spectrometry, and the expression derived for k_1 was

$$k_1 = 1.7\times10^{13} \exp(-227/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

We feel that the small temperature range investigated by Staricco et al. [1] does not lend itself to high accuracy in determining E_1, and that without data to confirm the sole remaining results of Wagner et al. [2,3], we make no recommendation for k_1.

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A9 $F + O_2 + M \rightarrow FO_2 + M$

The three-body reaction between fluorine atoms and molecular oxygen has received little attention, there being only three absolute determinations of k_1 (1,3,4).

$$F + O_2 + M \rightarrow FO_2 + M \quad (1)$$

$$(\Delta H^\circ_{298} = -66.36 \text{ kJ mol}^{-1}; -15.86 \text{ kcal mol}^{-1})$$

Producing F atoms by a microwave discharge in a stream of 0.1% F_2/He, Zetsch [1] added O_2 in excess and followed F and F_2 mass spectrometrically. These experiments were conducted at total concentrations $\sim4\times10^{-7}$ mol cm^{-3} and over the temperature range 272–362 K. Assuming F atom removal to be via the sequence

$$F + O_2 + M \rightarrow FO_2 + M \quad (1)$$

$$F + FO_2 \rightarrow F_2 + O_2 \quad (2)$$

the author used the steady-state approximation for FO_2, giving $-d[F]/dt = 2k_1[F][O_2][M]$. At 300 K, $k_1(M=He)$ was given as 1.7×10^{15} cm^6 mol^{-2} s^{-1}, and over the temperature range of this study, the apparent activation energy E_1 was -5.43 kJ mol^{-1} (-1.3 kcal mol^{-1}), corresponding almost to a T^{-2} dependence.

Lopez et al. [2] assumed this activation energy to be approximately zero, in a study of the photochemical fluorination of CF_2O, using a static system.

A discharge flow system was also used by Arutyanov et al. [3]. The flow of F atoms (generated by passing 5% F_2/He mixtures through a discharge) was mixed with streams of O_2 and He (or Ar, or N_2) at total pressures of 0.5–5 mm Hg (66.7–666.5 Pa), and [F] followed by e.s.r. spectrometry. By determining the variation of ln[F] with [M], the authors obtained $k_1(M=He)=(2.54\pm0.7)\times10^{15}$, $k_1(M=Ar)=(2.18\pm0.7)\times10^{15}$, $k_1(M=N_2)=(5.08\pm1.5)\times10^{15}$, and $k_1(M=O_2)\leqslant1.81\times10^{15}$ cm^6 mol^{-2} s^{-1} at (293±2) K. These values were derived on the assumption (made on the basis of the work of Zetzsch [1]) that reaction 2 is fast.

The final study was made by Chen et al. [4], flash photolysing F_2(25–125 mm Hg; 3.3–16.7 kPa)/O_2(2.5 mm Hg; 333.3 Pa)/HF(6×10^{-3}–1×10^{-1} mm Hg; 0.8–13.3 Pa) mixtures between 250–350 nm. [F] was determined by u.v. absorption, and the reaction followed by the decay of i.r. chemiluminescence (2.7 μm) from vibrationally excited HF. The kinetics of HF* formation and removal were described by the reaction sequence.

$$F + O_2 + M \rightarrow FO_2^* + M \quad (1)$$

$$FO_2^* + HF \rightleftharpoons HF^* + FO_2$$

$$F + O_2 + HF \rightarrow FO_2 + HF^*$$

$$FO_2^* + M \rightarrow FO_2 + M$$

$$HF^* + M \rightarrow HF + M$$

From this mechanism the authors derived an expression for the exponential decay constant for the i.r. chemiluminescence in terms of [F_2], [HF], and [O_2]. Graphical solution of this expression, under conditions of fixed [O_2] and low [HF] and [F], gave $k_1(M=F_2)=(1.92\pm0.15)\times10^{15}$ cm^6 mol^{-2} s^{-1}, and $k_1(M=O_2)=(5.80\pm0.73)\times10^{15}$ cm^6 mol^{-2} s^{-1} (298 K). Under conditions of constant [F_2]/[O_2] ratio, with constant [HF] and [F], they obtained $k_1(M=F_2)=(1.81\pm0.22)\times10^{15}$ cm^6 mol^{-2} s^{-1}, and $k_1(M=O_2)=(5.44\pm1.1)\times10^{15}$ cm^6 mol^{-2} s^{-1}. The latter values were presented in their table of results, together with the values $k_1(M=HF)=(9.07\pm1.8)\times10^{17}$, $k_1(M=Ar)=(3.05\pm0.33)\times10^{15}$, and $k_1(M=He)=(1.96\pm0.22)\times10^{15}$ cm^6 mol^{-2} s^{-1}, the latter two values being obtained from further experiments with up to 100 mm Hg(13.3 kPa) Ar or He.

The reasonable agreement between the room temperature values of $k_1(M=He)$ [1,3,4] over a total pressure range of 0.5–127.5 mm Hg(0.07–17 kPa) indicates that the fall-off region must be at still higher pressures. If the low activation energy determined by Zetzsch [1] is correct, then the low variation with temperature allows an average value of $k_1(M=He)=(2.07\pm0.5)\times10^{15}$ cm^6 mol^{-2} s^{-1} to be recommended, for 291–300 K.

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A10 $FO + FO \rightarrow F + F + O_2$

The second order kinetics of FO radical removal has been studied at room temperature only in discharge flow sytems

$$FO + FO \rightarrow F + F + O_2 \qquad (1)$$

$$(\Delta H^\circ_{298} = -59.75 \text{ kJ mol}^{-1};\ -14.28 \text{ kcal mol}^{-1})$$

Wagner et al. [3,4] used mass spectrometry to follow FO radicals generated by the reaction.

$$F + O_3 \rightarrow FO + O_2 \qquad (2)$$

at pressures 2.8–6.2 mm Hg (374–826 Pa). By comparing experimental [FO] profiles with those generated by Runge-Kutta integration of the rate equations from reactions 1 and 2, they obtained, to within a factor of 2, the value $k_1 = 10^{13}$ cm^3 mol^{-1} s^{-1} at 298 K.

A study by Clyne and Watson [2] into the detection of FO showed the FO decay to be rapid and bimolecular, with an estimated k_1 at 298 K lying between 1.2×10^{12} and 1.2×10^{13} cm^3 mol^{-1} s^{-1}. Further study by these authors [5], using an F_2-discharge flow system and mass spectrometry, gave a mean value over five runs of $k_1 = (5.12 \pm 1.69) \times 10^{12}$ cm^3 mol^{-1} s^{-1} (298 K).

The only available high temperature data on reaction 1 are from the shock tube study of Lin and Bauer [1]. F_2O(0.258%, 1.17%, 1.94%, 5.15% and 7.43%)/Ar mixtures at reflected shock pressures between 1.56 and 2.36 m Hg (208–314 kPa) were analysed for the yield of O_2 by mass spectrometry. Computer analysis of the O_2 yields, according to the mechanism

$$F_2O + M \rightleftharpoons F + FO + M \qquad (3)$$

$$FO + FO \rightarrow F + F + O_2 \qquad (1)$$

showed the O_2 yield to be less sensitive to k_3 than to k_1 over the temperature interval 1000–1100 K, owing to the equilibration of reaction 3. Little variation in k_1 over this range led these authors to give $k_1 = 1.26 \times 10^{12}$ cm^3 mol^{-1} s^{-1}, to within ±30% (1000–1100 K), which value Clyne and Watson [5] considered incompatible with their own and those of Wagner et al. [3].

We make no recommendation for the value of k_1.

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A11 $O + F_2 \rightarrow F + FO$

There has been only one group of research workers to study reaction 1, between oxygen atoms and fluorine, i.e., that of Krech et al. [1,2].

$$O + F_2 \rightarrow F + FO \qquad (1)$$

$$\Delta H^\circ_{298} = -61.476 \text{ kJ mol}^{-1}\ (-14.69 \text{ kcal mol}^{-1})$$

This is in contrast to the much-studied reaction 2, which is important in atmospheric studies.

$$O + Cl_2 \rightarrow Cl + ClO \qquad (2)$$

O atoms were produced by passing 100% O_2 (1) or O_2/excess He mixtures [2] through a discharge. A single experiment using the rapid titration reaction N+NO [2] gave a result consistent with those obtained by the latter. Total pressures were 3.75–5.25 mm Hg (500–700 Pa), and the pseudo first order decay of O atoms was followed by e.s.r. spectroscopy. Over the temperature range 461–523 K the expressions $k_1 = 2.5 \times 10^{13} \exp(-5700/T)$ cm^3 mol^{-1} s^{-1} (1) and $k_1 = 9.77 \times 10^{12} \exp\{-(5210 \pm 760)/T\}$ cm^3 mol^{-1} s^{-1} (2) were presented.

The abnormally high activation energies of those expressions were attributed to the low polarisability of the F_2 molecule.

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A12 $OH + F_2 \rightarrow HF + F + O$

The reaction between fluorine and OH is considered to be responsible for the high burning velocities in the H_2O/F_2 flame [1]

$$OH + F_2 \rightarrow HF + F + O \qquad (1)$$

$$\Delta H^\circ_{298} = 15.820 \text{ kJ mol}^{-1} (3.781 \text{ kcal mol}^{-1})$$

Nosova et al. [2] studied the temperature dependence of the ignition limits of H_2O/F_2 flames. F_2(30–50%)/H_2O mixtures were used at 1 atm (101 kPa) pressure over the temperature range 770–830 K. A mechanism for the overall reactions was assumed, in which reaction 1, as the most endothermic chain propagation reaction, was taken as being rate determining, by analogy with reaction 2 in H_2/O_2 flames.

$$H + O_2 \rightarrow OH + O \qquad (2)$$

From ignition limit data they obtained $k_1 = 7.0 \times 10^{13} \exp(-9000/T)$ cm^3 mol^{-1} s^{-1}, somewhat lower than the result obtained from burning velocity measurements, $k_1 = 2.0 \times 10^{15} \exp(-9000/T)$ cm^3 mol^{-1} s^{-1}. The discrepancy is attributed by the authors to poor reproducibility of the ignition pressure measurements.

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A13 $F + F_2O \rightarrow FO + F_2$

The abstraction of fluorine from fluorine monoxide is an important step in the chain mechanism for the decomposition of the latter.

$$F + F_2O \rightarrow FO + F_2 \quad (1)$$

$$\Delta H^{\circ}_{298} = 5.356 \text{ kJ mol}^{-1} \text{ (1.280 kcal mol}^{-1}\text{)}$$

Warnatz et al. [4] studied the reaction directly in a flow system at 300 K, producing F atoms by discharge through F_2 or by an $N+NF_2$ titration. The reaction was followed mass-spectrometrically, though no further details are given, except that no reaction was observed, and the authors set an upper limit of $k_1 \leqslant 10^9$ cm^3 mol^{-1} s^{-1}.

Czarnowski and Schumacher [3,5] studied the decomposition of F_2O(5.6–100%)/M mixtures, where M = O_2, N_2, F_2, He or SiF_4 in a static pyrolysis system at total pressures of 1.33–99.8 kPa. The reaction was followed manometrically. They obtained the following expression for the rate of F_2O disappearance:

$$-d[F_2O]/dt = k_2[F_2O] + k_1 k_2^{1/2}[F_2O]^{3/2}/k_3^{1/2}$$

$$F_2O + M \rightarrow F + FO + M \quad (2)$$

$$F + F + M \rightarrow F_2 + M \quad (3)$$

Using their own value for k_2 and taking k_3 from [2] they obtained $k_1 = 5.1 \times 10^{10} \exp(-3000/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 501–583 K.

Blauer et al. [1] obtained $k_1 = 6.3 \times 10^{17} \exp(-16\,600/T)$ cm^3 mol^{-1} s^{-1} from an analog computer simulation of F_2O decomposition. Although both this expression and that of Czarnowski and Schumacher fall below the limit of Warnatz et al. at 300 K there is no agreement between them, and we make no recommendation for k_1.

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A14 $F_2O_2 + M \rightarrow F + FO_2 + M$

The thermal decomposition of F_2O_2 has been studied by Schumacher and Frisch [3]. It decomposes quite rapidly at room temperature, and it was necessary for them to work at low temperatures (213–248 K) in order to measure the reaction rate in their static system.

$$F_2O_2 + M \rightarrow F + FO_2 + M; \quad (1)$$

thermodynamic data unavailable for FO_2, F_2O_2.

They allowed F_2O_2 (0.33–53.3 kPa) to decompose, following the reaction manometrically, and assuming reaction 1 to be the rate determining step. They found the decomposition to be homogeneous, and pressure dependent, with a transition from second to first order kinetics beginning above about 3 kPa. Thus they extrapolated all their results to infinite pressure to obtain the first order rate constant $k_1^{\infty} = 1.2 \times 10^{14} \exp(-8500/T)$ s^{-1}. Applying an RRK treatment with $E_1 = 72.4$ kJ mol^{-1} (17.3 kcal mol^{-1}) and $s = 6$ gave $k_1^{\infty} = 5.9 \times 10^{12} \exp(-8700/T)$ s^{-1}.

Subsequently, they studied the effect of added third bodies [2] at 236 K, using F_2O_2(2.1–25%)/M mixtures at total pressures of 4.39–75.4 kPa. The relative efficiencies obtained were F_2O_2:O_2:F_2:N_2:CO_2:Ar:He = 1:1.2:0.33:0.21:0.45:0.40:0.07.

The mechanism of the F_2O_2 decomposition was explored later by Lin and Bauer [5] who used the Evans-Polanyi rule to obtain $E_1 = 100 \pm 45$ kJ mol^{-1} (24±10 kcal mol^{-1}). Benson [4] has considered reaction 2 a possible path, but Lin and Bauer reject this on energetic grounds, with E_2 estimated to be ~290 kJ mol^{-1} (70 kcal mol^{-1}).

$$F_2O_2 + M \rightarrow FO + FO + M \quad (2)$$

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A15 $N_2F_4 + M \rightarrow NF_2 + NF_2 + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	92.885	198.61	-5.899	-10.288
300	92.893	198.62	-5.798	-10.189
500	92.237	197.17	0.663	- 3.950
1000	86.341	189.25	5.376	0.462
1500	78.889	183.22	6.823	1.732
2000	71.010	178.69	7.479	2.264
2500	62.957	175.10	7.831	2.519
3000	54.815	172.13	8.036	2.646
3500	46.635	169.61	8.164	2.706
4000	38.405	167.41	8.243	2.727
4500	30.171	165.47	8.293	2.725
5000	21.912	163.73	8.323	2.710

SI Units: $\log(K_p/\text{Pa}) = \log(K_p/\text{atm}) + 5.006$

$\log(K_c/\text{mol m}^{-3}) = \log(K_c/\text{mol cm}^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^\infty = 1.39 \times 10^{15} \exp(-9990/T)\ s^{-1}$

Temperature Range: 300-500 K.

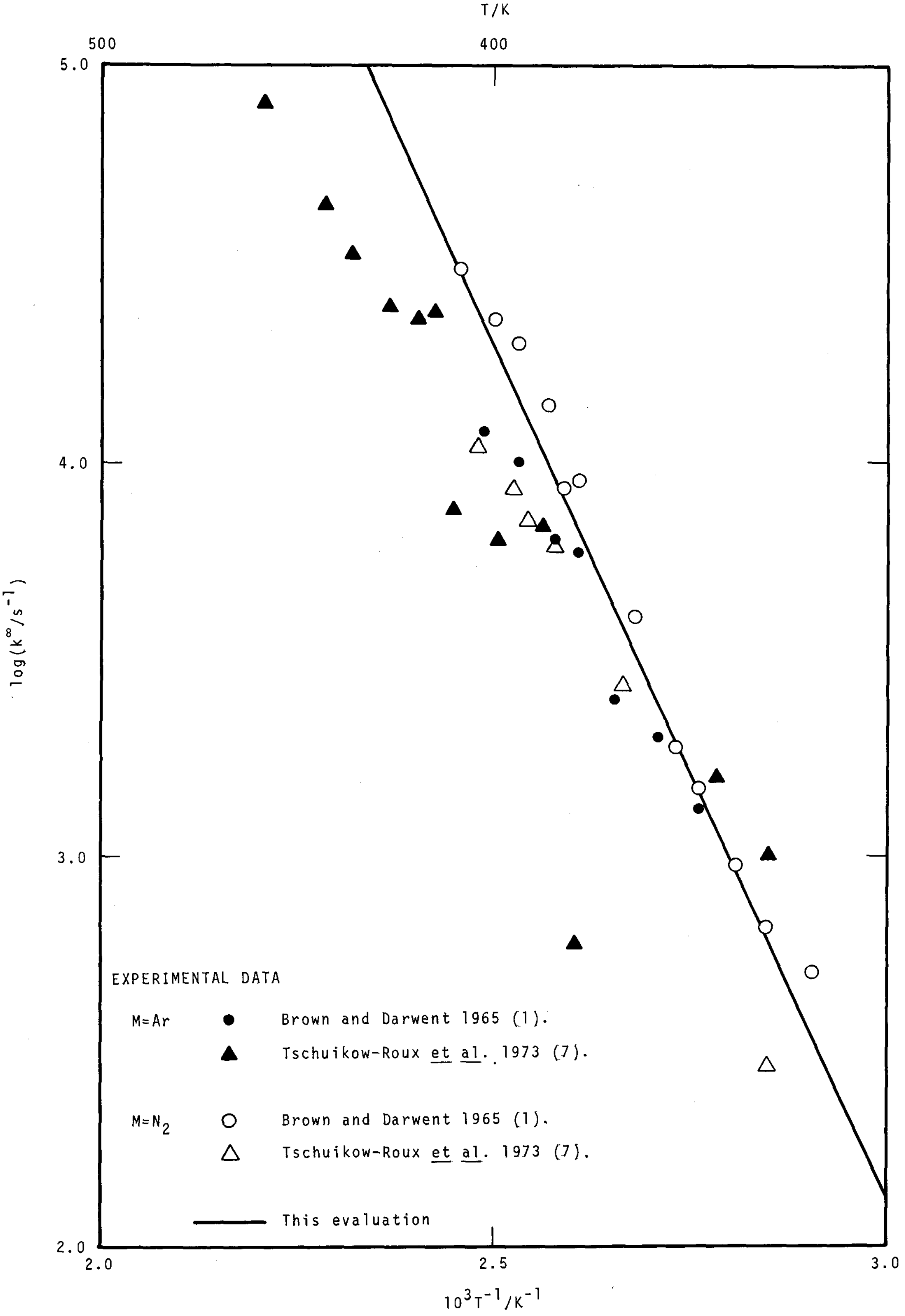
Suggested Error Limits for Calculated Rate Constant: less than a factor of 2 over this range.

Rate Parameters: $\log(A/s^{-1}) = 15.143 \pm 0.28$

$E/J\ mol^{-1} = 83\ 060 \pm 8030$

$E/cal\ mol^{-1} = 19\ 850 \pm 1920$

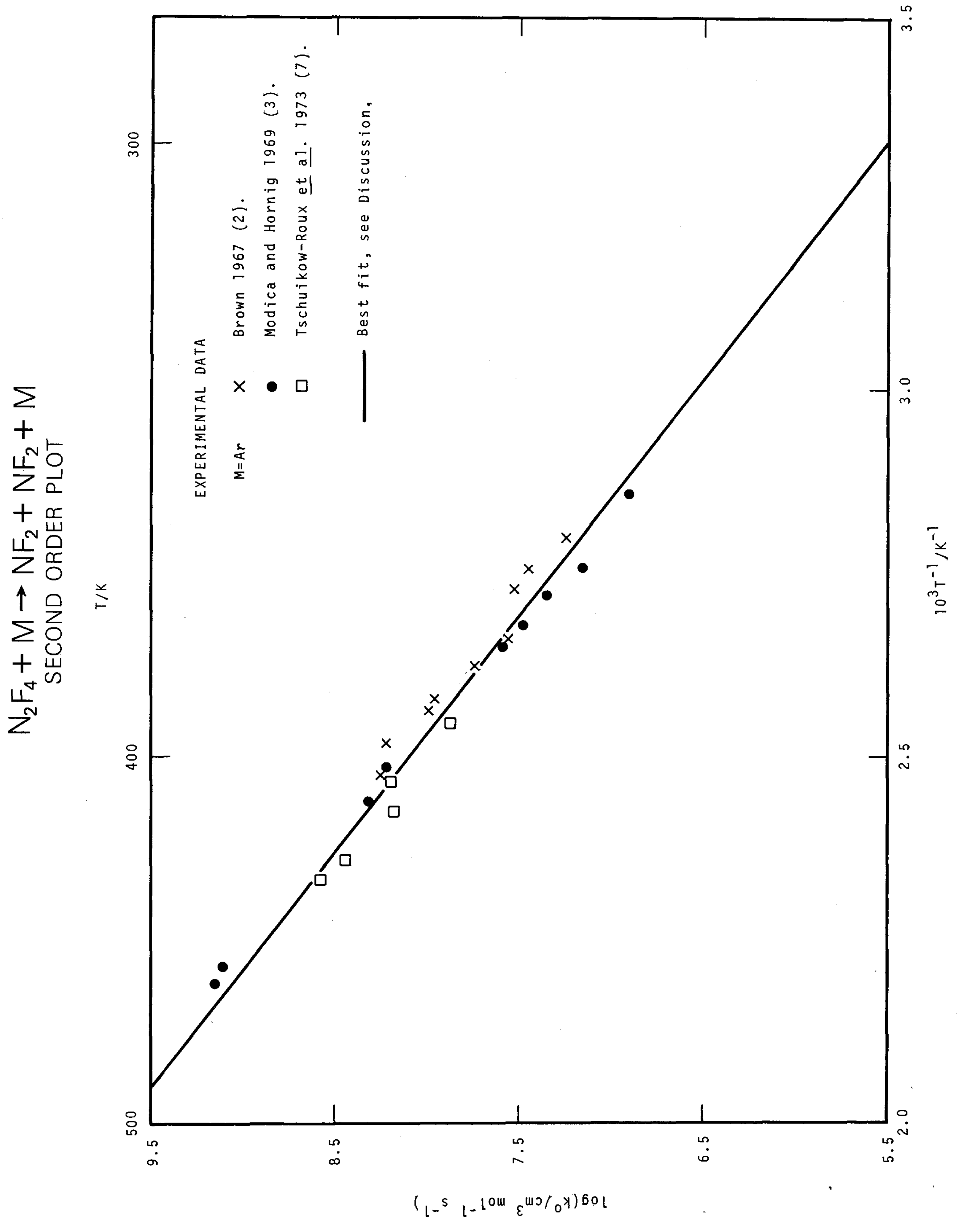
$N_2F_4 + M \rightarrow NF_2 + NF_2 + M$
FIRST ORDER PLOT



$N_2F_4 + M \rightarrow NF_2 + NF_2 + M$

EXPERIMENTAL DATA

Rate Constant k (s^{-1})		Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^{∞}				
5.1×10^{2}	$M=N_2$	344	Shock tube study. N_2F_4 (1%)/Ar or N_2 mixtures at total pressures 0.6-6.0 atm. (60.8-608 kPa). Incident shocks. $[NF_2]$ monitored by u.v. absorption spectroscopy at 260 nm. BROWN and DARWENT 1965 (1)	Below 175 kPa, reaction was in second-order region with both third bodies. Above this pressure a gradual transition to first order kinetics was observed, although no limiting value was obtained for k_1^{∞}. This was deduced by extrapolating the results to infinite pressure. $N_2F_4 + M \rightarrow NF_2 + NF_2 + M$ 1 From these results, authors obtained the following expressions:- $k_1^{\infty}(M=N_2)=9.6\times10^{14}\exp(-9800/T)\ s^{-1}$ and $k_1^{\infty}(M=Ar)=3.0\times10^{13}\exp(-8600/T)\ s^{-1}$. Quoted by (3, 6).
6.6×10^{2}		351		
9.5×10^{2}		356		
1.5×10^{3}		362		
1.9×10^{3}		366		
4.1×10^{3}		373		
9.0×10^{3}		382		
8.6×10^{3}		386		
1.4×10^{4}		389		
2.0×10^{4}		395		
2.3×10^{4}		400		
3.1×10^{4}		407		
1.3×10^{3}	$M=Ar$	362		
2.0×10^{3}		369		
2.5×10^{3}		377		
5.9×10^{3}		383		
6.3×10^{3}		388		
1.0×10^{4}		395		
1.2×10^{4}		402		
$3.4\times10^{13}\exp(-9000/T)$	$M=N_2$	All.	Theoretical study, based on statistical reaction rate theory. KECK and KALELKAR 1968 (3)	Authors note agreement with expression of (1) at 380 K. Order of reaction with respect to N_2 given as 0.7.
1.0×10^{3}	$M=Ar$	351	Shock tube study. N_2F_4(0.1-1%)/Ar or N_2 mixtures at total pressures of 0.69-12.0 atm, (69.9-1216 kPa). Incident shocks. $[NF_2]$ monitored by u.v. absorption spectroscopy at 260 nm. TSCHUIKOW-ROUX, MacFADDEN, JUNG and ARMSTRONG 1973 (7)	Results of M=Ar taken only above 2 atm pressure, where the transition to first-order kinetics begins. Values of k_1 obtained extrapolated to infinite pressure to obtain limiting first-order rate constant k_1^{∞}. Authors derive the following expressions:- $k_1^{\infty}(M=Ar)=2.3\times10^{15}\exp(-10\ 000/T)\ s^{-1}$ and $k_1^{\infty}(M=N_2)=1.2\times10^{15}\exp(-10\ 000/T)\ s^{-1}$, although they admit to a lot of scatter in the N_2 data. Also quoted is the expression $k_1^{\infty}(M=N_2)=2.0\times10^{15}\exp(-10\ 000/T)\ s^{-1}$, derived from data in (1).
1.6×10^{3}		359		
6.0×10^{2}		384		
7.0×10^{3}		390		
6.3×10^{3}		399		
7.6×10^{3}		408		
2.4×10^{4}		412		
2.3×10^{4}		416		
2.5×10^{4}		422		
3.4×10^{4}		431		
4.5×10^{4}		438		
8.1×10^{4}		453		
2.9×10^{2}	$M=N_2$	351		
2.7×10^{3}		375		
6.1×10^{3}		388		
7.1×10^{3}		393		
8.6×10^{3}		396		
1.1×10^{4}		403		


N₂F₄ + M → NF₂ + NF₂ + M
SECOND ORDER PLOT
T/K
300
400
500
EXPERIMENTAL DATA
M=Ar
× Brown 1967 (2).
● Modica and Hornig 1969 (3).
□ Tschuikow-Roux et al. 1973 (7).
— Best fit, see Discussion.
10³T⁻¹/K⁻¹
2.0
2.5
3.0
3.5
log(k⁰/cm³ mol⁻¹ s⁻¹)
9.5
8.5
7.5
6.5
5.5

$N_2F_4 + M \rightarrow NF_2 + NF_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o				
1.8×10^{7}	M=Ar	357	Shock tube study. No details available. BROWN 1967 (2)	Some of BROWN's Ph.D. work published in (1), but no details of the second-order reaction given there. These results taken from graph in (7).
2.8×10^{7}		362		
3.3×10^{7}		366		
3.8×10^{7}		376		
5.9×10^{7}		380		
9.6×10^{7}		386		
9.8×10^{7}		389		
1.7×10^{8}		397		
1.8×10^{8}		403		
8.2×10^{6}	M=Ar	350	Shock tube study. N_2F_4 (0.5-20%)/Ar(He, SF_6) mixtures at total pressures of 0.58-2.7 atm (58.8-274 kPa). Incident shocks. $[NF_2]$ monitored by u.v. absorption at 260 nm. MODICA and HORNIG 1968 (4)	Reaction found to be completely second order over the pressure range studied. No evidence of complicating side reactions. Value of k_1 for M=He, SF_6 and N_2F_4 were also calculated, the latter from rich N_2F_4/Ar mixtures, but no details of individual rate constants given. $N_2F_4 + M \rightarrow NF_2 + NF_2 + M$ 1 Two expressions derived, one from experimental data using simple collision theory, k_1(M=Ar)= $1.5\times10^{15}T^{0.5}\exp(-7700/T)$ $cm^3\ mol^{-1}\ s^{-1}$, and other from classical collision theory, taking N_2F_4 dissociation energy as 77.0 kJ mol^{-1} (18.4 kcal mol^{-1}), k_1(M=Ar)= $3.0\times10^{11}T^{0.5}(9300/T)^4\exp(-9300/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Simpler expression quoted by (1,6,7). Relative third body efficiences given as Ar:He:SF_6:N_2F_4 = 1:1.2:1.7:1.8. Quoted by (6). Used by (5).
1.5×10^{7}		362		
2.3×10^{7}		368		
3.1×10^{7}		373		
4.0×10^{7}		378		
1.7×10^{8}		402		
2.2×10^{8}		410		
1.3×10^{9}		450		
1.4×10^{9}		456		
7.6×10^{7}	M=Ar	393	Shock tube study. N_2F_4 (0.1-1%)/Ar(N_2) mixtures at total pressures of 0.69-12.0 atm(69.9-1216 kPa). Incident shocks. $[NF_2]$ monitored by u.v. absorption at 260 nm. TSCHUIKOW-ROUX, MacFADDEN, JUNG and ARMSTRONG 1973 (7)	Characteristic unimolecular behaviour shown in Ar, with first-order kinetics prevailing above 4 atm (see above), and a limiting second-order rate obtained below 2 atm. With N_2 as third body, only first order kinetics shown. Data combined with those of (2 and 4) to give $k_1=3.6\times10^{16}\exp(-7700/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (M=Ar) over the temperature range 330-480 K. Using the data from (7) alone we obtain $k_1=1.7\times10^{16}\exp(-7600/T)$ $cm^3\ mol^{-1}\ s^{-1}$, although plot could show slight curvature
1.6×10^{8}		405		
1.5×10^{8}		411		
2.9×10^{8}		424		
3.9×10^{8}		428		

$N_2F_4 + M \rightarrow NF_2 + NF_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		TSCHUIKOW-ROUX, MacFADDEN, JUNG and ARMSTRONG - continued	due to deviations from second order kinetics.

Discussion

Tetrafluorohydrazine exists as a stable compound only at temperatures below 300 K. Above this temperature decomposition occurs at a measurable rate to give the difluoramino radical NF_2.

$$N_2F_4 + M \rightarrow NF_2 + NF_2 + M \qquad (1)$$

The rate of decomposition increases steadily with temperature, until above 500 K dissociation is extremely rapid. Thus the reaction can only be studied within a narrow temperature range. There have however, been a number of studies, all in shock tubes, over a sufficiently wide pressure range to examine both the first and second order decompositions.

2nd Order Rate Constant k_1°

The pressure range for the transition from second to first order kinetics has not been clarified by the three studies reporting second order kinetics [2,4,7]. Below 2 atm, the reaction seems to be definitely in its second order region, but Tschuikow-Roux et al. [7] report a fall-off above this pressure, whereas Modica and Hornig [4] maintain second order kinetics persist up to 2.7 atm with a variety of third bodies. Few details are available of Brown's work [2].

The agreement between the three determinations is generally good, although the data of Tschuikow-Roux et al. are slightly lower than the rest and show a small amount of curvature, possibly indicating a pressure effect. All of the experimental values of k_1° lie well below the values from the RRKM calculation made by Tschuikow-Roux et al., the difference being attributed to inadequate knowledge of the transition state complex. The data can be fitted by the Arrhenius expression k_1° $(M=Ar)=6.3\times10^{15}$ $\exp(-7100/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 300-500 K. The derived activation energy, 59.03 kJ mol^{-1}, is therefore well below the endothermicity of the reaction and suggests that the dissociation would require the participation of approximately ten vibrational modes. This contrasts with a calculated value of approximately three modes, obtained from the internal energy of vibration [8]. We suspect that this large discrepancy can be attributed to an incomplete understanding of the chemistry of the system, and we therefore do not make any recommendation for k_1° at present.

1st Order Rate Constant k_1^∞

The two studies of the first order kinetics of reaction 1 [1,7] indicate that the transition to first order kinetics occurs at approximately 2 atm although neither author finds a limiting rate constant up to 12 atm for $M=Ar$ or N_2.

The agreement for $M=N_2$ is reasonable, to within a factor of 2. The results for $M=Ar$ are less concordant: to within a factor of 4. Although the overall scatter for k_1^∞ is large, we nevertheless recommend $k_1^\infty=1.39\times10^{15}$ $\exp(-9990/T)$ s^{-1} over the temperature range 300-500 K, within uncertainty limits of less than a factor of 2.

Using RRKM theory, Tsang [6] attempted to calculate k_1^∞ from the data of [1] and [4]. In spite of trying four different models for the transition state, he could only obtain a reasonable fit to the data by assuming a value significantly lower than that currently accepted (JANAF) for the N-N bond dissociation energy.

Relative Efficiencies of Third Bodies

There is little information available on third body efficiencies. All studies of the second order rate constant used Ar as third body, although Modica and Hornig [4] report the ratio $Ar:He:SF_6:N_2F_4=1:1.2:1.7:1.8$. Tsang [6] calculated the ratios in the first-order and transition regions to be $Ar:He:SF_6:N_2F_4:=1:1:1.6:3.5$. The experimental data on the first order region give N_2 and Ar as being approximately equally efficient, although Tsang gives the ratio $N_2:Ar=1.54:1$ from his calculations.

Rate of the Reverse Reaction

There exists just one determination of the reverse rate constant k_{-1}, by Clyne and Connor [5].

$$NF_2 + NF_2 + M \rightarrow N_2F_4 + M \qquad (-1)$$

They used a flow system, producing NF_2 radicals by thermal dissociation of N_2F_4 at 473 K (3-17% in Ar, He, SF_6 and O_2). Total pressures ranged from 113-526 Pa. $[NF_2]$ was followed by u.v. absorption spectrometry at 260 nm. In this pressure range the reaction was found to be entirely third order when $[NF_2]<[M]/10$. Above this value, a complex order in M was observed, and such results were discarded. At 293 K, a value of $k_{-1}(M=Ar)=4.7\times10^{15}$ cm^6 mol^{-2} s^{-1}

was obtained and the following ratio of third body efficiencies:– Ar:He:O_2:SF_6 = 1:0.6:0.8:2.2, and NO was estimated to have a relative efficiency of ~0.5. Using our own value of $k_1(M=Ar) = 2.8 \times 10^5$ cm^3 mol^{-1} s^{-1} at 298 K, and the equilibrium constant, we obtain $k_{-1} = 5.5 \times 10^{15}$ cm^6 mol^{-2} s^{-1} at 298 K, in good agreement with Clyne's value at 293 K which we recommend with error limits of ±50%.

Tsang [6] calculated values of k_{-1} over the temperature range 200–1800 K and pressure range 1.33 Pa–13.3 MPa, but found difficulty in reconciling the kinetics data with a calculation based on the thermodynamic data for the reaction.

References

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[4] Modica, A. P., and Hornig, D. F., J. Chem. Phys. **49**, 629 (1968).

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[6] Tsang, W., NBS Report 10904 (1972), p. 202. Eds. T. B. Douglas and C. W. Beckett.

[7] Tschuikow-Roux, E., MacFadden, K. O., Jung, K. H., and Armstrong, D. A., J. Phys. Chem. **77**, 734 (1973).

[8] Troe, J., 15th Combustion Symp., 667 (1975).

A16 $NF_3 + M \rightarrow NF_2 + F + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	252.671	147.833	-36.545	-40.933
300	252.693	147.896	-36.271	-40.662
500	253.935	151.231	-18.629	-23.242
1000	253.877	151.339	- 5.355	-10.269
1500	252.546	150.277	- 0.944	- 6.034
2000	250.856	149.306	1.248	- 3.967
2500	249.015	148.490	2.554	- 2.758
3000	247.090	147.791	3.422	- 1.969
3500	245.132	147.185	4.030	- 1.428
4000	243.136	146.653	4.486	- 1.030
4500	241.128	146.176	4.837	- 0.730
5000	239.107	145.750	5.116	- 0.497

SI Units: $\log(K_p/\mathrm{Pa}) = \log(K_p/\mathrm{atm}) + 5.006$

$\log(K_c/\mathrm{mol\ m^{-3}}) = \log(K_c/\mathrm{mol\ cm^{-3}}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 4.1 \times 10^{16} \exp(-24\,160/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ (M=Ar)

$= 6.8 \times 10^{-8} \exp(-24\,160/T)\ \mathrm{cm^3\ molecule\ s^{-1}}$ (M=Ar)

Temperature Range: 1100-1800 K

Suggested Error Limits for Calculated Rate Constant: a factor of two.

Note: This expression is that of Evans and Tschuikow-Roux (8, 9).

Rate Parameters:

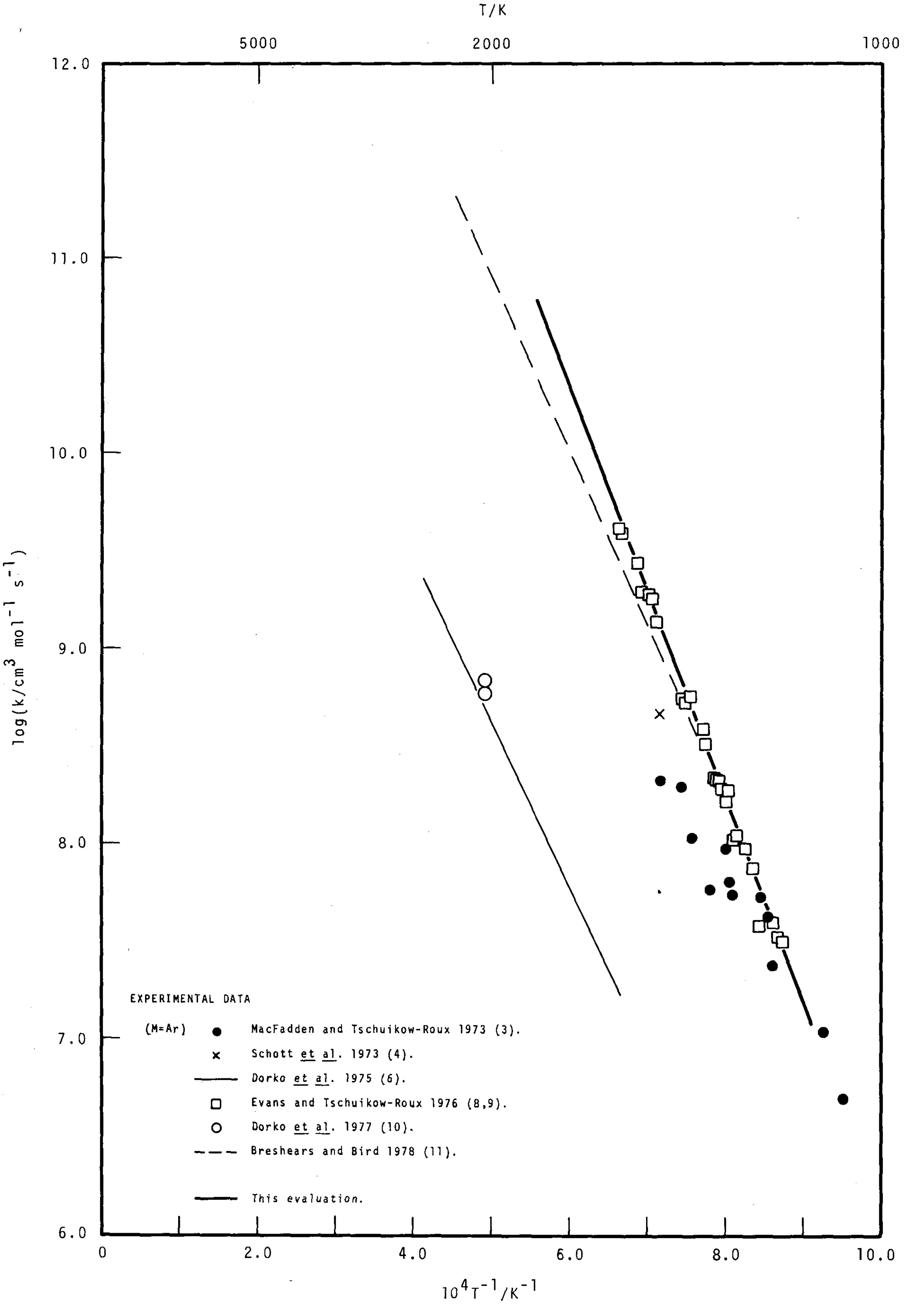
$\log(A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 16.61 \pm 0.30$

$\log(A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = -7.17 \pm 0.30$

$E/\mathrm{J\ mol^{-1}} = 200\,830 \pm 36\,000$

$E/\mathrm{cal\ mol^{-1}} = 48\,000 \pm 8\,000$

$NF_3 + M \rightarrow NF_2 + F + M$



$NF_3 + M \rightarrow NF_2 + F + M$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
		1500-1800	Shock tube study. N_2F_4 (0.25-2%)/Ne mixtures at total pressures of 0.34-0.44 atm (34.4-44.6 kPa). Reflected shocks. Reaction followed by t.o.f. mass spectrometry. DIESEN 1966 (1)	System designed to study NF_2 decomposition. Significant amounts of NF_3 produced, reaching a maximum after 250 μs, then dying away. Author claimed reaction 1 was reaction removing NF_3, and on the basis of his reaction scheme found $k_1/k_2 \sim 5$, but made no absolute determination of k_1. $NF_2 + M \rightarrow NF + F + M$ 2 $NF_2 + NF \rightarrow N_2F + F_2$ $NF_2 + N_2F \rightarrow NF_3 + N_2$ $NF_2 + F_2 \rightarrow NF_3 + F$ $NF_3 + M \rightarrow NF_2 + F + M$ 1
5.1×10^6	M=Ar	1050	Shock tube study. NF_3 (1-2%)/Ar mixtures at total pressures of 274-606 kPa. Incident shocks. [NF_2] monitored by u.v. absorption spectroscopy at 260 nm. MACFADDEN and TSCHUIKOW-ROUX 1973 (3)	Reaction found to be second order over the entire pressure range. Authors found $k_1 = 1.3 \times 10^{13} \exp(-15\ 300/T)$ cm^3 mol^{-1} s^{-1}. All secondary reactions were assumed to be negligible over the temperature-time region used, an assumption confirmed by theoretical calculations. Quoted by (4, 6).
1.1×10^7		1080		
2.4×10^7		1160		
4.4×10^7		1170		
5.4×10^7		1180		
5.8×10^7		1230		
6.5×10^7		1240		
9.5×10^7		1250		
6.0×10^7		1280		
1.1×10^8		1320		
2.0×10^8		1340		
2.1×10^8		1390		
4.8×10^8	M=Ar	1400	Shock tube study. NF_3(∼5%)/Ar mixtures at 4.0 kPa pressure. Incident shocks. [NF_2] monitored by u.v. absorption spectroscopy at 260 nm. SCHOTT, BLAIR and MORGAN 1973 (4)	Reaction studied over the temperature range 1100-1500 K, but only the result at 1400 K given. Authors attribute lower value of k_1 in (3) to possible first-order contribution at the higher pressures used there.
$6.9 \times 10^{12} \exp(-19\ 420/T)$	M=Ar	1500-2400	Shock tube study. NF_3(0.25-1%)/Ar mixtures at 0.8-60 atm. (81-6078 kPa) pressure. Reflected shocks. [NF_2] followed by i.r. emission spectroscopy at 5.18 μm. DORKO, GRIMM, SCHELLER and MUELLER 1975 (6)	Details of over 100 individual experiments given only graphically. From these, apparent second order rate constants were derived giving an expression $k_1 = 5.0 \times 10^{14} \exp(-28\ 500/T)$ cm^3 mol^{-1} s^{-1}. However, since the authors observed the transition to first order kinetics beginning above 10 atm, separate expressions were determined by extrapolating to zero and infinite pressure. The second order expression is the one

$NF_3 + M \rightarrow NF_2 + F + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		DORKO, GRIMM, SCHELLER and MUELLER continued	given in the first column, the limiting first order expression was $k_1^{\infty}=2.0\times10^{11}\exp(-28\ 430/T)\ s^{-1}$.
3.11×10^{7}	1144	Shock tube study. NF_3(1%)/Ar mixtures at total pressures of 0.80-1.81 atm (81.0-183.4 kPa). Incident shocks. $[NF_2]$ monitored by u.v. absorption spectroscopy at 260 nm, and i.r. emission spectroscopy at 5.17 μm. EVANS and TSCHUIKOW-ROUX 1976 (8 and 9)	Rate constants obtained are limiting low-pressure values. No details of derivation given in (8), but in (9) authors describe method, including corrections for k_{-1} $NF_2 + F + M \rightarrow NF_3 + M$ -1 and for variation in temperature and density during course of reaction. Authors fit expression $k_1(M=Ar)=4.07\times10^{16}\exp\{-(24\ 160\pm400)/T)\ cm^3\ mol^{-1}\ s^{-1}$ to these data. Observed activation energy in good agreemet with theoretical value at low-pressure limit.
3.22×10^{7}	1151		
3.91×10^{7}	1162		
3.78×10^{7}	1184		
7.45×10^{7}	1196		
9.28×10^{7}	1209		
1.08×10^{8}	1226		
1.05×10^{8}	1230		
1.83×10^{8}	1244		
1.64×10^{8}	1246		
1.87×10^{8}	1259		
2.01×10^{8}	1260		
2.03×10^{8}	1265		
2.04×10^{8} M=Ar	1269		
3.21×10^{8}	1289		
3.83×10^{8}	1295		
5.54×10^{8}	1324		
5.17×10^{8}	1332		
5.38×10^{8}	1338		
1.33×10^{9}	1402		
1.74×10^{9}	1418		
1.83×10^{9}	1423		
1.89×10^{9}	1440		
2.72×10^{9}	1456		
3.85×10^{9}	1495		
4.15×10^{9}	1505		
5.90×10^{8}	2029	Shock tube study. NF_3 (0.5%)/Ar mixture at 7.05 atm (714.2 kPa) behind reflected shock. Reaction followed by monitoring i.r. emission by NF_3 at 5.18 μ, and u.v. emission at 270 nm. DORKO, GRIMM and MUELLER 1977 (10)	Experiments performed to check reliability of i.r. emission technique. First order rate constant of $2.5\times10^4\ s^{-1}$ obtained from which we have derived upper value of k_1 presented here. $NF_3 + M \rightarrow NF_2 + F + M$ 1 From u.v. emission, value obtained as $2.9\times10^4\ s^{-1}$, giving lower value of k_1. Disagreement between these data and those of (9) discussed, being attributed to failure to allow for u.v. emission in latter's u.v. absorption technique.
6.85×10^{8}	2029		
$2.31\times10^{15}\exp(-20\ 500/T)$ M=Ar	1330-2000	Shock tube study. NF_3(5% and 10%)/Ar mixtures behind incident shocks, 0.1-0.5 atm (10.1-50.7 kPa). Density gradient followed by laser schlieren technique. BRESHEARS and BIRD 1978 (11)	Second order kinetics assumed. No systematic difference noted between values of k_1 from either mixtures. Pre-publication reference reported by (6).

Discussion

Like ammonia, nitrogen trifluoride is stable over a wide temperature range, its decomposition only becoming important above 1000 K.

$$NF_3 + M \rightarrow NF_2 + F + M \qquad (1)$$

A preliminary estimate of the rate of the reaction was made by Diesen [1], while studying the decomposition of NF_2 radicals in Ne. From mass spectrometric evidence he estimated $k_1 \sim 5k_2$, which, using his value for k_2 gave $k_1 = 1.1 \times 10^7$ cm^3 mol^{-1} s^{-1} at 1500 K.

$$NF_2 + M \rightarrow NF + F + M \qquad (2)$$

Subsequent studies have all used shock tubes, [3,4,6,8,9,10,11] shock-heating NF_3/Ar mixtures over a wide pressure range, and using both incident and reflected shocks. Even at the highest pressures used (60 atm), no evidence was found that a limiting first order rate had been reached, and only Dorko et al. [6] went to pressures high enough to observe a fall-off in the second order rate constant. Their second order rate constant, obtained by extrapolation to zero pressure, lies approximately two orders of magnitude below the other values, which are in good agreement over a wide temperature range. Simple Lindemann theory was used to obtain the rate constants, and the authors themselves admit that the A factors for both high and low pressure expressions are considerably too low, although the activation energy agrees well with the results of others. Despite their subsequent work [10], in which they attributed the difference between their work [6,10] and that of [9] to failures in spectrometric techniques, the general agrement between the data of Breshears and Bird [11], obtained independently of spectroscopic considerations, with those of [4,8 and 9], lead us to disregard Dorko's work [6,10]. The low activation energies shown by this and other decompositions of species of the type N_xF_y are similar to those seen in decompositions of N_xH_y, (e.g., Vol. 2, pp. 461, 497). This phenomenon has not yet received an entirely satisfactory explanation. One of the most recent studies, that of Evans and Tschuikow-Roux [8,9] gives a higher activation energy than earlier work, and is also in better agreement with theory. This is probably associated with the fact that their NF_3 concentrations were lower than those used by Breshears and Bird [11]. For this reason we recommend the expression of [8 and 9].

$$k_1^\circ = 4.1 \times 10^{16} \exp(-24\,160/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (M=Ar)}$$

over the temperature range 1100–1800 K, with error limits of a factor of two.

Rate of the Reverse Reaction

There have been two determinations of the rate of the reverse reaction -1 [2,5].

$$NF_2 + F + M \rightarrow NF_3 + M \qquad (-1)$$

The work of Warnatz et al. [2] is reported by [7]. They obtained $k_{-1}(M=He) = 5 \times 10^{16}$ cm^6 mol^{-2} s^{-1} at 300 K, following the reaction mass spectrometrically at a total pressure of 466 Pa, but no further details are available. Clyne and Watson [5] also used mass spectrometric detection, coupled to a flow system, in which N atoms were generated by a discharge through 100% N_2 at about 120 Pa pressure. NF_2, formed by the thermal decomposition of N_2F_4, was added in excess downstream, initially to form F atoms by the rapid reaction 3.

$$N + NF_2 \rightarrow N_2 + 2F \qquad (3)$$

After >10 ms, NF_3 was detectable. The subsequent reaction 4 is unimportant as the bond energy NF_2–F is greater than that of F–F.

$$NF_3 + F \rightarrow NF_2 + F_2 \qquad (4)$$

They obtain $k_{-1}(M=N_2) = 3.2 \times 10^{17}$ cm^6 mol^{-2} s^{-1} at 298 K. Schott et al. [4] calculate $k_{-1}(M=Ar) = 1.4 \times 10^{15}$ cm^6 mol^{-2} s^{-1} at 1400 K from k_1 and the equilibrium constant. In view of the lack of agreement we make no recommendation at 300 K, but recommend the expression $k_{-1} = 1.9 \times 10^{14} \exp(4500/T)$ cm^6 mol^{-2} s^{-1} over the temperature range 1000–2000 K, with error limits of a factor of two, derived from k_1 and the equilibrium constant.

References

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A17 $NF_2 + M \rightarrow NF + F + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	285.60	123.97	-43.559	-47.947
300	285.62	124.05	-43.250	-47.641
500	287.42	128.77	-23.300	-27.913
1000	289.38	131.64	- 8.239	-13.153
1500	290.34	132.43	- 3.193	- 8.263
2000	291.07	132.86	- 0.662	- 5.877
2500	291.78	133.17	0.860	- 4.452
3000	292.53	133.44	1.877	- 3.514
3500	293.34	133.70	2.605	- 2.853
4000	294.25	133.93	3.154	- 2.362
4500	295.24	134.17	3.581	- 1.986
5000	296.33	134.40	3.925	- 1.688

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 7.6 \times 10^{14} \exp(-25\,700/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)

$= 1.3 \times 10^{-9} \exp(-25\,700/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar)

Temperature Range: 1500-2500 K

Suggested Error Limits for Calculated Rate Constant: A factor of three over the entire temperature range.

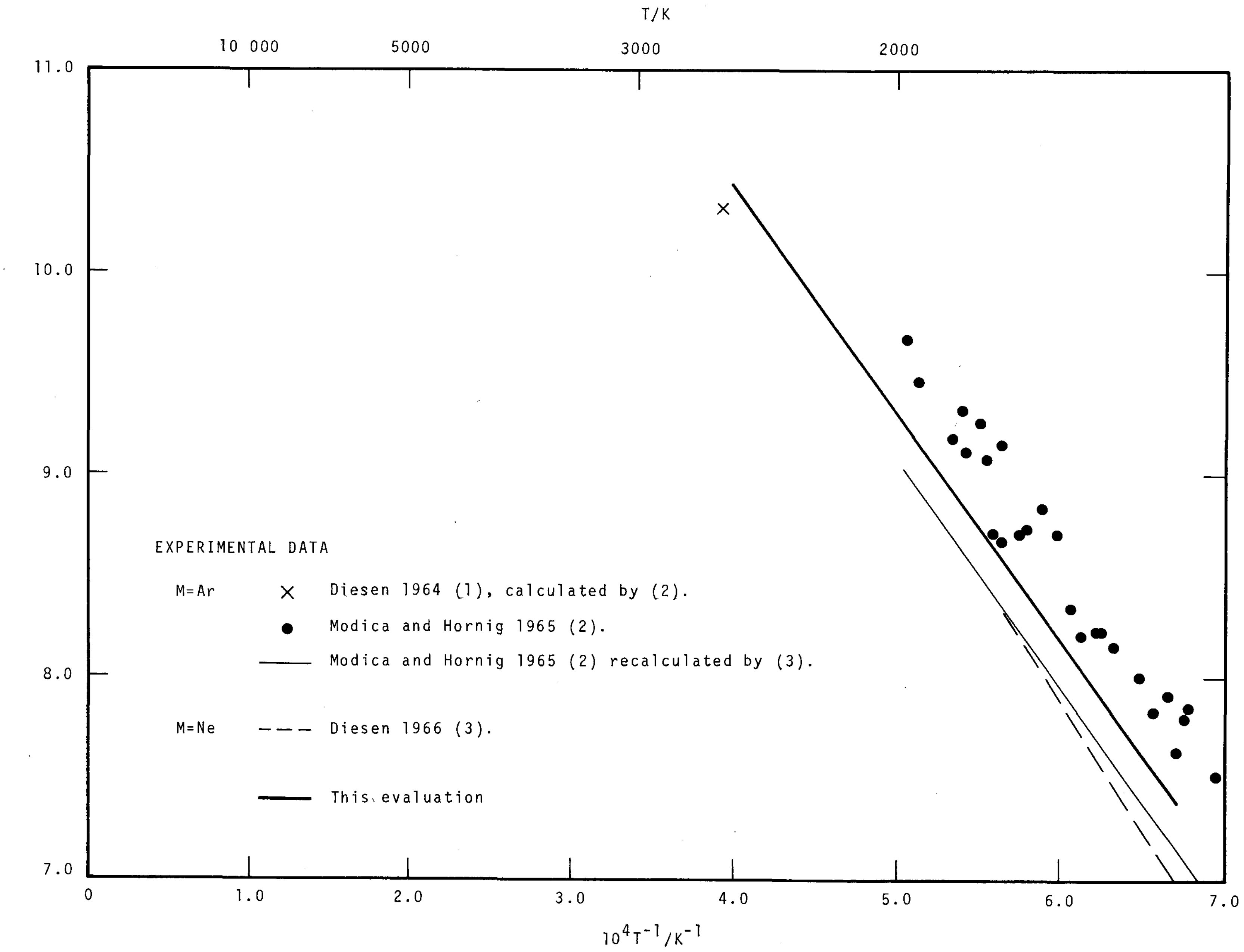
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1})$ = 14.88 ±0.50

$\log(A/cm^3\ molecule^{-1}\ s^{-1})$ = -8.89 ±0.50

$E/J\ mol^{-1}$ = 213 700 ±21 000

$E/cal\ mol^{-1}$ = 51 000 ±5000

$NF_2 + M \rightarrow NF + F + M$



$NF_2 + M \rightarrow NF + F + M$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o			
	2200-3000	Shock tube study. N_2F_4 (0.25-1%)/Ar mixtures at ∿15.0 kPa pressure. Reflected shocks. Reaction followed by t.o.f. mass spectrometry. DIESEN 1964 (1)	N_2F_4 dissociates very rapidly to NF_2. No evidence found for NF_3 formation, so author presumed decomposition takes precedence over disproportionation. $NF_2 + M \rightarrow NF + F + M$ 1 $NF_2 + NF_2 \rightarrow NF_3 + NF$ 2 Value of k_1 determined, but not quoted, just used to determine k_3. $NF + NF \rightarrow N_2 + 2F$ 3 k_1 calculated as 2.0×10^{10} cm^3 mol^{-1} s^{-1} at 2550 K in (2) from these data.
3.3×10^{7} M=Ar	1440	Shock tube study. N_2F_4 (0.5-1%)/Ar mixtures at total pressures of 150-221 kPa. Incident shocks. $[NF_2]$ monitored by u.v. absorption spectroscopy at 260 nm. MODICA and HORNIG 1965 (2)	Reaction found to be proceeding under second order conditions. Expression for k_1 given as 1.6×10^{13} $T^{\frac{1}{2}}\exp(-24\ 100/T)$ cm^3 mol^{-1} s^{-1} Quoted by (5). Used by (4). Data recalculated in (3) to give k_1 = $6.0 \times 10^{14}\exp(-26\ 200/T)$ cm^3 mol^{-1} s^{-1} on the grounds that below 2000 K, reaction 2 becomes more important, and a chain involving NF_3 and NF radicals is set up.
7.0×10^{7}	1475		
6.1×10^{7}	1480		
4.3×10^{7}	1490		
8.2×10^{7}	1500		
6.7×10^{7}	1520		
9.8×10^{7}	1540		
1.4×10^{8}	1580		
1.7×10^{8}	1600		
1.7×10^{8}	1605		
1.6×10^{8}	1630		
2.2×10^{8}	1650		
5.0×10^{8}	1670		
5.0×10^{8}	1675		
6.8×10^{8}	1700		
5.4×10^{8}	1725		
5.1×10^{8}	1740		
1.4×10^{9}	1770		
4.7×10^{8}	1775		
5.1×10^{8}	1790		
1.2×10^{9}	1800		
1.8×10^{9}	1815		
1.3×10^{9}	1840		
2.1×10^{9}	1850		
1.5×10^{9}	1875		
2.9×10^{9}	1950		
4.7×10^{9}	1975		
$2.2 \times 10^{15}\exp(-28\ 700/T)$ M=Ne	1500-1800	Shock tube study. N_2F_4 (0.25-2%)/Ne mixtures at pressures of ∿35.0 kPa. Reflected shocks. Reaction followed by t.o.f. mass spectrometry. DIESEN 1966 (3)	Results evaluated on the basis of a chain mechanism involving both NF and N_2F radicals. Estimations of k_4, k_5 and k_6 were made ∿10^{12} cm^3 mol^{-1} s^{-1} enabling the expression for k_1 (M=Ne) to be calculated. $NF + NF_2 \rightarrow N_2F + F_2$ 4 $N_2F + NF_2 \rightarrow NF_3 + N_2$ 5 $F_2 + NF_2 \rightarrow NF_3 + F$ 6 $NF_2 + M \rightarrow NF + F + M$ 1 Used by (4).

$NF_2 + M \rightarrow NF + F + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^∞			
$4.5\times10^{10}\exp(-29\ 000/T)\ s^{-1}$	All	Theoretical study, from unimolecular reaction rate theory. KECK and KALELKAR 1968 (4)	Value reported as being within 25% of k_1^∞ at 1700 K, presumably that determined by (2 and 3).

REVIEW ARTICLE

		Review of shock tube literature. STREHLOW 1969 (5)	Quotes (2) and mentions work from (3) although no value of k_1.

Discussion

Above 500 K, tetrafluorohydrazine decomposes very rapidly to give difluoramino radicals, NF_2. These react further, either by disproportionation (Section A20) or by reactions with other radicals produced following decomposition. The decomposition reactions predominate at higher temperatures.

$$NF_2 + M \rightarrow NF + F + M \quad (1)$$

$$NF_2 + NF_2 \rightarrow NF_3 + NF \quad (2)$$

The three experimental studies of NF_2 decomposition have all utilised shock tubes, Diesen [1,3] coupling his to a t.o.f. mass spectrometer, Modica and Hornig [2] following NF_2 decay spectroscopically. All experiments were at fairly low pressures ($\leqslant 2$ atm) and no evidence of any first order contribution to the decomposition was observed. Modica and Hornig were unable to consider secondary reactions in their system, but Diesen noticed NF_3 formed as an intermediate below 2000 K, and concluded that at lower temperatures a chain mechanism involving NF_3, NF and N_2F must operate. On this basis, he recalculated the results of Modica and Hornig [2], bringing them more into line with his own.

Although the reaction mechanism needs clarifying, we recommend as an interim value $k_1^\circ(M=Ar)=7.6\times10^{14}\exp(-25\ 700/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 1500–2500 K, with error limits of a factor of three. Within these limits, $k_1^\circ(M=Ar)=k_1^\circ(M=Ne)$.

References

[1] Diesen, R. W., J. Chem. Phys. **41**, 3256 (1964).
[2] Modica, A. P., and Hornig, D. F., J. Chem. Phys. **43**, 2739 (1965).
[3] Diesen, R. W., J. Chem. Phys. **45**, 759 (1966).
[4] Keck, J., and Kalelkar, A., J. Chem. Phys. **49**, 3211 (1968).
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A18 $NF_2 + F_2 \rightarrow NF_3 + F$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-94.851	-33.246	14.881
300	-94.847	-33.217	14.785
500	-93.713	-30.393	8.203
1000	-90.098	-25.397	3.379
1500	-86.517	-22.489	1.838
2000	-83.128	-20.535	1.098
2500	-79.956	-19.117	0.672
3000	-76.994	-18.037	0.399
3500	-74.249	-17.192	0.210
4000	-71.718	-16.514	0.074
4500	-69.417	-15.966	-0.029
5000	-67.321	-15.527	-0.108

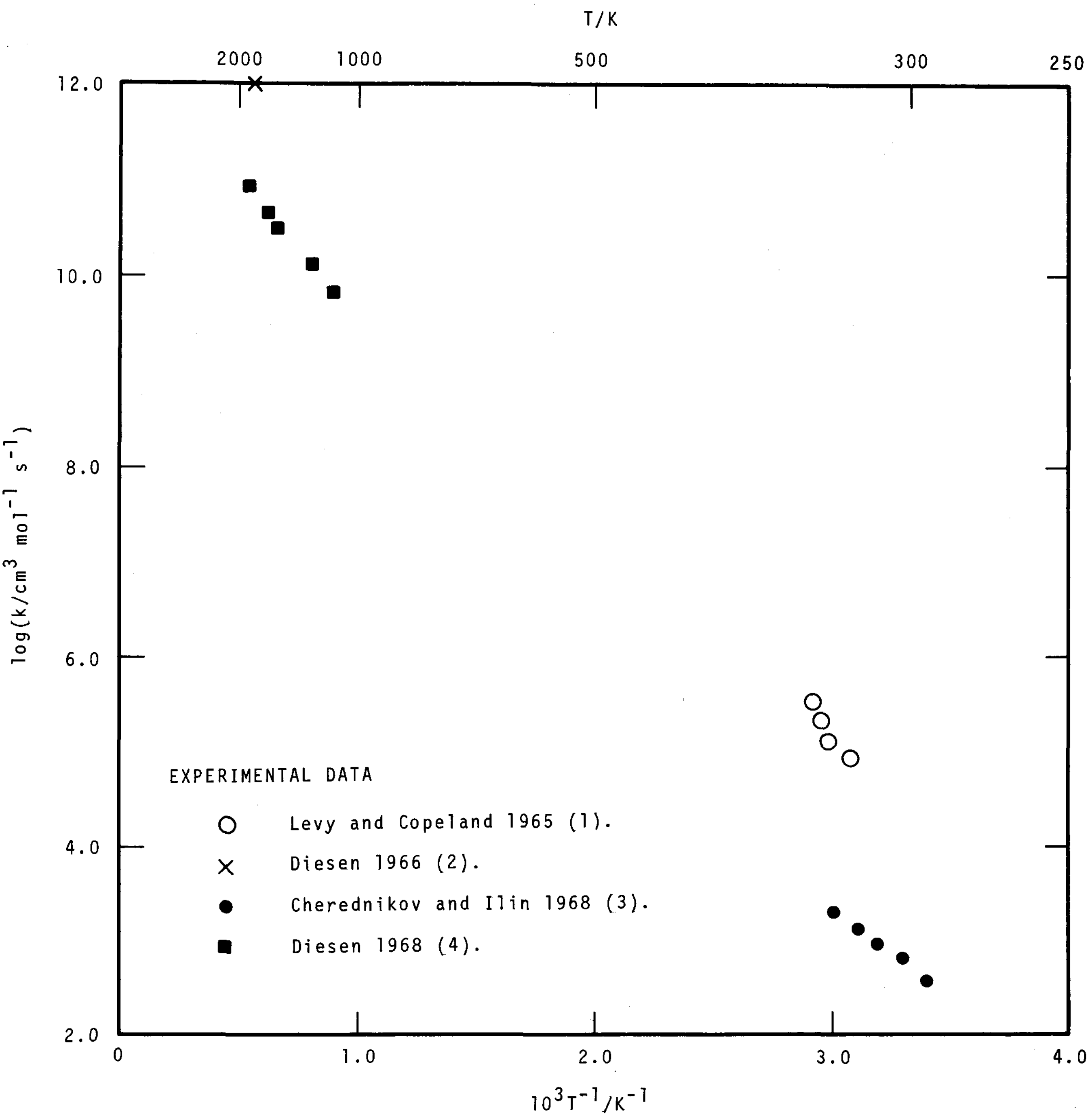
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
8.4x10^4	325	Static system. N_2F_4(6.67-66.7 kPa)/F_2(6.67-26.7 kPa)/N_2(0-88.0 kPa) mixtures. [F_2] followed by u.v. absorption spectroscopy at 284.9 nm. LEVY and COPELAND 1965 (1)	Under the conditions of the experiment, N_2F_4 is not completely dissociated to NF_2. The authors were in fact measuring the reaction of an N_2F_4/NF_2 mixture, and obtained the rate constant $k_{overall}$=1.6x10^{14} exp(-10 000)/T)cm$^{3/2}$ mol$^{-1/2}$ s^{-1}. The N_2F_4 dissociation was corrected using JANAF data to obtain the values of k_1 shown. $NF_2 + F_2 \rightarrow NF_3 + F$ 1 Authors used these to obtain the expression k_1=1.4x10^{11}exp(-4650/T) cm^3 mol^{-1} s^{-1}. Quoted by (4, 6).
1.3x10^5	335		
2.2x10^5	348		
3.4x10^5	359		

$NF_2 + F_2 \rightarrow NF_3 + F$



$NF_2 + F_2 \rightarrow NF_3 + F$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature	Method and Reference	Comments
$\sim 1\times10^{12}$	1800	Shock tube study. N_2F_4 (0.25-2%)/Ne mixtures at total pressures of 34.4-44.5 kPa. Reflected shocks. Reaction followed mass spectrometrically. DIESEN 1966 (2)	During a study of NF_2 dissociation, author noticed NF_3 formation, attributed by him to the following reaction sequence: $NF_2 + M \rightarrow NF + F + M$ $NF_2 + NF \rightarrow N_2F + F_2$ $NF_2 + N_2F \rightarrow NF_3 + N_2$ $NF_2 + F_2 \rightarrow NF_3 + F$ 1 On the basis of this scheme, author estimated k_1 as shown. Quoted by (6).
3.8×10^{2}	294	Static system. N_2F_4 (6.34-40.8 kPa)/F_2(12.9-50.6 kPa) mixtures, total pressure 50.0-56.9 kPa. Reaction followed by gas chromatography. CHEREDNIKOV and ILIN 1968 (3)	Again, results expressed in terms of the reaction of an N_2F_4/NF_2 mixture, giving $k_{overall}=1.2\times10^{12}\exp(-9000/T)$ $cm^{1.5}\ mol^{-0.5}\ s^{-1}$. No attempt is made to convert these results to allow for the N_2F_4/NF_2 equilibrium. The values of k_1 given are calculated from the authors' $k_{overall}$ and values of the equilibrium constant K_2 in the JANAF tables. From the authors' data we derive $k_1=5.5\times10^{8}\exp(-4200/T)$ $cm^3\ mol^{-1}\ s^{-1}$. $N_2F_4 + M \rightarrow NF_2 + NF_2 + M$ 2
5.9×10^{2}	303		
9.2×10^{2}	313		
1.3×10^{3}	322		
2.0×10^{3}	333		
7.9×10^{9}	1100	Shock tube study. N_2F_4 (<1%)/F_2(<1%)/Ne mixtures at 51.7-74.1 kPa total pressure. Reflected shocks. Reaction followed mass spectrometrically. DIESEN 1968 (4)	At these temperatures, conversion of N_2F_4 to NF_2 is practically instantaneous, and no secondary calculations were required to produce a rate constant. Quoted by (6). Used by (7). Expression $k_1=4.8\times10^{12}\exp(-7300/T)$ $cm^3\ mol^{-1}\ s^{-1}$ derived by (5).
1.3×10^{10}	1250		
3.2×10^{10}	1500		
4.9×10^{10}	1600		
9.0×10^{10}	1800		

Discussion

Unlike other reactions of the type NX_2+X_2 where X is H, O,Cl, Br or I, reaction 1 is exothermic and energetically favoured over its reverse, due to the strength of the N–F bond.

$$NF_2 + F_2 \rightarrow NF_3 + F \qquad (1)$$

Its rate has been studied at both high and low temperatures, in shock tubes in the former case, in static systems in the latter, with a variety of methods used for following the reaction. The two low temperature studies suffer from the effect of the N_2F_4/NF_2 equilibrium. The actual measured rate constant is for the reaction of F_2 with a mixture of NF_2 and N_2F_4, and the reaction order is apparently 3/2. Levy and Copeland [1] corrected for the N_2F_4/NF_2 equilibrium, and we have made a similar correction to the data of Cherednikov and Ilin [3]. The agreement is not good, the difference being at least two orders of magnitude.

Neither expression extrapolates well to the shock tube work of Diesen [4], whose activation energy lies midway between the other two. In these circumstances, we can make no recommendation for k_1.

Rate of the Reverse Reaction

There have been no experimental determinations of the rate of reaction –1

$$NF_3 + F \rightarrow NF_2 + F_2 \qquad (-1)$$

MacFadden and Tschuikow-Roux [7] give a value $k_{-1}= 8.8\times10^{13}\exp(-18\,000/T)$ $cm^3\ mol^{-1}\ s^{-1}$ calculated from Diesen's expression for k_1 [4] and the equilibrium constant, but we make no recommendation.

References

[1] Levy, J. B., and Copeland, B. K. W., J. Phys. Chem. **69**, 3700 (1965).
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[3] Cherednikov, V. N., and Ilin, E. K., Zh. Neorg. Khim. **13**, 3397 (1968). English translation, p. 1750.
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Miscellaneous Reactions Involving F/N Species

A19 NF + NF → N_2 + 2F

The disproportionation of NF radicals was proposed by Diesen [1] as the second stage in the decomposition of NF_2 radicals.

$$NF_2 + M \rightarrow NF + F + M \qquad (2)$$

$$NF + NF \rightarrow N_2 + 2F; \qquad (1)$$

$$\Delta H^\circ_{298} = -340.08 \text{ kJ mol}^{-1} \ (-81.280 \text{ kcal mol}^{-1})$$

The decomposition was followed in a shock tube coupled to a mass spectrometer. N_2F_4(0.25–1%)/Ar mixtures at 15.2 kPa pressure were shock-heated, and sampling for the mass spectrometer was made from behind the reflected shocks. Over the temperature range studied, 2200-3000 K, no evidence was found for further complicating reactions leading to NF_3. He found k_1 to be independent of temperature over the temperature range, $k_1=2.5\times10^{13}$ cm^3 mol^{-1} s^{-1}, with error limits of a factor of 2.

Reference

[1] Diesen, R. W., J. Chem. Phys. **41**, 3256 (1964).

A20 NF_2 + NF_2 → NF_3 + NF

The disproportionation of difluoramino radicals is the rate determining step in their decomposition at temperatures below 1000 K [1,3].

$$NF_2 + NF_2 \rightarrow NF_3 + NF; \qquad (1)$$

$$\Delta H^\circ_{298} = 32.928 \text{ kJ mol}^{-1} \ (7.870 \text{ kcal mol}^{-1})$$

Modica and Hornig [1] ruled out any contribution from reaction 1 in their study of NF_2 dissociation above 1400 K, finding the reaction first order in NF_2. Over the temperature range 623–753 K, Cherednikov et al. [2] found the overall stoichiometry to be

$$6NF_2 \rightarrow 4NF_3 + N_2$$

As they were unable to analyse for NF in the reaction mixture, they concluded from thermodynamic considerations that the initiation reaction was

$$NF_2 + NF_2 \rightarrow N_2 + 2F_2. \qquad (2)$$

They used a static system, allowing N_2F_4 at 20.0–160 kPa pressure to decompose, and periodically analysing the mixture gas chromatographically. (Conversion of N_2F_4 to NF_2 was found to be 100% at the temperatures used.) The quoted rate constant is divided by 3 to take account of the stoichiometry, and again by 2 to comply with our definition $-d[NF_2]/dt=2k_1[NF_2]^2$. This gives $k_1=1.7\times10^7$ exp(–11 800/T) cm^3 mol^{-1} s^{-1} over the quoted temperature range.

Corbin and Levy [3] comment on the low A factor obtained here. They used a similar static system, with the pressure of N_2F_4 ranging from 4.0–93.3 kPa and a temperature range of 578–791 K. The reaction mixture was sampled periodically by gas chromatography. Reaction 1 was considered the most likely initiation reaction, but the authors were unable to decide which of two subsequent paths prevailed, and chose an average stoichiometry of 2.25 with which to correct the overall k. Dividing this value of k_1 by 2 to comply with our definition gives $k_1=5.0\times10^{11}$ exp(–18 600/T) cm^3 mol^{-1} s^{-1}. The agreement with Cherednikov et al. is reasonable around 650–750 K, but owing to the considerable discrepancy outside this temperature range, and lack of information on the reaction mechanism, no recommendation is made.

References

[1] Modica, A. P., and Hornig, D. F., J. Chem. Phys. **43**, 2739 (1965).
[2] Cherednikov, V. N., Pereverzev, V. S., and Ryabov, V. P., Zh. Neorg. Khim. **14**, 873 (1969). English translation, p. 454.
[3] Corbin, W., and Levy, J. B., Int. J. Chem. Kinet. **7**, 679 (1975).

A21 H + NF_3 → NF_2 + HF

Abstraction of fluorine atoms from NF_3 by hydrogen atoms has been studied in any detail only by Rabideau [2].

$$H + NF_3 \rightarrow NF_2 + HF; \qquad (1)$$

$$\Delta H^\circ_{298} = -316.77 \text{ kJ mol}^{-1} \ (-75.710 \text{ kcal mol}^{-1})$$

He used a flow system, following the reaction by e.s.r. spectroscopy. H atoms were produced by a discharge through H_2 (1–3%)/He mixtures at total pressures of 304–350 Pa. NF_3 was added downstream at 37.8–65.3 Pa pressure. Below 473 K, it was not possible to detect any reaction, giving an upper limit of $k_1<2.6\times10^8$ cm^3 mol^{-1} s^{-1} at 473 K. Over the temperature range 476–599 K the expression $k_1=6.0\times10^{14}$ exp(–6700/T) cm^3 mol^{-1} s^{-1} was obtained.

Reaction 1 is also believed to be important in HF chemical laser systems, producing HF in a vibrationally excited state [1].

References

[1] Lin, M. C., J. Phys. Chem. **75**, 284 (1971).
[2] Rabideau, S. W., J. Mag. Resonance **11**, 163 (1973).

A22 $NO + F + M \rightarrow NOF + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-234.89	-121.30	34.816	39.205
300	-234.91	-121.37	34.561	38.952
500	-236.51	-125.57	18.149	22.762
1000	-238.07	-127.89	5.756	10.670
1500	-238.72	-128.42	1.605	6.696
2000	-239.16	-128.68	-0.474	4.741
2500	-239.53	-128.85	-1.724	3.588
3000	-239.90	-128.99	-2.559	2.832
3500	-240.30	-129.11	-3.157	2.301
4000	-240.70	-129.23	-3.606	1.910
4500	-241.14	-129.34	-3.954	1.614
5000	-241.62	-129.45	-4.234	1.379

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.006$
$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

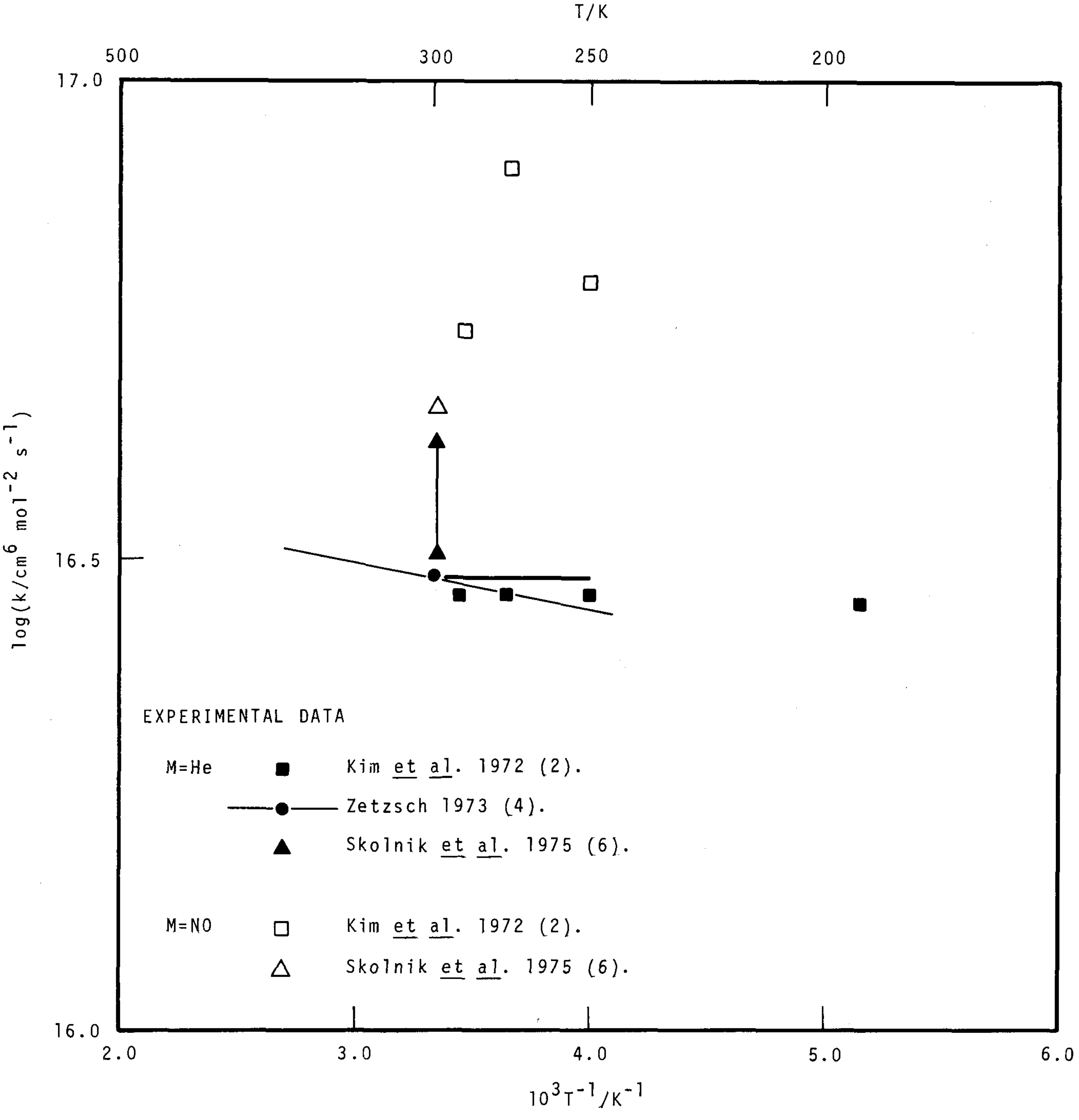
RECOMMENDED RATE CONSTANT

$k = 3.0 \times 10^{16}\ cm^6\ mol^{-2}\ s^{-1}$ (M=He)
$= 8.4 \times 10^{-32}\ cm^6\ molecule^{-2}\ s^{-1}$ (M=He)

Temperature Range: 250-300 K

Suggested Error Limits for Calculated Rate Constant: ±60%

$NO + F + M \rightarrow NOF + M$



NO + F + M → NOF + M

EXPERIMENTAL DATA

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
$2.8x10^{16}$	M=He	195	Discharge flow system. F_2 (<0.03%)/He mixtures at total pressures of 95.1-755 Pa. NO added downstream at 4.61-43.6 Pa pressure. [F] and [NO] monitored by e.s.r. spectroscopy. KIM, MACLEAN and VALANCE 1972 (2)	To eliminate effects of F and F_2 as third bodies, $[F_2]$ kept low in the discharge. A high total pressure was used to avoid any contribution from the second order reaction 2. $NO + F_2 \rightarrow NOF + F$ 2 $NO + F + M \rightarrow NOF + M$ 1 The following rate constant expressions were obtained:- $k_1(M=He) = 3.0x10^{16}exp(-11/T)$ and $k_1(M=NO) = 4.5x10^{16}exp(+110/T)$ cm^6 mol^{-2} s^{-1}. k_1(M=He) used by (3) at 298 K as M=Ar. Quoted by (6, 8).
$2.9x10^{16}$		250		
$2.9x10^{16}$		273		
$2.9x10^{16}$		288		
$6.2x10^{16}$	M=NO	250		
$8.3x10^{16}$		273		
$5.5x10^{16}$		288		
		298	Flow system. F_2(<0.5%)/Ar mixtures at a total pressure of 493 Pa. NO added downstream in excess. In some experiments RX added further downstream, where RX = CH_4, CH_3F, CH_2F_2, CHF_3, $CHClF_2$, HCl, $CBrF_3$, NH_3 or PH_3. Reaction followed by monitoring NOF emission. POLLOCK and JONES 1973 (3)	F atoms generated by reaction 2. No attempt made to determine k_1 directly, only as ratio k_1/k_3. $RH + F \rightarrow HF + R$ 3 $k_1/k_3 = 5.3x10^2$(M=CH_3F); $2.0x10^3$ (CH_2F_2); $1.5x10^5$(M=CHF_3); $2.0x10^4$ (M=$CHClF_2$); $3.9x10^3$(M=HCl); $7.0x10^6$(M=$CBrF_3$); $5.1x10^4$(M=NH_3); $2.1x10^4$ cm^3 mol^{-1}(M=PH_3); k_1/k_3 $\leqslant 4.5x10^2$ cm^3 mol^{-1}(M=CH_4). Using our values for k_3(RH=HCl and CH_4, this Vol. sections E2 and A6) we obtain k_1(M=HCl)= $2.73x10^{16}$ and $k_1(M=CH_4) \leqslant 1.8x10^{16}$ cm^6 mol^{-2} s^{-1}. Quoted by (8).
$3.0x10^{16}$	M=He	300	Discharge flow system. F_2 (0.1%)/Ar mixtures at total pressures of 0.21-3.47 kPa. NO added downstream so that [NO]:[F]∿10. Reaction followed mass spectrometrically. ZETZSCH 1973 (4)	Some experiments performed at 1.67 kPa over the temperature range 244-375 K, giving E_1=0.85 kJ mol^{-1} (0.2 kcal mol^{-1}). No value for A_1 is quoted but we obtain an expression $k_1=4.2x10^{16}$ exp(-100/T) cm^6 mol^{-2} s^{-1}. No F_2 was observed and thus any recombination of F atoms was ruled out. Quoted by (7).
$4.8x10^{16}$	M=NO	300	Discharge flow system. CF_4 /He or Ar mixtures at ∿60 Pa pressure. NO(5.66-100%) /M mixtures added downstream at 36.7-540 Pa pressure. [NOF] monitored by emission spectroscopy at 615-625 nm.	$[CF_4]$ kept low in discharge so that its effect as a third body could be ignored. He used as carrier gas for CF_4 except in some determinations of k_1(M=Ar), the lower figure given being for He carrier. $NO + F + M \rightarrow NOF + M$ 1
$3.2-4.2x10^{16}$	M=He	300		
$2.5-3.2x10^{16}$	M=Ar	300		
$2.1x10^{16}$	M=Ne	300		
$3.9x10^{16}$	M=N_2	300		
$1.3x10^{17}$	M=CO	300		
$1.6x10^{17}$	M=CF_4	300		
$1.4x10^{17}$	M=SF_6	300		
$1.1x10^{17}$	M=C_2F_6	300		

$NO + F + M \rightarrow NOF + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		SKOLNIK, VEYSEY, AHMED and JONES 1975 (6)	k_1(M=He) determined (a) by varying [He] with [NO] fixed (upper value) and (b) by varying [NO] with [He] fixed (lower value). Quoted by (8).

REVIEW ARTICLE

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Review of F atom reactions. JONES and SKOLNIK 1976 (8)	Quotes (2, 3, 6). Also refers to work on hot ^{18}F atom reactions (5) in which it was shown that reaction occurs only in the absence of third bodies. $NO + {}^{18}F \rightarrow NO^{18}F$ 1'

Discussion

The reaction between nitric oxide and fluorine atoms occurs in NO/F_2 flames as a means of removal of F atoms.

$$NO + F + M \rightarrow NOF + M \qquad (1)$$

This mechanism in NO/F_2 flames was first suggested by Rapp and Johnston [1], who estimated $k_1 \sim 2.10^{14}$ $cm^6\ mol^{-2}\ s^{-1}$ at flame temperatures, but were unable to make a more accurate assessment. The reaction has been studied recently in discharge flow systems [2,4,6], where by removing the discharge, reaction 2 may be studied under the same conditions [2,4].

$$NO + F_2 \rightarrow NOF + F \qquad (2)$$

All three studies have used helium as third body. The agreement is reasonable, especially if only the lower value of Skolnik et al. is considered [6]. However, the error involved between the two values is only 50%. The temperature dependent studies [2,4] show only a small activation energy, negligible over the narrow temperature range in which the reaction has been studied. We therefore recommend a value of $k_1(M=He) = 3.0 \times 10^{16}$ $cm^6\ mol^{-2}\ s^{-1}$ over the temperature range 250–300 K with error limits of ±60%.

The data for M=NO [2,6] show much greater scatter, and we make no recommendation for $k_1(M=NO)$. The data for other third bodies are given in the table [6].

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A23 $NO + F_2 \rightarrow NOF + F$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-77.069	-6.711	13.152
300	-77.065	-6.690	13.069
500	-76.287	-4.736	7.723
1000	-74.295	-1.954	3.780
1500	-72.689	-0.636	2.499
2000	-71.429	0.092	1.872
2500	-70.475	0.523	1.502
3000	-69.806	0.766	1.257
3500	-69.413	0.879	1.083
4000	-69.283	0.912	0.954
4500	-69.429	0.875	0.854
5000	-69.831	0.778	0.774

RECOMMENDED RATE CONSTANT

$k = 4.2 \times 10^{11} \exp(-1150/T)$ cm^3 mol^{-1} s^{-1}

$= 7.0 \times 10^{-13} \exp(-1150/T)$ cm^3 $molecule^{-1}$ s^{-1}

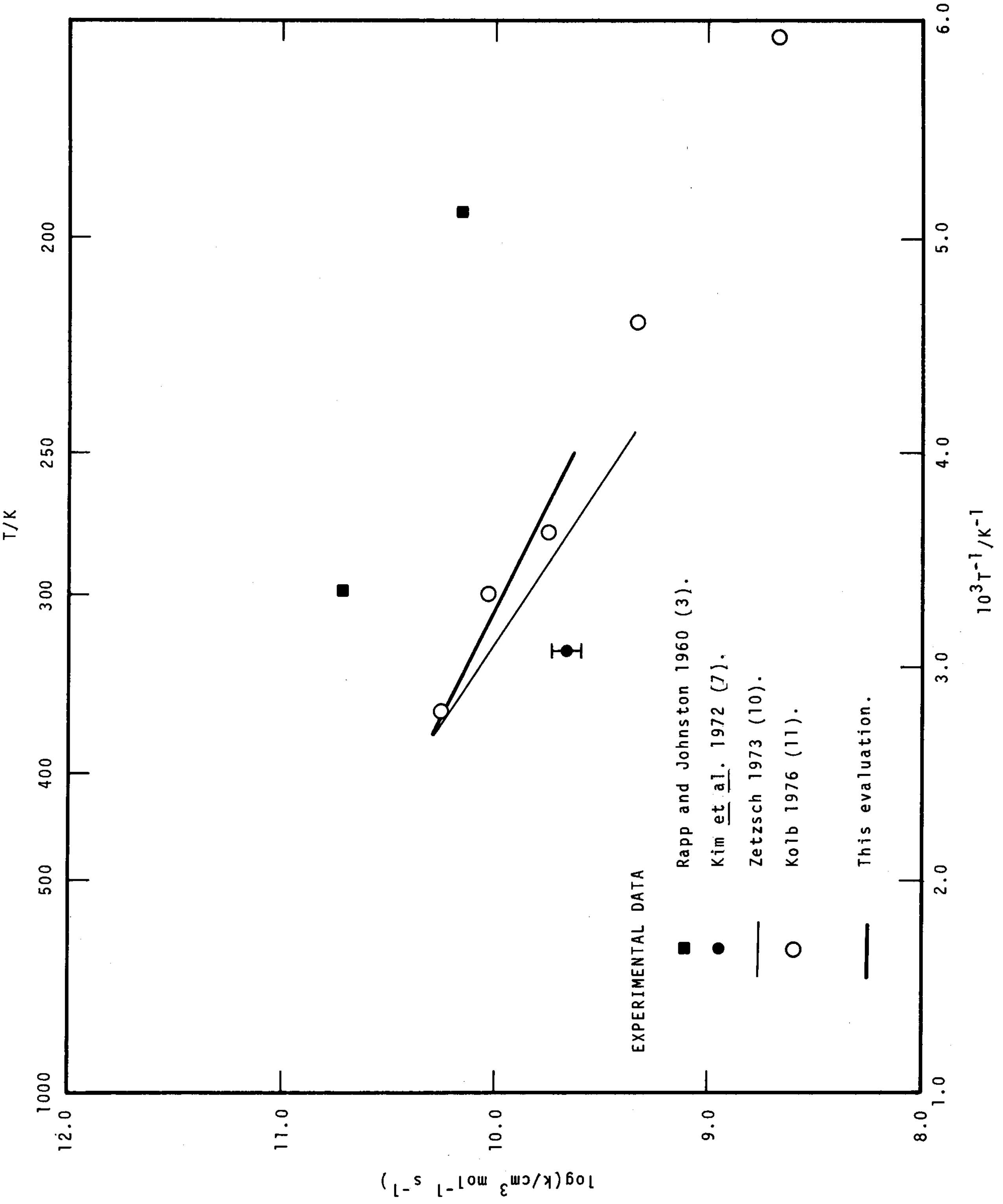
Temperature Range: 250-375 K

Suggested Error Limits for Calculated Rate Constant: A factor of 3.

Note: This expression is that of KOLB (11).

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 11.62 \pm 0.50$
$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -12.16 \pm 0.50$
$E/J\ mol^{-1} = 9600 \pm 2500$
$E/cal\ mol^{-1} = 2300 \pm 600$

$NO + F_2 \rightarrow NOF + F$



$NO + F_2 \rightarrow NOF + F$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1.5×10^{10} 5.37×10^{10}	195 300	Flame study. F_2(0.1%)/N_2 (387-667 Pa)/NO (15.7%)/N_2 (17.8-57.4 Pa) diffusion flames. Reaction followed by time exposure photography. RAPP and JOHNSTON 1960 (3)	Reaction 1 was assumed to be the initiation reaction, followed by the fast reaction 2. $NO + F_2 \rightarrow NOF + F$ 1 $NO + F (+M) \rightarrow NOF (+M)$ 2 By comparing the A factor of 6×10^{11} $cm^3\ mol^{-1}\ s^{-1}$ with calculated value of A_1 (2, 3), authors assumed rate constant measured was k_1. They obtained the expression $k_1 = 6 \times 10^{11} \exp(-750/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the given temperature range. Quoted by (4, 5, 7, 8, 11). Used by (9).
$(4.75 \pm 0.7) \times 10^9$	325	Flame study. F_2(<1%)/NO (<2%)/He mixtures at total pressures of 0.35-2.49 kPa. [F] monitored by e.s.r. spectroscopy. KIM, MACLEAN and VALANCE 1972 (7)	By measuring just the initial rate of reaction 1, authors were able to ignore reaction 2, although the value of k_1 obtained was checked by inserting their own values of k_2 (7) into data obtained at a later stage of the reaction. Quoted by (11).
	300	Flow system. NO added to F_2/N_2 stream ($[F_2]:[N_2]$ ratios 1.3×10^{-1}) such that $0 \leqslant [NO]:[F_2] \leqslant 2.0$. Total pressure 40 mm Hg(5.3 kPa). Laser Raman scattering used to determine $[F_2]$ at 510.2 nm, and [NOF] at 537.1 nm. HOELL, ALLARIO, JARRETT and SEALS 1973 (9)	Authors compared variation of $[F_2]$ with [NO], giving change in $[F_2]$ due to reaction sequence 1 and 2. $NO + F_2 \rightarrow NOF + F$ 1 $NO + F (+M) \rightarrow NOF (+M)$ 2 Theoretical modelling gave $k_2/k_1 < 5$, and probably ~ 1. As we have no recommendation for $k_2(M=N_2)$ (this Volume, section A22), we do not derive any definite value for k_1 from this result.
$1.1 \times 10^{12} \exp(-1500/T)$	244-375	Flow system. F_2(<0.1%)/He mixtures at total pressures of 0.21-3.47 kPa. NO added downstream so that $[NO] = 10\ [F_2]$. [F] and $[F_2]$ followed by mass spectrometry. ZETZSCH 1973 (10)	Reaction 1 followed immediately by reaction 2. k_2 determined in same study and used to determine k_1 from measurements of competitive rates of reactions 1 and 2 above for NO. Used by (12).

$NO + F_2 \rightarrow NOF + F$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$4.7x10^8$ $2.2x10^9$ $5.7x10^9$ $1.1x10^{10}$ $1.8x10^{10}$	169 217 276 300 359	Flow system. F_2(3.7%)/N_2 mixtures at total pressures of 133-533 Pa. NO added downstream so that $[F_2]$>> [NO]. [NO] followed by resonance fluorescence at 226 nm. KOLB 1976 (11)	In this temperature range, and under the experimental conditions chosen, author believed that reaction 2 had no effect on [NO] decay. From these data, he obtained the expression k_1=4.2x 10^{11}exp(-1150/T) cm^3 mol^{-1} s^{-1}.

Discussion

Reaction 1 is the principal initiation reaction in NO/F_2 flames and is also a convenient source of F atoms to initiate the H_2/F_2 reaction in the HF chemical laser [6].

$$NO + F_2 \rightarrow NOF + F \tag{1}$$

Of the five studies of reaction 1, two have been flame studies. Rapp and Johnston [3] used the diffusion flame method of Polanyi [1], with F_2 as the fuel in an NO atmosphere, following the reaction by time exposure photography. This method assumes transport by flow is small compared to that by diffusion and produces results around an order of magnitude higher than the other three studies.

More recently, Kim et al. [7] used a more orthodox flame study to obtain k_1/k_2, and a discharge flow study of the subsequent reaction 2, from which a value of k_2 was obtained and used in calculating k_1.

$$NO + F + M \rightarrow NOF + M \tag{2}$$

There is a difference of a factor of two between this study and that of Zetzsch [10], using a flow system, and also requiring the rate of reaction 2 to obtain k_1. His expression for k_1 is in reasonable agreement with that of Kolb [11] around room temperature. Kolb eliminated the effect of reaction 2 by making $[F_2] >> [NO]$, in contrast to Zetzsch's system. His activation energy $E_1 = 9.6$ kJ mol^{-1} (2.3 kcal mol^{-1}), falls midway between that of Rapp and Johnston [3], and Zetzsch [10]. We also feel that this direct determination is likely to be more accurate than in the other studies in which reaction 2 is involved. Thus we recommend the expression of Kolb [11],

$$k_1 = 4.2 \times 10^{11} \exp(-1150/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 250–375 K, with error limits of a factor of 3.

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A24 $NO_3F + M \rightarrow NO_3 + F + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	139.578	118.328	-18.273	-22.662
300	139.587	118.357	-18.121	-22.512
500	140.248	120.085	- 8.378	-12.991
1000	140.444	120.499	- 1.041	- 5.955
1500	139.465	119.725	1.398	- 3.693
2000	138.001	118.884	2.606	- 2.609
2500	136.302	118.131	3.323	- 1.989
3000	134.486	117.470	3.794	- 1.596
3500	132.599	116.884	4.126	- 1.332
4000	130.662	116.370	4.373	- 1.143
4500	128.696	115.905	4.560	- 1.008
5000	126.708	115.487	4.709	- 0.904

SI Units: $\log(K_p/\mathrm{Pa}) = \log(K_p/\mathrm{atm}) + 5.006$

$\log(K_c/\mathrm{mol\ m^{-3}}) = \log(K_c/\mathrm{mol\ cm^{-3}}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^{\infty} = 1.6 \times 10^{15} \exp(-16\ 000/T)\ s^{-1}$

Temperature Range: 350-390 K.

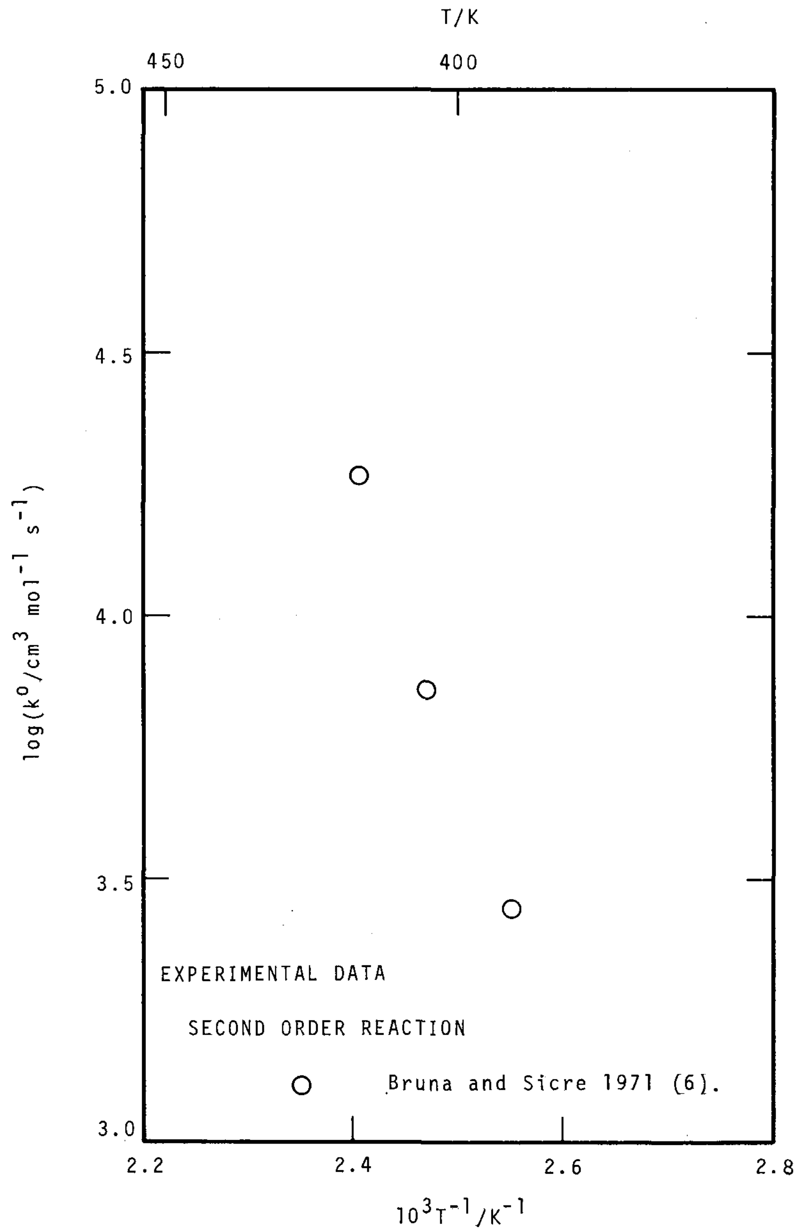
Suggested Error Limits for Calculated Rate Constant: ±30%.

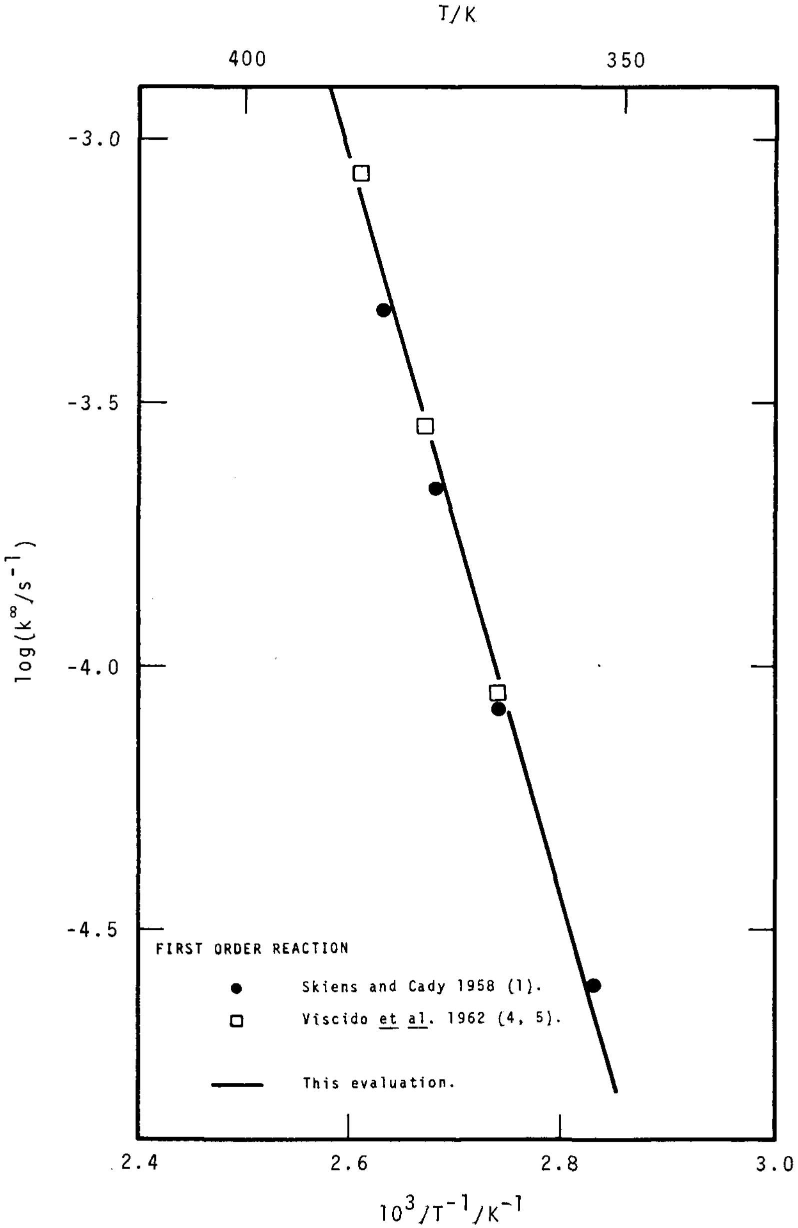
Rate Parameters: $\log(A/s^{-1})$ = 15.20 ±0.20

$E/\mathrm{J\ mol^{-1}}$ = 133 000 ±20 000

$E/\mathrm{cal\ mol^{-1}}$ = 32 000 ±5000

$NO_3F + M \rightarrow NO_3 + F + M$





$NO_3F + M \rightarrow NO_3 + F + M$

EXPERIMENTAL DATA

Rate Constant k (s^{-1})		Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^∞				
2.5×10^{-5}	$M=NO_3F$	353	Static system. NO_3F at 0.25-31.9 kPa pressure. In some experiments O_2,Ar,NO_2 or F_2 added. Reaction followed manometrically. SKIENS and CADY 1958 (1)	Products found to be O_2 and NO_2F. Authors proposed the following mechanism, with reaction 1 the rate determining step:- $NO_3F + M \rightarrow NO_3 + F + M$ 1 $NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$ 2 $NO_2 + F + M \rightarrow NO_2F$ 3 Pressure dependence of rate constants extrapolated to infinite pressure. Reaction was found to be entirely homogeneous and first order over pressure range studied. Of the added gases, NO_2 and F_2 accelerated the reaction rate, NO_2 by up to a factor of 50, while O_2 and Ar both reduced it by half. No further attempt was made to determine rate constants. An overall expression $k_1^\infty = 5.8\times10^{13}\exp(-14\ 900/T)\ s^{-1}$ was determined for $M=NO_3F$.
8.4×10^{-5}		364		
2.2×10^{-4}		373		
4.9×10^{-4}		380		
8.8×10^{-5}	$M=NO_3F$	363	Static system. NO_3F at 0.08-53.3 kPa pressure. In some experiments N_2,O_2,Ar, CO_2, NO_2F or F_2 added. Reaction followed manometrically. SICRE and SCHUMACHER 1962 (2) VISCIDO, SICRE and SCHUMACHER 1962 (4) VISCIDO, SICRE and SCHUMACHER 1963 (5)	Results generally in agreement with those of (1). An overall expression $k_1^\infty=2.5\times10^{15}\exp(-16\ 200/T)\ s^{-1}$ was derived. From the experiments with added inert gases, the following relative third body efficiencies were obtained: $NO_3F:N_2:O_2:Ar:CO_2:NO_2F$ = 1:0.14:0.15:0.15:0.25:0.90. This is in contrast to the results of (1). Quoted by (6).
2.9×10^{-4}		373		
8.8×10^{-4}		383		

$NO_3F + M \rightarrow NO_3 + F + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o			
2.8×10^3 M=NO_3F	393	Static system. NO_3F at 61.3-2660 Pa pressure. Reaction followed manometrically. BRUNA and SICRE 1971 (6)	Reaction followed at low pressures to obtain second order k_1, otherwise system as used previously (4). $NO_3F + M \rightarrow NO_3 + F + M$ 1 Some experiments carried out at 383 K, but rate too small to be measurable. From the results given, authors derived the expression $k_1^o=8.7\times10^{20}\exp(-15\ 800/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the temperature range studied. The results were compared with theoretical calculations by both Lindemann-Hinshelwood and RRKM theories, giving the following expressions for k_1, of which the latter is only in error by a factor of two at 400 K:- k_1(Lindemann-Hinshelwood) $=2.55\times10^{17}\exp(-13\ 870/T)\ cm^3\ mol^{-1}\ s^{-1}$; k_1(RRKM all vibrational)$=1.01\times10^{21}\exp(-15\ 250/T)\ cm^3\ mol^{-1}\ s^{-1}$; k_1 (RRKM vibration/rotation) $= 1.63\times10^{20}\exp(-15\ 450/T)\ cm^3\ mol^{-1}\ s^{-1}$.
7.3×10^3	403		
1.9×10^4	413		

Discussion

Nitroxy fluoride (fluorine nitrate) decomposes readily at temperatures not much above ambient. Its pyrolysis is thus easily studied, the products being nitryl fluoride and oxygen, if the reaction is allowed to proceed slowly, or nitrosyl fluoride and oxygen under conditions of spark ignition [1].

The slow reaction is conveniently studied around 350-400 K. Skiens and Cady [1] used an aluminium reaction vessel, identifying products from their melting and boiling points, and hence ascertaining the overall stoichiometry. In some experiments the reactor was packed with aluminium turnings, but no change in overall rate was noted, and the reaction was concluded to be a homogeneous, first order reaction. They postulated the following reaction mechanism:

$$NO_3F + M \rightarrow NO_3 + F + M \qquad (1)$$

$$2NO_3 \rightarrow 2NO_2 + O_2 \qquad (2)$$

$$NO_2 + F + M \rightarrow NO_2F + M \qquad (3)$$

and claimed they had measured k_1, the first step being rate determining.

Their results were confirmed by Viscido et al. [4] using similar techniques. Later, Bruna and Sicre [6] extended the measurements to much lower pressures to obtain the second order rate constant.

We recommend a value of $k_1^\infty = 1.6\times10^{15}\exp(-16\ 000/T)\ s^{-1}$ for the limiting first order rate constant, $M=NO_3F$, over the temperature range 350-390 K, with error limits of ±30%. No value is recommended for the second order rate constant k_1°.

Relative Third Body Efficiencies

Both Skiens and Cady [1] and Schumacher et al. [2,3,4] have considered the effect of additions of "inert" substances to the pyrolysis vessel. The former authors added Ar, O_2, F_2, H_2 and NO_2. Ar and O_2 retarded the reaction rate by about 50%, F_2 increased it by about a factor of 3, and NO_2 by a factor of 10-50. This, they concluded, must be due to the occurrence of reaction 4 (this Vol., section A29).

$$NO_3F + NO_2 \rightarrow NO_2F + NO_3 \qquad (4)$$

It was impossible to study the effect of H_2, as HF was formed, which attacked the glass of the i.r. cell used to analyse the products.

The effects of the inert third bodies added by Viscido et al. [4] are given in the table. Sicre and Schumacher [2] studied the effects of addition of fluorine over a wide pressure range. At high pressures they postulated a reaction between NO_3F and F_2 (section A30), but at low F_2 pressures ($<$1.33 kPa), an apparent doubling of the first order rate was noticed. This they attributed to a change in the reaction mechanism, leading to a stoichiometry of 2 for NO_3F disappearance:

$$NO_3F + M \rightarrow NO_3 + F + M \qquad (1)$$

$$NO_3 + F_2 \rightarrow NO_2F + FO \qquad (5)$$

$$NO_3F + FO \rightarrow NO_2F + O_2 + F \qquad (6)$$

with F atoms removed by recombination.

Addition of NO_2 confirmed the findings of Skiens and Cady [1], that a separate bimolecular reaction 4 was occurring [3] (see section A29).

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Miscellaneous Reactions Involving F/N/O Species

A25 $NO_2 + F + M \rightarrow NO_2F + M$

The formation of nitryl fluoride was studied by Zetzsch [1] in a discharge flow system, following a similar study on the NO/F reaction.

$$NO_2 + F + M \rightarrow NO_2F + M; \qquad (1)$$

$$\Delta H^\circ_{298} = -220.79 \text{ kJ mol}^{-1}(-52.77 \text{ kcal mol}^{-1})$$

F atoms were produced from a discharge through F_2(0.1%)/Ar mixtures at total pressures of 0.21–3.47 kPa. NO_2 was added downstream so that $[NO_2]/[F] \cong 10$. [F] was monitored by mass spectrometry, giving $k_1 = 2.3 \times 10^{17}$ cm^6 mol^{-2} s^{-1} at 300 K, as expected, faster than the NO_2/I or NO_2/Cl reactions. The reaction was also studied over the temperature range 248–368 K to obtain an activation energy $E_1 = 850 \pm 1250$ J mol^{-1} (200$\pm$300 cal mol^{-1}).

Reference

[1] Zetzsch, C., Proc. 1st European Combustion Symp. 35 (1973).

A26 $NO_2 + F_2 \rightarrow NO_2F + F$

The reaction between nitrogen dioxide and fluorine was originally used for the preparation of nitryl fluoride [1].

$$NO_2 + F_2 \rightarrow NO_2F + F; \qquad (1)$$

$$\Delta H^\circ_{298} = -62.969 \text{ kJ mol}^{-1}(-15.050 \text{ kcal mol}^{-1})$$

The only study of the rate of reaction 1 has been by Perrine and Johnston [2]. They mixed nitrogen dioxide and fluorine (no details of pressure given) in both glass and steel vessels. In the latter, there was clearly a heterogeneous component to the reaction, so all rate constant measurements were made in glass vessels by following $[NO_2]$ by absorption of light at 436 nm. Fluorine atoms produced had to be removed either by reaction 2 or 3, both very much faster than reaction 1.

$$NO_2 + F + M \rightarrow NO_2F + M \qquad (2)$$

$$F + F + M \rightarrow F_2 + M \qquad (3)$$

Taking this into account, the rate constant for reaction 1 was found to be $k_1 = 1.59 \times 10^{12} \exp(-5300/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 300–343 K.

References

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[2] Perrine, R. L., and Johnston, H. S., J. Chem. Phys. **21**, 2202 (1953).

A27 $NO_2 + F_2O \rightarrow NO_2F + FO$

The reaction between nitrogen dioxide and F_2O proceeds *in a manner analogous to that between* NO_2 *and* Cl_2O (section B53), with an additional route leading to O_2 production [1].

$$NO_2 + F_2O \rightarrow NO_2F + FO; \qquad (1)$$

$$\Delta H^\circ_{298} = -57.614 \text{ kJ mol}^{-1}(-13.770 \text{ kcal mol}^{-1})$$

Reaction 1 was assumed to be the rate determining initiation reaction. De Staricco et al. [1] studied the reaction over the temperature range 333–353 K. An excess of F_2O(8.0–46.7 kPa) was used in a static system with NO_2(1.33–5.33 kPa), and the reaction followed manometrically. The following reaction scheme was suggested.

$$NO_2 + F_2O \rightarrow NO_2F + FO \qquad (1)$$

$$NO_2 + FO \rightarrow NO_2...FO \xrightarrow{M} NO_3F \qquad (2a)$$

$$\rightarrow NO_3 + F \qquad (2b)$$

$$2NO_3 \rightarrow 2NO_2 + O_2 \qquad (3)$$

$$NO_2 + F + M \rightarrow NO_2F + M \qquad (4)$$

By freezing down the products rapidly at 195 K, the intermediate species $NO_2...FO$ was isolated and its subsequent decay through *paths 2a and 2b followed. A rate* constant $k_1 = 1.28 \times 10^{11} \exp(-7800/T)$ cm^3 mol^{-1} s^{-1} was determined.

Reference

[1] de Staricco, E. R., Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. NF **39**, 337 (1963).

A28 $NF_2 + F_2O \rightarrow NF_3 + FO$

This reaction was studied by Rubinstein et al. [1] over the temperature range 393–463 K, using thermal decomposition of N_2F_4 to produce the NF_2 radicals in N_2F_4(2.10–4.73 kPa)/F_2O(5.43–13.2 kPa) mixtures.

$$NF_2 + F_2O \rightarrow NF_3 + FO; \qquad (1)$$

$$\Delta H^\circ_{298} = -89.496 \text{ kJ mol}^{-1} \ (-21.390 \text{ kcal mol}^{-1})$$

The reaction was followed manometrically. Final products were determined as NF_3 and NOF in a 3:1 ratio. No subsequent reaction was seen between NOF and F_2O, and the authors concluded reaction 1 to be rate-determining, with $k_1 = 3.0 \times 10^{12} T^{0.5} \exp(-11\ 100/T)$ cm^3 mol^{-1} s^{-1}.

Reference

[1] Rubinstein, M., Sicre, J. E., and Schumacher, H.-J., Z. Phys. Chem. NF **43**, 51 (1964).

A29 $NO_3F + NO_2 \rightarrow NO_2F + NO_3$

Reaction 1 was first put forward to account for the extremely high efficiency of NO_2 as a third body in the decomposition of nitroxy fluoride (1)

$$NO_3F + NO_2 \rightarrow NO_2F + NO_3; \qquad (1)$$

$$\Delta H^\circ_{298} = -81.211 \text{ kJ mol}^{-1} (-19.410 \text{ kcal mol}^{-1})$$

Skiens and Cady [1] found the rate of the decomposition increased by from 10 to 50 times on the addition of NO_2, but made no attempt to measure a second order rate constant. Viscido et al. [2] followed the reaction over the temperature range 353–383 K. They mixed NO_2 (1.33–5.35 kPa) and NO_3F(6.35–13.9 kPa) over this temperature range following the pressure changes, and analysing the products (NO_2F, O_2) by i.r. spectroscopy. They found $k_1 = 1.9 \times 10^{11} \exp(-14\ 300/T)$ cm^3 mol^{-1} s^{-1} over that temperature range.

References

[1] Skiens, W. E., and Cady, G. H., J. Amer. Chem. Soc. **80**, 5640 (1958).
[2] Viscido, L., Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. NF **32**, 182 (1962).

A30 $NO_3F + F_2 \rightarrow NO_2F + F + FO$

When fluorine was added to nitroxy fluoride in studies of the decomposition of the latter [1,2] Skiens and Cady [1] noted an increase in the apparent rate of decomposition by a factor of 3–3.5.

$$NO_3F + F_2 \rightarrow NO_2F + F + FO; \qquad (1)$$

$$\Delta H^\circ_{298} = 68.450 \text{ kJ mol}^{-1} (16.36 \text{ kcal mol}^{-1})$$

They noted that if the fluorine were to attack the NO_2 formed during the decomposition, the reaction chain would be broken, and thus fluorine would act as an inhibitor, not an accelerator of the decomposition. They therefore postulated a direct attack by F_2 on NO_3F, but gave no details.

Sicre and Schumacher [2] found that low pressures of F_2 added to NO_3F apparently doubled the decomposition rate by changing the decomposition mechanism (section A24). When pressures of 9.36–49.6 kPa F_2 were added to about 4.7 kPa NO_3F, a direct bimolecular reaction occurred between them, and reaction 1 was assumed to be the initial, rate determining step. Over the temperature range 363–383 K, they obtained $k_1 = 6.7 \times 10^{14} \exp(-11\ 400/T)$ cm^3 mol^{-1} s^{-1}.

References

[1] Skiens, W. E., and Cady, G. H., J. Amer. Chem. Soc. **80**, 5640 (1958).
[2] Sicre, J. E., and Schumacher, H. J., Z. Phys. Chem. NF **32**, 355 (1962).

A31 $COF_2 + M \rightarrow F + COF + M$

THERMODYNAMIC DATA

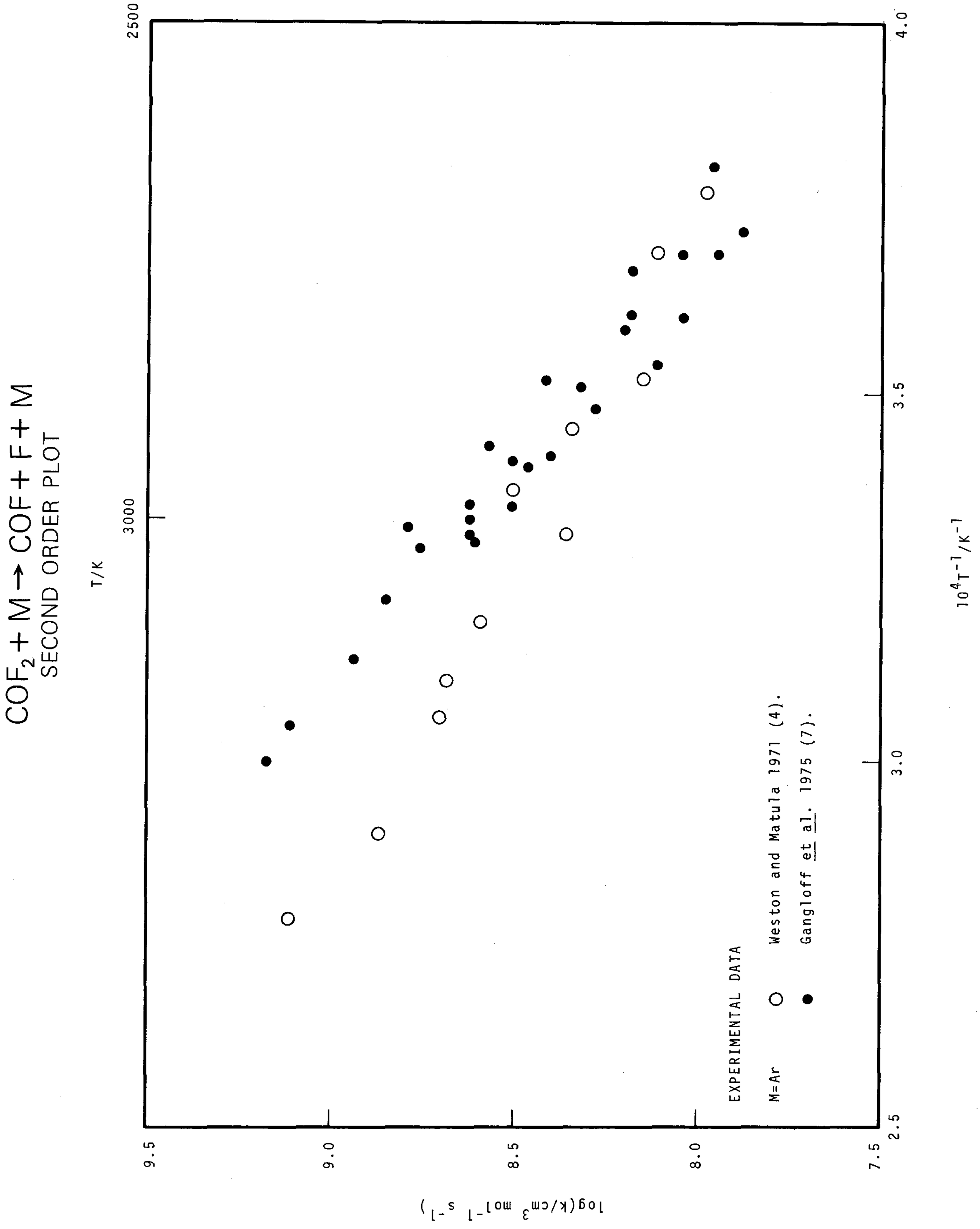
T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	546.26	148.24	-87.512	-91.900
300	546.29	148.32	-87.371	-91.762
500	548.31	153.67	-49.256	-53.869
1000	549.46	155.52	-20.578	-25.492
1500	548.68	154.92	-11.014	-16.104
2000	547.30	154.13	- 6.243	-11.458
2500	545.65	153.40	- 3.388	- 8.700
3000	543.86	152.75	- 1.491	- 6.882
3500	541.99	152.17	- 0.141	- 5.599
4000	540.08	151.66	0.869	- 4.647
4500	538.12	151.20	1.651	- 3.916
5000	536.14	150.78	2.275	- 3.338

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.



$COF_2 + M \rightarrow COF + F + M$
SECOND ORDER PLOT

$COF_2 + M \rightarrow F + COF + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o				
9.6×10^7	M=Ar	2650	Shock tube study. COF_2 (0.5-1.0%)/Ar mixtures at total pressures of 0.5-12 atm (50.6-1210 kPa). Incident and reflected shocks. $[COF_2]$ monitored by i.r. emission spectroscopy at 5.15 μm. WESTON and MATULA 1971 (4)	Observed rate constant plotted against pressure, and both k_1^o and k_1^∞ obtained from Lindemann theory. A least squares fit to the data gives $k_1^o=1.2\times10^{12}\exp(-25\ 000/T)\ cm^3\ mol^{-1}\ s^{-1}$. Authors found reaction in the fall off region between first and second order kinetics over the entire pressure range studied. $COF_2 + M \rightarrow F + COF + M$ 1 Quoted by (6, 7).
1.3×10^8		2710		
1.3×10^8		2760		
1.4×10^8		2840		
2.2×10^8		2895		
3.2×10^8		2965		
2.3×10^8		3020		
3.9×10^8		3130		
4.8×10^8		3215		
5.0×10^8		3265		
7.4×10^8		3445		
1.3×10^9		3590		
9.1×10^7	M=Ar	2625	Shock tube study. COF_2 (0.5-1.0%)/Ar mixtures at total pressures of 2.5-9.0 atm (253-909 kPa). Reflected shocks. In some experiments 1% CO added. $[COF_2]$ monitored by i.r. emission spectroscopy at 5.15 μm. GANGLOFF, MILKS, MALONEY, ADAMS and MATULA 1975 (7)	Second order kinetics found to fit observed rate constant over entire pressure range. Rate constants derived from initial reaction rate. Ignoring the results from runs with added CO, authors obtain $k_1^o=1.7\times10^{14}\exp(-38\ 900/T)\ cm^3\ mol^{-1}\ s^{-1}$. The addition of 1% CO had little effect on the apparent rate constant, reducing it just slightly, and a value of $k_2<6.7\times10^9T^{0.5}\exp(-11\ 600/T)\ cm^3\ mol^{-1}\ s^{-1}$ was assumed. $COF_2 + CO \rightarrow 2COF$ 2 Quoted by (5).
7.5×10^7		2681		
$*8.9\times10^7$		2706		
1.1×10^8		2710		
$*1.5\times10^8$		2725		
1.5×10^8		2770		
$*1.1\times10^8$		2774		
1.6×10^8		2786		
1.3×10^8		2825		
2.6×10^8		2841		
$*2.1\times10^8$		2849		
1.9×10^8		2874		
3.7×10^8		2915		
2.5×10^8		2924		
3.2×10^8		2933		
2.9×10^8		2941		
4.2×10^8		2985		
$*3.2\times10^8$		2985		
4.2×10^8		3003		
6.2×10^8		3012		
4.2×10^8		3021		
$*4.1\times10^8$		3030		
5.7×10^8		3040		
7.1×10^8		3106		
8.6×10^8		3185		
1.3×10^9		3279		
1.5×10^9		3333		

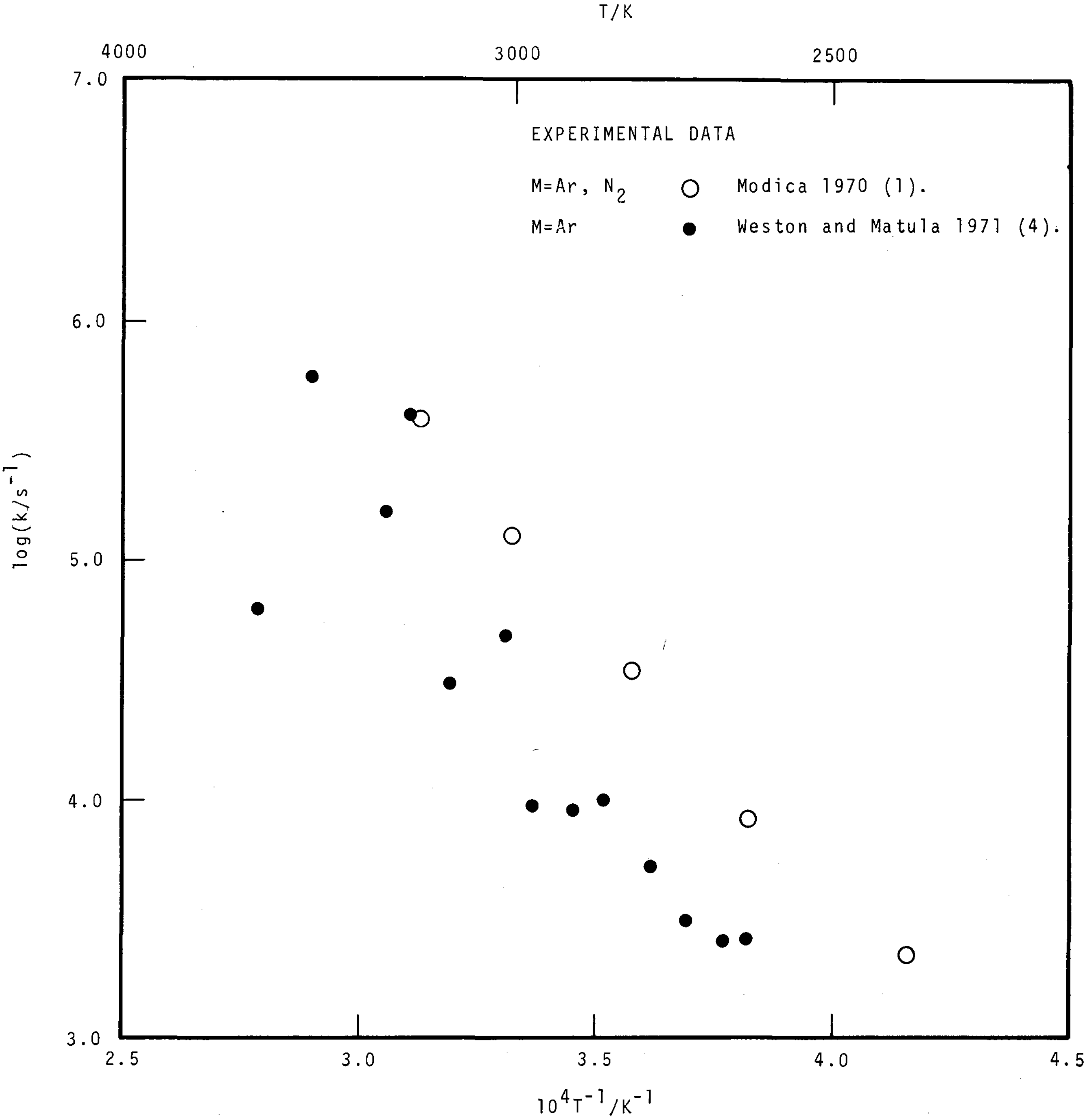
*1% CO added

REVIEW ARTICLE

$3.3\times10^{17}\exp(-30\ 700/T)$	M=Ar	2200-3600	Review of reaction in shock tubes. WAGNER 1971 (3)	Data of (1) at ~2 atm (203 kPa) recalculated to yield second order rate constant. First order constant also quoted. Not plotted on Arrhenius diagram.

$COF_2 + M \rightarrow COF + F + M$

FIRST ORDER PLOT



$COF_2 + M \rightarrow F + COF + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (s^{-1})		Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^∞				
2.2×10^3	M=Ar,N_2	2405	Shock tube study. COF_2 (0.25-2%)/Ar and COF_2(2%)/ N_2 mixtures at total pressures of 0.35-28.0 atm (35.4-2830 kPa). Incident and reflected shocks. $[COF_2]$ monitored by i.r. emission at 5.25 μm. MODICA 1970 (1)	Reaction found to be in transition region between first and second order kinetics over entire pressure range. First order rate constants determined from Lindemann theory, no attempt made to determine second order constants. Ar and N_2 equally effective as third bodies. Author gives $k_1^\infty=6.1\times10^{11}\exp(-46\ 300/T)\ s^{-1}$ from data obtained. $COF_2 + M \rightarrow F + COF + M$ 1 Data re-analysed in (3) to give second order rate constant $k_1^0=3.3\times10^{17}\exp(-30\ 700/T)\ cm^3\ mol^{-1}\ s^{-1}$. Quoted by (3,4,7).
8.5×10^3		2615		
3.5×10^4		2795		
1.3×10^5		3010		
4.0×10^5		3195		
2.6×10^3	M=Ar	2650	Shock tube study. COF_2 (0.5-1.0%)/Ar mixtures at total pressures of 0.5-12 atm (50.6-1210 kPa). Incident and reflected shocks. $[COF_2]$ monitored by i.r. emission spectroscopy at 5.15 μm. WESTON and MATULA 1971 (4)	k_1^0 and k_1^∞ derived from same experimental data by Lindemann theory. A least squares fit to the data gives $k_1^\infty=1.3\times10^{11}\exp(-46\ 900/T)\ s^{-1}$. A series of calculations were made testing the ability of RRK theory to describe the system at various pressures. In all cases, choosing $E_1=D_{COF-F}$ produced an activation energy far too high to fit the experimental data. Quoted by (6, 7).
3.1×10^3		2710		
5.3×10^3		2760		
1.0×10^4		2840		
9.0×10^3		2895		
9.5×10^3		2965		
4.9×10^4		3020		
3.1×10^4		3130		
4.1×10^5		3215		
1.6×10^5		3265		
5.9×10^5		3445		
6.4×10^4		3590		

Discussion

Carbonyl fluoride is a product in many fluorocarbon combustion systems, and its decomposition kinetics are thus of importance in the understanding of these systems. All the experimental investigations to date have been carried out in shock tubes over the temperature range 2500–3500 K. Agreement on pressure dependence and activation energy is not particularly good. All studies have followed COF_2 decomposition, there being no direct evidence on the nature of the products or details of the reaction mechanism.

$$COF_2 + M \rightarrow COF + F + M \qquad (1)$$

2nd Order Rate Constant k_1°

The two studies of Matula et al. [4,7] show good agreement up to 3000 K, but increasing divergence above that temperature. Although the pressure ranges covered are similar, Gangloff et al. [7] found second order kinetics operating, while Weston and Matula [4] found the reaction to be in the transition region between first and second order kinetics. We suspect that below 10 atm the kinetics approximate more to second than first order, but that the first order contribution cannot be ignored.

The energy of activation is so much lower than the reaction endothermicity, more so than expected for a molecule of this complexity, that we make no recommendation for k_1°. It seems likely that the decomposition mechanism may be more complex than assumed. We have ignored completely the expression of Wagner [3] derived from data of Modica [1] at ~2 atm. This gives values of k_1° four orders of magnitude higher than the other two studies, and it is hard to see a reason for such a large discrepancy.

1st Order Rate Constant k_1^∞

Both determinations of k_1^∞ [1,4] are derived from a Lindemann treatment of data obtained over a wide pressure range (0.3–30 atm). As might be expected, the agreement in activation energies is good, although the results of Weston and Matula for k_1^∞ [4] are consistently about a factor of three lower than those of Modica [1]. In both cases, RRK theory was also applied to the results. Modica obtained a good fit with $s=7$ but claimed that any value of $s>5$ would enable a reasonable fit to be obtained. Weston and Matula used $s=6$ but at all pressures the apparent activation energy obtained was higher than that observed. In recent studies using RRK theory, s is determined by the statistical method of Benson et al. [2].

As under second order conditions, the activation energy seems too low, and until the mechanism of the reaction is confirmed we suggest that the kinetic data be used only to characterise the COF_2 disappearance.

References

[1] Modica, A. P., J. Phys. Chem. **74**, 1194 (1970).
[2] Golden, D. M., Solly, R. F., and Benson, S. W., J. Phys. Chem. **75**, 1333 (1971).
[3] Wagner, H. Gg., Proc. 8th Int. Shock Tube Symp. Paper 4 (1971).
[4] Weston, D. M., and Matula, R. A., Combustion Sci. Tech. **4**, 37 (1971).
[5] Keating, E. L., and Matula, R. A., Eastern States Section Combustion Inst. Fall Meeting (1973).
[6] Biordi, J. C., Lazzara, C. P., and Papp, J., U.S. Bureau of Mines Report No. RI8029 (1975).
[7] Gangloff, H. J., Milks, D., Maloney, K. L., Adams, T. N., and Matula, R. A., J. Chem. Phys. **63**, 4915 (1975).

Miscellaneous Reactions Involving F/C Species

A32 CO + F + M → COF + M

Fluorine atoms react slowly with carbon monoxide to give as final products COF_2 and CO_2. Appelman and Clyne [1] observed the reaction to be a slow third order process and assumed reaction 1 to be the rate determining stage.

$$CO + F + M \rightarrow COF + M; \qquad (1)$$

$$\Delta H^\circ_{298} = -139.93 \text{ kJ mol}^{-1} \ (-33.443 \text{ kcal mol}^{-1})$$

F atoms were produced by a discharge through $F_2(<5\%)/Ar$ or He mixtures at ~130 Pa pressure. CO was added downstream in the flow system so that [CO]>[F], and the reaction was followed mass spectrometrically. Only COF_2 and CO_2 were observed in the mass spectrometer, so [F] was determined by titration with Cl_2, observing the ClF yield. It was not possible to vary the total pressure sufficiently to demonstrate conclusively the existence of a third order reaction, but the results seemed generally consistent with that theory with $k_1(M=He)=1.2\times10^{16}$ cm^6 mol^{-2} s^{-1} and $k_1(M=Ar)=2.1\times10^{16}$ cm^6 mol^{-2} s^{-1} at 296 K.

Arutyunov et al. [2] followed F atoms by e.s.r. spectroscopy in a flow system. F atoms were produced in an $F_2(5\%)/He$ or N_2 discharge at total pressures of 66.7–400 Pa, with CO added downstream at 26.7–40 Pa pressure. O_2 was also added at ~3 Pa to remove COF radicals which the authors suspected might otherwise generate more F atoms through reaction 2.

$$COF + F_2 \rightarrow COF_2 + F \qquad (2)$$

$$COF + O_2 \rightarrow COFO_2 \qquad (3)$$

They obtained $k_1(M=He)=2.3\times10^{16}$ cm^6 mol^{-2} s^{-1} and $k_1(M=N_2)=2.5\times10^{16}$ cm^6 mol^{-2} s^{-1} at 293 K. The value of $k_1(M=He)$ is higher than Clyne's, where regeneration of F atoms was not considered. However, in the absence of further evidence as to the relative importance of reaction 2, we recommend the value $k_1(M=He)=2\times10^{16}$ cm^6 mol^{-2} s^{-1} at 295 K, with error limits of a factor of two.

References

[1] Appelman, E. H., and Clyne, M. A. A., JCS Faraday I **71**, 2072 (1975).
[2] Arutyunov, V. S., Buben, S. N., and Chaikin, A. M., Reaction Kinet. Cat. Letts. **3**, 205 (1975).

A33 CO + F_2 → COF + F

The reaction between carbon monoxide and fluorine was considered by Heras et al. [1,2] to be the rate determining step in the formation of the peroxide $(COF)_2O_2$.

$$CO + F_2 \rightarrow COF + F; \qquad (1)$$

$$\Delta H^\circ_{298} = 17.895 \text{ kJ mol}^{-1} (4.277 \text{ kcal mol}^{-1})$$

CO and F_2 react at a measurable rate at room temperature. Heras et al. studied this reaction in the presence of O_2, leading to the formation of monofluorocarbonyl peroxide, a reaction which is explosive above 323 K. They used a static system, with $CO(1.60\text{–}27.2 \text{ kPa})/F_2(1.31\text{–}21.0 \text{ kPa})/O_2(3.35\text{–}71.4 \text{ kPa})$ mixtures, O_2 always in excess, at total pressures of 8.00–98.2 kPa, over the temperature range 288–318 K. In some experiments N_2 or CO_2 at 53.3 kPa or $(COF)_2O_2$ at 6.67–13.3 kPa were added to look for any third body effect. The reaction was followed manometrically and the authors concluded that reaction 1 was rate determining, with no third body effects. They gave $k_1=4.7\times10^{11}\exp(-3000/T)$ cm^3 mol^{-1} s^{-1}.

The reaction has been investigated more recently by Kaprilova et al. [3], looking for the effect of excited COF and COF_2 in any subsequent chain reaction. A static system was again used, with F_2 (0.13–2.67 kPa)/CO(0.13–6.67 kPa) mixtures over the temperature range 273–350 K. The reaction was followed manometrically. In some cases O_2 was added, and the authors showed that this retarded the initial reaction rate, reaching a limiting value where $[O_2]=0.1[F_2]$. Working under these conditions, and allowing for O_2 removal by reaction 2, the authors obtained $k_1=1.9\times10^2$ cm^3 mol^{-1} s^{-1} at 294 K.

$$COF + O_2 \rightarrow COFO_2 \qquad (2)$$

An overall activation energy of 62.3 kJ mol^{-1} (14.9 kcal mol^{-1}) was obtained, but no attempt was made to determine E_1.

In view of the enormous discrepancy in the results, no recommendation is made for k_1.

References

[1] Heras, J. M., Arvia, A. J., Aymonino, P. J., and Schumacher, H.-J., Z. Phys. Chem. NF **28**, 250 (1961).

[2] Heras, J. M., Arvia, A. J., Aymonino, P. J., and Schumacher, H.-J., Ann. Assoc. Quim. Argentina **50**, 120 (1962).

[3] Kaprilova, G. A., Buben, S. N., and Chaikin, A. M., Kin. i Kat. **16**, 591 (1975). English translation, p. 508.

A34 $CO + FO \rightarrow CO_2 + F$

There has been only one direct determination of the rate constant k_1 for the reaction of CO and FO, by Henrici et al. [2].

$$CO + FO \rightarrow CO_2 + F; \qquad (1)$$

$$\Delta H^\circ_{298} = -312.87 \text{ kJ mol}^{-1}(-74.777 \text{ kcal mol}^{-1})$$

They followed the reaction in a shock tube, producing FO radicals by shocking F_2O(0.51–3.19%)/CO(0.76–2.85%)/Ar mixtures at total pressures of 2.43–27.6 kPa, over the temperature range 800–1400 K. Under these conditions CO was assumed not to dissociate. Two separate experiments were undertaken. In one, the reaction behind a single-pulse shock was followed mass-spectrometrically, while in the other F_2O decay and CO_2 production were followed behind incident shocks, the former by u.v. absorption at 220 nm, and the latter by i.r. emission at 4.3 μm. Combining the results from the two sets of experiments, and using their own value for reaction 2, determined in the same study, they gave $k_1 = 7.5 \times 10^{10}$ cm^3 mol^{-1} s^{-1} over the temperature range 900–1400 K, with an error of a factor of 2.

$$F_2O + M \rightarrow F + FO + M \qquad (2)$$

A slight positive temperature dependence was observed in the experimental data, but the authors set $E_1 = 0$ since $D_{OH} >> D_{OF}$ and reaction 3, has only a small activation energy.

$$CO + OH \rightarrow CO_2 + H \qquad (3)$$

Arvia et al. [1] investigated the CO/F_2O system in quartz and glass vessels, but due to complicated wall reactions were unable to isolate the effects of reaction 1, producing an overall expression $k = (k_1k_4k_5/k_6)^{1/2} = 1.5 \times 10^{15}$ exp($-12\,800/T$) cm^3 mol^{-1} s^{-1} over the temperature range 423–473 K, based on a reaction mechanism of reactions 1, 4, 5, 6.

$$COF + F_2O \rightarrow COF_2 + FO \qquad (4)$$

$$CO + F_2O \rightarrow COF + FO \qquad (5)$$

$$COF + FO \rightarrow COF_2 + O \qquad (6)$$

References

[1] Arvia, A. J., Aymonino, P. J., and Schumacher, H.-J., Z. Phys. Chem. NF **51**, 170 (1966).

[2] Henrici, H., Lin, M. C., and Bauer, S. H., J. Chem. Phys. **52**, 5834 (1970).

A35 $CF_4 + M \rightarrow CF_3 + F + M$

Carbon tetrafluoride shows negligible decomposition at temperatures up to about 1500 K. Kochubei and Moin [2] found that in the presence of H_2, no reaction occurred to compete with reaction 2 in a flow system where the reaction time was 5 seconds.

$$CF_4 + M \rightarrow CF_3 + F + M; \qquad (1)$$

$$\Delta H^\circ_{298} = 541.82 \text{ kJ mol}^{-1}(129.50 \text{ kcal mol}^{-1})$$

$$H + CF_4 \rightarrow CF_3 + HF \qquad (2)$$

Modica and Sillers [1] studied the decomposition in a shock tube between 2200–3000 K, and were able to observe both CF_3 and CF_2 radicals, indicating a chain reaction occurring at these temperatures. They shocked CF_4(0.5–1%)/Ar mixtures and also pure CF_4 at pressures of 91.8–365 kPa. [CF_2] was monitored behind incident shocks by u.v. absorption at 266 nm. They found that the CF_3 dissociation rate, determined earlier in the same study, was three times as fast as the rate of formation of CF_2, and concluded that reaction 1 was rate determining. The reaction was second order over the entire pressure range studied. A least squares fit to the data for M=Ar gave $k_1^\circ = 6.2 \times 10^{34} T^{-4.64}$ exp($-61\,610/T$) cm^3 mol^{-1} s^{-1}, with the collision efficiencies for Ar and CF_4 reported to be roughly equal. This expression can be stated in Arrhenius form as $k_1^\circ = 1.2 \times 10^{17}$ exp($-51\,000/T$) cm^3 mol^{-1} s^{-1}.

References

[1] Modica, A. P., and Sillers, S. J., J. Chem. Phys. **48**, 3283 (1968).

[2] Kochubei, V. F., and Moin, F. B., Kin. i. Kat. **10**, 492 (1969). English translation p. 405.

Miscellaneous Reactions Involving F/S Species

A36 $SF_6 + M \rightarrow SF_5 + F + M$

Sulphur hexafluoride, stable and inert at room temperature, decomposes under shock tube conditions according to reaction 1.

$$SF_6 + M \rightarrow SF_5 + F + M; \qquad (1)$$

thermodynamic data unavailable for SF_5.

This dissociation was first studied by Bott and Jacobs [2]. They shocked SF_6(<0.1%)/Ar mixtures at total pressures of 0.13–4.50 atm (13.3–455 kPa). [SF_6] decay was monitored by i.r. emission spectroscopy behind incident shocks at 10.6 μm. Some runs were made at pressures up to 30 atm (3.03 MPa) by monitoring the u.v. absorption spectrum of SF_4 behind reflected shocks at 235 nm, as background radiation obscured the i.r. measurements. SF_4 is produced by the instantaneous decay of SF_5 in reaction 2.

$$SF_5 + M \rightarrow SF_4 + F + M \qquad (2)$$

RRK theory was applied to the first order rate constants obtained to give $k_1^\infty = 8.9\times10^{12}\exp(-38\,600/T)$ s^{-1} at infinite pressure over the temperature range 1650–2050 K. The rate constants obtained were in fact in the fall-off region between first and second order. The value of E_1 obtained is in good agreement with the SF_5-F dissociation energy [1].

In a similar investigation, Modica [3] shocked SF_6(1%)/Ar mixtures over the pressure range 1–3 atm (101–303 kPa), following the reaction mass-spectrometrically behind reflected shocks, and also monitoring [SF_4] by u.v. absorption spectroscopy at 266 nm. He obtained a value for the SF_5-F bond dissociation energy of 273 kJ mol^{-1}(65.2 kcal mol^{-1}). Although this is somewhat lower than that obtained by Bott and Jacobs, he found it possible to fit their data with an RRK calculation to give $k_1^\infty = 5.0\times10^{11}\exp(-32\,800/T)$ s^{-1}.

In view of the lack of confirmatory data, no recommendation is made for k_1.

References

[1] Curran, R. K., J. Chem. Phys. **34**, 1069 (1961).
[2] Bott, J. F., and Jacobs, J. A., J. Chem. Phys. **50**, 3850 (1969).
[3] Modica, A. P., J. Phys. Chem. **77**, 2713 (1973).

A37 $SF_4 + M \rightarrow SF_3 + F + M$

Sulphur tetrafluoride is the chief product of SF_6 dissociation. When shock heated itself, it decomposes further according to reaction 1.

$$SF_4 + M \rightarrow SF_3 + F + M; \qquad (1)$$

thermodynamic data unavailable for SF_3.

Bott [2] shocked SF_4(<0.1%)/Ar mixtures at total pressures of 0.55–3.48 atm (55.5–351 kPa). [SF_4] decay was monitored behind the incident shocks by i.r. emission spectroscopy at 11.45 μm. The results were treated as in the earlier SF_6 study [1], and RRK theory applied to give $k_1^\infty = 4.3\times10^{13}\exp(-40\,000/T)$ s^{-1} over the temperature range 1650–1950 K. The pre-exponential factor obtained is less than the 10^{15} predicted by transition state theory, which leads to a larger pressure dependence than shown by the experimental data, all of which were measured in the fall-off region between first and second order.

References

[1] Bott, J. F., and Jacobs, T. A., J. Chem. Phys. **50**, 3850 (1969).
[2] Bott, J. F., J. Chem. Phys. **54**, 181 (1971).

A38 $SF_3 + M \rightarrow SF_2 + F + M$

In his study of SF_4 dissociation, Bott [1] made a number of runs at 2050 K, and noticed that i.r. emission at 12.6 μm, attributed to SF_3, was beginning to decrease with temperature increase so that the SF_3 production no longer balanced the decomposition of the SF_4. He proposed that SF_3 itself was dissociating according to reaction 1.

$$SF_3 + M \rightarrow SF_2 + F + M \qquad (1)$$

To study this decomposition he shocked SF_4(0.1–0.3%)/Ar mixtures at 0.3–2.7 atm (30.3–277 kPa) pressure, following the SF_3 decay as before by i.r. emission spectroscopy at 12.6 μm. The reaction was found to be occurring entirely in its second order region, there was no pressure dependence, and over the temperature range 2050–2840 K he obtained $k_1^\circ = 4.3\times10^{15}\exp(-36\,200/T)$ cm^3 mol^{-1} s^{-1}.

Reference

[1] Bott, J. F., J. Chem. Phys. **54**, 181 (1971).

A39 $SF_5 + SF_5 \rightarrow SF_6 + SF_4$

The disproportionation of SF_5 radicals is believed to be the rate controlling step in the pyrolysis of disulphur decafluoride [3].

$$SF_5 + SF_5 \rightarrow SF_6 + SF_4 \qquad (1)$$

The pyrolysis of S_2F_{10} was first investigated by Trost and McIntosh [1]. They used a static system with S_2F_{10} at 3.67–52.7 kPa pressure, and studied the pyrolysis over the temperature range 434–455 K, following the reaction manometrically. The reaction rate was found to depend both on pressure and the surface-to-volume ratio of the vessel. Above about 30 kPa, first order conditions prevailed, and extrapolating these results to a surface-to-volume ratio of 0 they obtained $k_{\text{overall}} = 3.0\times10^{20}\exp(-24\,800/T)$ min^{-1}, assuming instantaneous decomposition of S_2F_{10} to SF_5 radicals. This expression is incompatible with their data, and was re-expressed by Benson and Bott [3] as $k_{\text{overall}} = 3.0\times10^{20}\exp(-24\,800/T)$ s^{-1}.

These data have been reinterpreted by Benson and Bott [3] using thermodynamic data for the S_2F_{10}/SF_5 equilibrium provided by Wilkins [2]. This gives an overall rate $k_{\text{overall}} = 5.6\times10^{18}\exp(-23\,000/T)$ s^{-1} and hence k_1 (from $k_{\text{overall}}/K_2) = 6.8\times10^{12}\exp(-9400/T)$ cm^3 mol^{-1} s^{-1}.

$$S_2F_{10} \rightleftharpoons SF_5 + SF_5 \qquad (2)$$

Benson and Bott consider this A factor to be too high for this type of reaction. As a large error was possible in the original entry E_{overall} due to the small temperature range considered, they recalculated the data again on the basis of $A_1 = 3\times10^{11}$ cm^3 mol^{-1} s^{-1} to give $k_1 = 3.0\times10^{11}\exp(-8000/T)$ cm^3 mol^{-1} s^{-1}.

In view of the uncertainties, no recommendation is made for k_1.

References

[1] Trost, W. R., and McIntosh, R. L., Can. J. Chem. **29**, 508 (1951).
[2] Wilkins, R. L., Aerospace Corp. Report No. TR-0158 (3240-20)-19 (1968).
[3] Benson, S. W., and Bott, J., Int. J. Chem. Kinet **1**, 451 (1969).

A40 $F_2S_2O_6 + M \rightarrow FSO_3 + FSO_3 + M$

At room temperature, fluorosulphuryl peroxide decomposes slowly to give the FSO_3 radical. Schumacher et al. [1,2] have studied the decomposition in the presence of N_2F_4 and NO_2 over the temperature range 258–288 K, and found in both cases that reaction 1 was rate determining.

$$F_2S_2O_6 + M \rightarrow FSO_3 + FSO_3 + M \qquad (1)$$

In the first study [1] $F_2S_2O_6$(1.33–8.00 kPa) was mixed with N_2F_4 (2.67–53.3 kPa) in a static system. In some experiments N_2(66.7 kPa) or O_2(40.0 kPa) were added. The reaction was followed manometrically. It was found that the overall rate was independent of $[N_2F_4]$, and first order with respect to $[F_2S_2O_6]$. No evidence was found of any second order contribution at this pressure. The authors give the expression $k_1 = 4.0 \times 10^{15} \exp(-12\,100/T)$ s^{-1} over the temperature range 258–288 K, which gives $k_1 < k_2$ in this range, in agreement with the experimental results.

$$N_2F_4 + M \rightarrow NF_2 + NF_2 + M \qquad (2)$$

Similar results were obtained for mixtures of $F_2S_2O_6$(0.8–5%)/NO_2(1.7–30%)/N_2 or O_2 at pressures of 80 kPa [2]. This time they obtained $k_1 = 3.0 \times 10^{15} \exp(-12\,000/T)$ s^{-1} over the temperature range 263–288 K. We recommend the expression $k_1 = 3.5 \times 10^{15} \exp(-12\,000/T)$ s^{-1} over the temperature range 260–290 K, with error limits of ±50%.

References

[1] von Ellenreider, G., Castellano, E., and Schumacher, H. J., Z. Phys. Chem. NF **57**, 19 (1968).

[2] von Ellenrieder, G., and Schumacher, H. J., Z. Phys. Chem. NF **59**, 157 (1968).

A41 $F_2SO_3 + M \rightarrow F + FSO_3 + M$

Fluorine fluorosulphate is stable at room temperature, but its decomposition can be studied at 373 K under normal static system conditions. Schumacher et al. have studied the decomposition both in the presence of SO_3 [1] and Cl_2 [2] and in both cases found reaction 1 to be rate-determining.

$$F_2SO_3 + M \rightarrow FSO_3 + F + M; \qquad (1)$$

thermodynamic data unavailable for F_2SO_3, FSO_3.

In the first case, mixtures of F_2SO_3(0.93–80.0 kPa) and SO_3(0.53–9.33 kPa) were heated in a static system to 364–394 K with added $F_2S_2O_6$(0.07–10.6 kPa) or inert gases (13.3–66.7 kPa). The reaction was followed manometrically. The authors found that $[SO_3]$ had no influence on the reaction rate, which was first order in F_2SO_3. No second order contribution was observed, and the authors obtained $k_1 = 1.4 \times 10^{15} \exp(-16\,600/T)$ s^{-1}, for $M = F_2SO_3$. Of the added gases, $F_2S_2O_6$ (the main product) exerted a catalytic effect, but the others considerably retarded the rate, viz., $F_2SO_3{:}F_2S_2O_6{:}SO_3{:}O_2{:}N_2{:}Ar{:}He =$ 1:2.2:0.7:0.63:0.25:0.12:0.06.

A similar situation occurred in the presence of Cl_2. F_2SO_3 (1–100%)/Cl_2(1–80%) mixtures were used, with CO_2 added in some cases to a total pressure of 66.7 kPa. Reaction 1 was again rate determining and in its first order region, with $k_1 = 6.5 \times 10^{14} \exp(-16\,400/T)$ s^{-1} over the temperature range 363–383 K. This gives a difference of 20–25% between the two expressions. We recommend the expression $k_1 = 1.0 \times 10^{15} \exp(-16\,500/T)$ s^{-1} over the temperature range 360–390 K, with error limits of ±50%.

References

[1] Czarnowski, J., Castellano, E., and Schumacher, H. J., Z. Phys. Chem. NF **57**, 249 (1968).

[2] von Ellenrieder, G., and Schumacher, H. J., Z. Phys. Chem. NF **60**, 49 (1968).

A42 $F_2SO_2 + M \rightarrow SO_2F + F + M$

Sulphuryl difluoride is the chief product in the oxidation of SF_6. Its own pyrolysis has been studied in a shock tube by Wray et al. [1].

$$F_2SO_2 + M \rightarrow SO_2\,F + F + M; \qquad (1)$$

thermodynamic data unavailable for SO_2F.

They shocked SO_2F_2(0.1%)/Ar mixtures at total pressures of 4.00–80.0 kPa and studied the reaction behind incident shocks over the temperature range 1900–2300 K. $[SO_2F_2]$ decay was monitored by i.r. emission spectroscopy at 11.7 μm. The reaction was found to be pressure dependent over the entire pressure range, and an attempt was made to fit an RRK expression to the data. The best fit was obtained with the expression $k_1 = 1 \times 10^{13} \exp(-41\,000/T)$ s^{-1}.

Reference

[1] Wray, K. L., and Feldman, E. V., AVCO Report No. AERL-RR-348 (1970). AD 716 627.

A43 $F_2S_2O_6 + NO \rightarrow FSO_3 + FSO_3NO$

Fluorosulphuryl peroxide reacts with nitric oxide at a measurable rate at room temperature. Using a static system, von Ellenreider and Schumacher chose to study the reaction over the temperature range 238–258 K [1].

$$F_2S_2O_6 + NO \rightarrow FSO_3 + FSO_3NO; \qquad (1)$$

thermodynamic data unavailable for $F_2S_2O_6$.

$F_2S_2O_6$(3.85–67.2%)/NO mixtures were used at 0.27–2.00 kPa pressure. The reaction was followed manometrically. A white solid was formed, which the authors concluded was FSO_3NO. It was the only product, the FSO_3 radical recombining to give $F_2S_2O_6$. From these results, the authors concluded that reaction 1 was the rate-determining step, with $k_1 = 2.8 \times 10^{10} \exp(-2600/T)$ $cm^3\ mol^{-1}\ s^{-1}$.

Reference

[1] von Ellenrieder, G., and Schumacher, H. J., Z. Phys. Chem. NF **59**, 151 (1968).

A44 $S + F_2 \rightarrow SF + F$

Clyne and Townsend have studied the reactions of sulphur atoms with halogen molecules [2] in a flow system. The reaction with fluorine is slow compared to that of other halogens although not as slow as the corresponding reaction of O atoms [1].

$$S + F_2 \rightarrow SF + F; \qquad (1)$$

thermodynamic data unavailable for SF.

Clyne and Townsend produced S atoms by a discharge through $SO_2(\sim 0.1\%)$/Ar mixtures, adding $F_2(5\%)$/He mixtures downstream so that $[F_2] \sim 1000[S]$, total pressure $\leqslant 530$ Pa. [S] monitored by resonance fluorescence at 180 nm, or by titration with O_2, [O] being followed at 130 nm.

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

The other products of the SO_2 discharge, SO and O atoms, were kept at low concentrations by using $[SO_2] \ngtr 20$ mPa. At 298 K they obtained $k_1 = (1.8 \pm 0.5) \times 10^{11}$ cm^3 mol^{-1} s^{-1}.

References

[1] Bemand, P. P., Ph. D. Thesis, London University (1974).

[2] Clyne, M. A. A., and Townsend, L. W., Int. J. Chem. Kinet., Symposium Edition **1**, 73 (1975).

B1 $Cl_2 + M \rightarrow Cl + Cl + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	242.580	107.190	-36.900	-41.288
300	242.597	107.257	-36.638	-41.029
500	244.521	112.165	-19.686	-24.299
1000	248.622	117.960	- 6.826	-11.740
1500	251.676	120.449	- 2.472	- 7.562
2000	254.094	121.851	- 0.272	- 5.487
2500	256,103	122.750	1.060	- 4.252
3000	257.751	123.353	1.956	- 3.435
3500	259.006	123.746	2.598	- 2.860
4000	259.935	123.989	3.082	- 2.434
4500	260.588	124.144	3.460	- 2.107
5000	261.082	124.252	3.762	- 1.851

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.0056$
$\log(K_c/mol\,m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

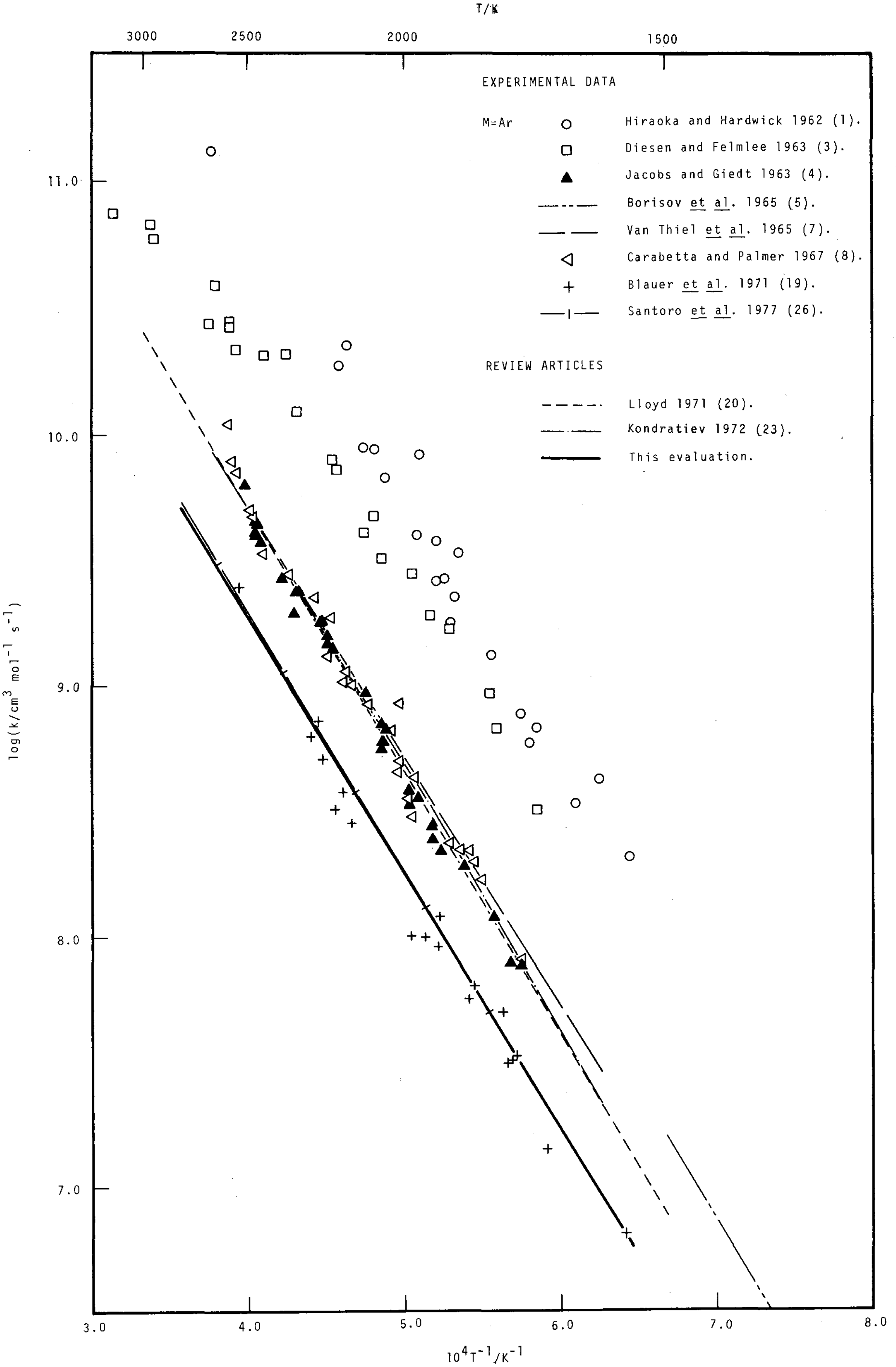
RECOMMENDED RATE CONSTANT

$k = 2.32 \times 10^{13} \exp(-23\ 630/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)
$= 3.85 \times 10^{-11} \exp(-23\ 630/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)
(k is defined by $-d[Cl_2]/dt = k[Cl_2][M]$)
Temperature Range: 1550-2800 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over quoted temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.366 \pm 0.18$
$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -10.414 \pm 0.18$
$E/J\ mol^{-1} = 196\ 470 \pm 23\ 930$
$E/cal\ mol^{-1} = 46\ 960 \pm 5\ 720$

$Cl_2 + M \rightarrow Cl + Cl + M$



$Cl_2 + M \rightarrow Cl + Cl + M$

EXPERIMENTAL DATA

	Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
(a)	3.4×10^{9}	M=Ar	1870	Shock tube study. Cl_2(4% (a), 20% (b), and 25% (c)) /Ar, and 25% Cl_2/He mixtures. Incident shock conditions. $[Cl_2]$ monitored by absorption ∿340-420 nm. HIRAOKA and HARDWICK 1962 (1)	Initial gradient of Cl_2 dissociation profile used to obtain k_1 $Cl_2 + M \rightarrow Cl + Cl + M$ 1 with correction made for enthalpy effect. Vibrational relaxation assumed sufficiently fast to be ignored. Authors fit results to form suggested by collision theory: $k_1 = AT^{\frac{1}{2}}\ (D/RT)^2\ \exp(-D/RT)$ $cm^3\ mol^{-1}\ s^{-1}$, where D is dissociation energy of Cl_2 at 0 K (238.7 $kJ\ mol^{-1}$; 57.06 $kcal\ mol^{-1}$). A given as 1.3×10^{12} $cm^3\ mol^{-1}\ s^{-1}$ $T^{-\frac{1}{2}}$ for mixtures (a), and 1.1×10^{12} for mixtures (b) and (c). TROE and WAGNER (11) report these data according to expression $k_1(M{=}Ar) = 1.7\times10^{15}\ \exp(-25\ 160/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (1600-2600 K).
	1.8×10^{9}		1890		
	8.4×10^{9}		1960		
	4.0×10^{9}		1970		
	6.8×10^{9}		2050		
	8.8×10^{9}		2080		
	9.0×10^{9}		2110		
	2.3×10^{10}		2160		
(b)	4.2×10^{8}		1600		
	7.7×10^{8}		1740		
	2.3×10^{9}		1880		
	2.7×10^{9}		1900		
	2.6×10^{9}		1920		
	3.8×10^{9}		1920		
	1.9×10^{10}		2180		
(c)	2.1×10^{8}		1550		
	3.4×10^{8}		1640		
	6.9×10^{8}		1710		
	5.9×10^{8}		1720		
	1.3×10^{9}		1800		
	1.3×10^{11}		2650		
	3.2×10^{8}	M=Ar	1710	Shock tube study. Cl_2/Kr (0.5%)/Ar mixtures behind reflected shocks. Total pressures 82-388 mm Hg (10.9-51.7 kPa). Dissociation followed by t.o.f. mass spectrometry. DIESEN and FELMLEE 1963 (3)	k_1 determined from initial slope of Cl_2 decay. Boundary layer effects considered to give possible systematic error of a factor 2. Authors give apparent activation energy of least-squares fit to their data as 171.5 $kJ\ mol^{-1}$ (41 $kcal\ mol^{-1}$). TROE and WAGNER (11) fit expression $k_1\ (M{=}Ar) = 8.7\times10^{13}\ \exp\{-(20\ 630\pm1010)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ (1700-2300 K) to these data.
	6.7×10^{8}		1790		
	9.2×10^{8}		1805		
	1.7×10^{9}		1890		
	1.9×10^{9}		1940		
	2.8×10^{9}		1980		
	3.2×10^{9}		2060		
	4.7×10^{9}		2085		
	4.1×10^{9} (2 pts.)		2110		
	7.3×10^{9}		2190		
	8.0×10^{9}		2205		
	1.24×10^{10}		2320		
	2.1×10^{10}		2360		
	2.1×10^{10}		2440		
	2.2×10^{10}		2550		
	2.7×10^{10}		2575		
	2.9×10^{10}		2575		
	3.9×10^{10}		2640		
	2.8×10^{10}		2670		
	6.0×10^{10}		2940		
	6.8×10^{10}		2960		
	7.5×10^{10}		3190		
(a)	7.59×10^{7}	M=Ar	1738	Shock tube study. Cl_2 (2% (a) and 4% (b))/Ar mixtures behind incident shocks. Cl_2 absorption followed at 364 nm. JACOBS and GIEDT 1963 (4)	Temperature assigned by authors to mixtures (a) given as $(3T_{2,0}-T_{2,eq})/4$, and to mixtures (b) $(7T_{2,0}-T_{2,eq})/8$, where $T_{2,0}$ and $T_{2,eq}$ are the initial and equilibrium post-shock temperatures, respectively, and differ by $\ngtr$100 K. Values of k_1 $Cl_2 + M \rightarrow Cl + Cl + M$ 1 obtained from slope of absorption profiles. Authors fit least-squares expressions $k_1(M{=}Ar) = 8.9\times10^{13}\exp(-24\ 310/T)$ $cm^3\ mol^{-1}\ s^{-1}$ and $8.5\times10^{13}\exp(-24\ 510/T)$
	1.21×10^{8}		1794		
	1.92×10^{8}		1860		
	2.45×10^{8}		1929		
	3.56×10^{8}		1964		
	3.81×10^{8}		1989		
	6.59×10^{8}		2049		
	5.89×10^{8}		2061		
	6.93×10^{8}		2061		
	1.49×10^{9}		2217		
	1.82×10^{9}		2238		
	1.80×10^{9}		2241		
	2.42×10^{9}		2310		
	2.36×10^{9}		2324		
	4.47×10^{9}		2469		
	4.06×10^{9}		2472		
	4.53×10^{9}		2475		
	6.45×10^{9}		2513		
(b)	7.82×10^{7}		1765		
	2.19×10^{8}		1912		

$Cl_2 + M \rightarrow Cl + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.74×10^{8} M=Ar	1936	JACOBS and GIEDT 1963 (4) continued.	$cm^3\ mol^{-1}\ s^{-1}$ to mixtures (a) and (b). Statistical error quoted as ±6%. Authors ascribe variation between two sets of data to errors in temperature assignment. If activation energy set as bond dissociation energy, classical form of $k_1(M{=}Ar)$ given (for mixtures (a)) as $3.13\times10^{12}(28\ 720/T)^{2.087}\exp(-28\ 720/T)\ cm^3\ mol^{-1}\ s^{-1}$. Used by (10,13,15,16 and 18). $k_1(M{=}Cl)=k_1(M{=}Cl_2)=k_1(M{=}Ar)$ estimated by JACOBS, COHEN and GIEDT (10), but in later study (13) they found $k_1(M{=}Cl)=10k_1(M{=}Ar)$, for 3500-5200 K. Used by (15 and 16). Simple Arrhenius expression for mixtures (a) used by (14 and 22).
3.40×10^{8}	1989		
5.62×10^{8}	2060		
9.40×10^{8}	2107		
1.38×10^{9}	2205		
1.55×10^{9}	2221		
1.94×10^{9}	2330		
2.72×10^{9}	2376		
3.79×10^{9}	2452		
4.12×10^{9}	2467		
	600-1500	Shock tube study. $Cl_2/CH_4/Ar$ mixtures, with CH_4/Cl_2 ratios 1 and 3.6. Reflected shock region, pressures 1-3 atm (101.3-304 kPa). Experiments also performed by expanding CH_4/Cl_2 mixtures into evacuated vessel. Ignition delay times determined from pressure measurements and emission from reaction. BORISOV, KOGARKO and SKACHKOV 1965 (5)	From variation of ignition delays with temperature, k_1 $Cl_2 + M \rightarrow Cl + Cl + M$ 1 obtained, using k_2 and k_3 from (2) $Cl + CH_4 \rightarrow CH_3 + HCl$ 2 $Cl_2 + CH_3 \rightarrow CH_3Cl + Cl$ 3 Least squares fit to data given as $k_1(M{=}CH_4{+}Cl_2)=1.10\times10^{14}\exp(-23\ 650/T)\ cm^3\ mol^{-1}\ s^{-1}$.
$4.57\times10^{13}\exp(-22\ 870/T)$ M=Ar	1600-2600	Shock tube study. Cl_2(5% and 10%)/Ar and Cl_2(5%)/CO_2(1%)/Ar mixtures. Incident shocks. Cl_2 absorption followed at 365 and 385 nm, and two-body recombination emission followed at 385, 410, 460 and 510 nm. VAN, THIEL, SEERY and BRITTON 1965 (7)	Vibrational relaxation of Cl_2 assumed complete. Corrections made for emission. Expression given here is for 5% Cl_2 mixtures, believed by authors to be best for $k_1(M{=}Ar)$. Expression for 10% Cl_2 mixtures given as $7.94\times10^{12}\exp(-17\ 990/T)\ cm^3\ mol^{-1}\ s^{-1}$. Although Cl_2 shown qualitatively to be more efficient than Ar as third body, large uncertainties in data did not allow authors to separate $k_1(M{=}Ar)$ from $k_1(M{=}Cl_2)$. LLOYD (20) presents individual data points after enlarging the authors' original graph.

$Cl_2 + M \rightarrow Cl + Cl + M$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
(a)	8.13×10^7	M=Ar	1738	Shock tube study. (a) Cl_2/Ar mixtures, in ratios 1:2 and 1:5, and (b) $Cl_2/Ar/O_2$ mixture in ratios 30:6:1. Emission at 500 nm used to monitor reaction. CARABETTA and PALMER 1967 (8)	Values of k_1 obtained from time taken for emission to reach ¼ of its equilibrium value. Beyond this time, corrections for reverse reaction -1 $Cl + Cl + M \rightarrow Cl_2 + M$ -1 necessary. Effective temperature T defined by $(3T_{2,0}-T_{2,eq})/4$ (see 4). Corrections for effects of changing density with time also made. Addition of oxygen (mixtures (b) found to have no effect. Authors gave expression to fit these data as $k_1(M{=}Ar) = 8.71\times10^{13}\exp(-24\ 310/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Used by (17). WAGNER (21) gives empirical expression $k_1(M{=}Ar) = 1.75\times10^{22}\ T^{-2.2}\exp(-28\ 680/T)$ $cm^3\ mol^{-1}s^{-1}$ as fit to these data.
	1.66×10^8		1819		
	1.95×10^8		1834		
	2.19×10^8		1866		
	2.34×10^8		1892		
	4.27×10^8		1974		
	3.02×10^8		1982		
	3.63×10^8		1989		
	8.51×10^8		2012		
	5.01×10^8		2014		
	4.57×10^8		2016		
	6.61×10^8		2032		
	8.32×10^8		2095		
	$1.0\ \times10^9$		2144		
	1.15×10^9		2162		
	1.05×10^9		2170		
	1.86×10^9		2207		
	1.32×10^9		2212		
	2.24×10^9		2256		
	3.39×10^9		2440		
	4.68×10^9		2473		
	5.01×10^9		2488		
	7.24×10^9		2547		
	1.10×10^{10}		2582		
(b)	2.19×10^8		1847		
	6.92×10^8		2109		
	2.75×10^9		2350		
	7.76×10^9		2566		
	6.5×10^6	M=Ar	1559	Shock tube study. 2%Cl_2/Ar mixtures, $[Cl_2]$ 7.9×10^{-7} to 2.88×10^{-6} mol cm^{-3} and [Ar] 3.9×10^{-5} to 1.41×10^{-4} mol cm^{-3}, and 2%Cl_2/2%HF/Ar mixtures. Incident shock conditions. Two-body emission followed at 500 nm. BLAUER, SOLOMON and ENGLEMAN 1971 (19)	k_1 determined from initial slopes of emission profiles, $Cl_2 + M \rightarrow Cl + Cl + M$ 1 the intensity being $\propto [Cl]^2$. Corrections made for density changes during reaction. Authors give expression $k_1(M{=}Ar) = 2.0\times10^{13}\exp\{-(23\ 380\pm760)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ as fit to these data.
	1.4×10^7		1692		
	3.3×10^7		1750		
	3.2×10^7		1759		
	3.1×10^7		1768		
	4.9×10^7		1776		
	6.3×10^7		1834		
	5.5×10^7		1847		
	1.2×10^8		1916		
	9.1×10^7		1921		
	9.9×10^7		1951		
	1.0×10^8		1986		
	2.8×10^8		2145		
	3.8×10^8		2176		
	3.2×10^8		2196		
	5.1×10^8		2236		
	7.2×10^8		2248		
	6.2×10^8		2274		
	2.45×10^9		2540		
	$(2.66\pm0.26)\times10^{13}\exp\{-(23\ 850\pm250)/T\}$ M=Ar		1700-2800	Shock tube study. Cl_2(5-20%)/Ar and Cl_2(20%)/He mixtures behind incident shocks. Reaction followed by laser schlieren densitometry. SANTORO, DIEBOLD and GOLDSMITH 1977 (26)	Dissociation rate constants derived from initial density gradients behind shock front. Computer fitting of data from various Cl_2/Ar mixtures showed single activation energy E_1 valid for both $k_1(M{=}Ar)$ and $k_1(M{=}Cl_2)$. Using this expression for $k_1(M{=}Cl_2)$, data from Cl_2/He mixtures gave $k_1(M{=}He)$.
	$(1.83\pm0.2)\times10^{14}\exp\{-(23\ 850\pm250)/T\}$ M=Cl_2		1700-2800		
	$(3.96^{+2.3}_{-1.4})\times10^{13}\exp\{-(24\ 460\pm1010)/T\}$ M=He		1700-2800		

$Cl_2 + M \rightarrow Cl + Cl + M$

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$8.71\times10^{13}\exp\{-(24\ 400\pm1000)/T\}$ M=Ar	1500-3000	Evaluation. Least-squares fits made for all current data (1,3,4,7,8). LLOYD 1971 (20)	Expression essentially as for JACOBS and GIEDT (4), with "more realistic" error limits of factor 2. Used by (25).
$7.24\times10^{24}T^{-3.5}\exp(-28\ 680/T)$	195-500	Review. Data of CARABETTA and PALMER (8) given as representative, and data for k_{-1} of CLYNE and STEDMAN (12) converted to give this expression. WAGNER 1971 (21) and TROE and WAGNER 1973 (24)	Expression not plotted.
$2.14\times10^{20}(1-\exp(-814/T))T^{-3/2}$ $\exp(-28\ 710/T)$ M=Ar	1600-2650	Evaluation. Least-squares fit to data of (4,9 and 8). KONDRATIEV 1972 (23)	Author notes that extrapolation to 298 K and conversion to k_{-1} $Cl + Cl + M \rightarrow Cl_2 + M \quad -1$ gives $k_{-1}=10^{16}\ cm^6\ mol^{-2}\ s^{-1}$, which compares well with measured values (6,9) of $4.27\times10^{15}\ cm^6\ mol^{-2}\ s^{-1}$.

Discussion

All of the data for the rate of dissociation of molecular chlorine

$$Cl_2 + M \rightarrow Cl + Cl + M \qquad (1)$$

have been obtained in shock tube systems, mostly using Ar as diluent. Various methods were used to follow the reaction: absorption spectrometry [1,4,7], t.o.f. mass spectrometry [3], two-body Cl recombination emission [5,8,19], and laser Schlieren densitometry [26].

The data of both Hiraoka and Hardwick [1] and Diesen and Felmlee [3] are an order of magnitude higher than the bulk of the data [4,7, and 8]. The error in the data of [1] probably arises from their failure to allow for Cl recombination emissions in the wavelength region of their Cl_2 absorption measurements: Van Thiel et al. [7] monitored Cl_2 absorption in the same region and made corrections for such emissions. The reflected shock techniques of Diesen and Felmlee [3], giving rise to boundary layer effects and subsequent contamination of their gas samples, are probably the cause of the high values obtained in this work. We have not given any weight to the data of [1 or 3].

The data of Borisov et al. [5], when extrapolated to ~3000 K, are also higher than those of [4,7 and 8], though only by ~80%. Nevertheless, as their results are the only experimental data below 1500 K, and as they were dependent upon k_2 and k_3

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (2)$$

$$Cl_2 + CH_3 \rightarrow CH_3Cl + Cl \qquad (3)$$

for which we have no data above 1000 K, we have not used them in this evaluation.

The data of Jacobs and Giedt [4], Van Thiel et al. [7], and Carabetta and Palmer [8] are in good agreement, and there is no systematic variation between the data of [8], in which no indication of their Cl_2 purity was given, and of [4 and 7], in which purified Cl_2 was used. Neither does there appear any large difference due to effects of the reverse reaction, despite [4 and 8] having kept low the degree of dissociation to reduce such effects, whereas [7] makes no specific mention of any similar precautions.

However, none of these authors have separated the effects of Cl_2 and Ar as collision partners. Jacobs et al. [10] estimated $k_1(M=Ar)=k_1(M=Cl_2)$ for the data of [4], whereas Van Thiel et al. [7] found Cl_2 qualitatively more efficient a third body than Ar. The recent work of Santoro et al. [26] gave $k_1(M=Cl_2)=6.9\ k_1(M=Ar)$, which is in line with the relative third body efficiencies of the other halogen molecules F_2 and Br_2 in their respective dissociations (see sections A1 and C1). Santoro et al. [26] showed their results from 20% Cl_2/Ar mixtures to be in good agreement with the data of [4,7 and 8]. With the Cl_2/Ar effectiveness ratio as high as 6.9, this means that Cl_2 must be diluted to ~2% in Ar before $k_1(M=Ar)$ approaches 90% of the overall dissociation rate constant, and the study by Blauer et al. [19] was indeed carried out with 2% Cl_2/Ar mixtures giving data in excellent agreement with [26].

We have therefore based our recommendation on the data of [19 and 26]. Lloyd [20] based his recommendation on the earlier work [4,7,8], using a least-squares fit, but his tabulation of the data of [8] appears to be incorrect: his values of log k_1 are all too high by 0.09, and this will have slightly affected the Arrhenius parameters he has obtained. Our recommended expression is

$$k_1(\mathrm{M=Ar}) = 2.32\times10^{13}\ \exp(-23\ 630/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

over the temperature range 1550–2800 K. Error limits of ±50% over this range must be taken into account. As Santoro et al. [26] have made the only separation between the effects of Cl_2, Ar and He, we make no recommendation for $k_1(\mathrm{M=Cl_2})$ or $k_1(\mathrm{M=He})$, but note that their value of 6.9 for $k_1(\mathrm{M=Cl_2})/k_1(\mathrm{M=Ar})$ gives good results for mixtures with high (~20%) Cl_2 concentrations in Ar, when compared with the data of [4,7 and 8].

The activation energy of this expression is notably lower than $\Delta H°$. This may be an artefact arising from the fitting of a simple Arrhenius expression to the data. The pre-exponential term may be strongly temperature dependent, although this is not obvious from the available data. There is no evidence to suggest that, alternatively, the reaction mechanism is more complex than assumed.

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B2 $Cl + Cl + M \rightarrow Cl_2 + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-242.580	-107.190	36.900	41.288
300	-242.597	-107.257	36.638	41.029
500	-244.521	-112.165	19.686	24.299
1000	-248.622	-117.960	6.826	11.740
1500	-251.676	-120.449	2.472	7.562
2000	-254.094	-121.851	0.272	5.487
2500	-256.103	-122.750	- 1.060	4.252
3000	-257.751	-123.353	- 1.956	3.435
3500	-259.006	-123.746	- 2.598	2.860
4000	-259.935	-123.989	- 3.082	2.434
4500	-260.588	-124.144	- 3.460	2.107
5000	-261.082	-124.252	- 3.762	1.851

SI Units: $\log(K_p/\text{Pa}^{-1}) = \log(K_p/\text{atm}^{-1}) - 5.0056$

$\log(K_c/\text{m}^3\ \text{mol}^{-1}) = \log(K_c/\text{cm}^3\ \text{mol}^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 2.23 \times 10^{14} \exp(906/T)$ cm^6 mol^{-2} s^{-1} (M=Ar)

$= 6.15 \times 10^{-34} \exp(906/T)$ cm^6 molecule^{-2} s^{-1} (M=Ar)

(k is defined by $-d[Cl]/dt = 2k[Cl]^2[M]$)

Temperature Range: 195-520 K

Suggested Error Limits for Calculated Rate Constant: ±40% over quoted temperature range.

Note: a recommendation for $k(M=Cl_2)$ is given in the Discussion.

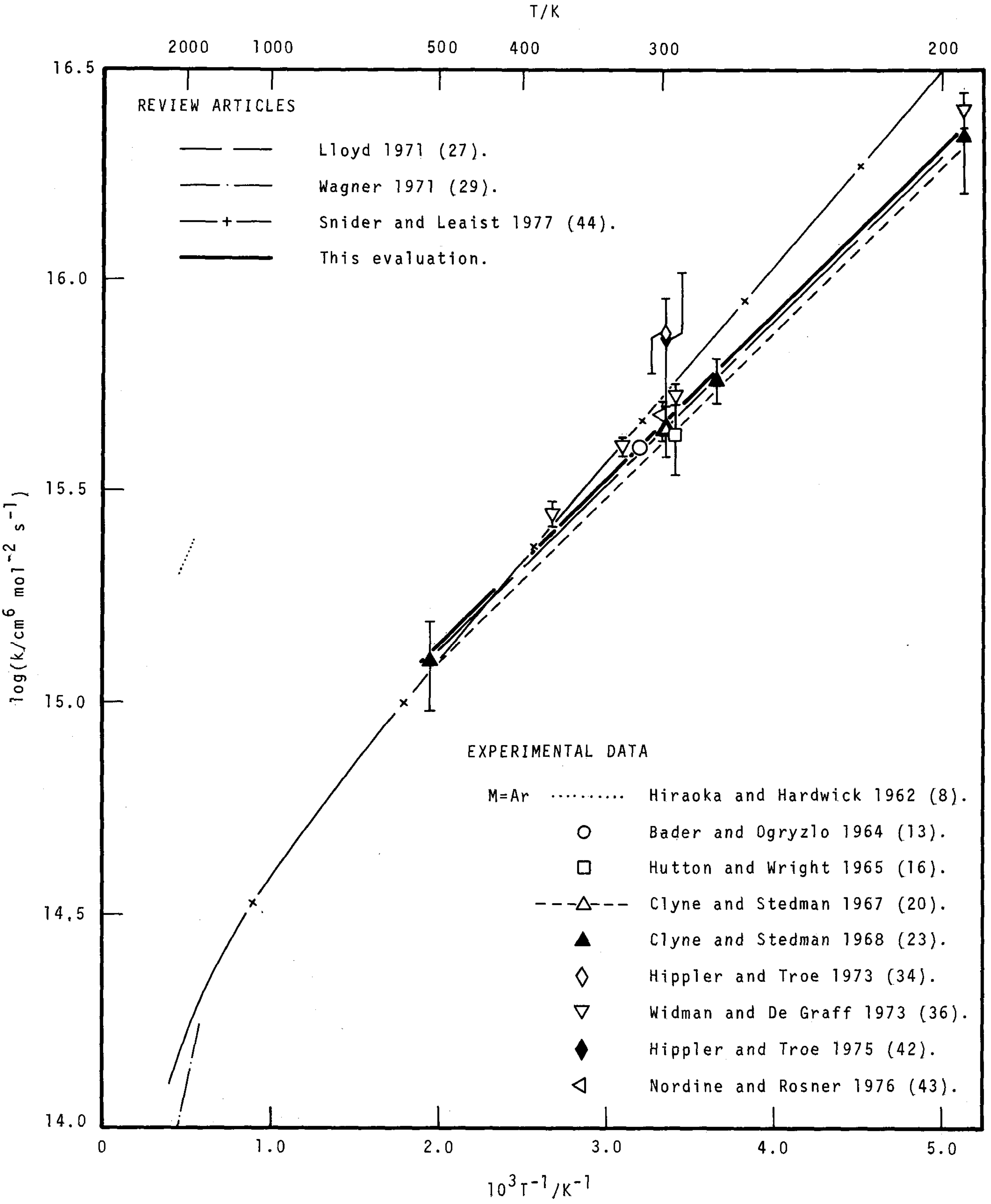
Rate Parameters: $\log(A/\text{cm}^6\ \text{mol}^{-2}\ \text{s}^{-1}) = 14.35 \pm 0.15$

$\log(A/\text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}) = -33.2 \pm 0.15$

$E/\text{J mol}^{-1} = -7530 \pm 1840$

$E/\text{cal mol}^{-1} = -1800 \pm 440$

$Cl + Cl + M \rightarrow Cl_2 + M$

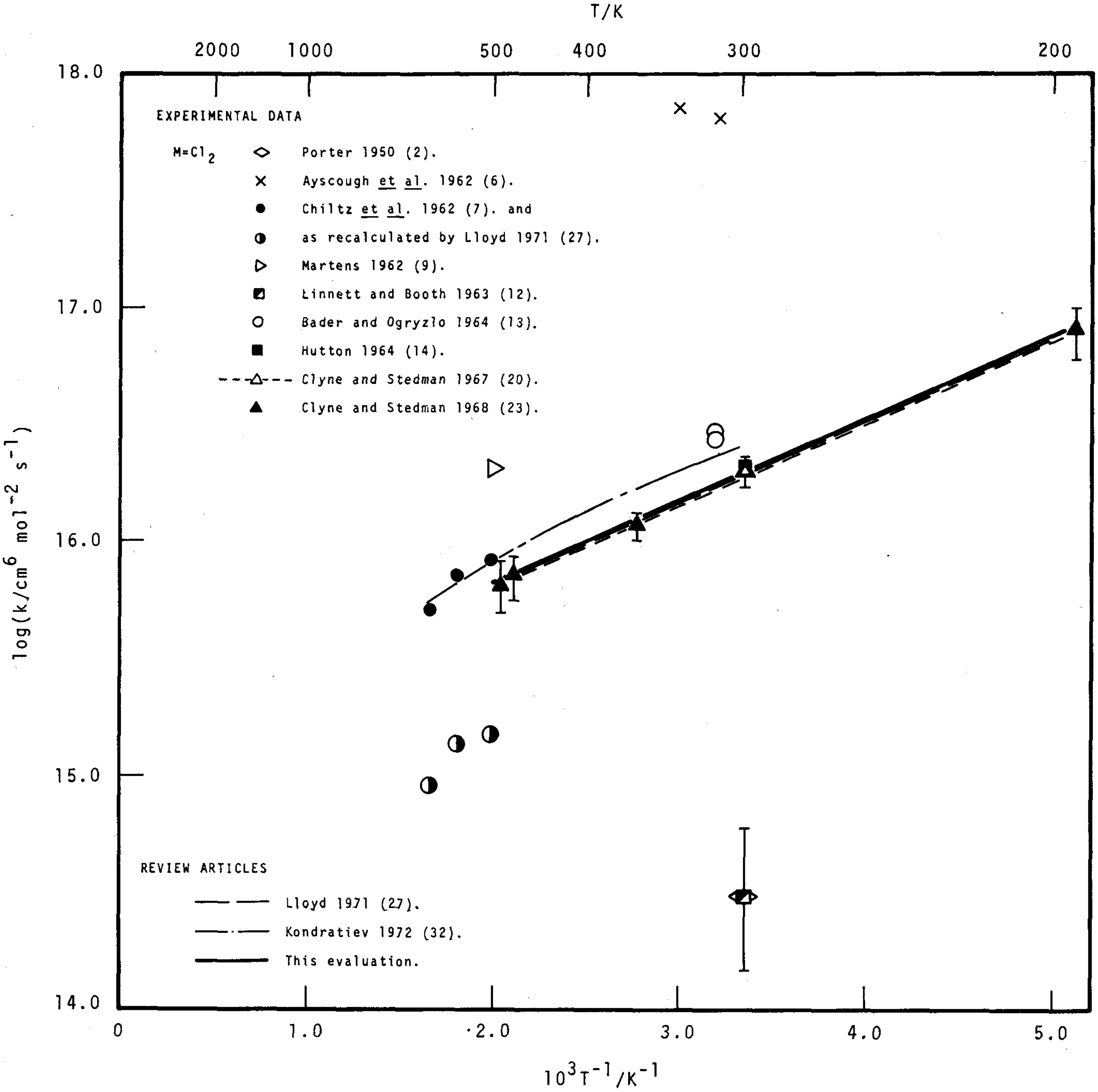


$Cl + Cl + M \rightarrow Cl_2 + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$\sim 3\times 10^{14}$ $M=Cl_2$	298	Flash photolysis study. Cl_2 at 10 mm Hg (1.3 kPa). Analysis by spectrographic means. PORTER 1950 (2)	Author estimates original decomposition of Cl_2 at 50%, and visual analysis of spectra gave half-life of Cl atoms as 3×10^{-2}s. Using the quoted $[Cl_2]$ pressure we have converted this to give k_1. Used by (5). $Cl + Cl + M \rightarrow Cl_2 + M$ 1
	293	Flash photolysis study. Cl_2(5 and 10 *mm* Hg; 0.65 and 1.3 kPa)/O_2(10-600 mm Hg; 1.3-80 kPa)/N_2 (0-600 mm Hg; 80 kPa) mixtures at total pressures 55-610 mm Hg (7.3-81.3 kPa). ClO followed by analysis of spectra in region 280 *nm*. PORTER and WRIGHT 1953 (4)	Corrections made for interference of Cl_2 in absorption by ClO. Temperature rise during reaction negligibly small under authors' conditions. Mechanism of ClO formation believed to be $Cl + Cl + O_2 \rightarrow 2ClO$ 2 $Cl + Cl + M \rightarrow Cl_2 + M$ 1 Rates of removal of Cl atoms by O_2 and by N_2 found to be in ratio 46:1, i.e. $(k_1(M=O_2)+k_2)/k_1(M=N_2)=46$. Authors included possibility that reaction 2 proceeded via $Cl + O_2 \rightarrow ClOO$ 3' $ClOO + Cl \rightarrow 2ClO$ 4 CLYNE and COXON (22) expressed this ratio as $K_3k_5/k_1(M=N_2) = 46$ $Cl + O_2 + M \rightleftharpoons ClOO + M$ 3,-3 $ClOO + Cl \rightarrow Cl_2 + O_2$ 5 and used $k_1(M=N_2)\sim 5\times 10^{15}$ $cm^6\ mol^{-2}\ s^{-1}$ at 300 K, without quoting source. JOHNSTON <u>et</u> <u>al</u>. (24) allowed for both reactions 4 and 5 and quoted $K_3(k_4+k_5)=46\ k_1(M=N_2)$.
$(6.50\pm 0.4)\times 10^{17}$ $(7.18\pm 0.4)\times 10^{17}$ } $M=Cl_2$	312.5 335.1	Static system. Cl_2(400 mm Hg; 53.3 kPa)/<u>cis</u>-$(CHCl)_2$(2.0 mm Hg; 267 Pa) photolysed with and without rotating sector (on/off ratio 1:4). Reaction monitored by pressure changes. AYSCOUGH, COCKER, DAINTON and HIRST 1962 (6)	*Wall termination by reaction w* $Cl + wall \rightarrow \frac{1}{2}Cl_2$ w reduced by high pressure of Cl_2 and adjustments to light beam *intensity. Values dependent upon* estimates for reaction volume, and authors consider uncertainties in k_1 to be underestimated.

$Cl + Cl + M \rightarrow Cl_2 + M$



$Cl + Cl + M \rightarrow Cl_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	500-600	Static system. CO(17.9-299.8 mm Hg; 2.39-40 kPa)/Cl_2(188.3-503.4 mm Hg; 25.1-67.1 kPa) mixtures, $[Cl_2]/[CO]$ ratios 0.96-19.72, irradiated. Several experiments performed with Ar ($[Ar]/[Cl_2]=1$), SF_6 ($[SF_6]/[Cl_2]=1$), and CCl_4 ($[CCl_4]/[Cl_2]= 0.22, 0.5$). Incident light intensity and pressure monitored, and $[Cl_2]$ measured by absorption at 366 nm. CHILTZ, ECKLING, GOLDFINGER, HUYBRECHTS, MARTENS and SIMOENS 1962 (7)	From initial slope of pressure variation authors obtained ratios $k_7(k_6/k_{-6}k_8)^{\frac{1}{2}}$ and k_1k_{-6}/k_6k_8 $Cl + CO \rightleftharpoons COCl$ 6,-6 $Cl_2 + COCl \rightarrow COCl_2 + Cl$ 7 $Cl + Cl + M \rightarrow Cl_2 + M$ 1 $Cl + COCl \rightarrow Cl_2 + CO$ 8 Values of $k_7(K_6/k_8)^{\frac{1}{2}}$ found within 50% of those of (1) but almost an order of magnitude below those of (3). Authors averaged values of k_8/K_6 of both (1 and 3), giving $k_1(M=Cl_2) = 7.94\times10^{15}$ (502.4 K), 7.08×10^{15} (552.3 K), and 5.01×10^{15} $cm^6\ mol^{-2}\ s^{-1}$ (598.9 K), all within error limits of a factor 3.2 in each direction. Mixtures with Ar and SF_6 showed $k_1(M=Ar, SF_6)<0.2\ k_1(M=Cl_2)$, and with CCl_4 that $k_1(M=CCl_4)\sim6.5\ k_1(M=Cl_2)$. LLOYD (27) used k_8/K_6 from (17) to give $k_1(M=Cl_2)=1.5\times10^{15}$, 1.35×10^{15} and 8.91×10^{14} $cm^6\ mol^{-2}\ s^{-1}$ at 502.4, 552.3 and 598.9 K, respectively.
		Shock tube study. Cl_2(4%, 20% and 25%)/Ar mixtures behind incident shocks. Absorption of Cl_2 420-340 nm used to follow reaction. HIRAOKA and HARDWICK 1962 (8)	Using dissociation data (see this Volume, section B1) from 4%Cl_2/Ar mixture, authors obtain expression $k_1(M=Ar)=3.6\times10^{12}(D/RT)^2(1-\exp(-813/T))^{-1}$ $cm^6\ mol^{-2}\ s^{-1}$, over the range 1870-2160 K, where D is Cl_2 dissociation energy at 0 K. Taking D as 238.7 kJ mol^{-1} (57.06 kcal mol^{-1}) authors give $k_1(M=Ar) = 2.5\times10^{15}$ $cm^6\ mol^{-2}\ s^{-1}$ at 1600 K.
$\sim2\times10^{16}$ $M=Cl_2$	$\sim$500	No details given. Measurement made in photochlorination of CO. MARTENS 1962 (9)	
	2550	Shock tube study. 1%Cl_2/Ar mixtures dissociated behind reflected shocks, then subjected to rapid expansion. Cl_2 absorption monitored. JACOBS, HARTUNIAN, GIEDT and WILKINS 1963 (11)	By comparing experimental data with theoretically computed profiles, using temperature dependence for k_1 $Cl + Cl + M \rightarrow Cl_2 + M$ 1 of (8), $k_1(M=Ar)$ found to be $<10^{14}$ $cm^6\ mol^{-2}\ s^{-1}$. Authors considered experiments only preliminary and gave no quantitative data.

$Cl + Cl + M \rightarrow Cl_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$(1.5-6)\times10^{14}$	$M=Cl_2$	298	Discharge flow system. Cl_2/Ar mixtures at total pressures 0.24-3 mm Hg (32-400 Pa). Cl atom decay followed by thermocouple probe. Reaction tube H_3BO_3 coated. LINNETT and BOOTH 1963 (12)	Authors assumed values for degree of Cl_2 dissociation in discharge, believed to be correct within a factor 2. BADER and OGRYZLO (13) consider these values incorrect by an order of magnitude. LLOYD (27) disregards this result.
4.0×10^{15}	M=Ar	313	Flow system. No details given. $[Cl_2]$ monitored by isothermal Ni wire calorimeter. Flow cell coated with H_3PO_4. BADER and OGRYZLO 1964 (13)	Surface recombination eliminated by extrapolation to zero pressure Second of two values for $k_1(M=Cl_2)$ is from later series of experiments than other three measurements, and is average of 10 determinations. Although authors' definition of k_1 specifically agrees with ours (see Discussion), values halved by (14 and 16) for comparison with their own data, and LLOYD (27) quotes a private communication of 1970 with OGRYZLO that these values should be half those quoted. $k_1(M=CO_2)=10^{16}\ cm^6\ mol^{-2}\ s^{-1}$ attributed to this work by (28 and 41). Value of $10^{15}\ cm^6\ mol^{-2}\ s^{-1}$ used by (30) for undefined M.
3.0×10^{15}	M=He	313		
2.7×10^{16}	$M=Cl_2$	313		
2.88×10^{16}		313		
2.04×10^{16}	$M=Cl_2$	298	Discharge flow system. Cl_2 dissociated by microwave discharge. Total pressures 0.33-2.03 mm Hg (44-270.6 Pa). [Cl] determined by titration with NOCl, and relative concentrations by monitoring intensity of red glow. H_2SO_4 coated vessel. HUTTON 1964 (14)	Low pressure experiments enabled k_w to be determined $Cl + wall \rightarrow \frac{1}{2}Cl_2$ w in order to allow for this effect. Used by (33).
$(4.25\pm0.8)\times10^{15}$	M=Ar	293	Discharge flow system. Cl_2/Ar mixtures passed through microwave discharge. $[Cl] < 1.2\times10^{-8}\ mol\ cm^{-3}$. Total pressures 0.33-2.03 mm Hg (44-270.6 Pa). Intensity of red recombination emission monitored, and [Cl] calibrated by titration with NOCl. Reaction	Authors analysed recombination rates according to mechanism $Cl + M \rightleftharpoons ClM$ 9,-9 $Cl + ClM \rightarrow Cl_2 + M$ 10 $Cl + wall \rightarrow \frac{1}{2}Cl_2$ w where M is Ar or Cl_2. Subsequently variation of k_1 with [Cl] obtained. Wall recombination allowed for by determining k_w in low pressure experiments. Used

$Cl + Cl + M \rightarrow Cl_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		cell walls coated with H_2SO_4 HUTTON and WRIGHT 1965 (16)	by (24) assuming $k_1(M=N_2)=k_1(M=Ar)$, and by (33) assuming $k_1(M=He)=k_1(M=Ar)$. (33) also attributes $k_1(M=O_2)=2.05\times10^{17}$ $cm^6\ mol^{-2}\ s^{-1}$ to this work.
$(4.4\pm0.6)\times10^{15}$ M=Ar $(2.0\pm0.3)\times10^{16}$ $M=Cl_2$ $2.0\times10^{14}\exp\{(906\pm352)/T\}$ M=Ar $1.26\times10^{15}\exp\{(805\pm302)/T\}$ $M=Cl_2$	298 298 195-500 195-500	Discharge flow system. Few details given. Recombination emission used to monitor [Cl]. CLYNE and STEDMAN 1967 (20)	Intensity I of recombination emission found as $\propto[Cl]^n$, where $2.0>n>1.0$. Authors also express temperature dependence of k_1 (M=Ar) as $AT^{-(3.0\pm0.5)}$, and of $k_1(M=Cl_2)$ as $BT^{-(2.7\pm0.5)}$. CREITZ (25) quotes $k_1(M=Cl_2)$ from this work as $9.72\times10^{22}T^{-2.7}$ $cm^6\ mol^{-2}\ s^{-1}$.
$(2.2\pm0.6)\times10^{16}$ M=Ar $(5.8\pm0.7)\times10^{15}$ $(4.4\pm0.5)\times10^{15}$ $(1.25\pm0.3)\times10^{15}$ $(8.0\pm2.0)\times10^{16}$ $M=Cl_2$ $(2.0\pm0.2)\times10^{16}$ $(1.15\pm0.15)\times10^{16}$ $(7.0\pm1.5)\times10^{15}$ $(6.5\pm1.6)\times10^{15}$	195 273 298 514 195 298 361 474 490	Discharge flow system. Cl_2 and Cl_2/Ar mixtures passed through discharge at total pressures of ∿1 mm Hg (133.3 Pa). [Cl] followed by monitoring recombination intensity, calibrated by titration with NOCl. Flow tube coated with H_3PO_4. CLYNE and STEDMAN 1968 (23)	Recombination at wall found negligible. Authors give as fits to these data $k_1(M=Ar)=2.0\times10^{14}\exp\{(906\pm352)/T\}$, or $4\times10^{15}(T/300)^{-(3.0\pm0.5)}$ $cm^6\ mol^{-2}\ s^{-1}$; and $k_1(M=Cl_2)=1.26\times10^{15}\exp\{(805\pm302)/T\}$, or $2\times10^{16}(T/300)^{-(2.7\pm0.5)}$ $cm^6\ mol^{-2}\ s^{-1}$. Used by (37). $k_1(M=Ar)$ given as $4\times10^{15}(T/298)^{-3}$ $cm^6\ mol^{-2}\ s^{-1}$ by WAGNER (29 and 35). Used by (31).
$(7.5\pm1.5)\times10^{15}$ M=Ar $(1.4\pm0.2)\times10^{15}$ M=He $(1.7\pm0.2)\times10^{15}$ M=Ne $(1.5\pm0.4)\times10^{16}$ $M=N_2$ $(2.1\pm0.4)\times10^{16}$ $M=SF_6$ $(5.7\pm1.0)\times10^{16}$ $M=SiF_4$ $(5.5\pm0.5)\times10^{16}$ $M=CF_4$ $(5.6\pm0.6)\times10^{16}$ $M=CO_2$ $(2.1\pm0.4)\times10^{16}$ $M=C_2F_6$	298 298 298 298 298 298 298 298 298	Flash photolysis study. Cl_2(3-10 mm Hg; 400-1333 Pa)/Ar, He, Ne or N_2 (1-4 atm; 101.3-405.2 kPa) and Cl_2(3-10 mm Hg; 400-1333 Pa)/SF_6, SiF_4, CF_4, CO_2 or C_2F_6 (0.5-3 atm; 50.7-304 kPa) mixtures. $[Cl_2]$ measured by absorption at 313 nm. HIPPLER and TROE 1973 (34)	At inert gas pressures below those given here, authors report perturbations of measurements, due partly to thermal effects. Contribution of $k_1(M=Cl_2)$ small enough to be ignored. $Cl + Cl + M \rightarrow Cl_2 + M$ 1
$(2.53\pm0.25)\times10^{16}$ M=Ar $(5.32\pm0.33)\times10^{15}$ $(4.02\pm0.20)\times10^{15}$ $(2.79\pm0.18)\times10^{15}$ $(2.77\pm0.26)\times10^{15}$ M=He $(2.28\pm0.13)\times10^{15}$ $(2.09\pm0.15)\times10^{15}$ $(6.85\pm0.45)\times10^{15}$ M=Ne $(3.78\pm0.37)\times10^{15}$ $(3.45\pm0.15)\times10^{15}$ $(3.06\pm0.30)\times10^{15}$ $(8.08\pm0.81)\times10^{15}$ $M=N_2$ $(6.09\pm0.29)\times10^{15}$ $(4.60\pm0.46)\times10^{15}$	195 293 323 373 205 293 373 195 293 327 373 293 323 373	Flash photolysis study. Cl_2(∿1 mm Hg; 133.3 Pa)/Ar, He, Ne, N_2, SF_6, CF_4 or CO_2 mixtures, with $[Cl_2]/[M]$ ratio $\sim2\times10^{-3}$ to 10^{-2}. Absorption of Cl_2 monitored at 365 nm. WIDMAN and DE GRAFF 1973 (36)	Thermal effects minimised by using only initial variation of Cl with time. Variation of $[Cl_2]/[M]$ over five-fold range showed contribution of $k_1(M=Cl_2)$ to be negligible for these experiments. Authors give expressions as least-squares fits to these data : $k_1(M=Ar)=2.50\times10^{14}\exp(910\pm25/T)$ or 4.17x

$Cl + Cl + M \rightarrow Cl_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
$(1.20\pm0.12)\times10^{16}$	M=SF$_6$	293	WIDMAN and DE GRAFF 1973 (36) continued.	$10^{24}T^{-(3.59\pm0.05)}$ cm^6 mol^{-2} s^{-1}; k_1(M=He) = $1.47\times10^{15}\exp(130\pm5/T)$ or $3.55\times10^{16}T^{-(0.48\pm0.01)}$ cm^6 mol^{-2} s^{-1}; k_1(M=Ne) = $1.26\times10^{15}\exp(330\pm10/T)$ or $5.50\times10^{18}T^{-(1.27\pm0.02)}$ cm^6 mol^{-2} s^{-1}; k_1(M=N$_2$) = $5.80\times10^{14}\exp(810\pm70/T)$ or $4.07\times10^{21}T^{-(2.32\pm0.02)}$ cm^6 mol^{-2} s^{-1}; k_1(M=SF$_6$) = $2.40\times10^{15}\exp(490\pm50/T)$ or $5.25\times10^{19}T^{-(1.47\pm0.02)}$ cm^6 mol^{-2} s^{-1}; k_1(M=CF$_4$) = $1.62\times10^{15}\exp(600\pm100/T)$ or $2.69\times10^{20}T^{-(1.77\pm0.04)}$ cm^6 mol^{-2} s^{-1}; k_1(M=CO$_2$) = $1.56\times10^{15}\exp(760\pm100/T)$ or $5.62\times10^{21}T^{-(2.22\pm0.02)}$ cm^6 mol^{-2} s^{-1}. k_1(M=N$_2$) used by (39).
$(1.10\pm0.04)\times10^{16}$		325		
$(8.48\pm0.80)\times10^{15}$		373		
$(1.23\pm0.12)\times10^{16}$	M=CF$_4$	293		
$(9.19\pm0.49)\times10^{15}$		323		
$(7.93\pm0.69)\times10^{15}$		373		
$(1.88\pm0.16)\times10^{16}$	M=CO$_2$	293		
$(1.57\pm0.05)\times10^{16}$		323		
$(1.27\pm0.09)\times10^{16}$		343		
$(1.12\pm0.09)\times10^{16}$		373		
$(1.7\pm0.2)\times10^{15}$	M=He	298	Flash photolysis study. Cl$_2$(3-10 mm Hg; 0.4-1.3 kPa)/He or N$_2$(1-100 atm; 0.1-10.1 MPa), or Ar(0.5-24 atm; 0.05-2.43 MPa), or CO$_2$(0.5-60 atm; 0.05-6.08 MPa), or Ne, SiF$_4$, CF$_4$, SF$_6$ or C$_2$F$_6$ (0.5-2 atm; 50.7-202.6 kPa) mixtures. [Cl$_2$] monitored by absorption at 313 nm. HIPPLER and TROE 1976 (42)	Growth of [Cl$_2$] after flash analysed according to d[Cl$_2$]/dt = $4k_1[M]\{[Cl_2]_\infty-[Cl_2]\}^2$, where $[Cl_2]_\infty$ is final value (also pre-flash value) of [Cl$_2$]. k_1(M=N$_2$) and k_1(M=CO$_2$) both passed through maxima with increasing pressure: values of these rate constants given for 1-2 atm (101.3-202.6 kPa) and 0.5-1 atm (50.7-101.3 kPa) respectively.
$(8\pm2)\times10^{15}$	M=N$_2$	298		
$(7.4\pm3)\times10^{15}$	M=Ar	298		
$(2\pm0.4)\times10^{16}$	M=CO$_2$	298		
$(1.7\pm0.5)\times10^{15}$	M=Ne	298		
$(1.3\pm0.3)\times10^{16}$	M=SiF$_4$	298		
$(1.2\pm0.3)\times10^{16}$	M=CF$_4$	298		
$(1.3\pm0.3)\times10^{16}$	M=SF$_6$	298		
$(1.3\pm0.3)\times10^{16}$	M=C$_2$F$_6$	298		
$(4.68\pm0.5)\times10^{15}$	M=Ar	300	F$_2$-discharge flow system. F$_2$(0.5-10%)/Ar mixtures passed through discharge, Cl$_2$(∿19 Pa) added, giving total pressures ∿143 Pa. Two-body Cl recombination afterglow followed at (630±5) nm. NORDINE and ROSNER 1976 (43)	Cl atoms produced by rapid reaction $F + Cl_2 \rightarrow ClF + Cl$ Second order plot of Cl decay used to determine k_1. Authors expressed rate constant as $2k_1$- the value presented here is half their value.

$Cl + Cl + M \rightarrow Cl_2 + M$

REVIEW ARTICLES

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.1 \times 10^{19} T^{-1}$ M=typical rocket exhaust products	1000-3500	Calculated on basis of data of HIRAOKA and HARDWICK (8), rather than those of JACOBS and GIEDT (10), who found T^{-2} dependence using their k_{-1} data. JENSEN and KURZIUS 1967 (21)	Authors base their preference for data of (8) over those of (10) on recommendation of FRISTROM and WESTENBERG (15). Authors assumed Cl_2 to be 3 times as efficient as Ar. Error factor given as 10. Expression reproduced by (19), and retained in later review by JENSEN and JONES (26), but with increased lower uncertainty factor of 0.03.
$2.19 \times 10^{14} \exp\{(900 \pm 250)/T\}$ M=Ar $1.26 \times 10^{15} \exp\{(810 \pm 200)/T\}$ $M=Cl_2$	200-500 200-500	Evaluation. Based on least-squares treatment of data of CLYNE and STEDMAN (23). LLOYD 1971 (27)	Alternative form of treatment gives $k_1(M=Ar) = 6.31 \times 10^{22} T^{-(2.9 \pm 0.5)}$ and $k_1(M=Cl_2) = 7.94 \times 10^{22} T^{-(2.7 \pm 0.5)}$ $cm^6\ mol^{-2}\ s^{-1}$. Error factors are ∿1.5 over the temperature range quoted, but large errors possible at very much higher temperatures. Arrhenius expressions recommended by (38 and 40). $Cl + Cl + M \rightarrow Cl_2 + M$ 1
$1.0 \times 10^{22} T^{-2.4}$ M=Ar	1700-2600	Review. Based on Cl_2 dissociation data of CARABETTA and PALMER (18). WAGNER 1971 (29)	Author presents expression in empirical form $k_1 = A(T/\bar{T})^n$, where $\bar{T}$ is mean temperature (2000 K) for which experimental data available. Expression misquoted in (35).
$7.94 \times 10^{21} T^{-(2.22 \pm 0.24)}$ $M=Cl_2$	300-600	Evaluation. Least-squares analysis of data of (7,13 and 14). KONDRATIEV 1972 (32)	
(a) $9.0 \times 10^{13} \exp(1210/T)$ (b) $4.8 \times 10^{20} T^{-2.0}$ (c) $3.0 \times 10^{14} \sinh(1070/T)$ M=Ar	195-2582 195-2582 195-2582	Expressions fitted to data of (18 and 36). SNIDER and LEAIST 1977 (44)	Expression (c) found to provide best fit to authors' selected data. Theoretical justification provided by authors.
$2.29 \times 10^{14} \exp\{(903 \pm 55)/T\}$ M=Ar	195-514	Review. Expression derived from least squares treatment of data of (23 and 36). WATSON 1977 (45)	Expression not shown on Arrhenius plot as is almost identical to our recommendation.

$Cl + Cl + M \rightarrow Cl_2 + M$

THIRD BODY COLLISION EFFICIENCIES

M=Ar	He	Cl_2	SF_6	CCl_4	Ne	N_2	CF_4	CO_2	SiF_4	C_2F_6	Temperature (K)	Reference
						EXPERIMENTAL DATA						
1		≥ 5	1	≥ 32.5							552.3	Chiltz *et al.* 1962 (7).
1	0.75	~ 7.0									313	Bader and Ogryzlo 1964 (13).
1		4.6									298	Clyne and Stedman 1967 (20) and 1968 (23).
1	0.19		2.8		0.23	2.0	7.3	7.5	7.6	2.8	298	Hippler and Troe 1973 (34).
1	0.43	3.8	2.26		0.71	1.52	2.31	3.53			293	Widman and De Graff 1973 (36).
						REVIEW ARTICLES						
1		3									1000-3500	Jensen and Kurzius 1967 (21).

Discussion

The rate of recombination of chlorine atoms has been studied principally by flash photolysis [2,4,34,36,42] and discharge flow [12,14,16,20,23,43] methods.

$$Cl + Cl + M \rightarrow Cl_2 + M \qquad (1)$$

Static systems [6,7] and shock tubes [8,11] have also been used, but the results of these studies are so widely different from the rest that we do not consider them further in this evaluation.

Of the flash photolysis studies using simple Cl_2/diluent mixtures [34,36,42], all used very low $[Cl_2]/[M]$ ratios to avoid the problems posed by the "thermal effect," due to heat released by the exothermic recombination reaction (see the discussion on iodine atom recombination, section D2).

Good agreement for k_1 values is obtained in the discharge flow systems between those studies in which the reaction was followed by isothermal calorimetry [13] and by the intensity of the two-body recombination emission [14,16,23].

For $k_1(M=Ar)$ the only data that disagree substantially with the remainder are those of Hippler and Troe [34,42], whose total pressures were considerably greater than those of [16,23,36 and 43]. Until the effects of pressure upon k_1 are better understood we base our recommendation upon the data of [13,16,20,23,36 and 43], giving the expression

$$k_1(M=Ar) = 2.23\times10^{14} \exp(906/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

with error limits of ±40%, over the temperature range 195–520 K.

There are considerably fewer results for $k_1(M=Cl_2)$ upon which to base our evaluation. The discharge flow results of Linnett and Booth [12] are nearly two orders of magnitude lower than those of Hutton [14], and Clyne and Stedman [20,23], and have not been used for this evaluation. Neither have we attached great weight to the results (by an undefined method) of Martens [9], or of Chiltz et al. [7] because of the uncertainty over their true values. As originally expressed they are in good agreement with [14 and 23], but Lloyd's interpretation [27] puts them almost an order of magnitude lower, and we cannot consider them as reliable. The correct interpretation of the results of Bader and Ogryzlo [13] is also uncertain—if these values do in fact represent $2k_1$ then the corrected values also agree well with those of [14,20 and 23]. But this then destroys the agreement for $k_1(M=Ar)$. Therefore we recommend that uncertainty limits of ±70%, larger than for $k_1(M=Ar)$, be used, to include the data of [13], with our recommended expression

$$k_1(M=Cl_2) = 1.25\times10^{15} \exp(820/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

based on the results of [14,20 and 23], for temperatures 195–500 K. This expression, and that for $k_1(M=Ar)$, are similar to those of Lloyd [27].

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B3 $HCl + M \rightarrow H + Cl + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	431.601	92.885	-70.762	-75.150
300	431.626	92.973	-70.296	-74.687
500	434.429	100.107	-40.155	-44.768
1000	440.956	109.278	-17.325	-22.239
1500	445.847	113.282	- 9.608	-14.698
2000	449.528	115.416	- 5.712	-10.927
2500	452.487	116.738	- 3.357	- 8.669
3000	454.973	117.646	- 1.776	- 7.167
3500	457.123	118.315	- 0.642	- 6.100
4000	459.030	118.822	0.214	- 5.304
4500	460.733	119.223	0.881	- 4.688
5000	462.265	119.550	1.415	- 4.198

SI Units: $\log(K_p/\mathrm{Pa}) = \log(K_p/\mathrm{atm}) + 5.0056$

$\log(K_c/\mathrm{mol\ m^{-3}}) = \log(K_c/\mathrm{mol\ cm^{-3}}) + 6.000$

RECOMMENDED RATE CONSTANT

$k = 4.4 \times 10^{13} \exp(-41\,140/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ (M=Ar)

$= 7.3 \times 10^{-11} \exp(-41\,140/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ (M=Ar)

Temperature Range: 2900-7000 K

Suggested Error Limits for Calculated Rate Constant: ±50% over given temperature range.

Rate Parameters:

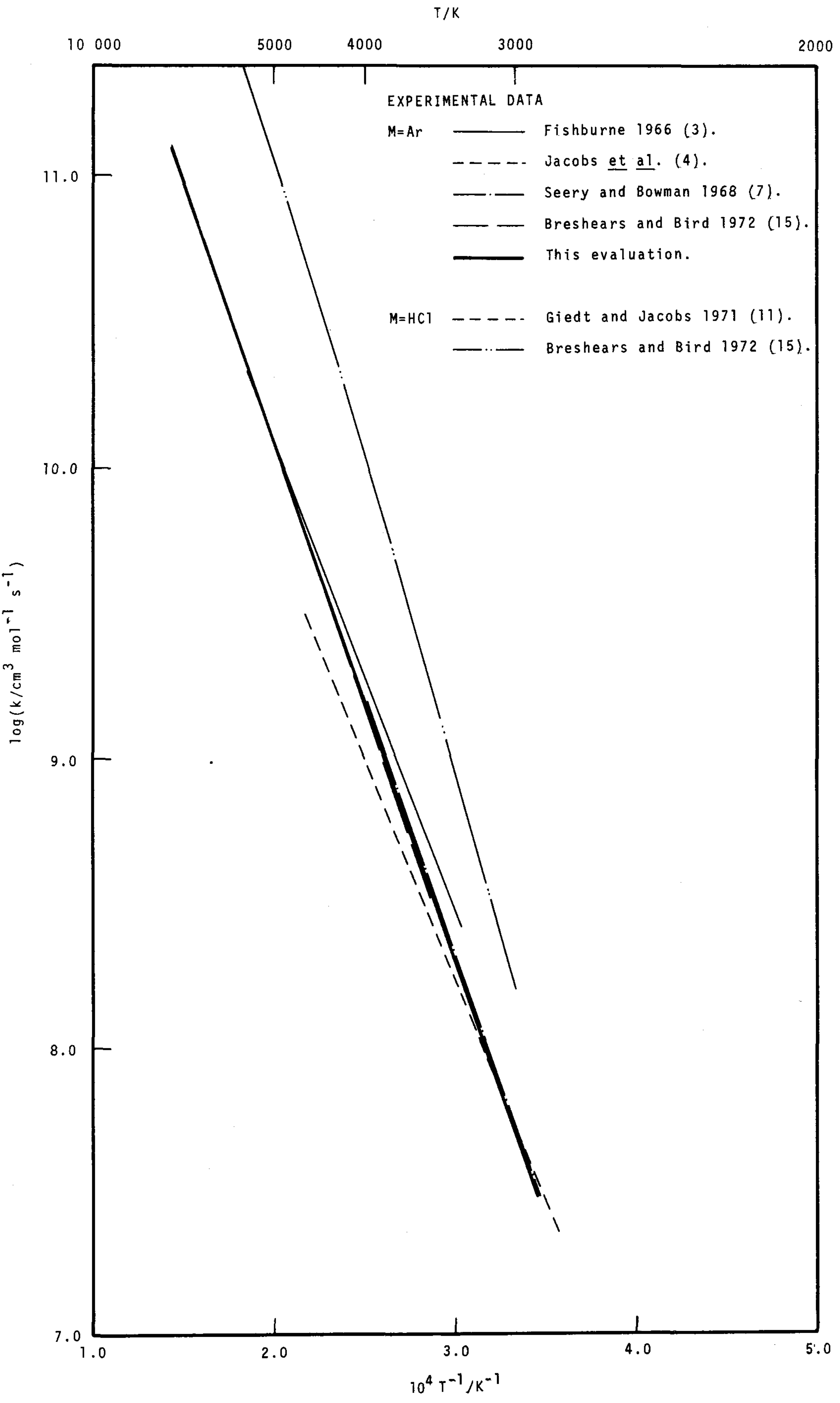
$\log(A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 13.64 \pm 0.2$

$\log(A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = -10.14 \pm 0.2$

$E/\mathrm{J\ mol^{-1}} = 342\,060 \pm 37\,920$

$E/\mathrm{cal\ mol^{-1}} = 81\,755 \pm 9\,060$

$HCl + M \rightarrow H + Cl + M$



$HCl + M \rightarrow H + Cl + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.92 \times 10^{11} T^{\frac{1}{2}} \exp(-35\ 080/T)$ M=Ar	3300-5400	Shock tube study. HCl(1% and 2%)/Ar and HCl(2%)/H_2 (1%)/Ar mixtures behind incident shocks. Total gas concentrations 2.1×10^{-6}-8.4×10^{-6} mol cm^{-3}. Dissociation followed by monitoring HCl ir emission at 3.46 μ. FISHBURNE 1966 (3)	HCl dissociation mechanism taken as $HCl + M \rightarrow H + Cl + M$ 1 $H + HCl \rightarrow H_2 + Cl$ 2 $Cl + HCl \rightarrow H + Cl_2$ 3 $H_2 + M \rightarrow H + H + M$ 4 Effects of reactions 3 and 4 minimised by using only first 10% of HCl decay. Effective rate constant k_{eff} for HCl dissociation given by $k_{eff}=k_1+k_2([H]/[M])$, with $k_{eff}=3.85 \times 10^{11} T^{\frac{1}{2}} \exp(-35\ 080/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Author took best value of k_1 as given by $k_1=k_{eff}/2$, in order for k_2/k_1 to agree with extrapolated data of STEINER and RIDEAL (1). No noticeable variation in k_{eff} between HF/Ar and HF/H_2/Ar mixtures.
$6.61 \times 10^{12} \exp(-35\ 230/T)$ M=Ar	2800-4600	Shock tube study. HCl(1% and 2%)/Ar mixtures. Incident shocks. Total pressures 0.7-2.4 atm (71-243 kPa). Ir emission from HCl followed at 4.2 μ. JACOBS, COHEN and GIEDT 1967 (4)	Rates of decomposition of HCl at constant density obtained at 20% and 40% reaction. Least-squares Arrhenius plots compared with plots computed according to mechanism $HCl + M \rightarrow H + Cl + M$ 1 $H + HCl \rightarrow H_2 + Cl$ 2 $Cl + HCl \rightarrow H + Cl_2$ 3 $H_2 + M \rightarrow H + H + M$ 4 $Cl_2 + M \rightarrow Cl + Cl + M$ 5 Preliminary fit to within factor of 2 given by $k_1=6.76 \times 10^{21} T^{-2} \exp(-51\ 410/T)$ $cm^3\ mol^{-1}\ s^{-1}$, but further analysis showed that better fit to apparent activation energies at both 20% and 40% reaction given by expression presented here. Used by (6 and 17). COHEN *et al.* (8, 9) quote further study that suggests $k_1(M=HCl) \approx k_1(M=Ar)$.
$4.2 \times 10^{13} \exp(-40\ 760/T)$ M=Ar	2900-4000	Shock tube study. HCl(1% and 2%)/Ar mixtures in incident shock region. Pressure range 1-2 atm (101-203 kPa). Vacuum uv absorption by HCl monitored	Initial slope of absorption profiles, up to 30% dissociation, used to determine k_1. Profiles computed using reactions 1 to 5 insensitive to fivefold alterations in k_2 to k_5, but highly

HCl + M → H + Cl + M

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		at 160.8 nm. SEERY and BOWMAN 1968 (7)	sensitive to twofold change in k_1. Vibrational relaxation of HCl sufficiently rapid to be ignored. Best fit using expression derived from collision theory given by k_1(M=Ar)=$3.5x10^{18}T^{-1}exp(-51\ 410/T)$ cm^3 mol^{-1} s^{-1}, but this not as good as simple Arrhenius expression given here.
$6.61x10^{12}exp(-35\ 230/T)$ M=HCl	1600-4600	Shock tube study. 100% HCl behind incident shocks. Pressure range 2.3-15.5 atm (233-1570 kPa). Two-body recombination emission from Cl followed at 400 and 466 nm. GIEDT and JACOBS 1971 (11)	Cl emission calibrated by equilibrium [Cl] levels and several shock-heated Cl_2/Ar mixtures. Good match between computed and experimental [Cl] profiles obtained using expression of JACOBS _et al_. (4).
$4.78x10^{13}exp(-41\ 600/T)$ M=Ar $1.76x10^{14}exp(-29\ 400/T)$ $exp(-3.72x10^7/T^2)$ M=HCl	(a)3500-7000 3000-7000 (b)3000-4000	Shock tube study. (a) HCl (5%,10% and 20%)/Ar mixtures and (b) 100% HCl under incident shock conditions. Pressures in region 1 atm (101 kPa). Laser-schlieren technique used to monitor density gradient during reaction. BRESHEARS and BIRD 1972 (15)	Non-zero minimum in schlieren deflection identified with state of vibrational equilibrium prior to HCl dissociation. Expressions to fit data chosen empirically, by least squares method. Extrapolation of k_1(M=HCl) derived from mixtures (b). Authors considered their data for k_1(M=HCl) possibly represent k_1(M=HCl) + k_6 HCl + HCl → H_2 + 2Cl 6

ISOTOPIC REACTION DCl + M → D + Cl + M

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$6.61x10^{12}exp(-35\ 230/T)$ M=Ar	2800-4600	Shock tube study. DCl(1% and 2%)Ar mixtures in incident shock region. Total pressures 0.7-2.4 atm (71-243 kPa). Ir emission from DCl monitored at 5.2 μ. JACOBS, COHEN and GIEDT 1967 (4)	Analysis as for reaction 1. To within an error factor of 2, fit to experimental data given by $k_{1D}=7.94x10^{21}T^{-2}exp(-51\ 930/T)$ cm^3 mol^{-1} s^{-1}, but again better fit given by expression with lower activation energy, as for HCl. DCl + M → D + Cl + M 1D Subsequent study by GIEDT and JACOBS (11), with temperatures down to 1600 K, showed this expression gave good fit to [Cl] profiles from 100% DCl mixtures.

Discussion

Determinations of the rate of HCl dissociation have been made only in shock tube systems

$$\mathrm{HCl + M \rightarrow H + Cl + M} \qquad (1)$$

In the earliest study, Fishburne [3] tried to minimise the effects of subsequent reactions

$$\mathrm{Cl + HCl \rightarrow H + Cl_2} \qquad (3)$$

$$\mathrm{H_2 + M \rightarrow H + H + M} \qquad (4)$$

by considering only the first 10% of the dissociation. Because the results for $k_1(\mathrm{M=Ar})$ of this study are rather higher than the rest [4,7,15] it appears that this technique was not entirely successful, i.e., that the resulting expression for $k_1(\mathrm{M=Ar})$ includes the effects of k_3 and k_4.

Of the remaining studies the results for $k_1(\mathrm{M=Ar})$ of Jacobs et al. [4] fall below those of Seery and Bowman [7] and Breshears and Bird [15], which may be a result of their analysis at 20% and 40% dissociation, rather than during the initial stages. The elegant laser-schlieren technique of Breshears and Bird [15] gave a very high time resolution of the dissociation, which removed the necessity for extrapolation back to zero time, as in the vacuum u.v. absorption study of Seery and Bowman [7]. Nevertheless, the latter investigation gave an expression for $k_1(\mathrm{M=Ar})$ in good agreement with that of [15], and consequently we recommend the expression

$$k_1(\mathrm{M=Ar}) = 4.4\times10^{13} \exp(-41\,140/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

for the temperature range 2900–7000 K. Error limits of ±50% should be recognised.

Although we feel that the determination by Breshears and Bird [15] of $k_1(\mathrm{M=HCl})$ is as precise as that for $k_1(\mathrm{M=Ar})$, the large discrepancy between their values and those of Giedt and Jacobs [11] has not been explained, and so we make no recommendation for $k_1(\mathrm{M=HCl})$.

The apparent discrepancy between the activation energy E of our recommended expression, and the enthalpy $\Delta H°$ may arise from the fitting of a simple Arrhenius expression to the data. The temperature range studied may be too small to show a strong temperature dependence of the pre-exponential factor. Alternatively the reaction mechanism may be more complex than assumed, although there is no evidence for this.

Rate of the Reverse Reaction

There have been no absolute determinations of the rate of the three-body reaction between hydrogen atoms and chlorine atoms

$$\mathrm{H + Cl + M \rightarrow HCl + M} \qquad (-1)$$

Boyd et al. [16] were able to put an upper limit of $k_{-1}(\mathrm{M=H_2O}) = 3\times10^{15}\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$ at 433 K, by comparing the experimental H_2 yield from Febetron radiolysis of 6% $\mathrm{HCl/H_2O}$ mixtures with the yield computed using an extensive reaction mechanism. The actual value used in this study was $10^{15}\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$, as suggested by Willis et al. [10], by analogy with related reactions discussed by Porter [2].

Jensen and Kurzius [5] also used a comparison of reaction −1 with reactions such as

$$\mathrm{H + F + M \rightarrow HF + M}$$

to estimate $k_{-1} = 1.1\times10^{19}T^{-1}\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$ (1000–3500 K), for use in problems of rocket exhaust modelling. This expression was used by Jensen and Pergament [13]. A later estimation by Jensen and Jones [12] gave $k_{-1} = 1.4\times10^{22}T^{-2}\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$ (1000–3500 K), an interim value, bearing in mind the agreement between the data for k_1 of Jacobs et al. [4] and of Seery and Bowman [7] at 3500 K. Wagner [14] used the data of [4] to give $k_{-1}(\mathrm{M=Ar}) = 3.3\times10^{21}T^{-2}\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$.

Using our expression for $k_1(\mathrm{M=Ar})$ together with the equilibrium constant, we obtain the expression

$$k_{-1}(\mathrm{M=Ar}) = 2.6\times10^{13} \exp(9940/T)\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}.$$

The error limits are ±50%, as for k_1.

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B4 $Cl + H_2 \rightarrow H + HCl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	4.38	5.75	-0.47
300	4.38	5.74	-0.46
500	4.07	4.97	-0.16
1000	3.52	4.13	0.03
1500	3.84	4.38	0.10
2000	4.28	4.63	0.13
2500	4.54	4.75	0.15
3000	4.59	4.77	0.17
3500	4.43	4.72	0.18
4000	4.00	4.61	0.19
4500	3.31	4.45	0.19
5000	2.38	4.25	0.20

RECOMMENDED RATE CONSTANT

$$k = 1.45 \times 10^{13} \exp(-2200/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 2.40 \times 10^{-11} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 200-650 K.

Suggested Error Limits for Calculated Rate Constant: ±50%

Note: Recommended expressions is that derived by LEE, MICHAEL, PAYNE, STIEF and WHYTOCK (86) extended to 650 K.

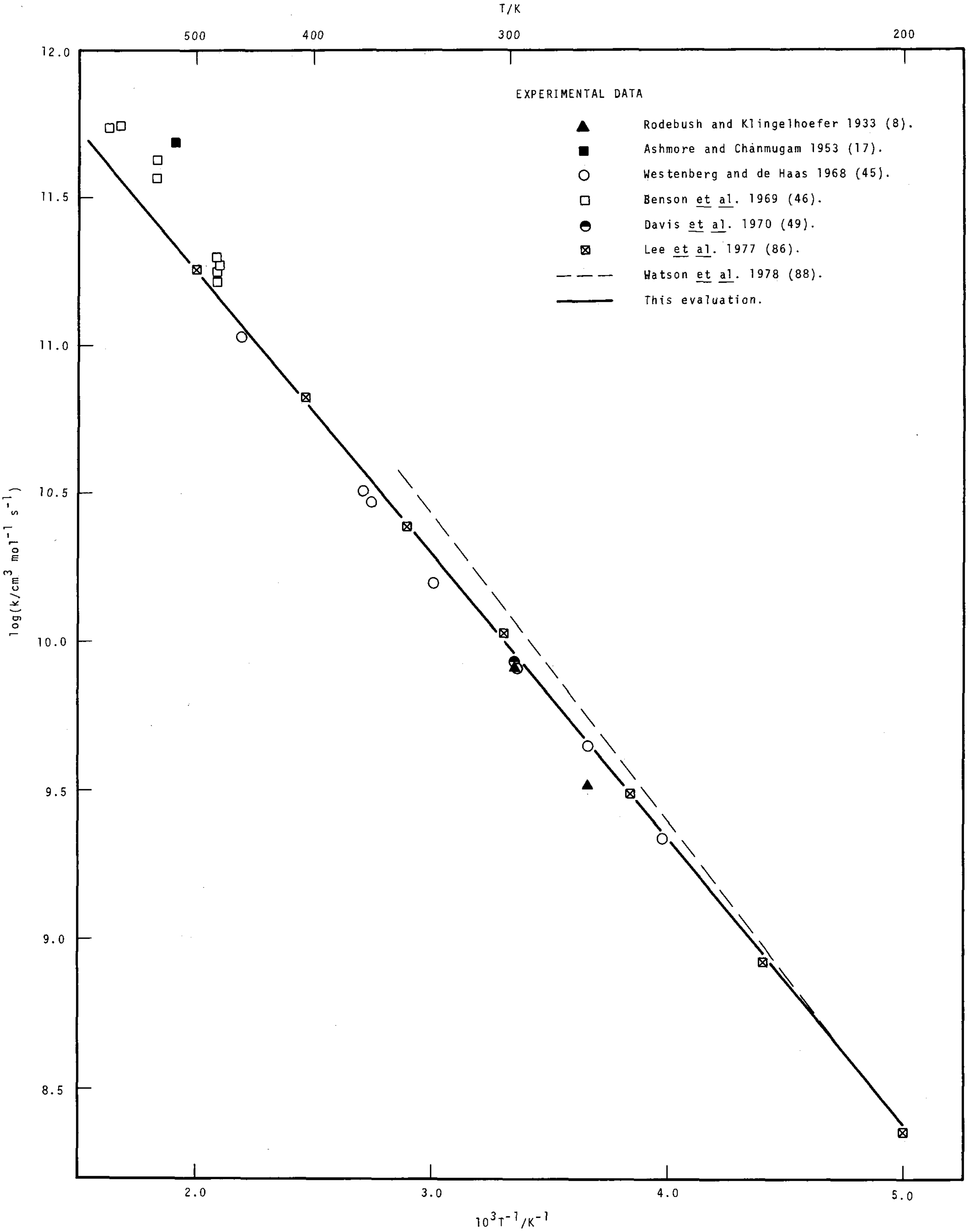
Rate Parameters: $\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.16 \pm 0.2$

$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -10.62 \pm 0.2$

$E/\text{J mol}^{-1} = 18\ 290 \pm 2220$

$E/\text{cal mol}^{-1} = 4\ 370 \pm 530$

$Cl + H_2 \rightarrow HCl + H$

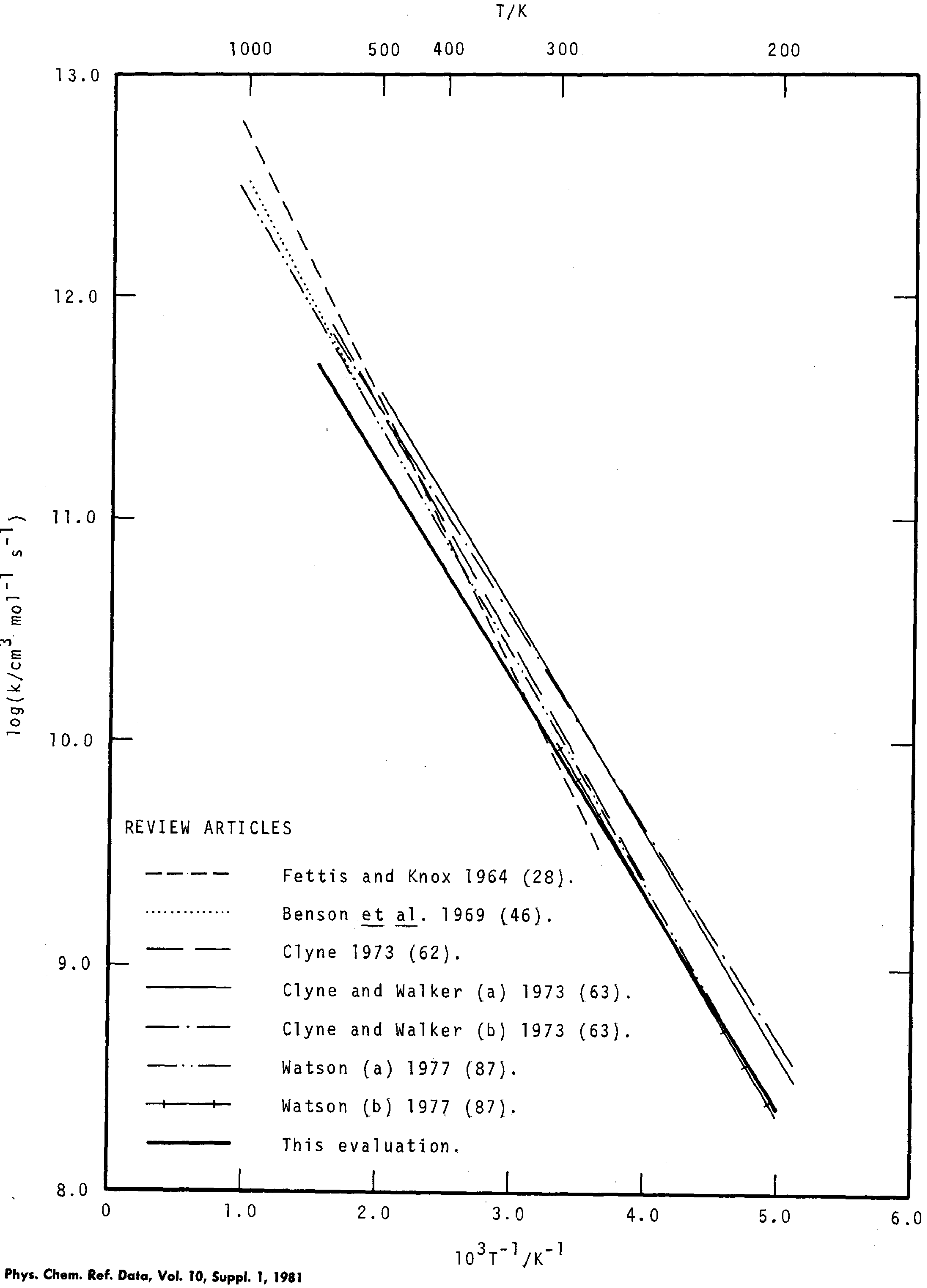


$Cl + H_2 \rightarrow H + HCl$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$3.3x10^9$ $8.2x10^9$	273 298	Discharge flow system. Pure Cl_2 at 40±5 Pa. [Cl] monitored with a Wrede-Harteck diffusion gauge. [HCl] determined titrimetrically. RODEBUSH and KLINGELHOEFER 1933 (8)	Complicating effects of surface recombination of atoms noted. Rate constants k_1 calculated $Cl + H_2 \rightarrow H + HCl$ 1 $H + Cl_2 \rightarrow Cl + HCl$ 2 assuming all H atoms rapidly scavenged by Cl_2 as in reaction 2. Authors compute E_1=25.5±4.2 kJ mol^{-1} (6.1±1.0 kcal mol^{-1}). Quoted by (10,12,13,33 and 59). Used by (34 and 46). Listed by (58 and 69).
	523	Static pyrolysis study. 1:1 mixtures of H_2 and Cl_2 at 13.3 and 18.7 kPa plus 0.8 kPa NOCl. Reaction progress and products monitored manometrically. ASHMORE and CHANMUGAM 1953 (17)	[Cl] essentially controlled by reactions 3 and 4. HCl yield $NO + Cl_2 \rightarrow Cl + NOCl$ 3 $Cl + NOCl \rightarrow NO + Cl_2$ 4 $Cl_2 \rightarrow Cl + Cl$ 5 $NOCl \rightarrow Cl + NO$ 6 $H + NOCl \rightarrow NO + HCl$ 7 calculated from overall pressure change and pressure of those residual gases condensable at 77 K. k_1 obtained using rate expression simplified by eliminating reactions 5 and 6 and assuming $\left\{\frac{k_2k_4[Cl_2]}{k_1k_7[H_2]}+\frac{k_4[NOCl]}{k_1[H_2]}\right\} > 6.7$ Using k_3=1.13x10^4 $cm^3\ mol^{-1}\ s^{-1}$ (18) and k_4=4.1x10^{12} $cm^3\ mol^{-1}\ s^{-1}$, extrapolated from the data of (16), authors compute k_1=(4.8 ±0.4)x10^{11} $cm^3\ mol^{-1}\ s^{-1}$ and E_1= 23.0±0.8 kJ mol^{-1} (5.5±0.2 kcal mol^{-1}) by combining their data $H + HCl \rightarrow Cl + H_2$ 8 with that of (8) and those derived from measurements of k_8 (13). Quoted by (20,22,25,27,33, 41,45,56,59,68,77 and 87). Misquoted by (32). Used by (19, 24,34,36,39,46 and 84). Listed by (58 and 69).
	293-488	Static photolysis system. $H_2/CH_4/Cl_2$ mixtures. Residual H_2 and CH_4 separated from products by distillation and adsorbed on silica gel for measurement.	Relative rates of reactions 1 and 9 measured. Authors assumed $Cl + H_2 \rightarrow H + HCl$ 1 $Cl + CH_4 \rightarrow CH_3 + HCl$ 9 that H and CH_3 were entirely scavenged by Cl_2. k_9/k_1 values only presented graphically in

$Cl + H_2 \rightarrow HCl + H$

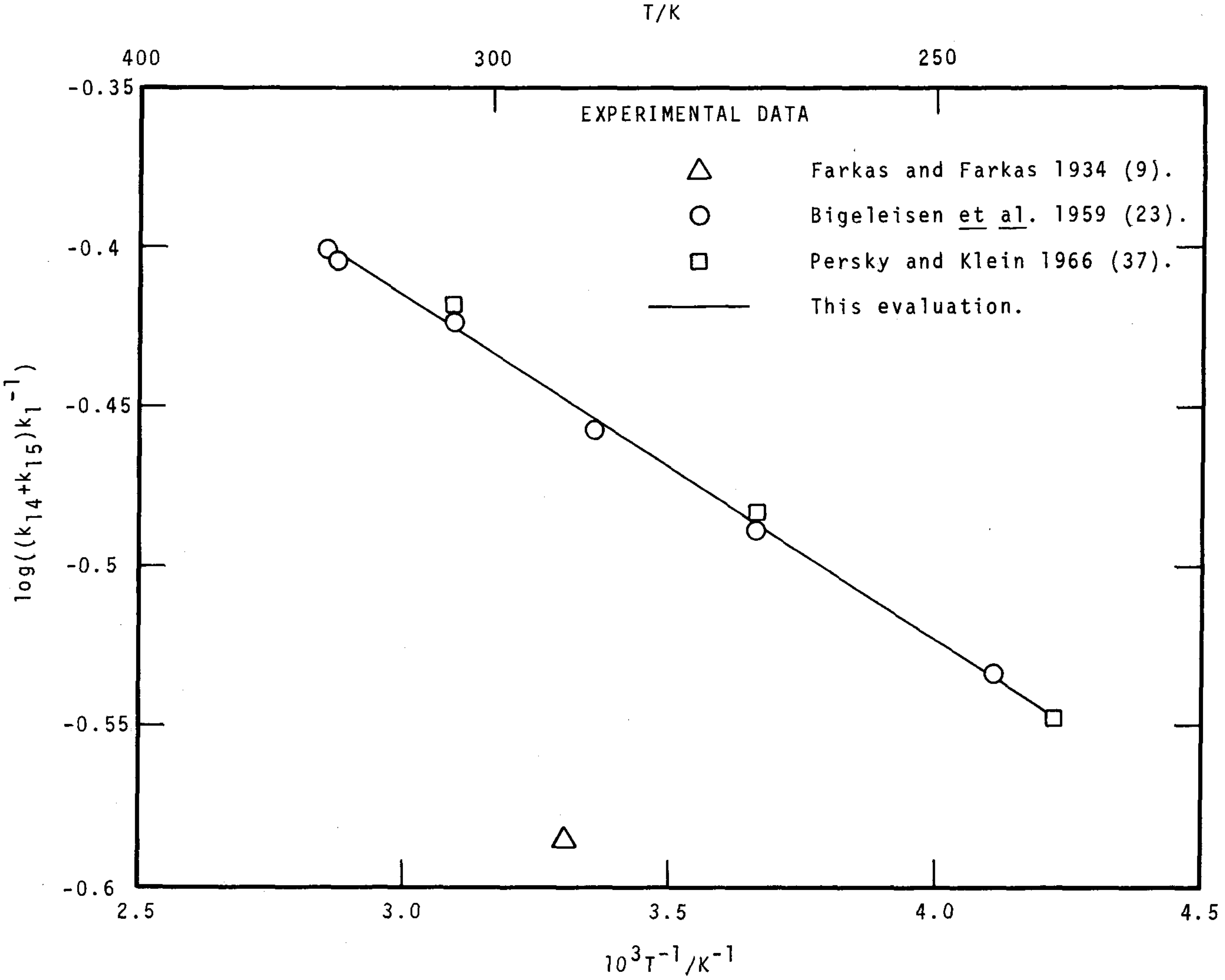


$Cl + H_2 \rightarrow H + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		PRITCHARD, PYKE and TROTMAN-DICKENSON 1954 (19) and 1955 (21)	Arrhenius form except for that at 373 K. T/K k_9/k_1 293 5.98 333 3.79 373 2.80±0.23 (Average of 6 determinations). 428 2.26 484 1.75 Concluded k_9/k_1=0.26 exp(855/T) in (19); this expression modified to k_9/k_1=0.32 exp{(830±75)/T} in (21); used to determine expression for k_9 by k_1 substitution from (17). Quoted by (49,68 and 82).
	196-599	Static photolysis system. $H_2/CH_4/Cl_2$ mixtures pressurised to ca. 70 kPa with N_2. Product HCl converted to benzene with diphenyl mercury. CH_3Cl and C_6H_6 analysed by g.l.c. KNOX and NELSON 1959 (24)	Relative rates of reactions 1 and 9 measured. H and CH_3 assumed to be scavenged by Cl_2. Data given in graphical form only. T/K k_9/k_1 196 20.3 206 17.5 241 8.93 295 5.93 334 3.83 374 2.82 404 2.38 464 1.62 599 1.13 Authors calculated k_9/k_1=0.30 exp (830±30/T); used to determine Arrhenius expression for k_9 by substituting that given by (17) for k_1. Quoted by (49,68 and 82).
$(2.17\pm0.09)\times10^{9}$ $(4.4\pm0.4)\times10^{9}$ $(8.1\pm0.4)\times10^{9}$ $(1.57\pm0.04)\times10^{10}$ $(2.94\pm0.01)\times10^{10}$ $(3.2\pm0.1)\times10^{10}$ $(1.07\pm0.07)\times10^{11}$	251 273 297 332 364 369 456	Discharge flow system. 0.5% Cl_2 in He or Ar plus excess H_2. $[^{35}Cl(^2P_{3/2})]$ and [H] measured by e.s.r. spectroscopy. WESTENBERG and DE HAAS 1968 (45)	Pseudo-first order conditions. Chlorine isotope effect assumed to be negligible. Large $[H_2]/[Cl]$ ratios chosen to eliminate complications from reactions 2 and 8. Authors calculate $k_1=(1.2\pm0.3)\times10^{13}\exp\{-(2165\pm100)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Misquoted by (65,66). Used by (46,52,55,61,62,70). Listed by (69,87). Quoted by (48,49,53, 57,59,60,76,77,81 and 86).
	476-610	Static pyrolysis study. $H_2/I_2/Cl_2$ mixtures at various total pressures in range 3.06-72.11 kPa. [ICl] and overall optical density monitored spectrophotometrically at 415 and 260 nm respectively.	ICl formed quantitatively before H_2 admitted to reaction vessel. [Cl] controlled by reactions 10 and 11 maintained in equilibrium heterogeneously. $I_2 \rightleftarrows I + I$ 10 $ICl \rightleftarrows I + Cl$ 11 $Cl + H_2 \rightarrow H + HCl$ 1

Cl + HD → H + DCl / D + HCl

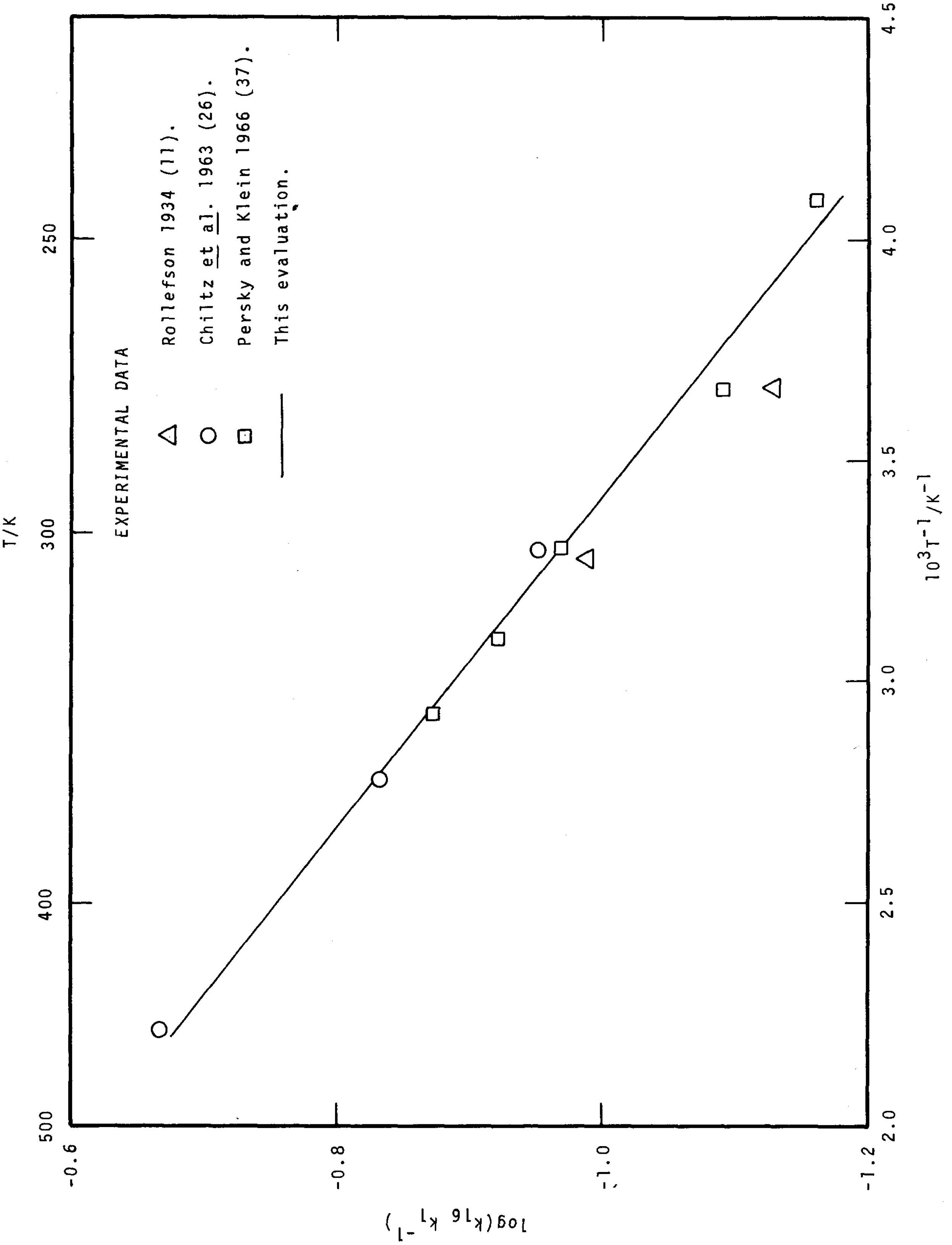


$Cl + H_2 \rightarrow H + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BENSON, CRUICKSHANK and SHAW 1969 (46)	$H + I_2 \rightarrow I + HI$ 12 $Cl + HI \rightarrow I + HCl$ 13 Authors assume H atoms produced in reaction 1 are scavenged entirely by I_2 to form HI, which is subsequently converted by reaction 13 to HCl. k_1 calculated incorporating corrections for depletion of $[H_2]$, increase in $[I_2]$ and finite [HI] during reaction, and using K_{10} and K_{11} values of unspecified origin. $k_1/cm^3mol^{-1}s^{-1}$ — T/K $1.862x10^{11}$ — 476 $1.629x10^{11}$ — 479 $1.780x10^{11}$ — 479 $1.980x10^{11}$ — 479 $3.649x10^{11}$ — 545 $4.238x10^{11}$ — 545 $5.200x10^{11}$ (3 points) — 593.8 $5.490x10^{11}$ — 593.8 $5.520x10^{11}$ (2 points) — 593.8 $5.560x10^{11}$ — 593.8 $5.600x10^{11}$ — 593.8 $5.851x10^{11}$ (2 points) — 593.8 $5.410x10^{11}$ — 610.3 $5.460x10^{11}$ — 610.3 Packed vessel runs at 545 K omitted by authors in calculating $\log(k_1/cm^3\ mol^{-1}\ s^{-1})=13.67\pm0.15-(1155\pm45)/T$. Quoted by (47,50, 59,69,77,80,81,86 and 87). Used by (74).
$8.43x10^9$	298	Repetitive flash photolysis technique. Mixtures of 8.5 Pa CCl_4, 2000 Pa He, plus H_2 at pressure in range 66-670 Pa. [Cl] measured by resonance fluorescence spectroscopy. DAVIS, BRAUN and BASS 1970 (49)	Data for each run accumulated over 20-30 flashes. <1% CCl_4 decomposed per flash, producing $[Cl]\approx1.7x10^{-13}$ mol cm^{-3}. Authors assumed CCl_4 deactivated all $Cl(^2P_{\frac{1}{2}})$ to ground state $Cl(^2P_{3/2})$ before reaction. k_1 independent of He pressure in range 0.93-13.0 kPa. WATSON (87) modifies k_1 to $(7.53\pm0.6)x10^9\ cm^3\ mol^{-1}\ s^{-1}$.
	Unspecified	Unknown. ROZLOVSKII, MAL'TSEVA and FROLOV 1973 (65)	Authors report $k_1=7.95x10^{13}\exp(-3430/T)\ cm^3\ mol^{-1}\ s^{-1}$ as calculated by ROZLOVSKII (30) from the data of MARKEVICH (14) on the slow reaction of H_2 and Cl_2. This expression is in poor agreement with all other data and is not plotted.

$Cl + D_2 \rightarrow DCl + D$



$Cl + H_2 \rightarrow H + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(2.29\pm0.26)x10^8$ $(8.37\pm0.66)x10^8$ $(3.06\pm0.18)x10^9$ $(1.07\pm0.08)x10^{10}$ $(2.43\pm0.22)x10^{10}$ $(6.62\pm0.66)x10^{10}$ $(1.81\pm0.14)x10^{11}$	200 227 260 302 345 406 500	Flash photolysis study. Phosgene (10.7-53.3 Pa)/H_2 (0.02-5.33 kPa)/Ar mixtures at total pressures of 2.7-27 kPa photolysed at λ>143 nm with flash energies 9-182 J. [Cl], typically 1.7-8.3x10^{-13} mol cm^{-3}, monitored by resonance fluorescence. LEE, MICHAEL, PAYNE, STIEF and WHYTOCK 1977 (86)	He substituted for Ar at 227 K. Results corrected for Cl atom diffusion. Pseudo-first order conditions giving k_1 values independent of H_2 pressure, total pressure and flash energy. Secondary reactions of Cl therefore considered negligible. Authors derive $k_1=(1.60\pm0.25)x10^{13}\ exp(-(2230\pm60)/T)\ cm^3\ mol^{-1}\ s^{-1}$ from their own data, and recommend $k_1=(1.45\pm0.19)x10^{13}\ exp(-(2200\pm40)/T)\ cm^3\ mol^{-1}\ s^{-1}$ for 200-500 K by combining their data and those of (45,49 and 88).
$(3.3\pm0.3)x10^{13}\ exp(-(2375\pm100)/T)$	213-350	Flash photolysis study. Experimental details unavailable. [Cl] monitored by resonance fluorescence. WATSON, DAVIS, MACHADO, CONAWAY and OH 1978 (88) reported by WATSON (87) and LEE, MICHAEL, PAYNE, STIEF and WHYTOCK (86)	As yet unpublished study. Arrhenius expression listed is that derived by authors from rate constants obtained at six temperatures. Individual rate constants depicted graphically in (86). Quoted by (72,82 and 83).

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
See comments	Low temperature (unspecified)	Estimated value BODENSTEIN 1931 (6)	Estimates collision efficiency of 10^{-4}, presumably at room temperature by combining data of (1,2, 4,5 and 7). Remarkably accurate for its publication date.
$(8.3\pm0.6)x10^{13}\ exp\{-(2760\pm70)/T\}$	273-1071	Suggested expression. FETTIS and KNOX 1964 (28)	Based on (8,17) and the data of (13) for the reverse reaction combined with the thermodynamic equilibrium constant. Quoted by (33,34,35,38,42,49,82,86,87). Used by (39,44,47,55 and 63). Listed by (58,69 and 79).
$1.0x10^{14}\ exp-(2820/T)$	Unspecified	Suggested expression. FRISTROM and WESTENBERG 1965 (31)	Based on (8,17) and the data of (13) for k_8 combined with the $H + HCl \rightarrow Cl + H_2$ 8 thermodynamic equilibrium constant. Not plotted. Gives similar k_1 values to expression of FETTIS and KNOX (28). Used by (40).

$Cl + H_2 \rightarrow H + HCl$

REVIEW ARTICLES - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
9.0×10^{13} exp-(2820/T)	1000-3500	Recommended expression. JENSEN and KURZIUS 1967 (40)	Based on (28) and (31). Authors considered expression valid at high temperatures despite the lack of data available for k_1 and k_8 above 523 K and 1071 K respectively. Not plotted. Expression gives similar values to that of FETTIS and KNOX (28). Quoted by (54).
4.8×10^{13} exp(-2650/T)	559-1003	Suggested expression. BENSON, CRUICKSHANK and SHAW 1969 (46)	Authors combine their own data (see (46) in main table above) with that of (8,17 and 45), together with that of (13) after recalculation, and (34) for the reverse reaction, using the known thermodynamic equilibrium constant. Quoted by (49,78,82). Listed by (69).
3.7×10^{13} exp(-2400/T)	250-610	Recommended expression. CLYNE 1973 (62)	Apparently based on (8,17,45,46 and 49). Printers error results in E_1 being given incorrectly as 2400 J mol^{-1} (575 cal mol^{-1}).
(a) $(3.40\pm0.9)\times10^{13}$exp{-(2257±69)/T} (b) $(2.23\pm0.4)\times10^{13}$exp{-(2146±51)/T}	195-496 195-610	Suggested expressions. CLYNE and WALKER 1973 (63)	Expression (a), based on (45,49) and reverse reaction data (34), preferred by authors to expression (b), which is based on same data, plus that of (46). These evaluations also suggested by WATSON (69). Used by (75). Quoted by (82,86 and 87).
(a) $(3.4\pm0.9)\times10^{13}$exp(-(2254±69)/T) (b) $(2.2\pm0.4)\times10^{13}$exp(-(2146±51)/T)	195-496 195-610	Suggested expressions. WATSON 1974 (69)	Author suggests the use of either of these expressions, which are those derived by CLYNE and WALKER (63). (Minor misquotation error for E_1 in expression (a)).
(a) 2.8×10^{13} exp(-(2340±30)/T) (b) 2.1×10^{13} exp(-2290/T)	213-1071 200-300	Preferred expressions. WATSON 1977 (87)	Expression (a) obtained by combining data from (46,88), and k_8 values from (13) (as modified by (46)) plus thermodynamic data. Expression (b) evaluated by including k_1 determinations from (86). Expression (b) also preferred by HUDSON (85).

$Cl + H_2 \rightarrow H + HCl$

ISOTOPIC REACTIONS CL + HD → D + HCL AND CL + HD → H + DCL

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	303	Static photolysis study. H_2/HD/Cl_2 mixtures (ratio 1:1.38:1.25) at 3.87 kPa. Hydrogen separated and D-content assessed from thermal conductivity measurements. FARKAS and FARKAS 1934 (9)	Amount of D_2 contamination in HD unknown. Estimates of Cl + H_2 → H + HCl 1 Cl + HD → H + DCl 14 Cl + HD → D + HCl 15 $(k_{14}+k_{15})/k_1$ appeared to decrease with increasing extents of reaction. Extrapolating to 0% conversion gives $(k_{14}+k_{15})/k_1$= 0.26±0.03. Quoted by (15).
	243-351	Static photolysis system. H_2/HD/Cl_2 mixtures at λ>390 nm. Amount of residual hydrogen estimated by volume and its D-content measured mass spectrometrically. BIGELEISEN, KLEIN, WESTON and WOLFSBERG 1959 (23)	Authors assume no HD or H_2 formation by reverse of reactions H + HCl → Cl + H_2 8 14 and 15, or by either reaction 8 or termolecular H and D atom recombination. Rate of reactions 14 plus 15 measured relative to that of reaction 1. T/K $(k_{14}+k_{15})/k_1$ Average of: 243.2 0.293±0.003 4 points 273.2 0.324±0.005 6 points 298.2 0.349±0.007 5 points 323.2 0.377±0.005 5 points 348.2 0.394±0.006 5 points 350.7 0.398±0.008 3 points Concluded $(k_{14}+k_{15})/k_1$=(0.81±0.02) exp{-(247±3)/T}. Quoted by (37 and 59).
	236-323	Static photolysis system. H_2/HT/Cl_2 plus HD (21%) mixtures irradiated with visible light from low pressure Hg arc. Analysis as in (22). PERSKY and KLEIN 1966 (37)	All hydrogen atoms assumed to be scavenged by Cl_2. $(k_{14}+k_{15})/k_1$ calculated. T/K $(k_{14}+k_{15})/k_1$ 236.7 0.283±0.001 273.2 0.329±0.002 323.2 0.383±0.003 Authors calculated $(k_{14}+k_{15})/k_1$= (0.81±0.02) exp{-(247±3)/T}, identical to that given in previous entry (23). Listed by (79).
	510	Flash initiated chemical laser. H_2/HD/Cl_2 mixture in ratio 3:25:8 at 4.8 kPa and H_2/D_2/Cl_2 mixture, ratio 5:24:8 at 4.9 kPa. 2000 J flash. Stimulated emission monitored of $P_2(6)$ and $P_2(8)$ bands of HCl and DCl respectively. CORNEIL and PIMENTEL 1968 (43)	Population inversion in vibrationally excited HCl and DCl Cl + H_2 → H + HCl 1 H + Cl_2 → Cl + HCl 2 Cl + HD → H + DCl 14 Cl + HD → D + HCl 15 Cl + D_2 → D + DCl 16 D + Cl_2 → Cl + DCl 17 produced by reactions 2 and 17 following reactions 1 and 14, and 15 respectively. Comparing

$Cl + H_2 \rightarrow H + HCl$

ISOTOPIC REACTIONS - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		CORNEIL and PIMENTEL 1968 (43) continued.	band intensities from both experiments and using k_{16}/k_1=0.23 and $(k_{14}+k_{15})/k_1$=0.495, calculated for 510 K from (37), authors estimate k_{15}/k_{14}=1.9±0.4. Quoted by (59 and 60).
	297-443	Discharge flow system. 0.4% Cl_2 in He plus HD and NO_2 at ca. 40 Pa. $[H^{37}Cl]$ and $[D^{37}Cl]$ monitored mass spectrometrically. BAR YAAKOV, PERSKY and KLEIN 1973 (60)	Data corrected for small contribution to HCl and DCl products from H_2 and D_2 impurities. [DCl]/[HCl] measured as a function of $[NO_2]$. $Cl + HD \rightarrow H + DCl$ 14 $Cl + HD \rightarrow D + HCl$ 15 At high $[NO_2]$, [DCl]/[HCl] approaches limiting minimum value due to complete scavenging of H and D by NO_2 rather than by Cl_2. Then $[DCl]/[HCl]=k_{15}/k_{14}$. T/K k_{15}/k_{14} Average of: 297 1.75±0.08 3 points 343 1.62±0.09 5 points 393 1.44±0.08 4 points 398 1.48±0.04 2 points 443 1.36±0.05 2 points Calculated k_{15}/k_{14}=(0.81±0.04) exp{(231±25)/T}. Quoted by (73).

ISOTOPIC REACTION $Cl + D_2 \rightarrow D + DCl$

	273 and 305	Static photolysis system. $Cl_2/H_2/CO$ and $Cl_2/D_2/CO$ mixtures. Reaction mixture monitored manometrically at 273 K and 90 K. ROLLEFSON 1934 (11)	Relative rates of reaction of Cl with H_2 vs. CO and D_2 vs CO compared. Complex mechanism not completely understood by author. $Cl + H_2 \rightarrow H + HCl$ 1 $Cl + D_2 \rightarrow D + DCl$ 16 Deduced k_{16}/k_1=0.0746 and 0.103 at 273 K and 305 K respectively and derived k_{16}/k_1=1.5 exp(-820/T). Quoted by (59).
	303-451	Static photolysis system. $H_2/D_2/Cl_2$ mixtures at 16.3 kPa-26.4 kPa. $[H^{35}Cl]$ and $[D^{35}Cl]$ monitored continuously by mass spectrometry. CHILTZ, ECKLING, GOLDFINGER, HUYBRECHTS, JOHNSTON, MEYERS and VERBEKE 1963 (26)	Assumed that H and D scavenged entirely by Cl_2. Corrections due to memory effect towards HCl and DCl in mass spectrometer found necessary. Authors calculate and report with reservation, k_{16}/k_1=0.112, 0.147 and 0.214 at 303.3 K, 361.2 K and 451.1 K respectively. Quoted by (59).

$Cl + H_2 \rightarrow H + HCl$

ISOTOPIC REACTIONS - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	313-423	Static photolysis system. D_2/HCl and D_2/DCl mixtures plus radioactive Cl_2-36 at total pressure 6.0-10.7 kPa. Initial concentration ratios $[Cl_2]/[D_2]$=4-5, both $[DCl]/[D_2]$ and $[HCl]/[D_2]$ = 4-6. Residual D_2 measured manometrically. Activity of product HCl and DCl determined. KLEIN, PERSKY and WESTON 1964 (29)	Wall catalysed chlorine exchange negligible due to reaction vessel ageing. Rate constant ratios derived assuming all relevant chlorine isotope effects to be unimportant. Authors considered reactions 16-26 inc. and 2, and $Cl + D_2 \rightarrow D + DCl$ 16 $^{36}Cl + D_2 \rightarrow D + D^{36}Cl$ 17 $^{36}Cl + HCl \rightleftarrows Cl + H^{36}Cl$ 18 $^{36}Cl + DCl \rightleftarrows Cl + D^{36}Cl$ 19 $D + Cl_2 \rightarrow Cl + DCl$ 20 $D + {}^{36}Cl_2 \rightarrow Cl + D^{36}Cl$ 21 $D + {}^{36}Cl_2 \rightarrow {}^{36}Cl + DCl$ 22 $D + HCl \rightarrow Cl + HD$ 23 $D + HCl \rightarrow H + DCl$ 24 $D + D^{36}Cl \rightarrow {}^{36}Cl + D_2$ 25 $D + DCl \rightarrow Cl + D_2$ 26 $H + Cl_2 \rightarrow Cl + HCl$ 2 calculated the following k_{16}/k_{18} and k_{16}/k_{19} ratios T/K k_{16}/k_{18} k_{16}/k_{19} 312.5 1.59±0.10 13.7 ±1.0 368.2 1.81±0.12 9.09±0.7 423.2 1.67±0.07 6.85±0.4 from which $(E_{16}-E_{18})$=0.46±1.1 kJ mol^{-1} (0.11±0.27 kcal mol^{-1}) was derived.
	244-342	Static photolysis system. D_2/HD (18%) mixtures plus Cl_2. Experimental procedure as in (37) above. PERSKY and KLEIN 1966 (37)	Comments as above (37). Computed $k_{16}/(k_{14}+k_{15})$. Authors used T/K $k_{16}/(k_{14}+k_{15})$ 244.4 0.233±0.001 273.2 0.267±0.002 303.1 0.299±0.002 323.2 0.318±0.002 342.0 0.340±0.002 $(k_{14}+k_{15})/k_1$=0.81±0.02 exp{-(247±3)/T} (37) to derive k_{16}/k_1=(0.69 ±0.03) exp{-(568±9)/T}.

ISOTOPIC REACTIONS $Cl + HT \rightarrow H + TCl$ AND $Cl + HT \rightarrow T + HCl$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	234-307	(a) Static photolysis system. H_2/HT mixtures plus excess Cl_2 at 3.0-5.4 kPa. Hydrogen measured by volume and tritium content using a proportional flow counter.	High percentage reaction conversion, 56-94%. All H and T atoms assumed to be scavenged by Cl_2. Low tritium content (ca. 1-2%) ensured that in equilibrated tritiated hydrogen, $[T_2]$ was sufficiently low to contribute negligibly to reaction. Small correction due to presence of T_2 applied to counting data however. Results from methods (a) and (b)
	273-344	(b) Self-radiolysis of H_2/HT/Cl_2 mixtures at 4.3-5.2 kPa. Procedure and analysis as in (a).	

$Cl + H_2 \rightarrow H + HCl$

ISOTOPIC REACTIONS - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		JONES 1951 (15)	indistinguishable and therefore $Cl + HT \rightarrow H + TCl$ 27 $Cl + HT \rightarrow T + HCl$ 28 combined by author. T/K $(k_{27}+k_{28})/k_1$ Average of: 234.68 0.226±0.001 3 points 273.16 0.269±0.002 5 points 306.41 0.300±0.001 6 points 343.91 0.329±0.001 2 points Calculated $(k_{27}+k_{28})/k_1=(0.74\pm0.02)\exp\{-(278\pm4)/T\}$. Quoted by (23 and 59).
	243-323	Same experiments as those described in (37) under studies of reactions 14 and 15. Tritium content of samples assessed with an internal Geiger counter. PERSKY and KLEIN 1966 (37)	Comments as above (37). Deduced $(k_{18}+k_{19})/k_1$ and calculated T/K $(k_{27}+k_{28})/k_1$ 243.2 0.153±0.002 273.2 0.184±0.002 323.2 0.229±0.006 $(k_{27}+k_{28})/k_1=(0.79\pm0.02)\exp\{-(401\pm7)/T\}$.

ISOTOPIC REACTIONS $Cl + DT \rightarrow D + TCl$ AND $Cl + DT \rightarrow T + DCl$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	273.2 and 323.2	Method as in (37) above. $D_2/DT/Cl_2$ mixtures. PERSKY and KLEIN 1966 (37)	Comments as above (37). Authors measured $(k_{29}+k_{30})/k_{16}$ as $Cl + DT \rightarrow D + TCl$ 29 $Cl + DT \rightarrow T + DCl$ 30 0.549±0.008 and 0.597±0.005 at 273.2 K and 323.2 K respectively and used $k_{16}/k_1=(0.69\pm0.03)\exp\{-(568\pm9)/T\}$ (37) to derive $(k_{29}+k_{30})/k_1=0.65\exp(-716/T)$. Listed by (79).

ISOTOPIC REACTION $Cl + T_2 \rightarrow T + TCl$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	273.2 and 323.2	Method as in (37) above. $D_2/T_2/Cl_2$ mixtures. PERSKY and KLEIN 1966 (37)	Comments as above (37). Authors obtained $k_{31}/k_{16}=0.332\pm0.005$ and $Cl + D_2 \rightarrow D + DCl$ 16 $Cl + T_2 \rightarrow T + TCl$ 31 0.389±0.002 at 273.2 K and 323.2 K respectively and used $k_{16}/k_1=(0.69\pm0.03)\exp\{-(568\pm9)/T\}$ (37) to calculate $k_{31}/k_1=0.65\exp(-852/T)$. Listed by (79).

Discussion

Studies of the reaction of molecular hydrogen and chlorine to form HCl both in explosions and flames, and under the influence of irradiation by visible and ultraviolet light, have been carried out since the latter part of the last century. Early workers established the radical nature of the reaction and the importance of the now well established Nernst chain mechanism, of which the reaction

$$Cl + H_2 \rightarrow H + HCl \qquad (1)$$

is the slower of the two propagating steps. A summary of the results obtained in this pioneering era is given by Marshall [3] and Bodenstein [6]. The similarity of the bond dissociation energies of H_2 and HCl is reflected in the approximate thermoneutrality of reaction 1 ($\Delta H°=4.4$ kJ mol^{-1} at 298

K), and results in the rate of the reverse reaction, 8, being comparable at the same temperature.

$$\mathrm{H} + \mathrm{HCl} \rightarrow \mathrm{Cl} + \mathrm{H_2} \qquad (8)$$

Despite the importance of a knowledge of k_1 few direct determinations of the rate constant have been carried out. Moreover, only four relative rate studies have been made. Those of Pritchard, Pyke and Trotman-Dickenson [19,21] and of Knox and Nelson [24] were carried out to determine Arrhenius expressions for the reaction of Cl atoms and CH_4 and therefore provide no information on the magnitude of k_1. These relative rate studies are discussed elsewhere, in section B7. Both Ashmore and Chanmugam's study [17], and that of Benson, Cruickshank and Shaw [46], suffer from similar drawbacks, in that the reaction systems are sufficiently complex as to require either simplifying assumptions, or the inclusion of correction terms to enable the experimental data to be analysed. Furthermore values of other relevant rate or equilibrium constants must be assumed in deriving k_1. While more recent data provide no reason to question seriously the methods of data analysis employed, we prefer to regard the derived k_1 values with a degree of caution, and use them as an influential guide only.

In addition to the early work of Rodebush and Klingelhoefer [8], whose remarkably precise measurements of k_1 using a prototype discharge flow system are interesting if not reliable, there are four investigations of the absolute magnitude of k_1 to be considered [45,49,86,88]. Of these, that of Westenberg and de Haas [45] utilised e.s.r. to monitor the concentration of reacting $\mathrm{Cl}(^2\mathrm{P}_{3/2})$ atoms in the presence of an excess of molecular H_2, whereas each of the other three studies measured Cl atom concentration by resonance fluorescence, a technique now well established as being particularly reliable, due to its applicability to reacting systems operating under pseudo-first order conditions as a result of low concentrations of the labile reactants. The results of these four studies are in excellent agreement and they therefore form the basis of our recommended expression for k_1.

Earlier reviews by Clyne and Walker [63], and Watson [69], questioned the accuracy of the rate constant values derived by Westenberg and de Haas [45], suggesting that they were in error by a factor of two. This postulate was put forward to explain the discrepancy noted by these latter workers between the expression for k_1/k_8, as calculated from their data [45], and that for the equilibrium constant, computed from the accepted thermodynamic data. Several explanations have been advanced to rationalise this difficulty, both supporting and criticising the existing data for both k_1 and k_8. They are outlined in the discussion of reaction 8 (section B5) together with our own appraisal of the current situation. We now follow Lee and co-workers [86] in recommending the expression

$$k_1 = 1.45 \times 10^{13} \exp(-2200/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

based primarily on the data from [45,49,86,88], over the temperature range 200–650 K, with error limits for calculated rate constants of ±50%.

Isotopic Reactions

Studies have been made of the reactions of Cl atoms with all six of the isotopic forms of molecular hydrogen. No direct rate constant values have been obtained however, the majority of investigations being relative rate measurements using reaction 1 as the primary standard. Several of the isotope effects have been the subject of theoretical calculations [23,37], but their detailed consideration is beyond the scope of this evaluation.

Two reactions, 14 and 15, are possible for HD. Klein and

$$\mathrm{Cl} + \mathrm{HD} \rightarrow \mathrm{H} + \mathrm{DCl} \qquad (14)$$

$$\mathrm{Cl} + \mathrm{HD} \rightarrow \mathrm{D} + \mathrm{HCl} \qquad (15)$$

co-workers have carried out two independent studies of the variation of $(k_{14}+k_{15})/k_1$ with temperature [23,37]. They are in good agreement and can be adequately described in the range 235–360 K by the expression shown drawn through the data points in the figure.

$$(k_{14} + k_{15})/k_1 = 0.81 \exp(-248/T)$$

We consider the measurement of $(k_{14}+k_{15})/k_1$ by Farkas and Farkas [9] to be unreliable. Only one investigation of the variation of k_{15}/k_{14} with temperature has been made [60]. An earlier estimate [43] of k_{15}/k_{14} at 510 K is at odds with these later results.

Of the three studies of k_{16}/k_1 [11,26,37] we give that of

$$\mathrm{Cl} + \mathrm{D_2} \rightarrow \mathrm{D} + \mathrm{DCl} \qquad (16)$$

Rollefson [11] a low weighting. The other results are in good agreement and the combined data can be described by

$$k_{16}/k_1 = 0.81 \exp(-611/T)$$

in the temperature range 240–455 K.

HT, like HD, can react with Cl atoms by two routes. The

$$\mathrm{Cl} + \mathrm{HT} \rightarrow \mathrm{H} + \mathrm{TCl} \qquad (27)$$

$$\mathrm{Cl} + \mathrm{HT} \rightarrow \mathrm{T} + \mathrm{HCl} \qquad (28)$$

dependence of $(k_{27}+k_{28})/k_1$ on temperature has been investigated in two studies, [15 and 37], giving somewhat different conclusions. Persky and Klein [37] have criticised the results of Jones [15] on the grounds that the high specific activity of the HT used in the experiments may have led to radiation induced isotope exchange between HT and HCl. In view of the agreement between the concomitantly measured isotope effect for Cl plus HD with those of an independent study, we prefer the later data [37] but make no recommendation.

The reactions of Cl with DT and T_2 have each received only a single investigation [37]. As such we are unable to comment on

$$\mathrm{Cl} + \mathrm{DT} \rightarrow \mathrm{D} + \mathrm{TCl} \qquad (29)$$

$$\mathrm{Cl} + \mathrm{DT} \rightarrow \mathrm{T} + \mathrm{DCl} \qquad (30)$$

$$\mathrm{Cl} + \mathrm{T_2} \rightarrow \mathrm{T} + \mathrm{TCl} \qquad (31)$$

the accuracy of the data other than noting that they appear to follow the general isotope effect trends observed in the Cl atom/hydrogen system.

At the present time we consider that there are insufficient data to warrant our making a recommendation for any of the rate constants k_{14} to k_{16} and k_{27} to k_{31}, although the expressions for $(k_{14}+k_{15})/k_1$ and k_{16}/k_1 could be used with care on an interim basis.

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B5 $H + HCl \rightarrow Cl + H_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-4.38	-5.75	0.47
300	-4.38	-5.74	0.46
500	-4.07	-4.97	0.16
1000	-3.52	-4.13	-0.03
1500	-3.84	-4.38	-0.10
2000	-4.28	-4.63	-0.13
2500	-4.54	-4.75	-0.15
3000	-4.59	-4.77	-0.17
3500	-4.43	-4.72	-0.18
4000	-4.00	-4.61	-0.19
4500	-3.31	-4.45	-0.19
5000	-2.38	-4.25	-0.20

RECOMMENDED RATE CONSTANT

$$k = 7.97 \times 10^{12} \exp(-1710/T)\ cm^3\ mol^{-1}\ s^{-1}$$

$$= 1.32 \times 10^{-11} \exp(-1710/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

Temperature Range: 200-650 K

Suggested Error Limits for Calculated Rate Constant: ±50% over quoted temperature range.

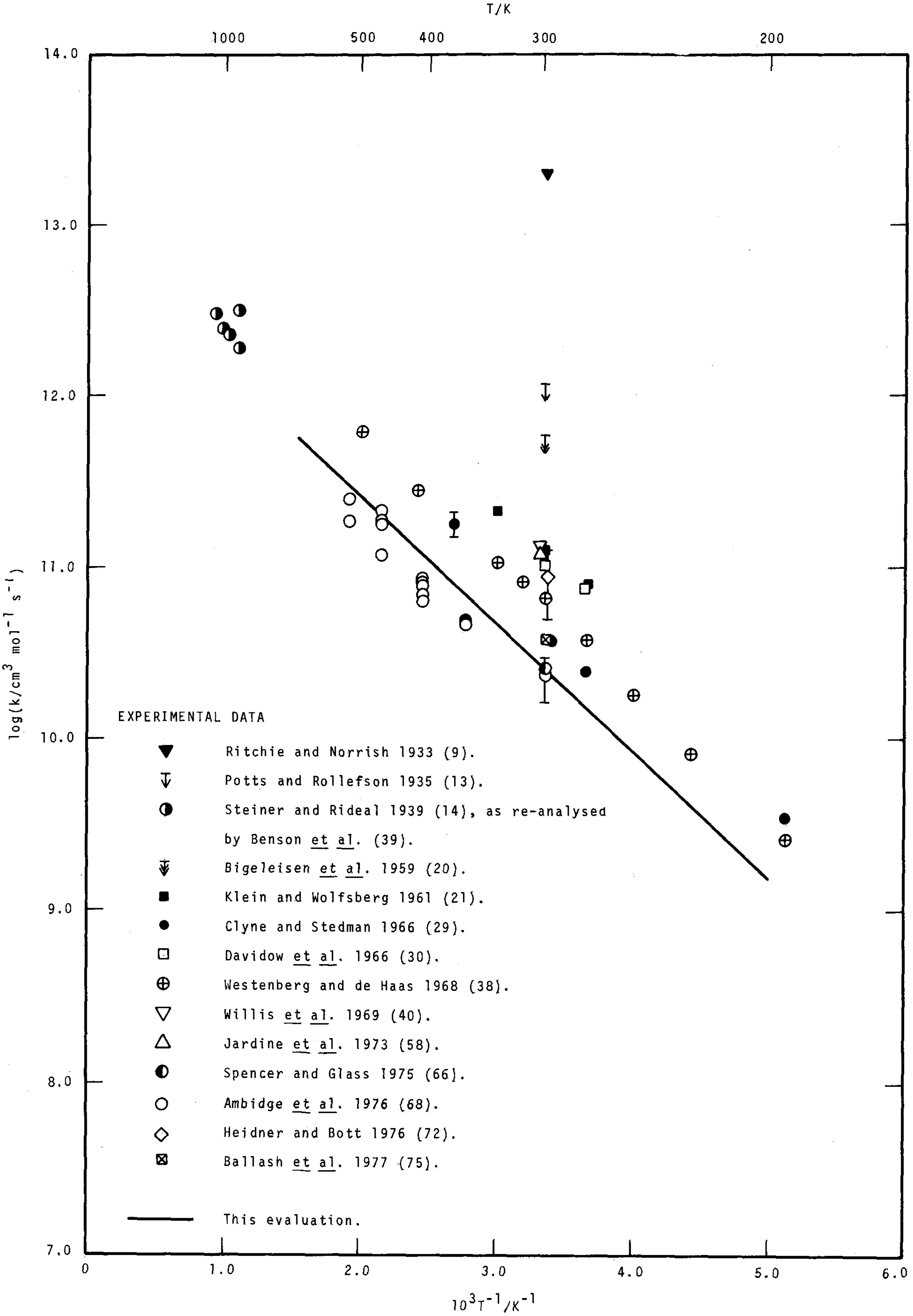
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 12.90 \pm 0.2$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -10.88 \pm 0.2$

$E/J\ mol^{-1} = 14\ 220 \pm 2220$

$E/cal\ mol^{-1} = 3\ 400 \pm 530$

$H + HCl \rightarrow Cl + H_2$

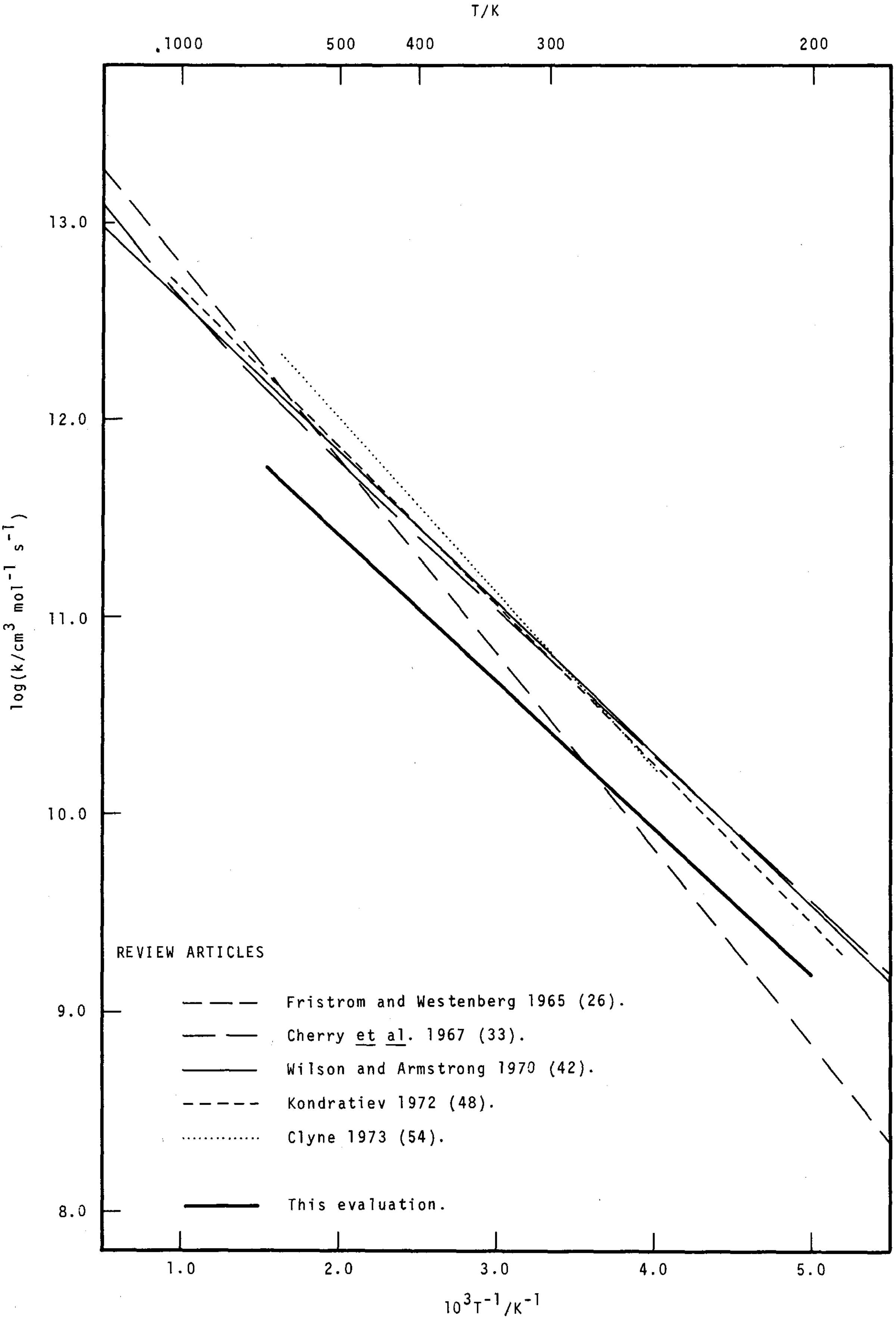


$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Static photolysis system. $H_2/Cl_2/HCl$ mixtures at λ= 406 nm, isolated by filter solutions. Unreacted [Cl_2] measured by absorption spectrophotometry at 365 nm using thermopile detector. RITCHIE and NORRISH 1933 (9)	Study of HCl photosynthesis. HCl quantum yields proportional to $1/I_{abs}^{0.4}$. Data fitted to empirical expression which was then compared to theoretical equation derived from postulated mechanism $H + HCl \rightarrow Cl + H_2$ 1 $Cl_2 + h\nu \rightarrow Cl + Cl$ 2 $Cl + H_2 \rightarrow H + HCl$ 3 $H + Cl_2 \rightarrow Cl + HCl$ 4 $Cl + Cl \rightarrow Cl_2$ 5 to obtain k_1/k_4=1.7. Authors assume collision efficiencies of reactions 1 and 4 approximately equal and quote value of 0.01 (7). Using our value, k_4=1.19x10^{13} $cm^3\ mol^{-1}\ s^{-1}$ (this Volume, section B6) we calculate k_1=2.0 x10^{13} $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (12 and 13).
	200-300	Static photolysis system. $H_2/Cl_2/HCl$ mixtures at unspecified wavelength. [H_2] monitored manometrically after immersing reaction vessel in liquid air. POTTS and ROLLEFSON 1935 (13)	HCl inhibited HCl photosynthesis study. Authors deduce HCl quantum yield independent of absorbed light intensity and obtain $k_1/k_4 \leqslant 0.1$ at unspecified temperature, but infer its acceptability at 298 K. Using our value k_4=1.19x10^{13} $cm^3\ mol^{-1}\ s^{-1}$ (this Volume, section B6) we calculate $k_1 \leqslant 1.19$x10^{12} $cm^3\ mol^{-1}\ s^{-1}$ at 298 K. Quoted by (12).
	901-1071 900	(a) Static pyrolysis study. Para-enriched H_2/HCl mixtures. Para-[H_2] determined by thermal conductivity measurements at liquid air temperature. (b) Static pyrolysis study. D_2/HCl mixtures. [HD] estimated from thermal conductivity measurements at liquid air temperature. STEINER and RIDEAL 1939 (14)	(a) Comparison of the rates of reaction 1 and the H atom catalysed para-ortho hydrogen conversion. Authors corrected data for minor participation by postulated bimolecular conversion reaction 6, and its reverse $para\text{-}H_2 + HCl \rightarrow ortho\text{-}H_2 + HCl$ 6 $H_2 \rightleftharpoons 2H$ 7 Authors obtain values for $k_1K_7^{0.5}$ at 901,960,1013 and 1071 K of 1.61,12.0,55.3 and 288 $cm^{1.5}\ mol^{-0.5}\ s^{-1}$ respectively, use K_7 values derived from the data of (6) and (11) to calculate k_1 values of 3.15x10^{12},

$H + HCl \rightarrow Cl + H_2$

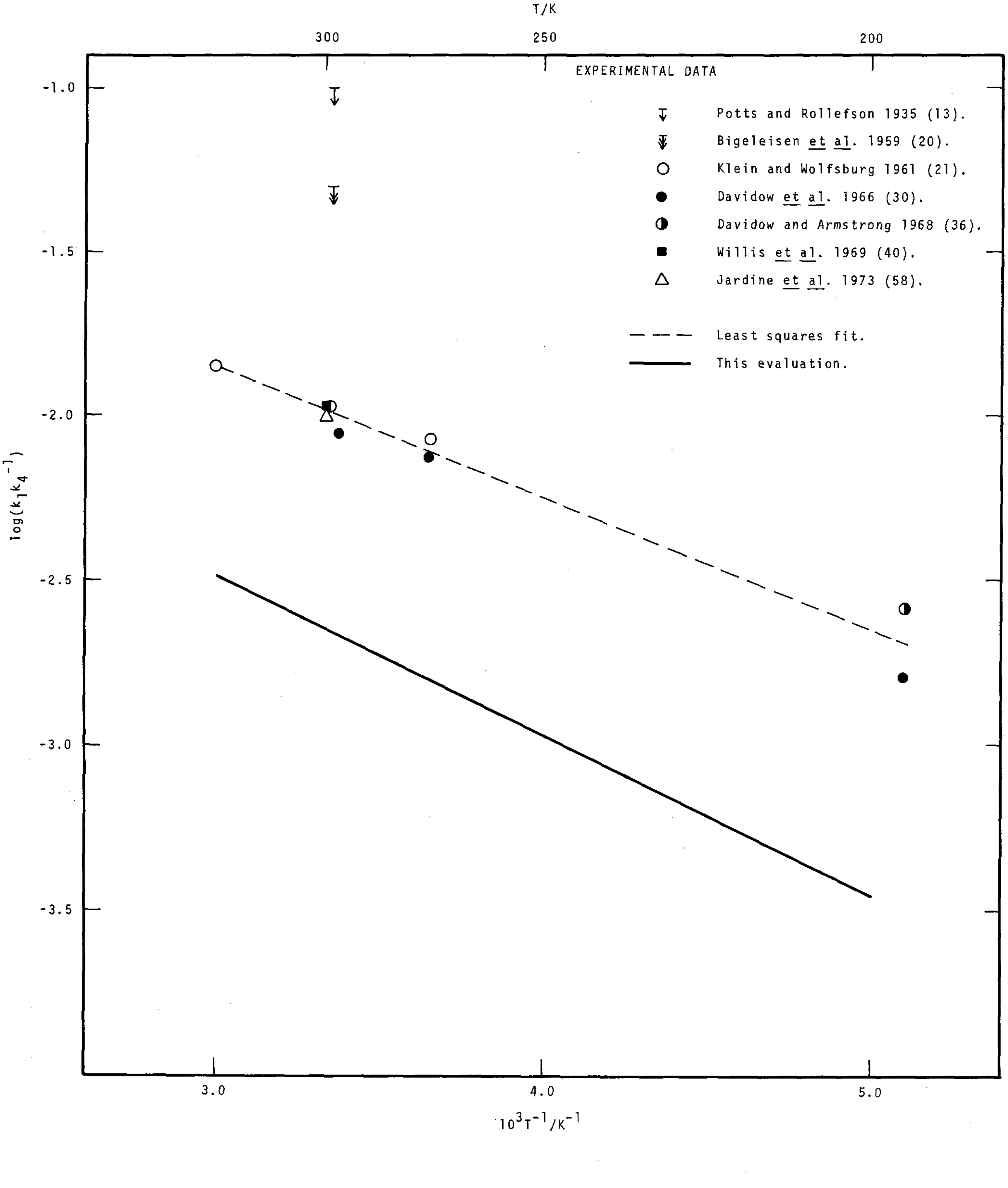


$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		STEINER and RIDEAL 1939 (14) continued.	$3.93x10^{12}$, $4.4x10^{12}$ and $5.7x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$, and thereby compute log $(A_1/cm^3\ mol^{-1}\ s^{-1})$= 13.75 and E_1=21.8 kJ mol^{-1} (5.2 kcal mol^{-1}). Recalculated by BENSON and co-workers (39) giving k_1 as $1.91x10^{12}$, $2.30x10^{12}$, $2.51 x10^{12}$ and $3.05x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ at these temperatures. (b) Exchange reactions of D_2 and HCl studied. Data corrected for postulated bimolecular reaction 8, allowing a value for k_1 of $D_2 + HCl \rightarrow HD + DCl$ 8 $3.2x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ to be calculated indirectly. Quoted by (28,29,38). Modified expression used by (25,31,59). Used by (25,42).
	298	Static photolysis system. $H_2/D_2/Cl_2$ mixture at λ>390 nm. $H_2/HD/D_2$ ratios measured by mass spectrometry. BIGELEISEN, KLEIN, WESTON and WOLFSBERG 1959 (20)	Photosynthesis of HCl and DCl. Authors estimated upper limit for $[HD]/[H_2]$ as $2x10^{-4}$ from data corrected for isotopic scrambling in mass spectrometer source and deduced $k_1/k_4 \leqslant 0.05$ by making both steady state and unspecified isotope effect assumptions, and neglecting termolecular combination reactions involving H, D and Cl. Using our value k_4=1.19 $x10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ (this Volume, section B6) we calculate $k_1 \leqslant 6.0x 10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (21).
	273-336	Static photolysis system. $H_2/Cl_2/TCl/HCl$ mixtures at λ>390 nm. Specific activity of product HT and that derived from TCl/HCl mixtures by reaction with Zn amalgam measured with Geiger gas counter. KLEIN and WOLFSBERG 1961 (21)	Authors used $k_3/(k_9+k_{10})$=1.35 exp(278/T) (17) and theoretically computed k_1/k_{11} ratio in $H + HCl \rightarrow Cl + H_2$ 1 $Cl + H_2 \rightarrow H + HCl$ 3 $H + Cl_2 \rightarrow Cl + HCl$ 4 $Cl + HT \rightarrow H + TCl$ 9 $Cl + HT \rightarrow T + HCl$ 10 $H + TCl \rightarrow Cl + HT$ 11 numerical integration of rate expression to calculate values for k_1/k_4 of $(8.42\pm0.7)x10^{-3}$, $(1.08\pm0.2)x10^{-2}$ and $(1.42\pm0.05) x10^{-2}$ at 273.5, 298.5 and 335.5 K respectively leading to k_1/k_4 =(0.143 ± 0.033) exp{-(775 ± 65)/T}.

H + HCl / H + Cl_2


T/K
300
250
200
EXPERIMENTAL DATA
↧ Potts and Rollefson 1935 (13).
↡ Bigeleisen et al. 1959 (20).
○ Klein and Wolfsburg 1961 (21).
● Davidow et al. 1966 (30).
◑ Davidow and Armstrong 1968 (36).
■ Willis et al. 1969 (40).
△ Jardine et al. 1973 (58).
— — — Least squares fit.
—— This evaluation.
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
log(k1k4-1)
3.0
4.0
5.0
10^3 T^-1/K^-1

$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		KLEIN and WOLFSBERG 1961 (12) continued.	Using our expression k_4=8.6x10^{13} exp(-590/T) $cm^3\ mol^{-1}\ s^{-1}$ we calculate k_1 values of 8.37x10^{10}, 1.30x10^{11} and 2.10x10^{11} $cm^3\ mol^{-1}\ s^{-1}$ at these temperatures. Quoted by (23,27,30,31,58 and 59).
	295 and 425	Static photolysis system. D_2/HCl mixtures at ca. 3.3 kPa photolysed with low pressure Hg lamp. (Effective λ=185 nm). $[H_2]$, [HD] and $[D_2]$ analysed by mass spectrometry. DE VRIES and KLEIN 1964 (24)	Results claimed to be pressure independent between 2.26 and 3.33 kPa. Contribution to products from translationally excited H atoms apparently overlooked. Application of steady-state analysis of multi-step mechanism $H + HCl \rightarrow Cl + H_2$ 1 $H + D_2 \rightarrow D + HD$ 12 to data yielded values for k_{12}/k_1 of 14±4 and ≥140 at 295 and 425 K respectively. Using log(k_{12}/ $cm^3\ mol^{-1}\ s^{-1}$)=13.51-(1870/T) (34) we calculate k_1=(1.1±0.4)x10^6 $cm^3\ mol^{-1}\ s^{-1}$ and ≤9.2x10^6 $cm^3\ mol^{-1}\ s^{-1}$ at these temperatures. Misquoted by (59). Not plotted.
(3.5±0.4)x10^9 (2.5±0.3)x10^{10} (3.8±0.4)x10^{10} (1.8±0.3)x10^{11}	195 273 294 373	Discharge flow system. HCl (typically 1.33 Pa) added to H atoms (typically 0.013 Pa) produced by discharging 0.02% H_2, in Ar at 133 Pa total pressure. [H] measured by adding NO and monitoring HNO chemiluminescence. CLYNE and STEDMAN 1966 (29)	Authors argue that low $[H_2]$ and small percentage conversion of H rendered reaction 3 unimportant. $Cl + H_2 \rightarrow H + HCl$ 3 Pseudo-first order conditions. Data combined with that from (14) to give curved Arrhenius plot described by k_1= (6.2±3.5)x$10^{11}T^{0.5}$ exp{-(1560±200)/T} $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (28,38,59). Used by (42).
	196-296	Radiolysis of $HCl/Cl_2/SF_6$ mixtures using both ^{60}Co and X-ray sources. $[H_2]$ presumably measured manometrically as in (22). DAVIDOW, LEE and ARMSTRONG 1966 (30)	Results independent of radiolysis source. Decreasing H_2 yield with $H + HCl \rightarrow Cl + H_2$ 1 $H + Cl_2 \rightarrow Cl + HCl$ 4 increasing $[Cl_2]/[HCl]$ attributed to competition of reactions 1 and 4 leading to k_1/k_4 values of (1.6±0.5)x10^{-3}, (7.5±0.5)x10^{-3} and (8.75±0.45)x10^{-3} at 196.2, 274.2 and 296.2 K respectively. Using our value, k_4=8.6x10^{13} exp(-590/T) $cm^3\ mol^{-1}\ s^{-1}$ (this Volume, section

$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		DAVIDOW, LEE and ARMSTRONG 1966 (30) continued.	B6) valid for temperatures between 250 and 730 K, we calculate k_1=7.5x10^{10} and 1.0x10^{11} cm^3 mol^{-1} s^{-1} at the two higher temperatures.
	196	Radiolysis system. Method given in (30). Cl_2/HCl mixtures in various ratios from 0.017 to 0.1. HCl pressure 73-85 kPa. DAVIDOW and ARMSTRONG 1968 (36)	Comments for (30) apply. Participation by H_2 forming reactions of hot H atoms and HCl^- allowed for by authors in calculating k_1/k_4=(2.6±0.7)x10^{-3} at 196±2 K. No value for k_4 available at this temperature. Quoted by (42).
(2.64±0.04)x10^9 (8.3 ±0.2)x10^9 (1.81±0.06)x10^{10} (3.8 ±0.1)x10^{10} (6.7 ±0.4)x10^{10} (8.3 ±0.7)x10^{10} (1.09±0.14)x10^{11} (2.84±0.26)x10^{11} (6.2 ±0.3)x10^{11}	195 226 250 273 297 314 333 413 497	Discharge flow system. HCl (3.41x10^{-10}-4.6x10^{-9} mol cm^{-3}) added to H atom flow from discharged H_2 (<0.1%) in He or Ar at total pressure 80-210 Pa. [H] monitored by e.s.r. spectrometry. WESTENBERG and DE HAAS 1968 (38)	Pseudo first-order conditions. Low [H] used to eliminate participation of reactions 3 and 4. Data at 413 and 497 K corrected for H atom longitudinal diffusion. Authors calculated k_1=(2.3±0.7)x10^{13} exp{-(1760±100)/T} cm^3 mol^{-1} s^{-1}. Quoted by (44,49,51,56,59, 61,62,63,64,73 and 76). Misquoted by (45,67). Used by (42,50,53,58,65 and 74).
	300	Radiolysis system. Febetron 705 pulsed electron radiolysis of Cl_2/HCl mixtures, ratio 4.6x10^{-3}-7.6x10^{-2}, at 93 and 160 kPa total pressure. Analysis of [H_2] as in (30) and by mass spectrometry. WILLIS, BOYD and ARMSTRONG 1969 (40)	As in (30) and (36) authors proposed that decreasing H_2 yield with increasing [Cl_2]/[HCl] ratio was due to competition for H between reactions 1 and 4. Derived k_1/k_4=0.0110 and 0.0103 from data obtained at 93 and 160 kPa respectively resulting in a quoted average value of 0.0107. Using our value k_4=1.20x10^{13} cm^3 mol^{-1} s^{-1} (this Volume, section B6) we calculate k_1=1.29x10^{11} cm^3 mol^{-1} s^{-1}. Quoted by (42).
	300	Static photolysis study. CO_2/HCl mixtures in (5.00 ±0.05):1 ratio plus Cl_2 at λ=184.9 nm. [H_2] measured manometrically as in (22). JARDINE, BALLASH and ARMSTRONG 1973 (58)	Thermalised H atom reactions studied after hot H moderation by CO_2. Data evaluated assuming fraction of hot H reacting with HCl is independent of [Cl_2], to give k_1/k_4=0.01±0.001. Using our value, k_4=1.20x10^{13} cm^3 mol^{-1} s^{-1} (this Volume, section B6), we calculate k_1=1.20x10^{11} cm^3 mol^{-1} s^{-1}.

$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2.6x10^{10}$	298	Discharge flow system. HCl ($1.07-2.86x10^{-9}$ mol cm^{-3}) added to H atoms ($1.69-36.0x10^{-11}$ mol cm^{-3}) in Ar at total pressure of 67-200 Pa. [H] and [Cl] monitored by e.s.r. spectroscopy. SPENCER and GLASS 1975 (66)	Pseudo first order conditions. Preliminary experiments established that wall combination of H with Cl atoms was unimportant. Effect of various wall coatings on reaction rate investigated. Stoichiometry, defined as [Cl] produced /[H] consumed, found to be dependent on H atom consumption rate. k_1 estimated by extrapolation to stoichiometry of unity. WATSON (77) suggests a more accurate extrapolation gives $3.1x10^{10}$ cm^3 mol^{-1} s^{-1}. Used by (71).
$2.91x10^{10}$	298	Discharge flow system. HCl ($2.8x10^{-11}-9.01x10^{-10}$ mol cm^{-3}) and SF_6($5.0x10^{-9}-6.06x10^{-8}$ mol cm^{-3}) added to H atoms in Ar. Initial [HCl]/[H] ratio in range 0.53-33.5. [H] and [HCl] monitored by e.s.r. and mass spectrometry respectively. AMBIDGE, BRADLEY and WHYTOCK 1976 (68)	Preliminary experiments in absence of SF_6 showed increase in k_1 at low [HCl]/[H] ratio (<25). Addition of excess SF_6 resulted in constant k_1 under all experimental conditions. Negligible depletion of [HCl] except in absence of SF_6 at low [HCl]/[H] ratios. k_1 found to be independent of added H_2. Authors analysed data in terms of reactions 1,1*,4,13 and 14. This $H + HCl \rightarrow Cl + H_2$ 1 $H + Cl_2 \rightarrow Cl + HCl^*$ 4 $Cl + wall \rightarrow \frac{1}{2}Cl_2$ 13 $H + HCl^* \rightarrow Cl + H_2$ 1* $HCl^* + M \rightarrow HCl + M$ 14 mechanism implies a stoichiometry of 2 when $[SF_6] >> [H]$, and experimental rate constants were therefore halved, giving those listed. Value at 298 K has been averaged to $(2.32±0.67)x10^{10}$ cm^3 mol^{-1} s^{-1} for plotting. Authors calculated $\log(k_1/cm^3\ mol^{-1}\ s^{-1}) = (12.67±0.10) - (695±37)/T$. Used by (70).
$1.96x10^{10}$	298		
$1.70x10^{10}$	298		
$2.95x10^{10}$	298		
$2.25x10^{10}$	298		
$1.68x10^{10}$	298		
$2.28x10^{10}$	298		
$2.41x10^{10}$	298		
$2.77x10^{10}$	298		
$2.32x10^{10}$	298		
$2.97x10^{10}$	298		
$1.65x10^{10}$	298		
$4.76x10^{10}$	360		
$4.82x10^{10}$	360		
$4.92x10^{10}$	360		
$6.45x10^{10}$	405		
$8.45x10^{10}$	405		
$8.30x10^{10}$	405		
$7.05x10^{10}$	405		
$2.21x10^{11}$	464		
$1.77x10^{11}$	464		
$1.79x10^{11}$	464		
$1.19x10^{11}$	464		
$1.90x10^{11}$	464		
$1.87x10^{11}$	521		
$2.50x10^{11}$	521		
$(9±4)x10^{10}$	295	Discharge flow system. Experimental details given by BOTT and HEIDNER (69). HCl(ca. $5x10^{-11}$ mol cm^{-3}) added to H atoms (ca. $5.4x10^{-11}$ mol cm^{-3}) produced by discharging H_2(13-160 Pa) in He at total	Peripheral results from study of H atom removal of HCl (v=1). Authors argue that high $[H_2]$/[HCl] ratio (100-2500) precludes complications from product Cl atoms. Fixed observation time method of kinetic analysis used to derive k_1.

$H + HCl \rightarrow Cl + H_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		pressure of 213-333 Pa. [HCl] measured by laser induced 1→0 fluorescence and [H] monitored by isothermal calorimetry. HEIDNER and BOTT 1976 (72)	
	298	Radiolysis study. ^{60}Co irradiated HCl ($1.6-6.5\times10^{-5}$ mol cm^{-3})/NO($0-8.4\times10^{-6}$) mixtures containing either none or 1.0-1.25 mol % SF_6. [H_2] yield measured manometrically as in (22). BALLASH, NAGRA and ARMSTRONG 1977 (75)	Added NO competes via reaction 15 with reaction 1 for thermal H atoms. $H + NO + M \rightarrow HNO + M$ (M=HCl) 15 Authors obtain $k_1/k_{15} = (2.8\pm0.3)\times10^{-6}$ mol cm^{-3} from experiments in which SF_6 was present as an electron scavenger. Analysis of data obtained in absence of SF_6 gave $k_1/k_{15} = (2.6\pm0.3)\times10^{-6}$ mol cm^{-3}. This expression used to calculate k_{15} value by substituting $k_1 = 6.6\times10^{10}$ cm^3 mol^{-1} s^{-1} (38). Using our value for $k_{15} = 1.5\times10^{16}$ cm^3 mol^{-1} s^{-1} (Volume 2, p.389) gives $k_1 = (3.9\pm2.0)\times10^{10}$ cm^3 mol^{-1} s^{-1}.

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
See Comments	Low temperature (unspecified)	Estimated value. BODENSTEIN 1931 (7)	Estimates collision efficiency of 10^{-4}, presumably at room temperature, by combining data of (1,2,4,5 and 8). Remarkably accurate for its publication date. Quoted by (9).
$5.8\times10^{13}\exp(-2265/T)$	Unspecified	Suggested expression. FRISTROM and WESTENBERG 1965 (26)	Expression derived by considering data from (14) with that obtained by combining experimental rate constants, k_3, for reverse reaction, (10,18), with known thermodynamic equilibrium constant. Quoted by (37).
$6.2\times10^{11}T^{0.5}\exp(-1560/T)$	Unspecified	Selected expression. CHERRY, GOLD and VAN NICE 1967 (33)	Expression selected is that derived by (29). Listings of (25,28 and 31) considered.

$H + HCl \rightarrow Cl + H_2$

REVIEW ARTICLES - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(2.3\pm0.7)\times10^{13}\exp\{-(1760\pm100)/T\}$	Unspecified	Suggested expression. WILSON and ARMSTRONG 1970 (42)	Based on (14,29 and 38).
$(2.95\pm1.2)\times10^{13}\exp\{-(1860\pm115)/T\}$	195-1070	Suggested expression. KONDRATIEV 1972 (48)	Based on (29) and the data of (14) as recalculated by (31).
$6.2\times10^{13}\exp(-2050/T)$	250-610	Recommended expression. CLYNE 1973 (54)	Apparently based on (14,29 and 38). Printers error results in E_1 being given incorrectly as 2050 J mol^{-1} (490 cal mol^{-1}).

ISOTOPIC REACTION D + HCL → CL + HD

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	900	Static pyrolysis study. D_2/HCl mixtures. [HD] estimated from thermal conductivity measurements at liquid air temperature. STEINER and RIDEAL 1939 (14)	Data corrected for postulated bimolecular reaction 8, allowing a value for k_{16} of 1.0×10^{12} cm^3 $D_2 + HCl \rightarrow HD + DCl$ 8 $D + HCl \rightarrow Cl + HD$ 16 mol^{-1} s^{-1} to be calculated indirectly. Quoted by (24). Used by (47).
	295 and 425	Static photolysis system. D_2/HCl mixtures at ca. 3.3 kPa photolysed with low pressure Hg lamp. [H_2], [HD] and [D_2] analysed mass spectrometrically. DE VRIES and KLEIN 1964 (24)	Comments in main table above for (24) apply. Authors deduced k_{16}/k_{17} to be zero, but with an $D + HCl \rightarrow H + DCl$ 17 upper limit of 0.9, and <10 at 295 and 425 K respectively. Quoted by (50).
$\leqslant (7\pm3)\times10^{10}$	295	Discharge flow system. Method identical to that described above (72). H atoms and H_2 replaced by D atoms and D_2. HEIDNER and BOTT 1976 (72)	Comments given above (72) apply. Authors derived $(k_{16}+k_{17})$ which $D + HCl \rightarrow Cl + HD$ 16 $D + HCl \rightarrow H + DCl$ 17 is therefore listed as maximum k_{16} value.

ISOTOPIC REACTION H + DCL → CL + HD

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	900	Static pyrolysis study. H_2/DCl mixtures. [HD] measured as in (14) above. STEINER and RIDEAL 1939 (14)	Data treated as noted above (14) giving $k_{18}=1.3\times10^{12}$ cm^3 mol^{-1} s^{-1}. $H + DCl \rightarrow Cl + HD$ 18

$H + HCl \rightarrow Cl + H_2$

ISOTOPIC REACTION $H + DCL \rightarrow CL + HD$ - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	300-498	Static photolysis study. 2.67 kPa each of H_2 and DCl at λ=184.9 nm. [HD] and [D_2] monitored by mass spectrometry. WOOD 1972 (50)	Measurements confined to extents of reaction <0.6% DCl decomposition. Contribution to product yields from 'hot' D atoms noted. Values of k_{18}/k_{19}, given below, $H + DCl \rightarrow D + HCl$ 19 $D + DCl \rightarrow Cl + D_2$ 20 $D + H_2 \rightarrow H + HD$ 21 determined using (i) $k_{20}=6.4\times10^{12}$ $\exp(-1915/T)$ cm^3 mol^{-1} s^{-1}, itself calculated using transition state theory from the expression for k_1 given by (38); and (ii) $k_{21}=4.4\times10^{13}$ $\exp(-3830/T)$ cm^3 mol^{-1} s^{-1} (35). k_{18}/k_{19} values. Limits given encompass individual values. Number of determinations other than one given in parenthesis. T/K k_{18}/k_{19} 300 18.2 301 19.55±0.85 (2) 302 20.35±0.15 (2) 303 18.6 348 38.8 ±6.6 (3) 394 56.5 398 55.6±14.8 (12) 448 56.05±5.55 (2) 498 70.1 Authors calculated $k_{18}/k_{19}=(850\pm200)\exp\{-(1120\pm90)/T\}$ from these data. Quoted by (60). Used by (47).
$\leqslant(7\pm4)\times10^{10}$	295	Discharge flow system. Experimental details identical to those given in main table (72). HCl replaced by DCl. HEIDNER and BOTT 1976 (72)	Comments given above (72) apply. Authors derived $(k_{18}+k_{19})$ which $H + DCl \rightarrow Cl + HD$ 18 $H + DCl \rightarrow D + HCl$ 19 is therefore listed as maximum k_{18} value.

ISOTOPIC REACTION $D + DCL \rightarrow CL + D_2$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	295	Static photolysis system. H_2/DCl mixtures photolysed with low pressure Hg lamp. [H_2], [HD] and [D_2] analysed mass spectrometrically. DE VRIES and KLEIN 1964 (24)	Application of steady state analysis of multi-step mechanism $D + DCl \rightarrow Cl + D_2$ 20 $D + HD \rightarrow D + H_2$ 22 to data yielded $k_{20}/k_{22}=0.015$, and $k_{20}/k_{21}=(6.3\pm2.5)\times10^{-3}$ by assuming $k_{16}/k_{17}=k_{18}/k_{19}$. See comments above on this paper.

$H + HCl \rightarrow Cl + H_2$

ISOTOPIC REACTION $D + DCL \rightarrow CL + D_2$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	288	Radiolysis system. Febetron 705 (dose rate 0.5-1.0 $\times10^{27}$ eV $g^{-1}\ s^{-1}$) irradiation of Cl_2/DCl mixtures at 160 kPa total pressure. Total dose 1.6 Mrad. $[D_2]$ monitored mass spectrometrically. JARDINE, ARMSTRONG, BOYD and WILLIS 1971 (43)	Authors assumed that decrease in D_2 yield with increasing $[Cl_2]$/ $D + DCl \rightarrow Cl + D_2$ 20 $D + Cl_2 \rightarrow Cl + DCl$ 23 [DCl] ratio was due to competition between reactions 20 and 23. Derived $k_{20}/k_{23}=2.90\times10^{-3}$ at 288 K.
$(2\pm1)\times10^{10}$	295	Discharge flow system. Method identical to that described in main table (72), but with H, H_2 and HCl replaced by D, D_2 and DCl. HEIDNER and BOTT 1976 (72)	Comments above (72) apply.

ISOTOPIC REACTION $D + HCL \rightarrow H + DCL$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	295 and 425	Static photolysis system. Details given above (24). DE VRIES and KLEIN 1964 (24)	Comments noted above (24). Authors obtained k_{16}/k_{17} as zero, $D + HCl \rightarrow Cl + HD$ 16 $D + HCl \rightarrow H + DCl$ 17 but with an upper limit of 0.9, at 295 K, and <10 at 425 K.
$\leq3.6\times10^{8}$	295 1000	Discharge flow system. Excess HCl (ca. 2.6-11.1 $\times10^{-10}$ mol cm^{-3}) added to D atoms (ca. 2.8-20$\times10^{-11}$ mol cm^{-3}) plus impurity H atoms (ca. 0.22-13.6$\times10^{-12}$ mol cm^{-3}) in Ar at total pressures ca. 280 Pa. [H], [D] and [Cl] monitored by e.p.r. spectrometry. ENDO and GLASS 1976 (71)	Halocarbon coated flow tube. Data analysed in terms of reactions $D + HCl \rightarrow H + DCl$ 17 $D + HCl \rightleftharpoons Cl + HD$ 16,-16 $H + HCl \rightarrow Cl + H_2$ 1 1,16 and 17, using $k_1/(k_{16}+k_{17})=0.67\pm0.04$, estimated from thermodynamic data and reverse rate constant measurements of PERSKY and co-workers (32,52), and $k_1=2.6\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ (66) at 295 K. Data at 1000 K computer simulated using mechanism comprising reactions $Cl + H_2 \rightarrow H + HCl$ 3 $H + DCl \rightleftharpoons Cl + HD$ 18,-18 $D + DCl \rightleftharpoons Cl + D_2$ 20,-20 1,3,16,-16,18,-18,20 and -20 with $k_{16}=1.5\times10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ (38) and kinetic isotope effects (32,52) extrapolated to this temperature. Atom decay between furnace and spectrometer cavity

$H + HCl \rightarrow Cl + H_2$

ISOTOPIC REACTION D + HCL → H + DCL – CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		ENDO and GLASS 1976 (71) continued.	ignored. Derived $0.025\ k_{16} < k_{17} < 0.1\ k_{16}$ giving $k_{17} = (9.6 \pm 5.4) \times 10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ and hence $E_{17} > 16.7\ kJ\ mol^{-1}$.
$\leq (7 \pm 3) \times 10^{10}$	295	Discharge flow system. Method identical to that described above using reactants D, D_2 and HCl (72). HEIDNER and BOTT 1976 (72)	Comments given above (72). Authors derived $(k_{16} + k_{17})$, which is therefore listed as maximum k_{17} value.

ISOTOPIC REACTION H + DCL → D + HCL

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	300-498	Static photolysis study. 1:1 mixture of H_2 and DCl, total pressure 5.33 kPa, photolysed at λ=184.9 nm. $[HD]$ and $[D_2]$ monitored mass spectrometrically. WOOD 1972 (50)	Comments noted above (50). Author derived the following k_{19}/k_{18} values and calculated k_{19}/k_{18} $H + DCl \rightarrow Cl + HD$ 18 $H + DCl \rightarrow D + HCl$ 19 $= (1.2 \pm 0.3) \times 10^{-3} \exp\{(1120 \pm 90)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. T/K — k_{19}/k_{18} 300 — 0.0549 301 — 0.0512±0.0022 302 — 0.0491±0.0004 303 — 0.0538 348 — 0.0258±0.005 394 — 0.0177 398 — 0.0180±0.005 448 — 0.0178±0.002 498 — 0.0143 Quoted by (60). Used by (47).
$< (7 \pm 4) \times 10^{10}$	295	Discharge flow system. Details as above (72). *HEIDNER and BOTT 1976 (72)*	Comments given above (72). Authors derived $(k_{18} + k_{19})$ which is therefore listed as maximum k_{19} value.

Discussion

The reaction between hydrogen atoms and hydrogen chloride is the reverse of the slower of the two chain propagating reactions

$$H + HCl \rightarrow Cl + H_2 \qquad (1)$$

active in the well-known Nernst mechanism for the conversion of molecular hydrogen and chlorine to hydrogen chloride. As reaction 1 is very nearly thermoneutral it was quickly realised that its rate would most likely be similar to that of reaction 3, and that it could therefore act as an inhibiting step in the H_2/Cl_2 reaction,

$$Cl + H_2 \rightarrow H + HCl \qquad (3)$$

especially at large extents of conversion where product HCl could divert H atoms that would otherwise propagate the reaction chain by reaction 4.

$$H + Cl_2 \rightarrow Cl + HCl \qquad (4)$$

The early studies of Ritchie and Norrish [9] and Potts and Rollefson [13] attempted to investigate the extent of this inhibiting action by matching experimental observations to rate laws derived to describe the overall reaction. In this aim these studies met with only limited success; in particular, the assumptions used by Ritchie and Norrish [9], together with their data, have been justly criticised [12,13].

Steiner and Rideal's investigation [14] of the H atom catalysed ortho-para-hydrogen conversion in the presence of HCl gave the first useful quantitative data from which k_1 could be derived. Benson, Cruickshank and Shaw [39] have pointed out however that the data were evaluated using K_7

values, since revised, pertaining to "normal" H_2 containing equilibrium proportions of the

$$H_2 \rightleftharpoons 2H \qquad (7)$$

ortho and para forms, whereas values of K_7 commensurate with a nonequilibrium, constantly changing ortho-para mixture should have been used. They therefore recalculated the k_1 values from the data and, in addition, reduced them by a factor of two, on the basis of a report [19] that the presence of small adventitious amounts of O_2 reduces the rate of hydrogen exchange. The resulting k_1 values are in fair agreement with those extrapolated from more recent work at lower temperatures. They must be viewed with caution however in the light of the uncertainty regarding the effect of O_2.

Few direct measurements of k_1 have been made, and all have been performed using the discharge flow method. The two earliest studies, by Clyne and Stedman [29] and by Westenberg and de Haas [38] are in quite good agreement, despite an apparent curvature in the Arrhenius plot of the data from [29]. Difficulties arise however when the simple Arrhenius expression that best fits these data sets is combined with the recommended expression for k_3 (section B4) to obtain an expression for the apparent equilibrium constant $K'=k_3/k_1$. The values of K' thus calculated are a factor of approximately two to three smaller than those derived from the currently accepted thermodynamic data [46] given by

$$K = 1.82 \exp(-491/T)$$

in the same temperature range as that of the rate data. Westenberg and de Haas [38] first pointed out this discrepancy and speculated that its origin lay in the greater probability of obtaining rotationally excited HCl in reaction 3, than of obtaining excited H_2 in reaction 1. Snider, however, proposed [41] an alternative explanation, based on the postulated preferential formation of $Cl(^2P_{1/2})$ in reaction 1. Galante and Gislason [57] rejected this proposal, arguing instead that in the experiments in question, the two spin-orbit states of chlorine were in equilibrium. In addition they discussed the hypothesis given in [38], citing the lack of rotational excitation in HF formed in the analogous reaction of F with H_2, and the results of classical trajectory studies that indicated the ineffectiveness of rotational excitation in promoting reaction. They proposed in turn that the experimental measurements of k_1 were too high by a factor of two as a result of Cl atom scavenging of an additional H atom at the wall.

Although initially [54] favouring Snider's hypothesis, Clyne and Walker subsequently questioned not only Galante and Gislason's reasoning, but argued that the measurements of k_3 were at fault rather than those of k_1 [55]. Their proposal resurrected a potential complication in some investigations of reaction 3, previously rejected by Westenberg and de Haas, in which Cl atoms could be regenerated by the fast reaction of product H atoms with molecular chlorine present in the system

$$Cl + H_2 \rightarrow H + HCl \qquad (3)$$

$$H + Cl_2 \rightarrow Cl + HCl \qquad (4)$$

Some studies of reaction 3 have been carried out in Cl_2-free systems however (see section B4), so this explanation would be inapplicable in those cases.

More recently Spencer and Glass re-investigated reaction 1 in flow tubes treated with various wall coatings [66]. They showed that the removal rate of H atoms and the reaction stoichiometry ([Cl] formed / [H] removed) was dependent on the nature of the reactor surface. Their results demonstrated that the detailed mechanism proposed by Galante and Gislason could not be operative in their system, but that Cl atoms, produced in reaction 1, can react with HCl, largely at the wall, to give a produce, thought to be HCl_2, that reacts further to consume a second H atom. It was therefore concluded that the earlier k_1 values of Westenberg and de Haas [38] and Clyne and Stedman [29] were too high.

Even more recently Ambidge and co-workers [68] studied reaction 1 in an HF-wall treated flow system, where Cl atoms are thought to decay primarily to Cl_2. The authors therefore analysed their results in terms of a mechanism incorporating not only reaction 4, but the reaction of vibrationally excited HCl, formed by reaction 4, with H atoms, and its deactivation by a bath gas or at the wall. This mechanism leads to a stoichiometry in excess of unity and leads to k_1 values in good agreement with those calculated via the thermodynamic data from the recommended expression for k_3, and the measurement of Spencer and Glass at 298 K. The apparent discrepancy between the equilibrium constant K and the ratio k_1/k_3 therefore appears to have been resolved for the present. We consider that at the present time the quality and extent of the experimental data for k_3 is superior to that for k_1 and therefore prefer to make a recommendation for k_1 based on that for k_3 and the accepted thermodynamic data. The expression is

$$k_1 = 7.97\times10^{12} \exp(-1710/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for use in the temperature range 200–650 K with error limits of ±50%.

Not yet discussed are the several relative rate measurements for k_1. These fall into two groups. The sole member of the first of these is a study by de Vries and Klein of the rate of reaction 1 relative to that of 12 [24]. Using the expression for k_{12} recommended

$$H + D_2 \rightarrow D + HD \qquad (12)$$

by Schofield [34] leads to computed k_1 values several orders of magnitude lower than those directly measured. It seems doubtful that the expression for k_{12} could be in error to such a large degree, notwithstanding reported curvature in the Arrhenius plot due to tunnelling at temperatures below 450 K [35], and we therefore reject these data. The most probable cause of error is the neglect of the effects of reactions of translationally excited hydrogen atoms.

The second group of measurements comprises those of k_1/k_4 using both photolytic [20,21,58] and radiolytic [30,36,40] methods. The self-consistency of the data is quite good, particularly at 298 K. A least squares fit to the data gives

$$\log(k_1/k_4) = -0.66-398/T$$

When we combine the recommended expressions for k_1 and k_4 (section B6) however we obtain

$$\log(k_1/k_4) = -1.03-486/T$$

which gives calculated k_1/k_4 values some five to six times lower than those found experimentally at the same temperatures. The reason for this discrepancy is not clear. We believe however that the more recent direct measurements of k_1, k_3 and k_4 are not grossly in error and therefore prefer our calculated expression for k_1/k_4. Experimentally this ratio was obtained by essentially two groups of workers only. The radiolysis method employed by one of these is inherently less reliable than many other techniques, due to the considerable complexity of the reaction systems. It is probably fortuitous that the photolysis data is in such good agreement. The most recent relative rate measurements from the radiolysis studies [75],

$$H + NO + M \rightarrow HNO + M \qquad (15)$$

k_1/k_{15}, gives, in contrast, a value for k_1 in fair agreement with that calculated from the recommended k_1 expression, when our value (Volume 2, p. 389) for k_{15} is substituted.

Isotopic Reactions

The information available on the isotopic variations of reaction 1 is sparse. We can reject outright that of de Vries and Klein [24] on the grounds that they have omitted to consider the influence of reactions of "hot" H and D atoms, and that their method of data analysis has been shown to lead to wildly inaccurate values for k_1. Similar doubts, but of a lesser magnitude, have been raised [71] about Wood's data [50]. In view of the limited number of relative and absolute rate constant measurements, we are unable to make any recommendations for any of these reactions.

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B6 $H + Cl_2 \rightarrow Cl + HCl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-189.01	14.30	33.86
300	-189.02	14.28	33.65
500	-189.90	12.05	20.16
1000	-192.32	8.68	10.50
1500	-194.16	7.16	7.11
2000	-195.43	6.43	5.44
2500	-196.37	6.00	4.42
3000	-197.21	5.70	3.73
3500	-198.11	5.43	3.24
4000	-199.09	5.16	2.87
4500	-200.14	4.92	2.58
5000	-201.18	4.70	2.35

RECOMMENDED RATE CONSTANT

$k = 8.6 \times 10^{13} \exp(-590/T)$ cm^3 mol^{-1} s^{-1}

$= 1.4 \times 10^{-10} \exp(-590/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 250-730 K

Suggested Error Limits for Calculated Rate Constant: ±50%

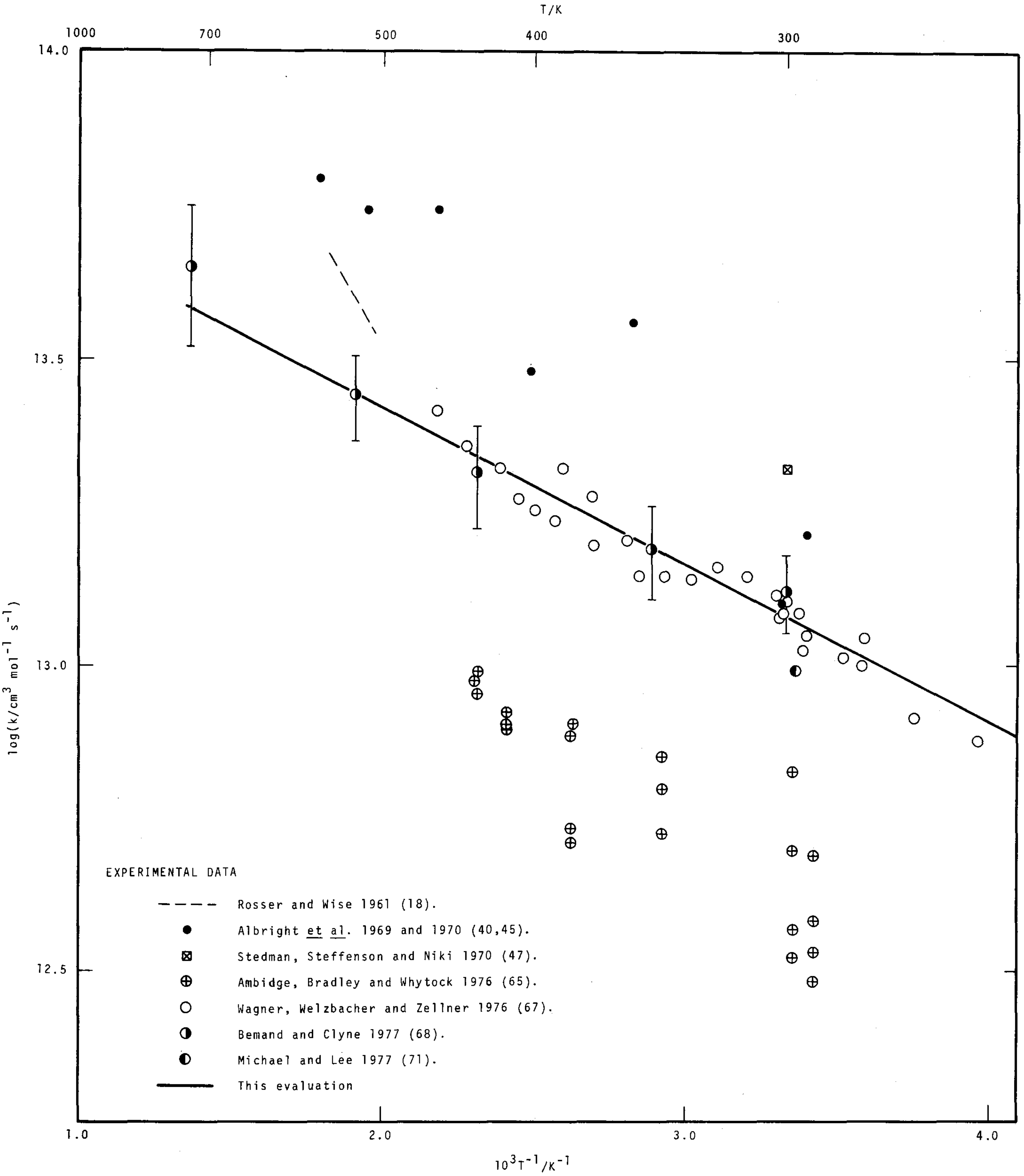
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.93 \pm 0.36$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.85 \pm 0.36$

$E/J\ mol^{-1} = 4\ 905 \pm 2\ 555$

$E/cal\ mol^{-1} = 1\ 170 \pm 610$

$H + Cl_2 \rightarrow HCl + Cl$



$H + Cl_2 \rightarrow Cl + HCl$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Static photolysis system. $H_2/Cl_2/HCl$ mixtures at λ= 406 nm, isolated by filter solutions. Unreacted $[Cl_2]$ measured at 365 nm using thermopile detector. RITCHIE and NORRISH 1933 (7)	Study of HCl photosynthesis. HCl quantum yields proportional to $I^{-0.4}$. Data fitted to empirical expression which was then compared to theoretical equation derived from postulated mechanism $H + Cl_2 \rightarrow Cl + HCl$ 1 $Cl_2 + h\nu \rightarrow Cl + Cl$ 2 $Cl + H_2 \rightarrow H + HCl$ 3 $H + HCl \rightarrow Cl + H_2$ 4 $Cl + Cl \rightarrow Cl_2$ 5 to obtain k_1/k_4=0.59. This value used by authors to assign an approximate value to the collision efficiency for reaction 4. Quoted by (9). Not plotted.
	200-300	Static photolysis system. $H_2/Cl_2/HCl$ mixtures at unspecified wavelength. $[H_2]$ monitored manometrically at liquid air temperature. POTTS and ROLLEFSON 1935 (10)	HCl inhibited HCl photosynthesis study. HCl quantum yield thought to be independent of absorbed light intensity. Authors deduce $k_1/k_4 \geq 10$ at unspecified temperature but infer its validity at 298 K. This ratio used by authors to derive the collision efficiency of reaction 4. Not plotted.
	298	Static photolysis system. H_2/D_2 mixture in ratio 15.7 :1, plus Cl_2, at λ>390 nm. $H_2/D_2/HD$ ratios measured by mass spectrometry. BIGELEISEN, KLEIN, WESTON and WOLFSBERG 1959 (14)	HCl and DCl photosynthesis. Authors estimated upper limit for $[HD]/[H_2]$ as 2×10^{-4} from data corrected for isotopic scrambling in mass spectrometer source. Deduced $k_1/k_4 \geq 20$ by making both steady state and unspecified isotope effect assumptions, and by neglecting termolecular combination reactions involving H, D and Cl. Concluded E_1<16.74 kJ mol^{-1} (4.0 kcal mol^{-1}) using A_1/A_4=10 (9) and E_4=18.83 kJ mol^{-1} (4.5 kcal mol^{-1}), computed from E_3=23.0 kJ mol^{-1} (5.5 kcal mol^{-1}) (13) and thermodynamic data. Listed by (29).

$H + Cl_2 \rightarrow Cl + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	508-548	Static pyrolysis system. Excess H_2 plus Cl_2 ($\sim$650 Pa) and NO_2 ($\sim$216 Pa) mixtures. [Cl_2] and [NO_2] determined from spectrophotometric measurements at 330 nm and 420 nm. ROSSER and WISE 1961 (18)	Data corrected for observed induction period and finite mixing times. Assumed that reaction chain lengths were long $H + Cl_2 \rightarrow Cl + HCl$ 1 $H + NO_2 \rightarrow NO + OH$ 6 and that reaction rate of NO_2 with Cl_2 was negligible. Amended Arrhenius expression calculated by authors given in erratum (19) as k_1/k_6=6.25 exp(-1575/T) and used by them to derive value for k_6. Using the most recent expression for k_6 from CLYNE and MONKHOUSE (69), k_6=2.8x10^{14} exp(-410/T) cm^3 mol^{-1} s^{-1} gives k_1= 1.75x10^{15} exp(-1985/T) cm^3 mol^{-1} s^{-1}.
	273-336	Static photolysis system. $H_2/Cl_2/TCl/HCl$ mixtures at λ>390 nm. Specific activity of product HT and that produced from TCl/HCl mixtures by reaction with Zn amalgam measured with Geiger gas counter. KLEIN and WOLFSBERG 1961 (17)	Authors used $k_3/(k_7+k_8)$=1.35 exp(278/T) (12) and theoretically $Cl + H_2 \rightarrow H + HCl$ 3 $H + HCl \rightarrow Cl + H_2$ 4 $Cl + HT \rightarrow H + TCl$ 7 $Cl + HT \rightarrow T + HCl$ 8 $H + TCl \rightarrow Cl + HT$ 9 computed k_4/k_9 ratio in numerical integration of rate expression, to calculate values for k_1/k_4 of 119±10, 93±16 and 70.4±2.0 at 273.5, 298.5 and 335.5 K respectively; concluded k_1/k_4=(7.0±2.0) exp{(775±65)/T}. Misquoted by (41). Quoted by (23,26,28,30,31, 37,43,48,49,57,60,67 and 72). Used by (35,38,39,42,51,53 and 59).
	196-296	Radiolysis of $HCl/Cl_2/SF_6$ mixtures using both X-ray and ^{60}Co sources. [H_2] presumably measured manometrically as in (20). DAVIDOW, LEE and ARMSTRONG 1966 (30)	Results independent of radiolysis source. Decreasing H_2 yield $H + Cl_2 \rightarrow Cl + HCl$ 1 $H + HCl \rightarrow Cl + H_2$ 4 with increasing [Cl_2]/[HCl] attributed to competition of reactions 1 and 4 leading to k_1/k_4 values of 690±220, 134±9 and 114±7 at 196.2, 274.2 and 296.2 K respectively. Quoted by (48 and 53).

$H + Cl_2 \rightarrow Cl + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	196	Radiolysis system. Method as in (30). Mixtures of Cl_2/HCl in ratios between 0.1 and 0.017. HCl pressure in range 73-85 kPa. DAVIDOW and ARMSTRONG 1968 (37)	Comments given for (30) above apply. Authors corrected data for H_2 formation by reaction of both HCl^- and hot H atoms with HCl, in calculating k_1/k_4=385 at 196±2 K. Quoted by (48).
	300	Radiolysis system. Febetron 705 pulsed electron radiolysis of Cl_2/HCl mixtures, ratio $4.6x10^{-3}$-$7.6x10^{-2}$, at 93 and 160 kPa total pressure. Analysis of $[H_2]$ as in (30) and by mass spectrometry. WILLIS, BOYD and ARMSTRONG 1969 (43)	Authors proposed that decrease in H_2 yields with increasing $[Cl_2]/[HCl]$ ratio was due to competition between reactions 1 and 4. Derived k_1/k_4=90.9 and 97.1 from the experiments at 93 and 160 kPa respectively giving an average value of 94. Quoted by (48).
$1.63x10^{13}$ $1.26x10^{13}$ $3.61x10^{13}$ $3.01x10^{13}$ $5.54x10^{13}$ $5.51x10^{13}$ $6.23x10^{13}$	294 301 354 402 458 511 557	Discharge flow system. H_2 (≤1%) in He plus He diluted Cl_2; $[Cl_2]$<0.1[H]; [He] at either 0.40 or 0.72 kPa; [H] between $5x10^{-11}$ and $3.3x10^{-10}$ mol cm^{-3}. [H], $[H_2]$ and $[Cl_2]$ monitored mass spectrometrically. ALBRIGHT, DODONOV, LAVROVSKAYA, MOROZOV and TAL'ROSE 1969 (40) and DODONOV, LAVROVSKAYA, MOROZOV, ALBRIGHT, TAL'ROSE and LYUBIMOVA 1970 (45)	Pseudo-first order conditions; [H] shown to be constant within 10%. Authors calculated k_1=$(3.73\pm0.35)x10^{14}$ exp{-(906±151)/T} $cm^3\ mol^{-1}\ s^{-1}$. Listed by (44,58). Quoted by (48,53,55,63,64,65,67 and 72). Used by (46, 56 and 62).
$(2.1\pm0.7)x10^{13}$	300	Discharge flow system. Cl_2 plus excess H_2 (∿0.2%) in He at pressures between 120 and 400 Pa. $[Cl_2]$ monitored mass spectrometrically. STEDMAN, STEFFENSON and NIKI 1970 (47)	Pseudo-first order conditions; assumed [H] constant. k_1 found to be independent of pressure within the range 120 to 400 Pa. Used by (61). Quoted by (65,67, 72).

$H + Cl_2 \rightarrow Cl + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	300	Static photolysis system. CO_2/HCl mixtures in (5.00±0.05):1 ratio plus Cl_2 at λ=184.9 nm. $[H_2]$ measured manometrically as in (20). JARDINE, BALLASH and ARMSTRONG 1973 (57)	Study of thermal H atom reactions following CO_2 moderation of photolytically produced hot H atoms. Data evaluated assuming fraction of hot H reacting with HCl is independent of $[Cl_2]$, giving k_1/k_4 = 100±10.
3.03×10^{12} 3.81×10^{12} 3.38×10^{12} 4.86×10^{12} 6.68×10^{12} 3.68×10^{12} 3.30×10^{12} 4.97×10^{12} 7.07×10^{12} 6.25×10^{12} 5.30×10^{12} 8.01×10^{12} 5.11×10^{12} 5.39×10^{12} 7.66×10^{12} 7.91×10^{12} 8.04×10^{12} 8.42×10^{12} 9.78×10^{12} 8.97×10^{12} 9.44×10^{12}	292 292 292 292 298 298 298 298 342 342 342 380 381 381 381 415 415 415 432 432 434	Discharge flow system. H atoms (ca. 10^{-11} mol cm^{-3}) in Ar reacted with Cl_2 ($1.07-1.92\times10^{-11}$ mol cm^{-3}), initial $[Cl_2]/[H]$ ratio 0.57-2.91, at total pressure ca. 530 Pa. H atoms monitored by esr spectroscopy. $[Cl_2]$ and product [HCl] measured mass spectrometrically. AMBIDGE, BRADLEY and WHYTOCK 1976 (65)	Effective rate constant for H atom removal calculated assuming pseudo-first order conditions. Measurements therefore confined to conditions with ≤10% Cl_2 consumption. Overall stoichiometry shown to depend on $[Cl_2]/[H]$, but to be independent of added HCl. Cl atoms not detected by esr under run conditions. Authors analysed data in terms of scheme consisting of reactions 1,10,11 and 12, where HCl* is vibrationally excited HCl, $H + Cl_2 \rightarrow Cl + HCl^*$ 1 $H + HCl^* \rightarrow Cl + H_2$ 10 $Cl \rightarrow \frac{1}{2}Cl_2$ (wall) 11 $HCl^* + Cl_2 \rightarrow HCl + Cl_2$ 12 deriving k_{12}/k_{10}=1.0±0.3 and k_1 values listed from computed stoichiometries. Authors calculated $k_1=(4.6\pm1.3)\times10^{13}\exp\{-(715\pm100)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Quoted by (67,68,70 and 72). Used by (66).
7.5×10^{12} 8.2×10^{12} $(1.11\pm0.01)\times10^{13}$ 1.00×10^{13} 1.03×10^{13} $(1.12\pm0.05)\times10^{13}$ $(1.06\pm0.02)\times10^{13}$ $(1.22\pm0.04)\times10^{13}$ $(1.27\pm0.07)\times10^{13}$ $(1.21\pm0.01)\times10^{13}$ $(1.20\pm0.11)\times10^{13}$ 1.30×10^{13} 1.40×10^{13} 1.45×10^{13} 1.38×10^{13} 1.40×10^{13} 1.40×10^{13} $(1.60\pm0.06)\times10^{13}$ 1.57×10^{13} 1.89×10^{13} 2.10×10^{13} 1.72×10^{13} 1.80×10^{13} 1.87×10^{13}	252 266 278 279 284 294 295 296 299 301 302 303 312 322 331 341 351 356 361 371 385 389 399 408	Discharge flow system. Cl_2 ($2.79\times10^{-11}-1.66\times10^{-10}$ mol cm^{-3}) added to H atoms ($5.43\times10^{-13}-4.14\times10^{-12}$ mol cm^{-3}) in He at total pressures from 245-653 Pa. [H] monitored by Lyman-α resonance fluorescence at 121.57 nm. WAGNER, WELZBACHER and ZELLNER 1976 (67)	Pseudo first order conditions. H atom fluorescence signal calibrated using titration of H with NO_2 and its linear dependence on [H] demonstrated. H removal by both wall adsorbed Cl_2, and secondary reactions, shown to be negligible. No pressure effect observed. Listed k_1 values are results of single determinations at all temperatures except those at 278, 294,295,296,299,301,302 and 256 K which are averages of 2,2,2,2,2,2,3 and 3 determinations respectively. Authors calculate $k_1=(8.7\pm1.7)\times10^{13}$ exp

$H + Cl_2 \rightarrow Cl + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2.10×10^{13} 2.28×10^{13} 2.60×10^{13}	418 438 458	WAGNER, WELZBACHER and ZELLNER 1976 (67) continued.	$\{-(600 \pm 70)/T\}$ cm^3 mol^{-1} s^{-1}. Quoted by (68,70 and 72).
$(1.32 \pm 0.19) \times 10^{13}$ $(1.55 \pm 0.27) \times 10^{13}$ $(2.06 \pm 0.39) \times 10^{13}$ $(2.76 \pm 0.43) \times 10^{13}$ $(4.47 \pm 1.17) \times 10^{13}$	300 346 432 523 730	Discharge flow system. Cl_2 $(4.43\text{-}40.0 \times 10^{-12}$ mol $cm^{-3})$ in Ar added to H atoms $(1.5\text{-}14.8 \times 10^{-13}$ mol $cm^{-3})$ in Ar. [H] monitored by Lyman-α resonance fluorescence at 121.6 nm. BEMAND and CLYNE 1977 (68)	Pseudo first order conditions. Fluorescence signal calibrated by generating H from known [NO] via reaction sequence 13,14 and $N + NO \rightarrow O + N_2$ 13 $O + H_2 \rightarrow OH + H$ 14 $O + OH \rightarrow O_2 + H$ 15 15, fast at 780 K. Listed k_1 values are the average of 21, 8, 11, 9 and 7 determinations at 300, 346,432,523 and 730 K respectively. Authors compute $k_1 = (8.5 \pm 1.4) \times 10^{13} \exp\{-(575 \pm 65)/T\}$ cm^3 mol^{-1} s^{-1}. Quoted by (67,70 and 72).
$(9.6 \pm 0.6) \times 10^{12}$	298	Discharge flow system. Excess Cl_2 $(1.56\text{-}33.2 \times 10^{-12}$ mol $cm^{-3})$ in He added to H atoms (ca. 1.7×10^{-13} mol cm^{-3}) in He at total pressure of 243 Pa. [H] monitored by Lyman-α resonance fluorescence. MICHAEL and LEE 1977 (71)	Pseudo first order conditions. 23 determinations of first order decay constant, corrected for axial diffusion, carried out and averaged to give listed value.

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See comments	Low temperature (unspecified)	Estimated value. BODENSTEIN 1931 (5)	Collision efficiency of 10^{-2}, presumably at room temperature, estimated by combining data of (1,2,3,4 and 6). Remarkably accurate for its publication date. Quoted by (7 and 8).
$8.73 \times 10^{13} \exp(-590/T)$	250-750	Recommended value. WATSON 1977 (72)	Recommended value based on (67 and 68). Measurements from (17, 40,47 and 65) also considered. Not plotted because of its similarity to our recommendation.

ISOTOPIC REACTION $D + CL_2 \rightarrow CL + DCL$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(7.2 \pm 3.0) \times 10^{12}$	300	Method and procedure identical to that in (47) above. STEDMAN, STEFFENSON and NIKI 1970 (47)	Comments given above, (47) apply.
	288	Radiolysis system. Febetron 705 (high dose rate $0.5\text{-}1.0 \times 10^{27}$ eV g^{-1} s^{-1}) irradiation of Cl_2/DCl mixtures at 160 kPa total pressure. Total dose 1.6 Mrad. $[D_2]$ monitored mass spectrometrically. JARDINE, ARMSTRONG, BOYD and WILLIS 1971 (50)	Authors assumed that decrease in D_2 yield with increasing $[Cl_2]/$ $D + Cl_2 \rightarrow Cl + DCl$ 1' $D + DCl \rightarrow Cl + D_2$ 4' $[DCl]$ ratio resulted from the competition between reactions 1' and 4'. Derived $k_1'/k_4' = 345$ at 288 K.

Discussion

The fast reaction of H atoms with Cl_2 comprises one of the two propagating steps of the Nernst chain mechanism responsible

$$H + Cl_2 \rightarrow Cl + HCl \qquad (1)$$

for the photochemical, pyrolytic and combustive combinations of H_2 and Cl_2. The large exothermicity results in a nonequilibrium energy distribution for the products. If the excitation energy is channelled into HCl vibration, then levels up to v=6 can be populated. Experimentally infra-red emission has been observed from excited HCl for levels up to this limit, and population distributions measured [15,16,21,22,24,32,52]. As a consequence of the population inversion, under appropriate conditions, this reaction may be used as the basis of the HCl chemical laser, the first of its type devised [27,33,34,36,42]. The measured population distributions enable the fractions of the available energy entering vibrational, rotational and translational product modes to be derived. The results show that the absolute efficiency for conversion of the reaction exoergicity into vibrational energy is low and it is therefore concluded that the potential energy surface appropriate to the reaction has a repulsive nature. Molecular beam studies substantiate this conclusion [54].

In contrast to the extensive series of experiments designed to characterise the dynamics of the reaction, there are only a few determinations of its rate. Indeed reliable rate constant data have only become available very recently.

Rosser and Wise [18] attempted to measure k_1 relative to k_6. Rate data for reaction 6 over an extended temperature range

$$H + NO_2 \rightarrow NO + OH \qquad (6)$$

are sparse. Using the latest expression for k_6 applicable to the temperature range of the relative rate experiments, derived by Clyne and Monkhouse [69], gives

$$k_1 = 1.75 \times 10^{15} \exp(-1985/T)\ cm^3\ mol^{-1}\ s^{-1} \qquad (A)$$

over the range 508–548 K. This expression gives rate constants that are in reasonable agreement with those subsequently measured, but in view of the complex nature of the reaction system employed we place a low weighting on these data in our evaluation of k_1.

All of the other relative rate measurements of reaction 1 have been carried out versus that of reaction 4. Both photolytic [7,10,14,17,57] and radiolytic [30,37,43] studies have been made

$$H + HCl \rightarrow Cl + H_2 \qquad (4)$$

yielding results that show a high degree of internal self-consistency, with the exception of the earlier work [7,10]. These data, outlined in greater detail in the discussion of reaction 4 (section B5), are fitted by the least squares expression

$$\log(k_1/k_4) = 0.66 + 398/T \qquad (B)$$

Substitution for k_4 would therefore allow k_1 to be calculated. The Arrhenius parameters for k_4 are in dispute however, and consequently we prefer to use expression B, or individual k_1/k_4 values, together with our recommended k_1 expression, to compute k_4 values.

The first direct measurement of the absolute value of k_1 over the temperature range 294–557 K, was carried out by Albright and co-workers [40,45] under pseudo-first order conditions, using a mass spectrometer to monitor the decay of molecular Cl_2 in the presence of an excess of H atoms. Their data are in quite good agreement with those of later workers [67,68] at ca. 300 K but at higher temperatures the discrepancy increases. Their derived activation energy and *A*-factor, 7.53 kJ mol^{-1} and $(3.73\pm0.35)\times10^{14}$ cm^3 mol^{-1} s^{-1}, respectively, are the highest yet proposed for this reaction.

Stedman, Steffenson and Niki [47] used the same technique to measure k_1 at 300 K. Their value is ca. 16% higher than that calculated using the expression obtained by Albright et al. [40,45].

Four direct determinations of k_1 have been made in which the reaction was followed by monitoring the changing H atom concentration. In the first of these Ambidge, Bradley and Whytock used e.s.r. spectrometry as the analytical tool [65]. Their data show considerable scatter and are in poor agreement with that of Wagner, Welzbacher and Zellner [67], Bemand and Clyne [68], and Michael and Lee [71], all of whom used the resonance fluorescence technique, producing mutually consistent results. Smaller H atom concentrations could be used in the latter experiments than in the former and complications due to the presence of vibrationally excited HCl, formed in reaction 1, were therefore considered to be negligible. On the other hand Ambidge and co-workers found it necessary to correct for removal of H by HCl*, but neglected the effects of both HCl* deactivation, and other reactions, at the wall. They also used a pseudo-first order treatment to analyse their data, obtained with the e.s.r. spectrometer operating at the limits of its sensitivity, despite having only a slight concentration excess of Cl_2 over H atoms. It is noticeable that their hydrogen atom decay plots do not extrapolate to the initial H atom concentration at the time zero. While we cannot positively specify the reason why these results do not agree with those of other studies, we feel that they are nevertheless less reliable.

The two data sets of Wagner and co-workers [67] and of Bemand and Clyne [68] give almost identical Arrhenius expressions for k_1. Care was taken in these experiments to ensure that the fluorescence signal was both correctly calibrated and linearly dependent upon H atom concentration. Moreover by using low atom concentrations, complications resulting from reactions of the products of reaction 1 and other side reactions are reduced to negligible levels. The room temperature rate constant value of Michael and Lee [71] is in reasonable agreement with both of these studies. We consider that the expression best describing k_1 should be based on the results of these three studies and have therefore derived

$$k_1 = 8.6\times10^{13} \exp(-590/T) \ cm^3 \ mol^{-1} \ s^{-1}$$

for use in the temperature range 250–730 K. We nevertheless recognise the difficulties involved in the measurement of the rate of such a rapid reaction even with the relatively sophisticated experimental techniques now available, and therefore suggest that suitable error limits for calculated values of k_1 would be ±50%.

$D + Cl_2 \rightarrow Cl + DCl$

Apart from the measurement by Jardine, Armstrong, Boyd and Willis of k_1' relative to k_4' at 288 K [50] there is but one determination of the value of k_1'. In this study Stedman, Steffenson

$$D + Cl_2 \rightarrow Cl + DCl \qquad (1')$$

$$D + DCl \rightarrow Cl + D_2 \qquad (4')$$

and Niki monitored the decay of Cl_2, in an excess of H atoms [47], employing a mass spectrometric technique also used by them to obtain k_1. Their value for this latter rate constant is however some 75% higher than our recommended value, calculated for the same temperature, 300 K, and we therefore feel that their k_1' value should be regarded with caution. It would perhaps be preferable to assume that the two measurements were subject to similar experimental error and that k_1' should best be calculated via the experimental rate constant ratio k_1'/k_1, found to be 0.34. Relative rate measurements yielding values for k_1/k_4 are mutually consistent,

$$H + HCl \rightarrow Cl + H_2 \qquad (4)$$

but are not in agreement with those calculated from the recommended expressions for k_1 and k_4. It therefore seems likely that the experiments of Jardine and co-workers [50], performed as an extension to their previous studies of k_1/k_4 [43], give a k_1'/k_4' value that is in error. Furthermore reliable determinations of k_4' are not available. In view of these difficulties no recommendation can be made for k_1'.

Rate of the Reverse Reaction

There are no experimental determinations of the rate constant for the reverse reaction between Cl and HCl. Fishburne

$$Cl + HCl \rightarrow H + Cl_2 \qquad (-1)$$

[31] has estimated the expression

$$k_{-1} = 1.8\times10^{14} \exp(-24\ 660/T) \ cm^3 \ mol^{-1} \ s^{-1}$$

from the data of Klein and Wolfsberg [17] for k_1/k_4, the thermodynamic equilibrium constant for the reactions 1, –1 and k_4 values taken from Steiner and Rideal [11]. Jacobs, Giedt and Cohen [38] studied the Cl atom induced HCl decomposition in a shock tube, but measured no k_{-1} values directly, preferring to match their experimental results with those computed using k_{-1} values calculated from Klein and Wolfsberg's data [17] in a manner analogous to that used by Fishburne [31]. Combining our recommended Arrhenius expression for k_1 with the relevant thermodynamic data leads us to derive the following recommended expression for k_{-1}, with error limits of ±50%, over the temperature range 250–730 K.

$$k_{-1} = 1.0\times10^{14} \exp(-23\ 885/T) \ cm^3 \ mol^{-1} \ s^{-1}$$

Isotopic Exchange Reactions: $^{36}Cl + HCl \rightarrow Cl + H^{36}Cl$ and $^{36}Cl + DCl \rightarrow Cl + D^{36}Cl$

Klein, Persky and Weston have investigated chlorine atom exchange in HCl and DCl by photolysing $D_2/HCl/^{36}Cl_2$ and

$D_2/DCl/^{36}Cl_2$ mixtures in the pressure range 6.0–10.7 Pa [25]. Further details of the method and data analysis considerations are given in the notes for the Cl plus D_2 reaction (section B4). Measurement of both the D_2 remaining at the end of the photolysis and the activity of the product HCl and DCl enabled the following rate

$$^{36}Cl + HCl \rightarrow Cl + H^{36}Cl \quad (16)$$

$$^{36}Cl + DCl \rightarrow Cl + D^{36}Cl \quad (17)$$

$$Cl + D_2 \rightarrow D + DCl \quad (3')$$

constant ratios to be determined, from which the authors derived a

T/K	k_{16}/k_3'	k_{17}/k_3'
312.5	0.628±0.035	0.073±0.005
368.2	0.551±0.035	0.110±0.008
423.2	0.598±0.025	0.146±0.008

value for the mean activation energy difference $(E_{16}-E_3')$ of -0.46 ± 1.1 kJ mol^{-1} (-0.11 ± 0.27 kcal mol^{-1}). Using $(E_3'-E_3)=4.93\pm0.08$ kJ mol^{-1} (14) and $E_3=23.01\pm0.84$kJ mol^{-1} (13), they then calculated $E_{16}=27.5\pm2.1$ kJ mol^{-1} (6.57 ± 0.49 kcal mol^{-1}).

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B7 $Cl + CH_4 \rightarrow HCl + CH_3$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	6.958	29.319	0.329
300	6.979	29.690	0.336
500	8.602	33.962	0.875
1000	8.699	34.443	1.345
1500	6.205	32.464	1.479
2000	2.987	30.614	1.521
2500	- 0.431	29.091	1.529
3000	- 3.887	27.832	1.521
3500	- 7.318	26.769	1.507
4000	-10.698	25.870	1.491
4500	-14.008	25.096	1.473
5000	-17.238	24.409	1.455

RECOMMENDED RATE CONSTANT

$$k_1 = 1.10 \times 10^7 \; T^{1.97} \exp(-750/T) \; cm^3 \; mol^{-1} \; s^{-1}$$
$$= 1.83 \times 10^{-17} T^{1.97} \exp(-750/T) \; cm^3 \; molecule^{-1} \; s^{-1}$$

Temperature Range: 200-500 K

Suggested Error Limits for Calculated Rate Constant: ±35% in the temperature range quoted.

Rate Parameters:

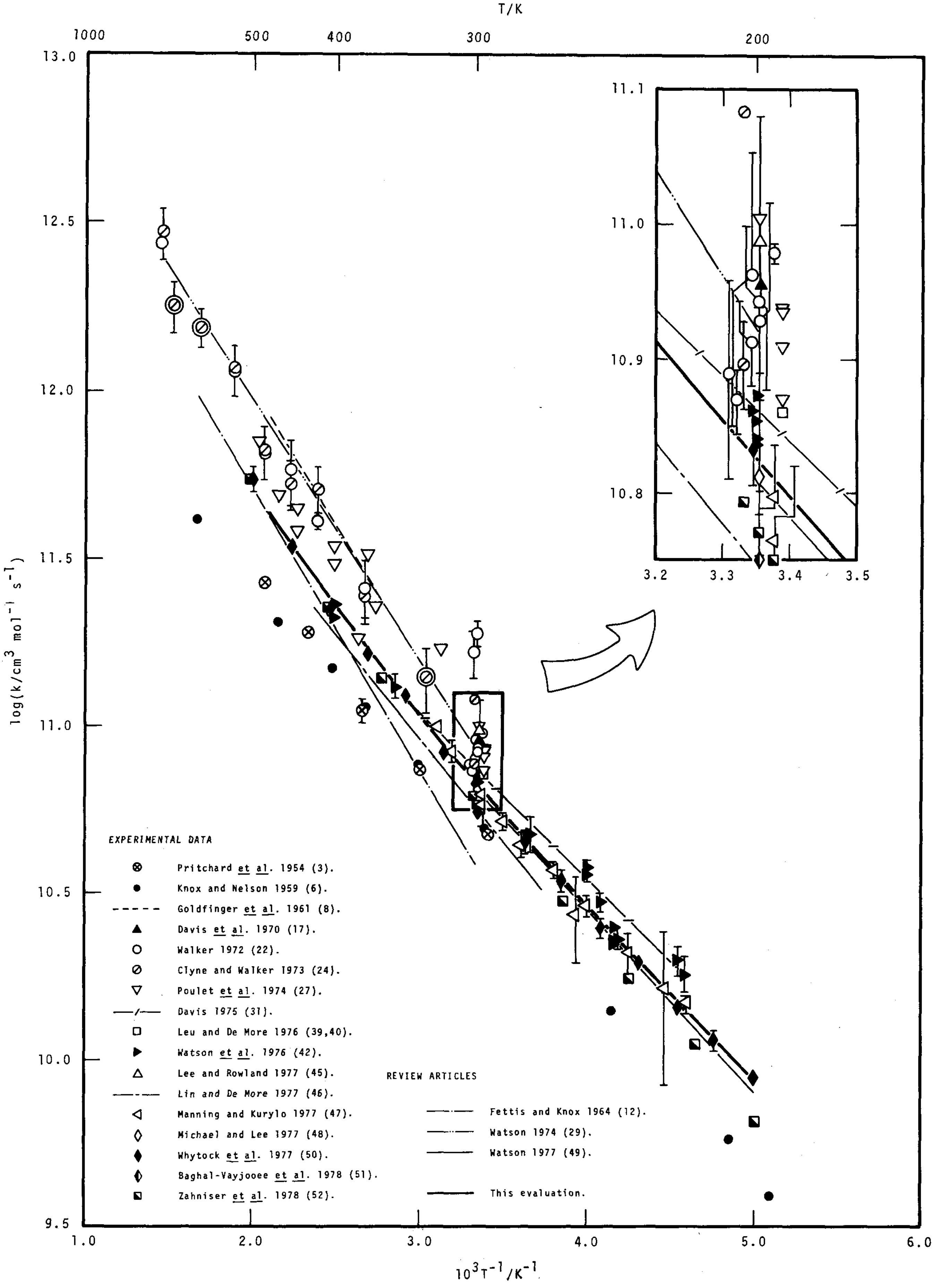
$\log(A' T^{1.97}/cm^3 \; mol^{-1} \; s^{-1}) = 7.041 + 1.97 \log T \pm 0.13$

$\log(A' T^{1.97}/cm^3 \; molecule^{-1} \; s^{-1}) = -16.738 + 1.97 \log T \pm 0.13$

$E'/J \; mol^{-1} = 6240 \pm 1660$

$E'/cal \; mol^{-1} = 1490 \pm 400$

$Cl + CH_4 \rightarrow HCl + CH_3$

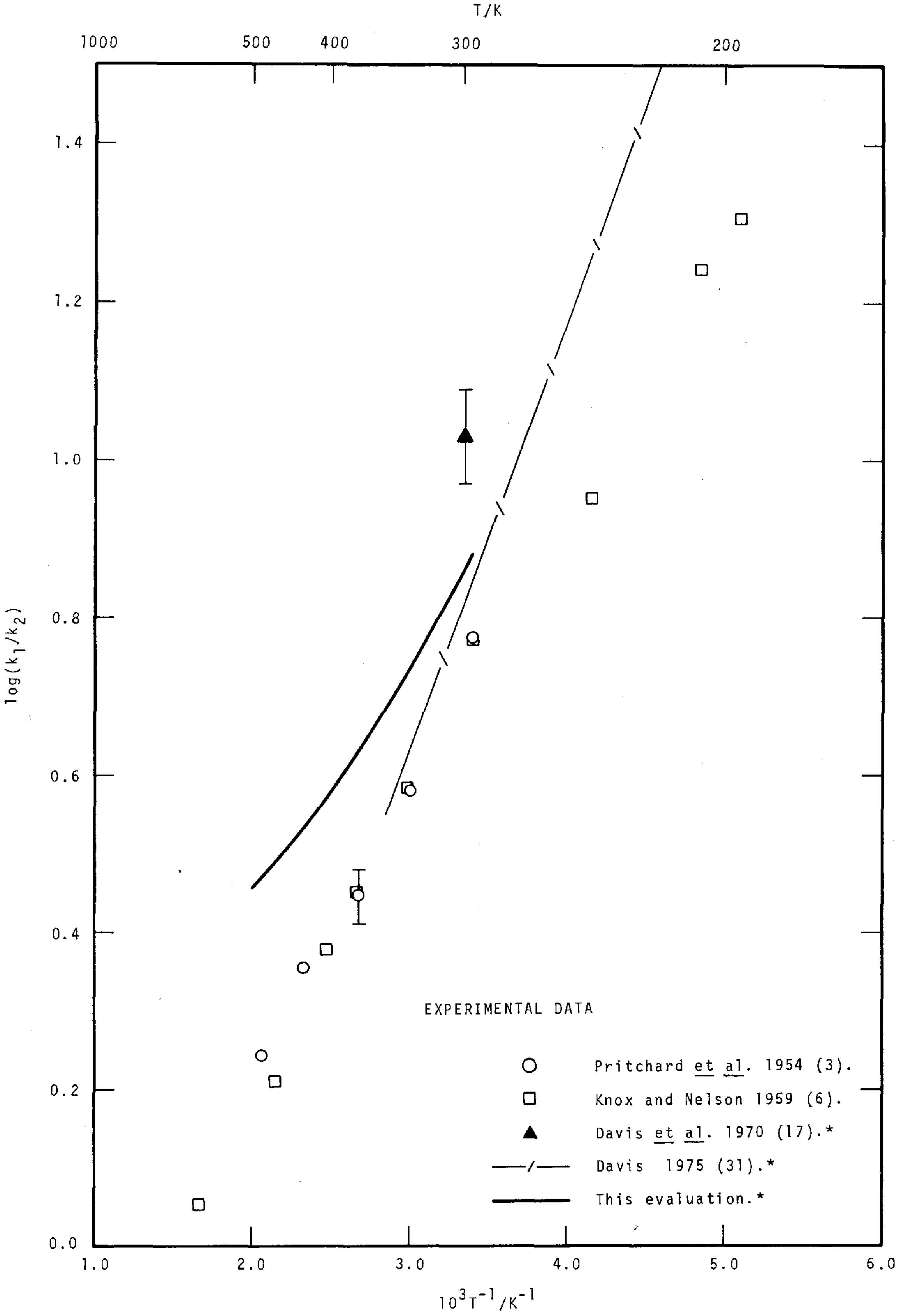


$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	273-488	Static photolysis system. $CH_4/H_2/Cl_2$ mixtures with typical initial concentrations (at 373 K) $[Cl_2] = (1.55\pm0.1)x10^{-6}$ mol cm^{-3}, $2.83x10^{-6} < [H_2] < 8.13x10^{-6}$ mol cm^{-3} and $2.80x10^{-6} < [CH_4] < 5.22x10^{-6}$ mol cm^{-3}. Residual CH_4 and H_2 removed by low temperature distillation and absorbed on silica gel for measurement. PRITCHARD, PYKE and TROTMAN-DICKENSON 1954 (3)	Ratios of initial and final concentrations of CH_4 and H_2 gave k_1/k_2 $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + H_2 \rightarrow HCl + H$ 2 Values of k_1/k_2, taken from graph, are 5.98 (293 K), 3.79 (333 K), 2.80 ± 0.23 (373 K) (average of 6 determinations), 2.26 (428 K), and 1.75 (484 K). Authors give Arrhenius expression $k_1/k_2 = 0.26 \exp(856/T)$ and use k_2 of ASHMORE and CHANMUGAM (2) to give $k_1 = 3.16x10^{14} \exp(-1910/T)$ cm^3 mol^{-1} s^{-1}, the pre-exponential factor being incorrect. PRITCHARD <u>et al</u>. (5) modified their original expression for k_1/k_2 to $0.32 \exp(830\pm75/T)$, and gave k_1 (correctly) as $2.6x10^{13} \exp(-1940/T)$ cm^3 mol^{-1} s^{-1}. Using our recommendation for k_2 (this Volume, section B4) we derive $k_1 = 4.76x10^{10}$ (293 K), $7.43x10^{10}$ (333 K), $(1.11\pm0.1)x10^{11}$ (373 K), $1.92x10^{11}$ (428 K), and $2.69x10^{11}$ cm^3 mol^{-1} s^{-1} (484 K) for this work.
	(a) 298-484 (b) 349-563	Static photolysis system. (a) $CH_4/CH_3Cl/Cl_2$ and (b) $CH_4/C_2H_6/Cl_2$ mixtures. Initial concentrations (a) $[CH_4]$ $3x10^{-6}$-$9x10^{-6}$ mol cm^{-3}, $[CH_3Cl]$ $2.5x10^{-6}$-$7.2x10^{-6}$ mol cm^{-3}, and (b) $[CH_4]$ $6.5x10^{-6}$-$8.1x10^{-6}$ mol cm^{-3}, $[C_2H_6]$ $1.4x10^{-6}$-$2.0x10^{-6}$ mol cm^{-3}. Residual CH_4 and C_2H_6 separated by distillation, HCl removed by KOH, and CH_3Cl separated. PRITCHARD, PYKE and TROTMAN-DICKENSON 1955 (5)	Analysis of kinetics of mixtures (b) as for $CH_4/H_2/Cl_2$ mixtures in (3) but for mixtures (a) two limiting cases treated: total inertness or total reactivity of CH_3Cl produced via $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ 3 gave 2 estimates for k_1/k_4 $Cl + CH_3Cl \rightarrow HCl + CH_2Cl$ 4 differing by up to 12%. Average result used to calculate E_1-E_4. Authors quote ratios k_1/k_4 and k_1/k_5 $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5 as $0.45 \exp\{-(250\pm75)/T\}$ and $0.21 \exp\{-(1430\pm190)/T\}$ respectively.

$Cl + CH_4$ / $Cl + H_2$



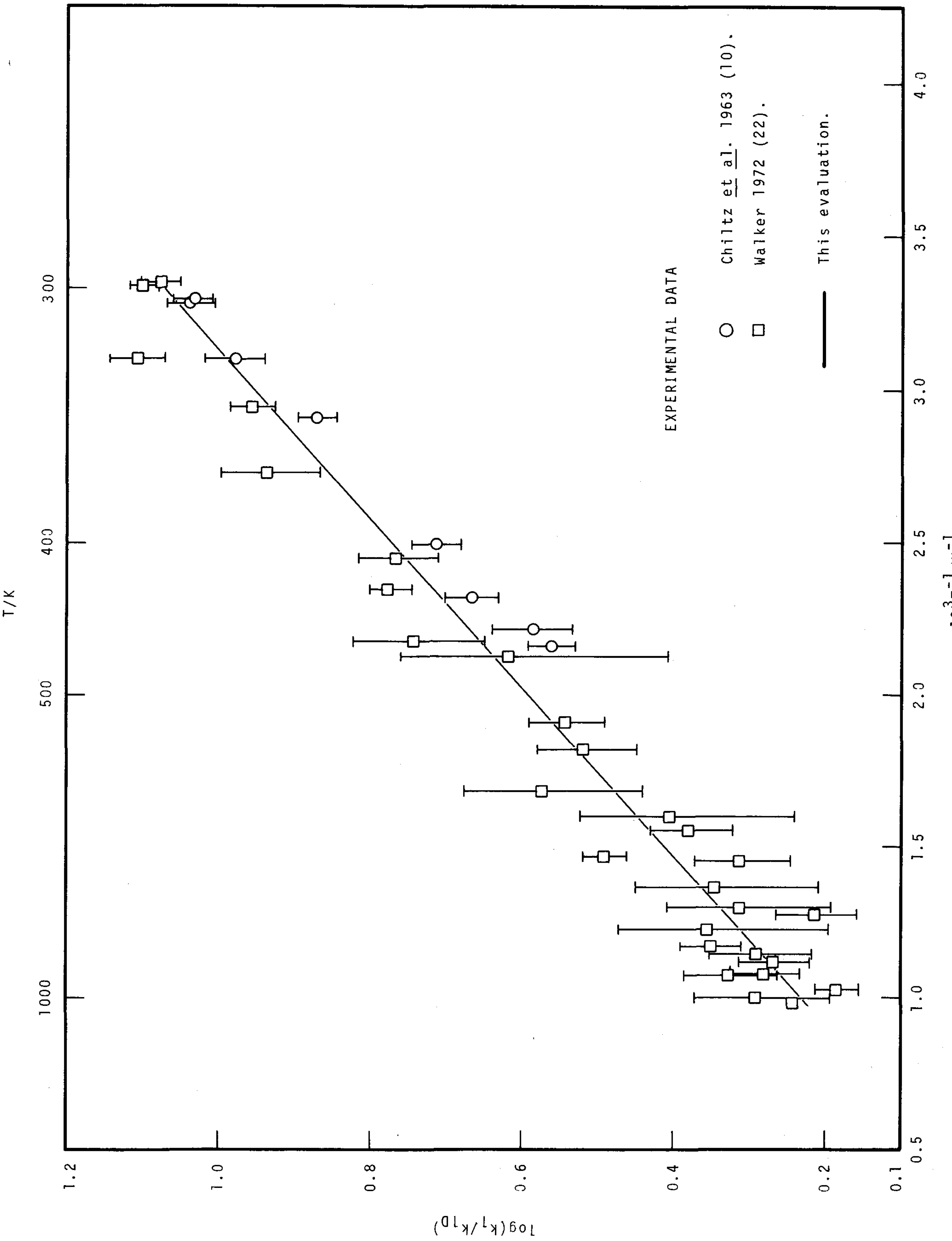
* Ratio obtained from absolute values of both k_1 and k_2.

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

<table>
<tr><th>Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)</th><th>Temperature (K)</th><th>Method and Reference</th><th>Comments</th></tr>
<tr><td></td><td>193-593</td><td>Static photolysis system. $CH_4/H_2/Cl_2$ and $CH_4/C_2H_6/Cl_2$ mixtures. Cl_2 pressures 0.025-0.25 mm Hg (3.3 -33.3 Pa), (CH_4+H_2) or $(CH_4+C_2H_6)$ pressures $\sim 10p_{Cl_2}$, and N_2 added to give total pressure ∿500 mm Hg (66.7 kPa). HCl product converted to benzene with diphenyl mercury, and CH_3Cl and C_2H_5Cl determined by gas chromatography.
KNOX and NELSON 1959 (6)</td><td>Relative rates of reactions 1 and 2, and 1 and 5, obtained from consumption of RH ($R=H, CH_3, C_2H_5$)
$Cl + CH_4 \rightarrow HCl + CH_3$ 1
$Cl + H_2 \rightarrow HCl + H$ 2
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5
Ratios k_1/k_2 and k_1/k_5 taken from graphs (6 and 4)
<table>
<tr><th>T/K</th><th>k_1/k_2</th><th>k_1/k_5</th></tr>
<tr><td>196</td><td>20.3</td><td></td></tr>
<tr><td>206</td><td>17.5</td><td></td></tr>
<tr><td>232</td><td></td><td>$4.8x10^{-4}$</td></tr>
<tr><td>241</td><td>8.93</td><td></td></tr>
<tr><td>275</td><td></td><td>$1.6x10^{-3}$</td></tr>
<tr><td>295</td><td>5.93</td><td></td></tr>
<tr><td>303</td><td></td><td>$2.0x10^{-3}$</td></tr>
<tr><td>330</td><td></td><td>$3.3x10^{-3}$</td></tr>
<tr><td>334</td><td>3.83</td><td></td></tr>
<tr><td>349</td><td></td><td>$4.1x10^{-3}$</td></tr>
<tr><td>374</td><td>2.82</td><td></td></tr>
<tr><td>404</td><td>2.38</td><td></td></tr>
<tr><td>420</td><td></td><td>$8.4x10^{-3}$</td></tr>
<tr><td>464</td><td>1.62</td><td>$1.1x10^{-2}$</td></tr>
<tr><td>599</td><td>1.13</td><td>$2.1x10^{-2}$</td></tr>
<tr><td>629</td><td></td><td>$2.4x10^{-2}$</td></tr>
</table>
Authors give least-squares fits to these data as $k_1/k_2=0.30\ exp(830\pm30/T)$ and $k_1/k_5=0.26\ exp\{-(1410\pm23)/T\}$. Earlier presentation of k_1/k_5 data by KNOX (4) gives $k_1/k_5=0.27\ exp\{-(1410\pm15)/T\}$. Using k_2 from (2) authors quote $k_1=2.4x10^{13}\ exp\{-(1940\pm30)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. This expression used by KNOX (9) in competitive chlorination in $CH_4/CHCl_3$ and CH_4/CH_2Cl_2 mixtures. Quoted by (19 and 23). Using our recommendation for k_2 (this Volume, section B4) we derive $k_1=3.93x10^9$ (196 K), $5.84x10^9$ (206 K), $1.41x10^{10}$ (241 K), $4.96x10^{10}$ (295 K), $7.66x10^{10}$ (334 K), $1.14x10^{11}$ (374 K), $1.49x10^{11}$ (404 K), $2.05x10^{11}$ (464 K), and $4.16x10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ (599 K).</td></tr>
<tr><td></td><td>360-475</td><td>Static photolysis system. $CH_4/C_2Cl_4/Cl_2$ mixtures. Pressures in similar $C_2HCl_5/C_2Cl_4/Cl_2$ mixtures given as $p_{C_2HCl_5}$, 14.4-87 mm Hg (1.92-11.6 kPa), $p_{C_2Cl_4}$ 17.5-88.1 mm Hg (2.34-11.8 kPa), and p_{Cl_2}</td><td>From initial rates of Cl_2 consumption and pressure change, straight line plots obtained of gradient k_1k_{-6}/k_6k_7
$Cl + CH_4 \rightarrow HCl + CH_3$ 1
$Cl + C_2Cl_4 \rightleftharpoons C_2Cl_5$ 6,-6
$Cl_2 + C_2Cl_5 \rightarrow C_2Cl_6 + Cl$ 7
Using E_1 of KNOX and NELSON (6)</td></tr>
</table>

Cl + CH_4 / Cl + CD_4


T/K
300
400
500
1000
EXPERIMENTAL DATA
○ Chiltz et al. 1963 (10).
□ Walker 1972 (22).
This evaluation.
$10^3T^{-1}/K^{-1}$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
$\log(k_1/k_{1D})$
1.2
1.0
0.8
0.6
0.4
0.2
0.1

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		16.4-232.5 mm Hg (2.18-31 kPa). Incident light intensity, pressure and Cl_2 absorption at 366 nm monitored. GOLDFINGER, HUYBRECHTS and MARTENS 1961 (8)	authors derive $k_1=5.0x10^{13}$ exp(-1940/T) $cm^3\ mol^{-1}\ s^{-1}$. Used by (13). ECKLING <u>et</u> <u>al</u>. (7) report results of this work as $k_1=1.26x10^{14}$ exp(-1940/T) $cm^3\ mol^{-1}\ s^{-1}$.
	303-599	Static photolysis system. CH_4(10.8-17.3 mm Hg; 1.4-2.3 kPa)/C_2F_5H (99.6-412.3 mm Hg; 13.3-55.0 kPa)/Cl_2 (5.3-10.7 mm Hg; 0.7-1.4 kPa) mixtures. Gas chromatography used to determine product yields of CH_3Cl and C_2F_5Cl. COOMBER and WHITTLE 1966 (14)	From relative CH_3Cl and C_2F_5Cl yields, authors obtained k_1/k_8 as (12.4±0.7) exp(730±20/T). $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + C_2F_5H \rightarrow HCl + C_2F_5$ 8
$(9.03\pm0.6)x10^{10}$	298	Flash photolysis study. CCl_4 (65 μ Hg; 8.5 Pa)/ CH_4(50-500 μ Hg; 6.6-66 Pa)/He (7-98 mm Hg; 0.93-13 kPa) mixtures. [Cl] followed by resonance fluorescence at 133.58 or 137.9 nm. DAVIS, BRAUN and BASS 1970 (17)	Fluorescence signal ∝ $[Cl]^{0.9}$ for range $10^{11}<[Cl]<10^{12}$ mol cm^{-3}. Pulse counting and repeated photolysis used to reduce random errors. Corrections (<15%) made for Cl losses by diffusion. All measurements made after 250 μs to allow for $Cl(^2P_{\frac{1}{2}})$ deactivation. k_2 also determined. $Cl + H_2 \rightarrow HCl + H$ 2 Expression $k_1=4.8x10^{13}$ exp(-1910/T) $cm^3\ mol^{-1}\ s^{-1}$ attributed to this study by CRUTZEN (26), and $5.3x10^{13}$ exp(-1910/T) $cm^3\ mol^{-1}\ s^{-1}$ by (28). WATSON (44) considers this value to be overestimated by ∿10%: other studies found fluorescence signal ∝ [Cl], which would give $k_1=8.13x10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$.
	298	Static photolysis system. $CH_4/C_2H_6/ICl$ (∿30 mm Hg; 4 kPa) mixtures at total pressures 60-120 mm Hg (8-16 kPa). $[CH_4]/[C_2H_6]$ ratio 6.25. Reaction products analysed by gas chromatography. KELLY, YU and WIJNEN 1970 (18)	From ratio of products CH_3Cl and C_2H_5Cl authors obtained $k_1/k_5=(8\pm0.8)x10^{-2}$ $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5 Assuming $A_1/A_5=1.0$ authors give $E_1-E_5=9.2$ kJ mol^{-1} (2.2 kcal mol^{-1}).

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
(a)	$(8.47\pm1.9)x10^{10}$	298	(a) Cl_2-discharge flow system. Cl_2(0.4-2%)/Ar mixtures in discharge, CH_4 added downstream. Total pressures 0.57-1.35 mm Hg (76-180 Pa). [Cl] calibrated by titration with NOCl, using afterglow at 520 nm and [NO], as determined by mass spectrometry, and [CH_4] monitored by mass spectrometry. (b) NO added to flow of ClO_2, CH_4 added downstream. Total pressures 0.86-1.15 mm Hg (115-153 Pa). [Cl] determined by NOCl titration, [CH_4], [ClO_2] by mass spectrometry. WALKER 1972 (22)	Author quotes mean room temperature value (over 28 measurements) for k_1 by method (a) as $(8.30\pm1.0)x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$. Method (b) used to eliminate Cl_2 and reaction 3, $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ 3 production of Cl being via $NO + ClO_2 \rightarrow ClO + NO_2$ $NO + ClO \rightarrow Cl + NO_2$ with NO in excess to minimise Cl removal via $Cl + ClO_2 \rightarrow 2ClO$ Mean room temperature value (7 measurements) by method (b) given as $(1.52\pm0.4)x10^{11}\ cm^3\ mol^{-1}\ s^{-1}$. Arrhenius form of these data given as $k_1=(3.12\pm0.5)x10^{13}\ exp\{-(1800\pm15)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ (298-686 K). Data too scattered to give meaning to alternative fit $k_1=2.51x10^{10}T\ exp(-1360/T)\ cm^3\ mol^{-1}\ s^{-1}$.
	$(8.76\pm1.2)x10^{10}$	298		
	$(8.17\pm0.6)x10^{10}$	299		
	$(9.19\pm2.1)x10^{10}$	299		
	$(7.39\pm0.4)x10^{10}$	301		
	$(7.77\pm1.3)x10^{10}$	302		
	$(1.40\pm0.1)x10^{11}$	329		
	$(2.60\pm0.5)x10^{11}$	374		
	$(4.08\pm0.2)x10^{11}$	418		
	$(5.85\pm1.3)x10^{11}$	449		
	$(6.61\pm0.7)x10^{11}$	484		
	$(1.15\pm0.2)x10^{12}$	530		
	$(1.55\pm0.3)x10^{12}$	591		
	$(1.80\pm0.4)x10^{12}$	654		
	$2.74x10^{12}$	686		
(b)	$(9.50\pm0.15)x10^{10}$	296		
	$(1.90\pm0.17)x10^{11}$	299		
	$(1.66\pm0.27)x10^{11}$	301		
(a)	$(7.89\pm0.6)x10^{10}$	300	(a) Cl_2-discharge flow system, and (b) flow system, NO added to ClO_2 stream. Method and conditions as for (22). CLYNE and WALKER 1973 (24)	Data slightly different from those in WALKER's thesis (22). Measurement of k_1 at 300 K by method (b) not considered accurate: estimate only given. Least mean squares fit given to these data as $k_1=(3.06\pm0.3)x10^{13}\ exp\{-(1790\pm40)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ (300-686 K). Used by (25,30,33, 34 and 35).
	$(1.40\pm0.3)x10^{11}$	329		
	$(2.42\pm0.4)x10^{11}$	374		
	$(5.08\pm0.9)x10^{11}$	418		
	$(5.32\pm0.9)x10^{11}$	449		
	$(6.63\pm1.2)x10^{11}$	484		
	$(1.16\pm0.2)x10^{12}$	530		
	$(1.55\pm0.2)x10^{12}$	591		
	$(1.80\pm0.3)x10^{12}$	654		
	$(2.96\pm0.5)x10^{12}$	686		
(b)	$\sim1.21x10^{11}$	300		
	$7.41x10^{10}$	295	Cl_2-discharge flow system. Cl_2/Ar mixtures through discharge, CH_4 added downstream through moveable inlet. Total pressures 0.67-1.2 mm Hg (89-160 Pa). [Cl] determined by NOCl titration, monitoring Cl_2 and NCl mass spectrometrically, and [CH_4] followed using mass spectrometry. Flow tube coated with H_3PO_4. POULET, LE BRAS and COMBOURIEU 1974 (27)	k_1 determined using large and moderate excesses of Cl atoms, using pseudo-first order and integrated expressions respectively. Authors give Arrhenius expression as $k_1=(1.11\pm0.1)x10^{13}\ exp\{-(1410\pm100)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ (295-490 K). $Cl + CH_4 \rightarrow HCl + CH_3$ 1
	$8.13x10^{10}$	295		
	$8.61x10^{10}$	295		
	$8.67x10^{10}$	295		
	$1.01x10^{11}$	298		
	$1.70x10^{11}$	320		
	$2.26x10^{11}$	366		
	$3.25x10^{11}$	371		
	$1.82x10^{11}$	380		
	$3.05x10^{11}$	401		
	$3.46x10^{11}$	401		
	$3.81x10^{11}$	442		
	$4.50x10^{11}$	442		
	$4.91x10^{11}$	464		
	$7.06x10^{11}$	490		

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$3.25x10^{12}$ exp(-1130/T)	218-350	No details available. DAVIS 1975 (31)	Reported as provisional data, subject to revision, by HAMPSON and GARVIN (32). Method probably as for previous study by DAVIS (17). Used by (36,37, 41 and 43).
$(7.23±0.18)x10^{10}$	295	Cl_2 discharge flow system. Cl_2 (1%-5%)/He mixtures passed through discharge and added to CH_4 through moveable inlet. Cl ($5.7 x10^{-10}$-$1.6x10^{-9}$ mol cm^{-3}) in excess by >factor 10. $[CH_4]$ decay followed by mass spectrometry, and [Cl] determined by (a) variation in $[Cl_2]$ upon activation of discharge, and (b) titration with NOCl. LEU and DE MORE 1976 (39 and 40)	Pseudo first order decay of CH_4 gave k_1 directly.
$(1.80±0.24)x10^{10}$ $(1.99±0.20)x10^{10}$ $(2.33±0.18)x10^{10}$ $(2.28±0.05)x10^{10}$ $(2.30±0.01)x10^{10}$ $(2.50±0.3\ )x10^{10}$ $(2.98±0.18)x10^{10}$ $(3.01±0.16)x10^{10}$ $(3.62±0.18)x10^{10}$ $(3.79±0.18)x10^{10}$ $(4.77±0.59)x10^{10}$ $(6.87±0.12)x10^{10}$ $(6.87±0.54)x10^{10}$ $(6.93±0.36)x10^{10}$ $(7.17±0.6\ )x10^{10}$ $(7.47±1.21)x10^{10}$ $(7.28±0.02)x10^{10}$ $(1.32±0.11)x10^{11}$ $(2.13±0.07)x10^{11}$ $(2.32±0.02)x10^{11}$	218 220 238.5 239 239 239 245 245 250 250 273 298 298 298 298 298 299 350 401 401	Flash photolysis study. CCl_4 (10-200 μ Hg; 1.3-26.7 Pa)/CH_4 (0-300 μ Hg; 40 Pa)/He (20-200 mm Hg; 2.7-26.7 kPa) or Ar (50 mm Hg; 6.7 kPa) mixtures. [Cl] followed by resonance fluorescence. WATSON, MACHADO, FISCHER and DAVIS 1976 (42)	Initial conditions $[CH_4]>>[Cl]$ chosen so that pseudo first order decay of Cl used to give k_1. Authors express these data by $k_1 = (4.48±0.45)x10^{12} \exp\{-(1230±50)/T\}$ cm^3 mol^{-1} s^{-1} (218-401 K). $Cl + CH_4 \rightarrow HCl + CH_3$ 1
	243-361	Static radiolysis study. $CClF_3/CH_4$ or $C_2H_6/O_2/C_2H_3Br$ mixtures at total pressures ∿5 atm (506.5 kPa). No individual reactant pressures given. $C_2H_3{}^{38}Cl$ yield determined. LEE and ROWLAND 1977 (45)	Reactions of ^{38}Cl atoms following $CClF_3$ radiolysis given as $^{38}Cl + C_2H_3Br \rightarrow C_2H_3Br^{38}Cl^*$ 9 $C_2H_3Br^{38}Cl^* \rightarrow C_2H_3{}^{38}Cl + Br$ $C_2H_3Br^{38}Cl^* + M \rightarrow C_2H_3Br^{38}Cl + M$ $C_2H_3Br^{38}Cl + O_2 \rightarrow$ products $^{38}Cl + CH_4 \rightarrow HCl + CH_3$ 1' $^{38}Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5' 'Hot' ^{38}Cl atoms thermalised by excess $CClF_3$. Addition of CH_4 or C_2H_6 reduces $C_2H_3{}^{38}Cl$ yield, hence ratios $k_{1'}/Bk_9$ and $k_{5'}/Bk_9$

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		LEE and ROWLAND 1977 (45) continued.	obtained, where B is parameter independent of [CH$_4$] provided [CH$_4$] << [CCl$_3$F]. Elimination of B gave ratios $k_{5'}/k_{1'}=(1700\pm300)$ at 243 K, (360 ± 40) at 298 K, and (150 ± 20) at 361 K. Authors used $k_{5'}=(3.31\pm0.3)x10^{13}$ cm^3 mol^{-1} s^{-1} (47) at 243 K to derive $k_{1'}=(1.93\pm0.4)x10^{10}$ cm^3 mol^{-1} s^{-1}. We have used WATSON's preferred value for k_5 at 298 K (49) to derive $k_{1'}=(9.70^{+0.5}_{-1.9})x10^{10}$ cm^3 mol^{-1} s^{-1}.
(a) $(6.38\pm4.82)x10^{12}$ exp{-(1415±200)/T} (b)	268-423 220-296	(a) Discharge flow system, using mass spectrometry, and (b) static photolysis system, using competitive chlorination of CH$_4$ and C$_2$H$_6$. LIN and DEMORE 1977 (46)	No details available. Results of method (b) given as $k_5/k_1=(4.16\pm0.35)$ exp{(1440±20)/T}. $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5 Authors used k_5 of WATSON and LEWIS to derive $k_1=(1.13\pm0.1)x10^{13}$ exp{-(1560±40)/T} cm^3 mol^{-1} s^{-1}, and data of systems (a) and (b) combined to give $k_1=8.85x10^{12}$ exp(-1510/T) cm^3 mol^{-1} s^{-1}. WATSON (49) reported ratio obtained in (b) and derived $k_1=1.05x10^{13}$ exp(-1500/T) cm^3 mol^{-1} s^{-1} (198-296 K) using his preferred value for k_5.
$(1.50\pm0.1)x10^{10}$ $(1.64\pm0.8)x10^{10}$ $(2.10\pm0.3)x10^{10}$ $(2.91\pm0.2)x10^{10}$ $(2.75\pm0.8)x10^{10}$ $(3.70\pm0.2)x10^{10}$ $(4.43\pm0.4)x10^{10}$ $(5.17\pm0.3)x10^{10}$ $(5.82\pm0.8)x10^{10}$ $(6.26\pm0.6)x10^{10}$ $(8.48\pm0.6)x10^{10}$ $(1.00\pm0.03)x10^{11}$	218 * 224 235 250 * 254 263 277 285 * 296 296 313 322	Flash photolysis study. CCl$_4$ (13 μ Hg; 1.73 Pa)/CH$_4$ mixtures at unspecified total pressures. [Cl] monitored by resonance fluorescence. MANNING and KURYLO 1977 (47)	Decay of [Cl] found independent of initial [Cl], indicating lack of secondary reactions with Cl atoms. Values of k_1 derived from pseudo first order kinetics, and corrected for C$_2$H$_6$ impurities (34 ppm in most cases, 500 ppm in those cases marked *). Corrections made using data for k_5 determined in same study. $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ 5 Data marked * not included in least squares fit giving $k_1=(4.78\pm0.9)x10^{12}$ exp{-(1270±50)/T} cm^3 mol^{-1} s^{-1}. Possibility of slight curvature of Arrhenius plot considered by authors. Value of k_1 at 298 K of $(6.44\pm1.2)x10^{10}$ cm^3 mol^{-1} s^{-1} derived from values of this work, of (42 and 52).

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(6.50 \pm 0.4) \times 10^{10}$	298	Cl_2-discharge flow system. Cl_2/He mixtures passed through discharge; excess CH_4 added downstream through moveable inlet. Initial $[Cl] \approx 8.3 \times 10^{-12}$ mol cm^{-3}. Total pressures 1.31 mm Hg (174.6 Pa). Resonance fluorescence used to monitor [Cl]. MICHAEL and LEE 1977 (48)	Pseudo first order decay of [Cl] used to derive k_1. Correction made for Cl removal by 32 ppm C_2H_6 impurity.
$(8.79 \pm 0.54) \times 10^{9}$	200	Flash photolysis flow system. $COCl_2$ (25-400 μ Hg; 3.33-53.3 Pa)/CH_4 (50-1505 μ Hg; 6.67-200.6 Pa) /Ar (15-300 mm Hg; 2-40 kPa) mixtures photolysed ⩾143 nm. $[COCl_2]:[CH_4]$ ratios varied 6.7×10^{-2}-3.0. [Cl] monitored by resonance fluorescence. WHYTOCK, LEE, MICHAEL, PAYNE and STIEF 1977 (50)	Resonance fluorescence signal taken to be ∝ [Cl]. Pseudo first order rate constants for Cl decay corrected for diffusion, determined independently in $COCl_2$/Ar mixtures. Wide range of flash intensities, and hence [Cl], covered. Correction also made to bimolecular rate constant for 32 ppm C_2H_6 impurity in CH_4. Curvature of Arrhenius plot fitted by overall expression $k_1 = 3.28 \times 10^5 T^{2.5} \exp(-608/T)$ cm^3 mol^{-1} s^{-1} (200-500 K), or by two separate Arrhenius expressions $k_1 = (3.92 \pm 0.48) \times 10^{12} \exp\{-(1229 \pm 27)/T\}$ cm^3 mol^{-1} s^{-1} (200-299 K), and $k_1 = (1.11 \pm 0.17) \times 10^{13} \exp\{-(1545 \pm 52)/T\}$ cm^3 mol^{-1} s^{-1} (299-500 K). Slightly different expressions reported by WATSON (49).
$(1.15 \pm 0.08) \times 10^{10}$	210		
$(1.41 \pm 0.11) \times 10^{10}$	220		
$(1.95 \pm 0.12) \times 10^{10}$	232		
$(2.48 \pm 0.16) \times 10^{10}$	245		
$(3.44 \pm 0.27) \times 10^{10}$	260		
$(4.51 \pm 0.36) \times 10^{10}$	276		
$(6.81 \pm 0.42) \times 10^{10}$	299		
$(8.31 \pm 0.3\ ) \times 10^{10}$	318		
$(1.23 \pm 0.08) \times 10^{11}$	343		
$(1.65 \pm 0.09) \times 10^{11}$	371		
$(2.27 \pm 0.17) \times 10^{11}$	404		
$(3.44 \pm 0.25) \times 10^{11}$	447		
$(5.46 \pm 0.44) \times 10^{11}$	500		
$(5.60 \pm 0.3) \times 10^{10}$	298	Very low pressure pyrolysis study. Cl_2(<1%)/He mixtures passed through discharge and added to CH_4 stream, so that $[CH_4] >> [Cl]$. Total pressures not reported. Reaction followed by mass spectrometry. BAGHAL-VAYJOOEE, COLUSSI and BENSON 1978 (51)	Authors assumed reverse reaction made negligible contribution to kinetics. No CH_3Cl found in products.

$Cl + CH_4 \rightarrow HCl + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(6.56\pm0.2)\times10^{9}$	200	Discharge flow system. Cl_2/He mixtures passed through discharge. CH_4 added downstream through moveable inlet, giving $1.7\times10^{-15} \leqslant [Cl] \leqslant 3.3\times10^{-13}$ mol cm^{-3}, and $1.3\times10^{-10} \leqslant [CH_4] \leqslant 1.7\times10^{-8}$ mol cm^{-3} at total pressures 2-4 mm Hg (266.6-533.2 Pa). Vacuum uv resonance fluorescence at 134.7 nm used to monitor [Cl] decay. ZAHNISER, BERQUIST and KAUFMAN 1978 (52)	Cl fluorescence calibrated by titrating ClO with NO. Pseudo first order decay of [Cl] found to be linear for up to factor of ∿50. Data of T<300 K expressed as $k_1=(4.94\pm0.4)\times10^{12}\exp\{-(1320\pm20)/T\}$ cm^3 mol^{-1} s^{-1}. Upward curvature for T>300 K, found to be greater than could be accounted for by experiemntal error, led authors to give overall expression $k_1=5.18\times10^{6}$ $T^{2.11}\exp(-795/T)$ cm^3 mol^{-1} s^{-1}. Data quoted before publication by (45,47 and 49).
$(1.12\pm0.04)\times10^{10}$	215		
$(1.77\pm0.02)\times10^{10}$	235		
$(3.00\pm0.1)\times10^{10}$	259		
$(5.63\pm0.2)\times10^{10}$	296		
$(5.90\pm0.2)\times10^{10}$	298		
$(6.20\pm0.1)\times10^{10}$	300		
$(1.38\pm0.02)\times10^{11}$	361		
$(2.28\pm0.09)\times10^{11}$	407		
$(5.48\pm0.2)\times10^{11}$	504		

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(2.4\pm0.8)\times10^{13}\exp\{-(1930\pm90)/T\}$	300-600	Review. Expression based on data of (5 and 6). FETTIS and KNOX 1964 (12)	Authors use $k_2=8.2\times10^{13}\exp(-2760/T)$ cm^3 mol^{-1} s^{-1} as standard from which to obtain k_1, using experimental ratios k_1/k_2. $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + H_2 \rightarrow HCl + H$ 2 Used by (20) without multiplication by 4 for each H atom. Reported by (15 and 21).
$(3.37\pm0.5)\times10^{13}\exp\{-(1790\pm37)/T\}$	298-686	Evaluation. Expression based on average of values of k_1 at 298 K of (17 and 24), and E_1 of (24). WATSON 1974 (29)	Data of (3 and 6) not used in this evaluation owing to the discrepancy between k_1/k_2 of these studies and of (17). Expression retained by (32).
$4.39\times10^{12}\exp\{-(1260\pm55)/T\}$	200-299	Evaluation. Review of reactions of atmospheric interest. WATSON 1977 (49)	Updating of author's earlier review (29). Recommended expression derived from data of (42,47,50 and 52), using least squares. Value at 298 K quoted as $(6.75\pm0.7)\times10^{10}$ cm^3 mol^{-1} s^{-1}. Used by HUDSON (44).

$Cl + CH_4 \rightarrow HCl + CH_3$

ISOTOPIC REACTION $CL + CD_4 \rightarrow DCL + CD_3$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	300-470	Static photolysis system. CH_4(18.7-38.1 mm Hg; 2.5-5.1 kPa)/CD_4 (72.1-236.3 mm Hg; 9.6-31.5 kPa)/Cl_2 (1.9-14.3 mm Hg; 0.25-1.9 kPa) mixtures. Product analysis by mass spectrometry. CHILTZ, ECKLING, GOLDFINGER, HUYBRECHTS, JOHNSTON, MEYERS and VERBEKE 1963 (10)	Mechanism of competitive reactions taken as $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + CD_4 \rightarrow DCl + CD_3$ 1D $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ 3 $CD_3 + Cl_2 \rightarrow CD_3Cl + Cl$ 3D i.e. assumptions are CH_3 and CD_3 only react via 3 and 3D respectively, and CH_3Cl and CD_3Cl react no further. From rates of change of CH_3Cl and CD_3Cl, ratio k_1/k_{1D} obtained: T/K $\log(k_1/k_{1D})$ 303.7 1.033±0.026 304.4 1.037±0.032 321.9 0.978±0.04 343.3 0.871±0.025 400.4 0.713±0.033 430.7 0.666±0.035 451.6 0.586±0.053 461.4 0.561±0.031 WALKER (22) attributes expression k_1/k_{1D}=0.48 exp(960/T) to this work.
	298-1018	Cl_2-discharge flow system. Cl_2/He mixtures in discharge, CH_4/CD_4 mixtures added downstream. Total pressures 0.55-1.2 mm Hg (73-160 Pa). $[CH_4]$ and $[CD_4]$ monitored by mass spectrometry. WALKER 1972 (22)	He used as carrier gas to avoid confusion between m/e=20(Ar^{++}) and 20(CD_4^+). Rate constant ratio k_1/k_{1D} found from relative rates of CH_4 and CD_4 decay. T/K k_1/k_{1D} 298 11.96±0.7 299 12.59±0.5 322 12.84±1.1 340 9.03±0.6 366 8.64±1.3 407 5.85±0.7 426 5.96±0.4 460 5.55±1.1 471 4.15±1.6 520 3.50±0.4 549 3.31±0.5 593 3.75±1.0 625 2.54±0.8 642 2.40±0.3 681 3.10±0.2 687 2.06±0.3 731 2.22±0.6 775 2.06±0.5 787 1.64±0.2 816 2.27±0.7 854 2.25±0.2 871 1.95±0.3 891 1.86±0.2 924 1.91±0.2 930 2.13±0.3 973 1.53±0.1 1000 1.96±0.4 1018 1.75±0.0 Arrhenius fits given to these data as k_1/k_{1D}=0.725 exp(880/T) (298-681 K), and k_1/k_{1D}=0.71 exp (880/T) (298-1018 K). Using his

$Cl + CH_4 \rightarrow HCl + CH_3$

ISOTOPIC REACTION CL + CD_4 → DCL + CD_3 - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		WALKER 1972 (22) continued.	own expression for k_1 (see Comments column for entry under reaction 1), author gives k_{1D}= $4.3x10^{13}$ exp(-2680/T) cm^3 mol^{-1} s^{-1} (298-681 K). These data also reported by CLYNE and WALKER (24).

ISOTOPIC REACTIONS CL + CH_2D_2 → HCL + CHD_2 AND CL + CH_2D_2 → DCL + CH_2D

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	250-344	Static photolysis system. CH_2D_2/Cl_2 mixtures, with CH_2D_2 in excess ($[CH_2D_2]/[Cl_2]$= 2 to 9). Mass spectrometry used to measure $[CHD_2Cl]$ and $[CH_2DCl]$. WIBERG and MOTELL 1963 (11)	Steady state approximation used for Cl atoms and CH_n radicals (n=1-3) so that mechanism described solely in terms of rate constants for reactions $Cl + CH_4 \rightarrow HCl + CH_3$ 1 $Cl + CH_3Cl \rightarrow HCl + CH_2Cl$ 4 $Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$ $Cl + CHCl_3 \rightarrow HCl + CCl_3$ Using values of k_1, k_4, etc. as first approximations to rate constants for deuterated species, e.g. k_{10} and k_{11}, $Cl + CH_2D_2 \rightarrow HCl + CHD_2$ 10 $\rightarrow DCl + CH_2D$ 11 comparison made between calculated and observed $[CHD_2Cl]/[CH_2DCl]$ ratios. Best fits to experimental data obtained for k_{10}/k_{11}=14.4 (250 K), 12.1 (273 K), 8.2 (325 K), and 7.1 (344 K). Authors give Arrhenius expression for k_{10}/k_{11} as 1.09 exp(654/T). Small amounts of CH_3D present in CH_2D_2 (2.9±0.4%) provided largest source of error. Secondary isotope effect assumed negligible.

Discussion

The reaction between chlorine atoms and methane

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (1)$$

is an important process in the behaviour of stratospheric Cl, because of the high (5×10^{-15}-10^{-12} mol cm^{-3} [33,34]) concentrations of CH_4. Reaction 1 provides a temporary sink for Cl atoms, thereby interrupting the cycle of ozone removal:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

Prior to any absolute measurement of k_1 there was excellent agreement over a wide temperature range between the data of Pritchard et al. [3] and Knox and Nelson [6] for the relative rate k_1/k_2

$$Cl + H_2 \rightarrow HCl + H \qquad (2)$$

Both sets of results were obtained in static photolysis systems, by comparing the overall consumption of CH_4 and of H_2.

However, absolute determinations of k_1 and k_2 at 298 K by Davis et al. [17] gave a ratio k_1/k_2 a factor of 2 higher than those of [3 and 6]. Moreover subsequent measurements of absolute values of both k_1 [22,27] and k_2 [16] agreed with the values of Davis.

But later work of Davis et al. [31,42] on both k_1 and k_2, in which lower values of k_1 and higher values of k_2 were reported, resulted in ratios k_1/k_2 in much better agreement (at least above 300 K) with the earlier results of Pritchard et al. [3] and Knox and Nelson [6]. These lower values of k_1 are now supported by the most recent studies [39,40,42,47,48,50,51,52].

These later studies are probably the more accurate, owing to the lower reactant concentrations detectable with the resonance fluorescence technique [42,47,48,50,52], thereby reducing the influence of secondary reactions.

Watson, in his excellent detailed review [49] has pointed out the strong effects upon the reaction rate of C_2H_6 impurities in CH_4 samples. Manning and Kurylo [47] and Whytock et al. [50] have taken particular care over this point, and with Zahniser et al. [52] have produced the lowest recent values of k_1 (although the latter present no details of CH_4 purity levels).

All the recent investigations that have covered a wide temperature range have noticed a curvature in their Arrhenius plots [47,50,52]. This probably explains discrepancies in the activation energies measured in previous studies over different temperature ranges: Clyne and Walker [24] *obtained* $E_1 = 14.9$ *kJ mol*$^{-1}$ *(3.56 kcal mol*$^{-1}$*) for 300–690 K*, whereas Watson et al. [42] obtained 10.2 kJ mol^{-1} (2.44 kcal mol^{-1}) for 218–400 K. Allowance for the curvature has been made either by fitting two separate linear expressions to the data, or by incorporating a large temperature exponent in the pre-exponential factor: 2.5 by [50], and 2.11 by [52]. We have found that a somewhat lower temperature dependence is sufficient to describe the modest curvature of these data: on the basis of the most recent data of [42,47,48,50,51 and 52] we recommend the expression

$$k_1 = 1.10\times10^7 T^{1.97} \exp(-750/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 200–500 K. Uncertainty limits of ±35% should be taken over this range.

$Cl + CD_4 \rightarrow DCl + CD_3$

The kinetic isotope effect for the chlorination of a C–H bond has been studied by Chiltz et al. [10] and Walker [22], both investigations determining the ratio k_1/k_{1D} over wide temperature ranges.

$$Cl + CD_4 \rightarrow DCl + CD_3 \qquad (1D)$$

The error limits on all of these data are such that there is general agreement, with those of Chiltz et al. [10] falling somewhat below, and having a slightly higher activation energy than, those of Walker [22]. A least-squares analysis of all the data gives the expression

$$k_1/k_{1D} = 0.74 \exp(832/T)$$

for temperatures 300–1020 K, which with our recommended expression for k_1 gives

$$k_{1D} = 1.49\times10^7 T^{1.97} \exp(-1580/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 300–500 K. Uncertainty limits of ±80% are recommended over these temperatures.

Rate of the Reverse Reaction

The data for the rate constant k_{-1}

$$CH_3 + HCl \rightarrow Cl + CH_4 \qquad (-1)$$

have been summarised and evaluated by Kerr and Parsonage [38], giving a preferred expression $k_{-1} = 2.34\times10^{11} \exp(-1160/T)$ cm^3 mol^{-1} s^{-1} (300–500 K), with quoted error limits of ±150%. At 298 K, this expression gives $k_{-1} = 4.77\times10^9$ cm^3 mol^{-1} s^{-1}. Using the Thermodynamic Data at the beginning of this section, we derive a value of k_{-1} at 298 K of 3.12×10^{10} cm^3 mol^{-1} s^{-1} from our recommended expression for k_1. The difference between these two values of k_{-1} is greater than can be explained by the uncertainties in k_1 or by the slightly lower value of k_{11}

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (11)$$

used by Kerr and Parsonage as compared with our recommended value for k_{11} (to be presented in Volume 5).

We believe that the discrepancy is due to differences in the thermodynamic data used for CH_3. Kerr and Parsonage [38] quote $\Delta H^\circ_{f,298}(CH_3)$ as 142.3 kJ mol^{-1} (34.0 kcal mol^{-1}), whereas the JANAF Tables give the value 145.7 kJ mol^{-1} (34.82 kcal mol^{-1}). If we assume that both our expression for k_1, and Kerr and Parsonage's expression for k_{-1} are correct, then we derive $\Delta H^\circ_{f,298}(CH_3)$ as 141.0 kJ mol^{-1} (33.70 kcal mol^{-1}). This value is only 418 J mol^{-1} (100 cal mol^{-1}) higher than the value for $\Delta H^\circ_{f,298}(CH_3)$ derived from a similar consideration of the forward and reverse rate constants of the reaction

$$H + CH_4 \rightarrow CH_3 + H_2$$

to be published in Volume 5 of this series.

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B8 O + HCl → Cl + OH

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	4.12	0.93	-0.68
300	4.12	0.93	-0.67
500	4.40	1.62	-0.38
1000	4.96	2.46	-0.13
1500	4.93	2.43	-0.05
2000	4.72	2.32	0.00
2500	4.52	2.23	0.02
3000	4.34	2.16	0.04
3500	4.13	2.10	0.05
4000	3.87	2.03	0.06
4500	3.52	1.94	0.06
5000	3.07	1.85	0.06

RECOMMENDED RATE CONSTANT

$k = 6.87 \times 10^{12} \exp(-3370/T)$ cm^3 mol^{-1} s^{-1}

$= 1.14 \times 10^{-11} \exp(-3370/T)$ cm^3 molecule^{-1} s^{-1}

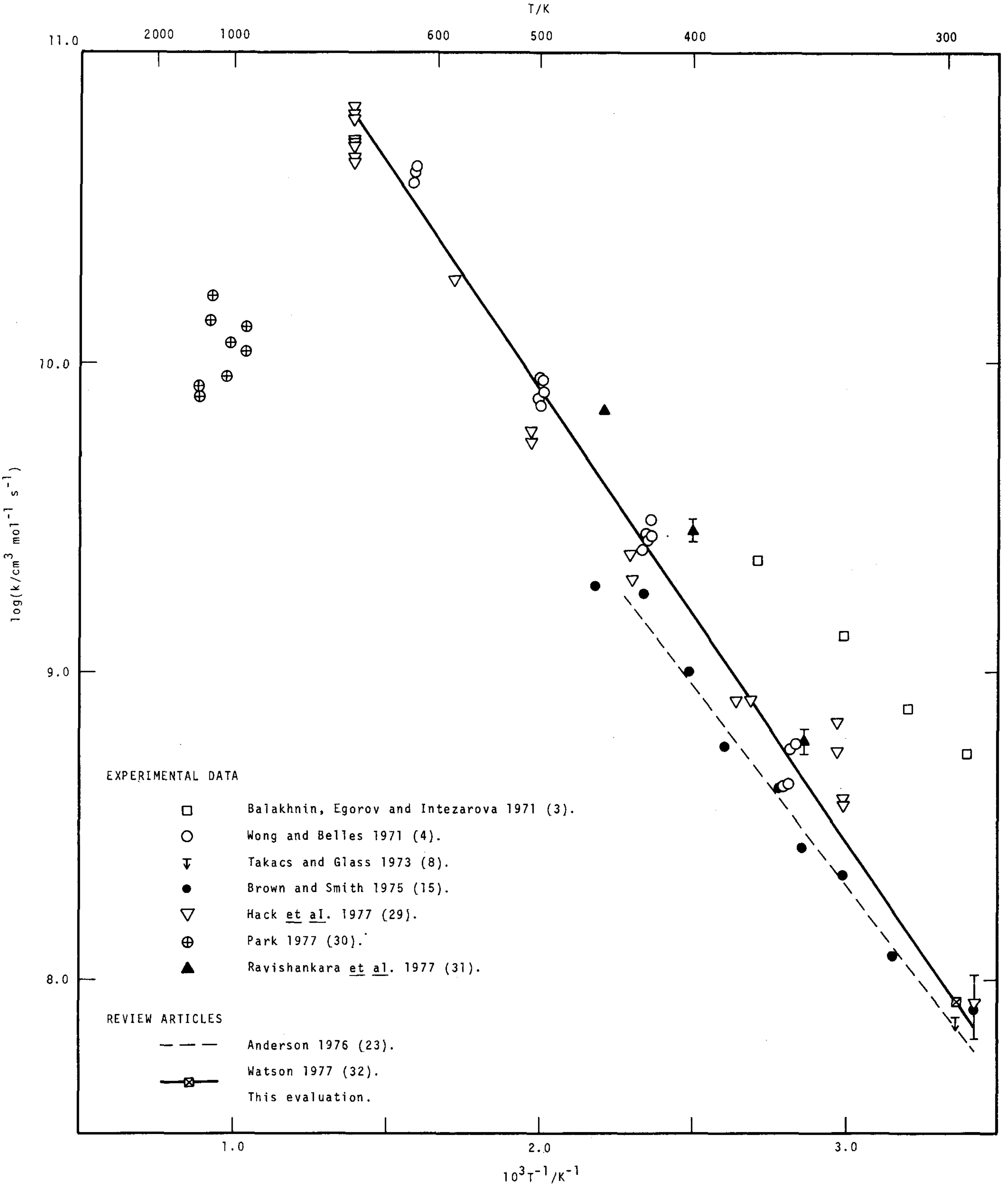
Temperature Range: 290-720 K.

Suggested Error Limits for Calculated Rate Constant: Factor of 2 at 290 K rising to a factor of 4 at 720 K.

Note: this expression is that of WATSON (32).

Rate Parameters:
$\log(A/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 12.837 \pm 1.2$
$\log(A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -10.943 \pm 1.2$
$E/\text{J mol}^{-1} = 28\ 020 \pm 8360$
$E/\text{cal mol}^{-1} = 6\ 700 \pm 2000$

$O + HCl \rightarrow Cl + OH$

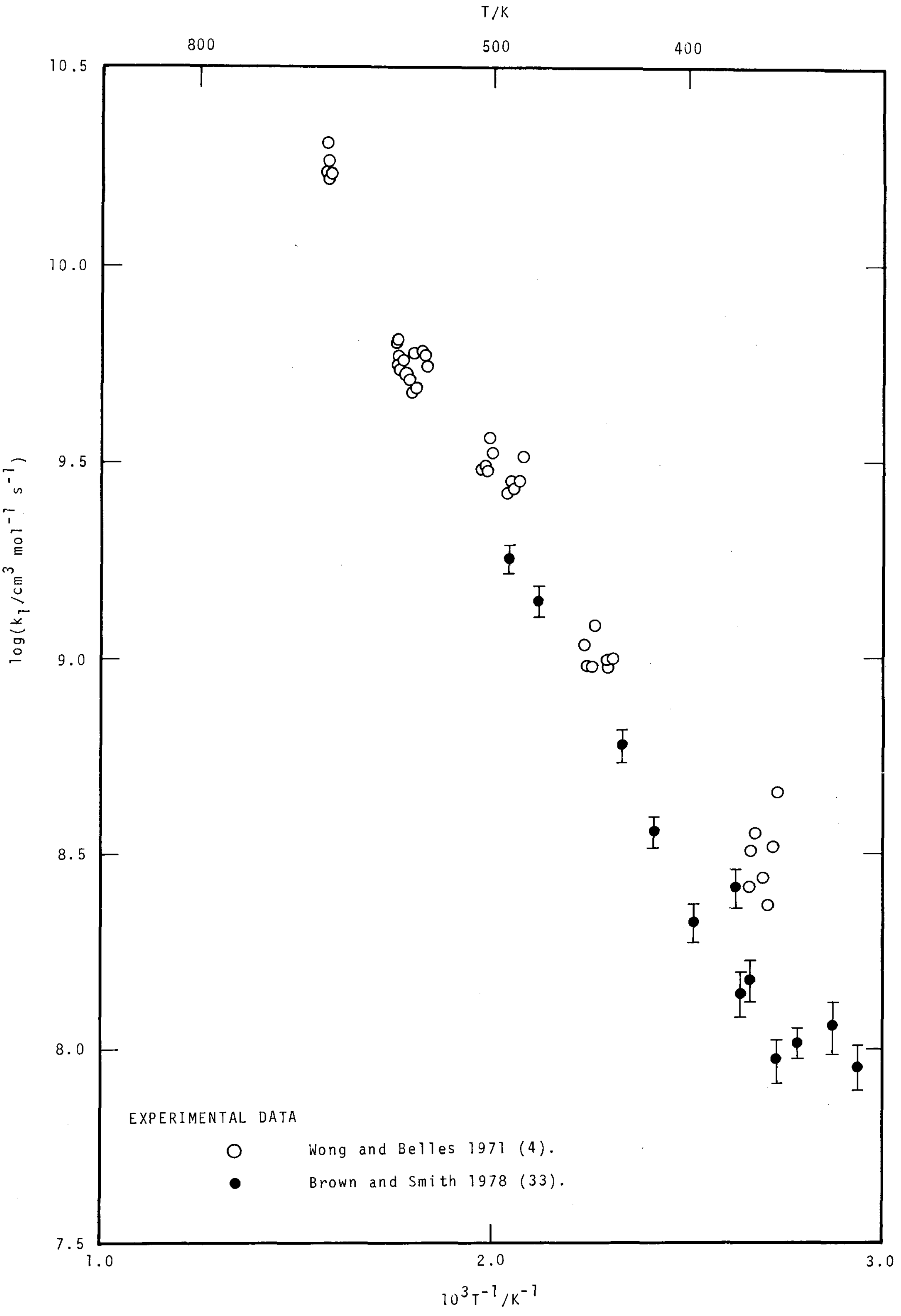


$O + HCl \rightarrow Cl + OH$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$5.4x10^8$ $7.6x10^8$ $1.3x10^9$ $2.3x10^9$	295 313 335 370	Discharge flow system. Excess HCl (6.7-13.3 Pa) added to O atoms ([O]<0.1 [HCl]) in Ar at 267 Pa total pressure. [O] and [Cl] monitored by esr spectroscopy. BALAKHNIN, EGOROV and INTEZAROVA 1971 (3)	Overall reaction stoichiometry, n, not measured but mechanism assumed to consist of reactions 1 to 4 inclusive, implying $O + HCl \rightarrow Cl + OH$ 1 $O + OH \rightarrow H + O_2$ 2 $OH + HCl \rightarrow Cl + H_2O$ 3 $O \rightarrow$ wall 4 $1 \leq n \leq 2$. Rate constants presented in graphical form only. Authors assume n=(1.5±0.5) and, hence calculated $k_1=(1.05\pm0.35)x10^{12}$ exp(-2265/T) cm^3 mol^{-1} s^{-1}. Quoted by (4,10,12,13,15,16,17,18,19,21,23). Listed by (27).
$5.81x10^8$ $5.56x10^8$ $4.32x10^8$ $4.23x10^8$ $2.75x10^9$ $3.11x10^9$ $2.68x10^9$ $2.82x10^9$ $2.47x10^9$ $8.02x10^9$ $8.82x10^9$ $8.95x10^9$ $7.24x10^9$ $7.62x10^9$ $4.28x10^{10}$ $4.06x10^{10}$ $3.74x10^{10}$	353 355 356 358 424 425 426 428 429 498 499 500 501 502 629 630 631	Discharge flow system. HCl added to O atoms ($5.68x10^{-10}$-$9.21x10^{-10}$mol cm^{-3}) in Ar at 107 Pa total pressure. [HCl] similar to [O]. [O], [HCl], [O_2], [H_2] and [H_2O] monitored mass spectrometrically. WONG and BELLES 1971 (4)	Stirred flow reactor. Authors propose reaction mechanism comprising reactions 1,2,3,5,6,7,8,9,10,11 and 12. Reactions 2 and 7 $O + O + M \rightarrow O_2 + M$ 5 $O + O_2 + M \rightarrow O_3 + M$ 6 $H + HCl \rightarrow Cl + H_2$ 7 $O + O_3 \rightarrow O_2 + O_2$ 8 $O + Cl_2 \rightarrow Cl + ClO$ 9 $Cl + Cl + M \rightarrow Cl_2 + M$ 10 $O + ClO \rightarrow Cl + O_2$ 11 $H + Cl_2 \rightarrow Cl + HCl$ 12 thought to be mainly responsible for O_2 and H_2 production respectively. Calculated $k_1=(1.13\pm0.16)x10^{13}$ exp{-(3575±65)/T} cm^3 mol^{-1} s^{-1} using values for k_5 and k_6 as recommended by JOHNSTON (2) and k_9 from CLYNE and COXON (1). Quoted by (12,15,17,19,22,23,25). Used by (26).
$<6x10^7$	298	Unspecified. TAKACS and GLASS 1973 (8)	Probably discharge flow system. Accredited to GLASS, unpublished results.
$(8.0\pm1.2)x10^7$ $(1.2\pm0.1)x10^8$ $(2.2\pm0.2)x10^8$ $(2.7\pm0.3)x10^8$ $(4.2\pm0.3)x10^8$ $(5.7\pm0.4)x10^8$ $(1.0\pm0.1)x10^9$ $(1.8\pm0.1)x10^9$ $(1.9\pm0.05)x10^9$	293 318 335 351 360 385 403 429 440	Discharge flow system. O atoms from titration of N atoms with NO mixed with excess HCl ([HCl]/[O]$_o$ in range 15-1270) in N_2 at 133-333 Pa total pressure. [O] monitored spectrophotometrically by O+NO afterglow.	Reaction mechanism assumed to consist of reactions 1,2,3,7,9, $Cl \rightarrow$ wall 13 11 and 13. Reaction 4 shown to be unimportant. Obtained k_{13}=4.1 s^{-1} and using this together with k_2=$2.5x10^{13}$ cm^3 mol^{-1} s^{-1} (5), k_3=$2.5x10^{12}$ exp(-530/T) cm^3 mol^{-1} s^{-1} (11), k_7=$6.1x10^{12}$ exp

$O + DCl \rightarrow Cl + OD$



$O + HCl \rightarrow Cl + OH$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BROWN and SMITH 1975 (15) and SMITH 1975 (20)	$(-1610/T)\ cm^3\ mol^{-1}\ s^{-1}$ (evaluated by authors), $k_9=6.1\times10^{12}\exp(-1810/T)\ cm^3\ mol^{-1}\ s^{-1}$ (7) and $k_{11}=3.2\times10^{13}\ cm^3\ mol^{-1}$ (6), authors calculated corrected k_1 values as listed and derived $k_1=(1.5^{+0.7}_{-0.5})\times10^{12}\exp\{-(2970\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Quoted by (13,14,17,23,28).
(a) 8.4×10^{7}	293	Discharge flow system. O_2 dissociated by 10-30% in microwave discharge. HCl ($4.53\times10^{-9}-1.1\times10^{-7}$ mol cm^{-3}) added downstream through moveable inlet, giving $3.4\leq[HCl]/[O]\leq80$. Total pressures 1.65-5.63 mm Hg (220.0-750.5 Pa). Esr spectrometry used to follow [O], [Cl] and [OH]. [O] calibrated by titration with NO_2. HACK, MEX and WAGNER 1977 (29)	Authors considered O atom removal to be by sequence $O + HCl \rightarrow Cl + OH$ 1 $O + OH \rightarrow H + O_2$ 2 $OH + HCl \rightarrow Cl + H_2O$ 3 and ignoring wall reactions, and assuming [OH] to be quasistationary, derived expression for stoichiometry n as $(1+k_2[O]/(k_2[O]+k_4[HCl]))$. Using $k_2=2.5\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ (5) and $k_3=4\times10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ as determined in same work, n found to vary between 1 and 2. Hence effective rate constant for O atom removal converted to values of k_1 indicated by (a). Values also derived from Cl atom production (b). Excellent agreement obtained between two methods. Values marked * indicated as being uncorrected for wall reaction. Expression given as $k_1=(5.2\pm1)\times10^{12}\exp\{-(3230\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Earlier presentation of these data (24) referred to by WATSON (32).
(b) $(8.4\pm2)\times10^{7}$	293		
3.7×10^{8} *	335		
3.9×10^{8} *	335		
5.5×10^{8} *	337		
6.8×10^{8} *	337		
8.0×10^{8}	373		
8.0×10^{8}	379		
1.99×10^{9}	435		
2.40×10^{9}	435		
5.56×10^{9}	509		
6.03×10^{9}	509		
1.85×10^{10}	585		
4.42×10^{10}	718		
4.55×10^{10}	718		
5.07×10^{10}	718		
5.21×10^{10}	718		
5.31×10^{10}	718		
6.10×10^{10}	718		
6.39×10^{10}	718		
6.77×10^{10}	718		
1.1×10^{10}	962	Shock tube study. Mixtures of $O_3/HCl/O_2$ and Ar subjected to reflected shock giving pressures of 405-810 kPa. [ClO] monitored spectroscopically at 253.7 nm. PARK 1977 (30)	ClO absorbance measurements converted to absolute concentrations using previously determined absorption cross section values (27) (see this Volume, section B15). ClO production and removal interpreted in $O + HCl \rightarrow Cl + OH$ 1 $OH + HCl \rightarrow Cl + H_2O$ 3 $O_3 + M \rightarrow O + O_2 + M$ -6 $O + ClO \rightarrow Cl + O_2$ 11 $Cl + O_3 \rightarrow ClO + O_2$ 14 terms of reactions 1,3,-6,11 and 14. Measurements restricted to
1.3×10^{10}	963		
1.2×10^{10}	1013		
9.1×10^{9}	1027		
1.7×10^{10}	1081		
1.4×10^{10}	1087		
7.7×10^{9}	1121		
8.5×10^{9}	1130		

O + HCl → Cl + OH

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		PARK 1977 (30) continued.	conditions where $(k_{14}[O_3]_{initial}/k_{-6}[M])<1$ and $(k_{11}[O_3]_{initial}/k_1[HCl])>1$. Non-stationary state computer modelling treatment applied to reaction scheme to generate k_1 values, which are only displayed graphically. Author deduces $k_1=(1.2\pm0.6)\times10^{10}$ cm^3 mol^{-1} s^{-1} at T=1050±150 K.
$(5.96\pm0.5)\times10^8$ $(2.89\pm0.2)\times10^9$ $(6.99\pm0.2)\times10^9$	350 401 454	Flash photolysis study. O_2 (150 μm Hg; 20 Pa)/HCl (0.25-2.0 mm Hg; 33.3-266.6 Pa)/Ar (100 mm Hg; 13.3 kPa) mixtures photolysed in vacuum uv, giving $[HCl]/[O]>10^4$. [O] monitored by resonance fluorescence. RAVISHANKARA, SMITH, WATSON and DAVIS 1977 (31)	$O(^1D)$ formed by photolysis rapidly quenched by Ar diluent. Values of k_1 determined from pseudo first order decay of [O]. $O + HCl \rightarrow Cl + OH$ 1 These data expressed as $k_1=(3.13\pm0.5)\times10^{13}$ $\exp\{-(3780\pm380)/T\}$ cm^3 mol^{-1} s^{-1}.
		REVIEW ARTICLES	
1.5×10^{12} $\exp\{-(2970\pm150)/T\}$	293-440	Preferred value is that of (15). ANDERSON 1976 (23)	This expression favoured over those of (3 and 4).
8.43×10^7 6.87×10^{12} $\exp\{-(3370\pm350)/T\}$	298 293-718	Evaluation. Preferred values based on those of (4,15,29 and 31). WATSON 1977 (32)	Data of BALAKHNIN <u>et al</u>. (3) not used.
		ISOTOPIC REACTION O + DCL → CL + OD	
4.56×10^8 3.30×10^8 2.33×10^8 2.75×10^8 3.57×10^8 3.24×10^8 2.60×10^8 1.00×10^9 9.9×10^8 9.4×10^8 1.21×10^9 9.6×10^8 9.6×10^8 1.09×10^9 3.31×10^9 2.83×10^9 2.71×10^9 2.82×10^9 2.63×10^9 3.36×10^9	366 368 369 371 374 375 376 432 435 436 442 443 445 447 480 483 486 489 491 500	Discharge flow system. DCl added to O atoms (5.47×10^{-10} -1.04×10^{-11} mol cm^{-3}) in Ar at 107 Pa total pressure. Similar [DCl] and [O]. [O], [DCl] and $[O_2]$ monitored mass spectrometrically. WONG and BELLES 1971 (4)	Stirred flow reactor. Analogous mechanism to that proposed by authors for reaction 1 assumed. k_1' values calculated by $O + DCl \rightarrow Cl + OD$ 1' gave method as for k_1 values. Derived $k_1'=(3.74\pm0.60)\times10^{12}$ $\exp\{-(3420\pm85)/T\}$ cm^3 mol^{-1} s^{-1}.

$O + HCl \rightarrow Cl + OH$

ISOTOPIC REACTION $O + DCL \rightarrow CL + OD$ - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
3.69×10^9	501	WONG and BELLES 1971 (4) continued.	
2.98×10^9	503		
3.10×10^9	504		
3.05×10^9	506		
5.56×10^9	546		
5.93×10^9	547		
6.06×10^9	549		
4.88×10^9	554		
6.00×10^9	555		
4.78×10^9	556		
5.17×10^9	560		
5.30×10^9	561		
5.32×10^9	562		
5.77×10^9	565		
5.39×10^9	566		
5.67×10^9	567		
5.95×10^9	568		
6.61×10^9	569		
6.46×10^9	570		
1.71×10^{10}	631		
1.74×10^{10}	632		
1.68×10^{10}	633		
1.85×10^{10}	634		
2.04×10^{10}	635		
$(9.03 \pm 1.2) \times 10^7$	340	Discharge flow system. O atoms produced by titrating N with NO, and DCl added downstream in excess ($151 < [DCl]/[O] < 1290$). Total pressures probably as in (15). NO_2 afterglow monitored. BROWN and SMITH 1978 (33)	Variation of NO_2 afterglow intensity with distance downstream from injection of DCl gave k_1' from first order plot. $O + DCl \rightarrow Cl + OD$ 1' Stoichiometry calculated as always <1.3. These data fitted by expression $k_1' = (2.33 \pm 0.5) \times 10^{12} \exp\{-(3520 \pm 250)/T\}$ cm^3 mol^{-1} s^{-1}.
$(1.14 \pm 0.2) \times 10^8$	348		
$(1.04 \pm 0.9) \times 10^8$	359		
$(9.33 \pm 1.2) \times 10^7$	366		
$(1.51 \pm 0.2) \times 10^8$	375		
$(1.39 \pm 0.2) \times 10^8$	378		
$(2.59 \pm 0.3) \times 10^8$	381		
$(2.11 \pm 0.2) \times 10^8$	397		
$(3.61 \pm 0.3) \times 10^8$	413		
$(6.02 \pm 0.6) \times 10^8$	429		
$(1.40 \pm 0.1) \times 10^9$	472		
$(1.81 \pm 0.2) \times 10^9$	489		

Discussion

Measurements of k_1, the rate constant for the reaction between HCl and oxygen atoms are complicated by the rapid reaction

$$O + HCl \rightarrow Cl + OH \qquad (1)$$

between product OH radicals and O atoms. Other secondary processes may also be important, including reactions 3 and 7.

$$O + OH \rightarrow H + O_2 \qquad (2)$$

$$OH + HCl \rightarrow Cl + H_2O \qquad (3)$$

$$H + HCl \rightarrow Cl + H_2 \qquad (7)$$

Thus if values of k_1 are to be correctly determined, either the secondary reactions must be eliminated, e.g., [31], or the stoichiometry n of the overall reaction must be known. None of the discharge flow studies of reaction 1 [3,4,15,29] reports an experimental value for n. All evaded this difficulty by assuming a reaction mechanism and, except for Balakhnin et al. [3], substituting literature values for the required rate constants in the kinetic expressions derived therefrom in order to calculate k_1.

Three other studies [9,14,18] have been carried out in which the reaction HCl ($v=1$) with O atoms has been investigated. Rate constants for HCl ($v=1$) relaxation have been obtained but their evaluation does not concern us here.

Balakhnin and co-workers [3] postulated a mechanism comprising reactions 1,2 and 3 plus O atom removal at the wall (reaction 4). This scheme predicts that n lies between one and two and they have therefore incorporated this uncertainty into the quoted error limits for their reported A-factor. Their k_1 values were obtained over a smaller temperature range than those of other workers and are larger by a factor of between 3 and 8. The explanation for this latter discrepancy is open to speculation. The corrected k_1 values of Wong and Belles [4] and of Brown and Smith [15] are in fair agreement. Both pairs of workers assumed that the secondary reactions 2,3,7,9 and 11 were important. Wong and Belles also included reactions 4,5,6,8,10 and 12 in their

$$O + O + M \rightarrow O_2 + M \qquad (5)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (6)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (8)$$

$$O + Cl_2 \rightarrow Cl + ClO \qquad (9)$$

$$Cl + Cl + M \rightarrow Cl_2 + M \qquad (10)$$

$$O + ClO \rightarrow Cl + O_2 \qquad (11)$$

$$H + Cl_2 \rightarrow Cl + HCl \qquad (12)$$

$$Cl \rightarrow \text{wall} \qquad (13)$$

scheme, but not 13, which was considered by Brown and Smith. These authors felt that had reaction 13 been included by Wong and Belles then the calculated rate constants would have been more closely in agreement with their own by virtue of the consequent larger correction for the effects of reactions 9 and 11.

The most recent discharge flow results of Hack et al. [29] are also in agreement with those of [4 and 15], with equal room temperature values being obtained from both O atom disappearance and Cl atom production. However the latest study [31], using the flash photolysis-resonance fluorescence technique, gave higher values of k_1. The linearity of the pseudo first order [O] decay plots was such that secondary reactions could be considered negligible. In contrast, these authors' data for reaction 3 (section B9) are in much better agreement with other determinations of k_3, e.g., [29], and so this difference is unlikely to be attributable to inaccuracies inherent in the technique.

In view of the unknown overall reaction stoichiometry and the necessity to make corrections, albeit not very large, for the effects of secondary reactions in the discharge flow studies, we find it difficult to differentiate, with regard to reliability, between the experimental studies. The agreement, especially at lower temperatures, of the results of [4,15 and 29], and the extrapolated data of [31] suggests that these data are to be preferred. We accordingly accept Watson's combination of these results [32], and recommend his expression for k_1 (over the temperature range 290–720 K).

$$k_1 = 6.87\times10^{12} \exp(-3370/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

We recommend error limits in k_1 of a factor of 2 at 290 K rising to a factor of 4 at 720 K.

Rate of the Reverse Reaction

There are no experimental determinations of the rate constant k_{-1}.

$$Cl + OH \rightarrow O + HCl \qquad (-1)$$

An expression for k_{-1} can however be obtained using the equilibrium constant $K_{1,-1}$ calculated from known thermodynamic data, and our recommended expression for k_1. In this way we calculate

$$k_{-1} = 5.9\times10^{12} \exp(-2860/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 290–720 K. Thus $\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.77\pm1.2$ and $E_{-1} = 23\ 740\pm8360$ J mol^{-1} (5680±2000 cal mol^{-1}), where the errors are assumed to arise only from errors in k_1 and not the equilibrium data.

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B9 $OH + HCl \rightarrow Cl + H_2O$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-67.94	-16.59	11.04
300	-67.95	-16.61	10.96
500	-68.40	-17.79	6.21
1000	-68.13	-17.51	2.64
1500	-67.42	-16.95	1.46
2000	-66.45	-16.40	0.88
2500	-65.27	-15.87	0.54
3000	-63.95	-15.38	0.31
3500	-62.55	-14.95	0.15
4000	-61.11	-14.57	0.04
4500	-59.81	-14.23	-0.05
5000	-58.28	-13.97	-0.12

RECOMMENDED RATE CONSTANT

$k = 2.25 \times 10^{12} \exp(-514/T)\ cm^3\ mol^{-1}\ s^{-1}$

$= 3.74 \times 10^{-12} \exp(-514/T)\ cm^3\ molecule^{-1}\ s^{-1}$

Temperature range: 210-500 K.

Suggested Error Limits for Calculated Rate Constant: ±20% at 298 K rising to ±50% at 210 and 500 K.

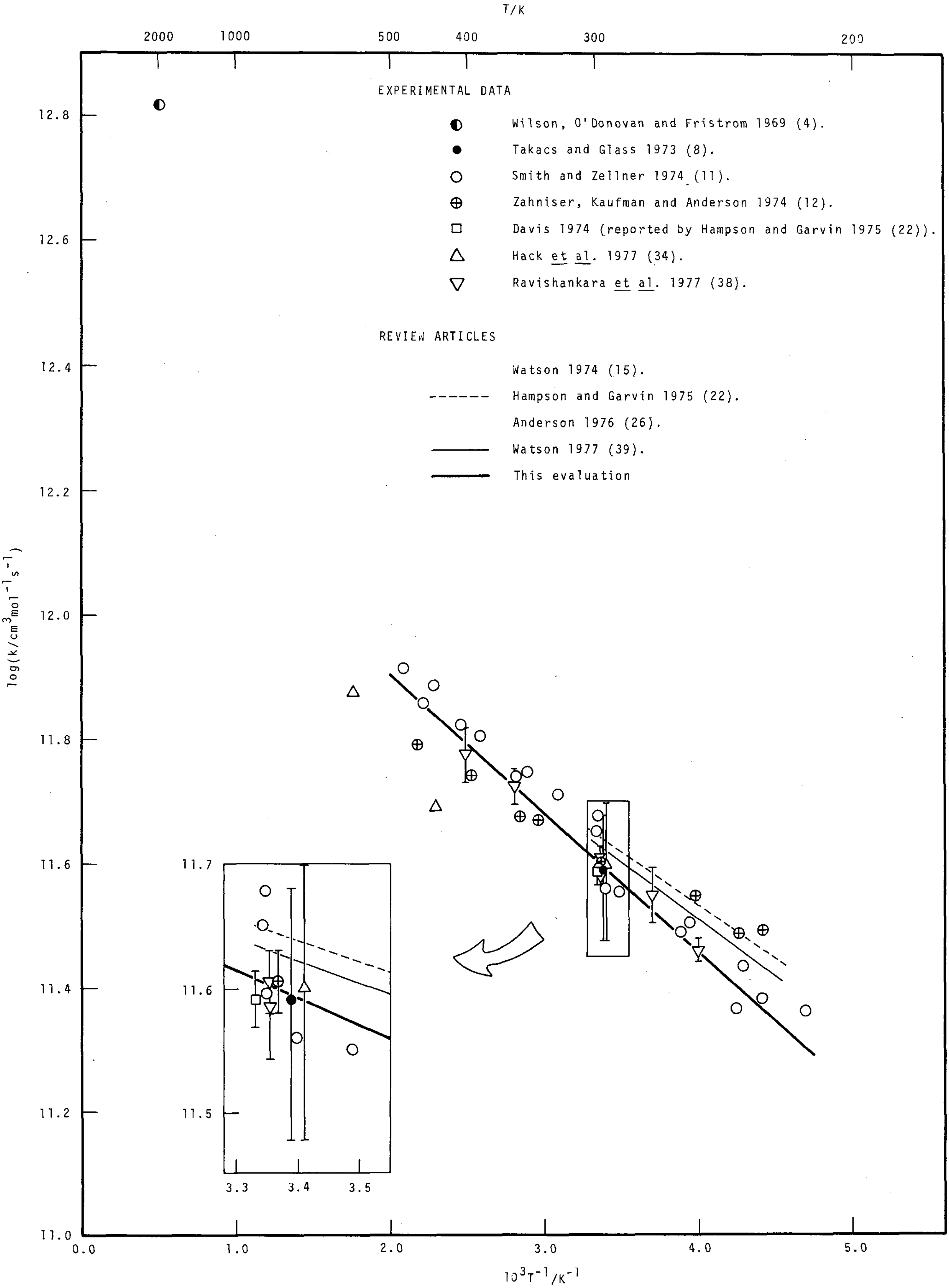
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 12.352 \pm 0.5$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -11.427 \pm 0.5$

$E/J\ mol^{-1} = 4\ 270 \pm 2\ 760$

$E/cal\ mol^{-1} = 1\ 020 \pm 660$

$OH + HCl \rightarrow Cl + H_2O$



$OH + HCl \rightarrow Cl + H_2O$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	1920-1940	Flame study. HCl inhibited CH_4/O_2 mixtures at 0.05 atm (5.07 kPa) total pressure. Concentration profiles of HCl, CO, CO_2 and other species determined by mass spectrometric probe. WILSON, O'DONOVAN and FRISTROM 1969 (4)	Authors computed OH concentration profiles using $k_2=4.52x10^{11}$ cm^3 mol^{-1} s^{-1} (2), and hence derived $k_1=7.7x10^{12}$ cm^3 mol^{-1} s^{-1}. $OH + HCl \rightarrow H_2O + Cl$ 1 $OH + CO \rightarrow CO_2 + H$ 2 Using our value, $k_2=3.89x10^{11}$ cm^3 mol^{-1} s^{-1} (Volume III, p.203), we calculate $k_1=6.6x10^{12}$ cm^3 mol^{-1} s^{-1}. This is probably a lower limit value due to HCl formation in flame. Reported by (6) with log k_1 error limits of ±0.7. Quoted by (8,10,11,12) Listed by (15,39) Used by (8,9,29).
	356-628	Discharge stirred-flow system. 1.83% O_2 in Ar at 0.8 mm Hg (105 Pa). OH from O+HCl. [O], [O_2], [H_2], [HCl] and [H_2O] measured by mass spectrometry. WONG and BELLES 1971 (5)	Investigation primarily aimed at measuring k(O+HCl). Estimated E_1=21 kJ mol^{-1} (5 kcal mol^{-1}) by unspecified method from H_2O yield. Quoted by (10,39).
$(3.9\pm0.9)x10^{11}$	295	Discharge flow system. HCl (ca. $7\text{-}15x10^{-10}$ mol cm^{-3}) added to OH (ca. $1.5\text{-}5.7x10^{-11}$ mol cm^{-3}) from $H+NO_2$, in Ar ($3.60\text{-}4.15x10^{-8}$ mol cm^{-3}). Total pressure 67-200 Pa. [OH] and [Cl] monitored by esr spectrometry. TAKACS and GLASS 1973 (8)	Kinetic measurements made in slight H atom excess. Minor effects of reactions 3,4 and 5 allowed for in k_1 calculation by $OH + OH \rightarrow H_2O + O$ 3 $OH + O \rightarrow H + O_2$ 4 $OH \rightarrow wall$ 5 computer fit of experimental data using $k_3=9.64x10^{11}$ cm^3 mol^{-1} s^{-1} and $k_5=60$ s^{-1} (7). Derived $k_1=1.3x10^{13}$ exp(-1045/T) cm^3 mol^{-1} s^{-1} using k_1 from (4). This expression used by (9,13) to calculate $k_1=1.2x10^{12}$ cm^3 mol^{-1} s^{-1} at 433 K, and misquoted by (14). Quoted by (11,12). Listed by (15,22,23,26,39).
$2.3x10^{11}$	212	Flash photolysis study. H_2O (13.3-66.7 Pa)/HCl and N_2O (1.3 kPa)/H_2 (1.3 kPa)/HCl mixtures at 1.3-2.7 kPa total pressure photolysed at λ>165 nm. [OH] monitored by resonance absorption. SMITH and ZELLNER 1974 (11)	k_1 values derived from [HCl] and observed exponential [OH] decay. OH side reactions considered unimportant. k_1 independent of OH source. Value marked * indicate N_2O+H_2 as OH source. Data only shown graphically. Authors calculate $k_1=(2.5\pm0.12)x10^{12}$ exp{-(530±25)/T} cm^3 mol^{-1}
$2.4x10^{11}$	226		
$2.7x10^{11}$	233		
$2.3x10^{11}$ *	235		
$3.2x10^{11}$	253		
$3.1x10^{11}$ *	257		
$3.6x10^{11}$	286		
$3.6x10^{11}$ *	294		
$3.9x10^{11}$	298		
$4.8x10^{11}$	298		
$4.5x10^{11}$ *	299		
$5.1x10^{11}$	323		
$5.6x10^{11}$	345		
$5.5x10^{11}$ *	354		

$OH + HCl \rightarrow Cl + H_2O$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$6.4\text{x}10^{11}$ $6.6\text{x}10^{11}$ $7.7\text{x}10^{11}$ $7.2\text{x}10^{11}$ $8.2\text{x}10^{11}$	386 404 436 450 480	SMITH and ZELLNER 1974 (11) continued.	s^{-1}. Quoted by (12,17,19,25). Listed by (15,22,26,39).
$3.11\text{x}10^{11}$ $3.07\text{x}10^{11}$ $3.52\text{x}10^{11}$ $(4.04\pm0.24)\text{x}10^{11}$ $4.67\text{x}10^{11}$ $4.74\text{x}10^{11}$ $5.51\text{x}10^{11}$ $6.21\text{x}10^{11}$	224 234 251 297 336 351 394 460	Discharge flow system. HCl ($8\text{x}10^{-11}$-$7\text{x}10^{-10}$ mol cm^{-3}) added to OH ($2\text{x}10^{-14}$-$2\text{x}10^{-12}$ mol cm^{-3}), from $H+NO_2$, in He($1\text{x}10^{-7}$-$3\text{x}10^{-7}$ mol cm^{-3}), total pressure 270-800 Pa. [OH] monitored by resonance fluorescence. ZAHNISER, KAUFMAN and ANDERSON 1974 (12)	Values of k_1 shown to be independent of total pressure, particular wall coating and presence of either excess NO_2 or excess H. Pseudo-first order conditions. Rate constants only presented graphically except for that at 297 K. Authors derive $k_1=(1.2\pm0.6)\text{x}10^{12}\exp\{-(310\pm10)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. This expression used by (17,18,20,27,28,30, 31,33,36,37) and a slightly modified pre-publication expression by (16). Listed by (15,22, 26,39). Quoted by (19 and 32).
$(3.9\pm0.2)\text{x}10^{11}$	300	No details given. DAVIS 1974, reported by HAMPSON and GARVIN (22), and DAVIS, SCHIFF and FISCHER 1975, reported by WATSON (39)	Probably flash photolysis - resonance fluorescence technique.
$(4.0\pm1.0)\text{x}10^{11}$ $4.9\text{x}10^{11}$ $7.5\text{x}10^{11}$	293 435 567	Discharge flow system. H atoms produced in discharge and NO_2 added downstream, to give $5\text{x}10^{-12}<[OH]<2\text{x}10^{-11}$ mol cm^{-3}. HCl added through moveable inlet such that $3.0<[HCl]/[OH]<21.0$ at total pressures 1.7-3.8 mm Hg (226.6-506.7 Pa). Cl and OH monitored by esr spectrometry. HACK, MEX and WAGNER 1977 (34)	Effective rate constant for OH removal obtained. Correction for reaction 4 considered <10% $OH + O \rightarrow H + O_2$ 4 Absence of further secondary reactions enabled k_1 to be obtained without corrections for stoichiometry (c.f. reaction 6, section B8). $O + HCl \rightarrow Cl + OH$ 6 Small temperature dependence quoted as $E_1=2.6$ kJ mol^{-1}.
$(2.89\pm0.1)\text{x}10^{11}$ * $(3.55\pm0.4)\text{x}10^{11}$ $(4.04\pm0.2)\text{x}10^{11}$ $(3.85\pm0.4)\text{x}10^{11}$ * $(5.30\pm0.4)\text{x}10^{11}$ $(5.96\pm0.6)\text{x}10^{11}$	250 270 298 298 356 402	Flash photolysis study. O_3 (50 µm Hg; 6.7 Pa)/H_2(100 µm Hg; 13.3 Pa)/He(40 mm Hg; 5.3 kPa), or H_2O(150 µm Hg; 20 Pa)/He(20 and 50 mm Hg; 2.7 and 6.7 kPa) mixtures, with added HCl (2.5 -20 µm Hg; 0.3-2.7 Pa), giving $[HCl]/[OH]>600$. Resonance fluoresence used	In O_3/H_2 mixtures, OH produced by sequence $O_3 + h\nu \rightarrow O(^1D) + O_2$ $O(^1D) + H_2 \rightarrow OH + H$ $H + O_3 \rightarrow OH + O_2$ Values of k_1 determined from pseudo first order decay of [OH], found to be linear over >2 mean life times. Insignificant variation between values

OH + HCl → Cl + H_2O

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		to follow [OH]. RAVISHANKARA, SMITH, WATSON and DAVIS 1977 (38)	obtained using H_2O or O_3/H_2 mixtures (latter indicated by *). These data expressed as $k_1=(1.99\pm0.2)\times10^{12}\ \exp\{-(470\pm40)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ $OH + HCl \rightarrow Cl + H_2O$ 1

REVIEW ARTICLES

$1.7\times10^{12}\ \exp\{-(400\pm100)/T\}$	220-300	Recommended expression. WATSON 1974 (15)	Based on (11) and (12). Listed by (22,26). Used by (21). Quoted by (24).
$1.7\times10^{12}\ \exp\{-(400\pm100)/T\}$	220-300	Preferred expression. HAMPSON and GARVIN 1975 (22)	Endorses WATSON's expression (15) after consideration of (8,11 and 12).
$1.7\times10^{12}\ \exp\{-(400\pm100)/T\}$	220-300	Preferred expression. ANDERSON 1976 (26)	Favours evaluation of WATSON (15) after consideration of (8,11,12 and 15).
$1.78\times10^{12}\ \exp\{-(425\pm50)/T\}$ $(4.0\pm0.4)\times10^{11}$	220-300 298	Recommended expression and value. WATSON 1977 (39)	k_1 at 298 K is an average of values from (8,11,12,38). Expression based on data of (11,12,38). Data of (4,5,8) rejected. Expression continued to be recommended by HUDSON (35), although it is incompatible with recommended room temperature value.

ISOTOPIC REACTION OH + DCL → HDO + CL

2.2×10^{11}	294	Flash photolysis study. DCl/H_2O(13.3-66.7 Pa) mixtures, total pressure 1.3-2.7 kPa, photolysed at λ>165 nm. [OH] monitored by resonance absorption. SMITH and ZELLNER 1974 (11)	Data analysed as for study of reaction 1 noted above (11) $OH + DCl \rightarrow Cl + HDO$ 1' OH side reactions considered unimportant. Rate constants only displayed graphically. Authors calculate $\log(k_1'/cm^3\ mol^{-1}\ s^{-1})=(12.5\pm0.2)-(340\pm16)/T$. Listed by (22).
1.9×10^{11}	298		
2.0×10^{11}	298		
2.1×10^{11}	298		
2.3×10^{11}	322		
2.7×10^{11}	333		
3.1×10^{11}	351		
3.3×10^{11}	355		
4.1×10^{11}	410		
4.4×10^{11}	414		
4.4×10^{11}	425		
5.4×10^{11}	463		

Discussion

Chlorine compounds are known to act as flame inhibitors, presumably by reducing the concentrations of reactive intermediates such as H, and to a lesser extent OH. It is probable that HCl plays a major role in these reaction sequences. HCl also acts as a reservoir for chlorine in the stratosphere, it being formed largely by H abstraction from methane by Cl atoms. Regeneration of Cl occurs mainly by reaction 1, and calculations show that for typical conditions at these altitudes, the HCl concentration is several orders of magnitude greater than that of Cl [24]. HCl therefore acts as an important moderator of the chemistry of the $Cl/ClO/O_3$ system [17], and the knowledge of a precise value for k_1 is of paramount importance in defining the extent of stratospheric ozone depletion.

$$OH + HCl \rightarrow Cl + H_2O \qquad (1)$$

The first attempted measurement of k_1 was carried out by Wilson, O'Donovan and Fristrom [4]. They studied the structure of CH_4/O_2 flames inhibited by HCl at 1920–1940 K, and derived a value for k_1 by monitoring the concentration profiles of various species including HCl, CO and CO_2, using mass spectrometry. They acknowledged that their value could be too low as a result of HCl being formed by Cl atom attack on CH_4. Their value is however higher than those calculated from extrapolations of lower temperature data [11,12], indicating the possible participation of an HCl consuming reaction (or reactions) not accounted for. In view of this disagreement, and the complex nature of the flame system and the difficulties of its interpretation, we place little reliance on this k_1 value.

Subsequently, three discharge flow system investigations of reaction 1 have been carried out [8,12,34]. All are in excellent agreement at room temperature, and furthermore, are consistent with that measured by Smith and Zellner [11] and Ravishankara et al. [38] using flash photolysis. In these studies the photolyses of both water vapour and N_2O/H_2 [11] and O_3/H_2 [38] mixtures were separately used to provide OH radicals. The same k_1 value, within experimental error, was obtained from both procedures. Experiments have also been carried out over the temperature range 212–567 K [11,12,34,38]. There is some uncertainty as to the exact value of the lower limit of the temperature range covered in [11] however, as table 2 of this paper quotes a value of 220 K, which is incompatible with the position of the lowest temperature point shown plotted in their Arrhenius diagram (figure 2) at ca. 212 K. The values determined for the temperature dependence at present appear to depend upon the technique used. The flash photolysis studies of Smith and Zellner [11] and Ravishankara et al. [38] have provided activation energies of 4.4 and 3.9 kJ mol^{-1} respectively, up to 70% higher than the value 2.6 kJ mol^{-1} obtained by both Zahniser et al. [12] and Hack et al. [34] using discharge flow systems. In view of the possibility of interference of secondary reactions in the latter, and the demonstrated independence of the flash photolysis results [11,38] upon OH radical generation methods, we prefer to base our recommended activation energy on these results. With a room temperature value derived from [8,11,12,34 and 38] we recommend the expression

$$k_1 = 2.25\times10^{12} \exp(-514/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for use over the temperature range 210–500 K, with suggested error limits for k_1 of $\pm20\%$ at 298 K, rising to $\pm50\%$ at 210 and 500 K. Previous reviewers have followed Watson [15] in recommending an expression with the slightly lower value for E_1/R of 400 K [22,26]. Clearly Wong and Belles' rough estimate of 2520 K for E_1/R [5] cannot be correct.

OH + DCl → Cl + HDO

Only Smith and Zellner [11] have performed experiments to measure rate constants for the isotopic reaction 1′.

$$OH + DCl \rightarrow Cl + HDO \qquad (1')$$

Employing an identical flash photolysis technique to that used to study reaction 1, they obtained $k_1' = (2.8\pm1.4)\times10^{12} \exp\{-(780\pm35)/T\}$ cm^3 mol^{-1} s^{-1} over the temperature range 298–470 K. Presumably similar causes of error were involved in both series of experiments, and it is probable that the optimum values for k_1' in this temperature range are best calculated using their derived equation for k_1'/k_1 together with our recommended expression for k_1, giving

$$k_1' = 2.58\times10^{12} \exp(-767/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Rate of the Reverse Reaction

There are no experimental determinations of the rate constant for reaction -1.

$$Cl + H_2O \rightarrow OH + HCl \qquad (-1)$$

Johnston and Parr estimated an activation energy, $E_{-1}=37.7$ kJ mol^{-1} (9.0 kcal mol^{-1}), using the BEBO method [1], and Jensen and Kurzius suggested $k_{-1}=3\times10^{13} \exp(-9560/T)$ cm^3 mol^{-1} s^{-1} by modifying the Arrhenius expression derived by them for k_6 to allow for the differences in reaction endothermicity and steric factors [3]. If we combine our expression for k_1 with the known thermodynamic

$$Cl + HCl \rightarrow H + Cl_2 \qquad (6)$$

data for the reactants and products, then we compute the following recommended expression for k_{-1} over the temperature range 210–500 K.

$$k_{-1} = 1.68\times10^{13} \exp(-8670/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Appropriate error limits are the same as those prescribed for k_1.

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B10 $Cl + O_3 \rightarrow ClO + O_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-162.75	27.68	29.958
300	-162.75	27.67	29.781
500	-163.28	26.40	18.436
1000	-166.01	22.65	9.855
1500	-168.56	20.57	6.943
2000	-170.67	19.35	5.468
2500	-172.28	18.62	4.572
3000	-173.40	18.22	3.970
3500	-174.06	18.00	3.539
4000	-174.35	17.93	3.214
4500	-174.34	17.93	2.961
5000	-174.12	17.97	2.758

RECOMMENDED RATE CONSTANT

$k_1 = 1.48 \times 10^{13} \exp(-210/T)$ cm^3 mol^{-1} s^{-1}

$= 2.45 \times 10^{-11} \exp(-210/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 200-400 K.

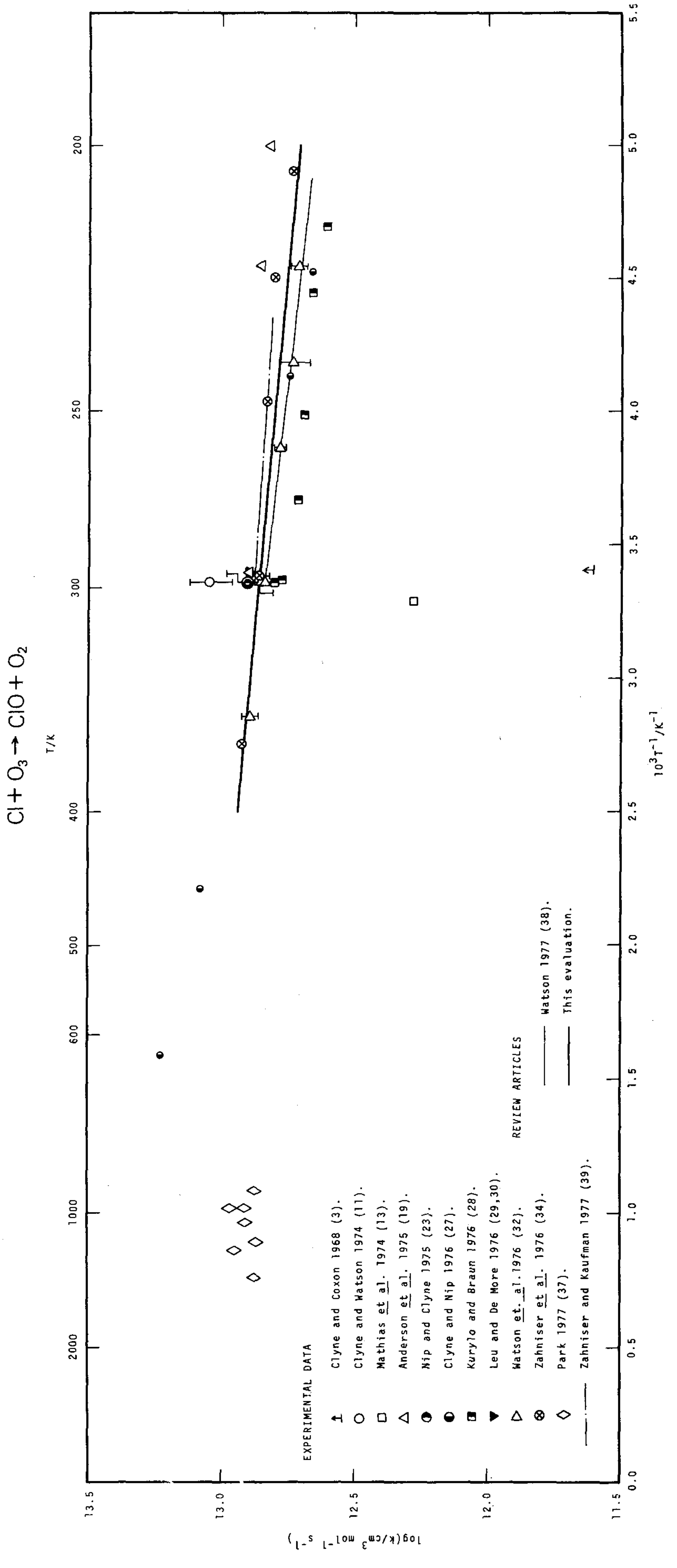
Suggested Error Limits for Calculated Rate Constant: ±40% over the quoted temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.169 \pm 0.15$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -10.611 \pm 0.15$

$E/J\ mol^{-1} = 1750 \pm 2300$

$E/cal\ mol^{-1} = 420 \pm 550$


Cl + O$_3$ → ClO + O$_2$
T/K
200
250
300
400
500
600
1000
2000
$10^3 T^{-1}/K^{-1}$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
log(k/cm^3 mol^{-1} s^{-1})
11.5
12.0
12.5
13.0
13.5
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Watson 1977 (38).
This evaluation.

$Cl + O_3 \rightarrow ClO + O_2$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$>4x10^{11}$	294	Discharge flow system. Cl_2/Ar mixtures passed through discharge. Excess O_3 added downstream through moveable inlet. Total pressures 1.36 mm Hg (181.3 Pa), [Cl] $=6.1x10^{-10}$ mol cm^{-3} and $5x10^{-10}<[O_3]<2.5x10^{-9}$ mol cm^{-3}. [Cl] measured by uv absorption at 250 nm, and chemiluminescence monitored. CLYNE and COXON 1968 (3)	Lower limit to k_1 obtained from estimated half reaction times at low $[O_3]$. $Cl + O_3 \rightarrow ClO + O_2$ 1 Used by (12).
$(1.11±0.2)x10^{13}$	298	Discharge flow system. O_3 ($5.7x10^{-13}$ to $2.1x10^{-12}$ mol cm^{-3}) added downstream to Cl stream ($5.3x10^{-12} \leqslant [Cl] \leqslant 2.3x10^{-11}$ mol cm^{-3}) at total pressures 120 Pa. Relative $[O_3]$ measured by mass spectrometry, calibrated by NO titration, and [Cl] measured by O_3 consumption in excess of O_3. CLYNE and WATSON 1974 (11)	Pseudo-first order decay of O_3 gave k_1. Authors suggest possible large random errors due to indirect measurement of $[O_3]$. This result is that of WATSON (7). Reported by CLYNE (6). Used by (15,18,22,24,25 and 26) and preferred by WATSON (16).
	305	Static photolysis study. Cl_2 (0.51-5.13 mm Hg; 68-684 Pa)/O_3 (1.9-27.0 mm Hg; 0.25-3.6 kPa)/O_2 (1.0-97 mm Hg; 0.13-12.9 kPa)/C_2Cl_4 (1.0-10.0 mm Hg; 0.13-1.3 kPa) mixtures. Initial $[O_3]/[O_2]$ ratios $2.2x10^{-3}$-27 and average $[C_2Cl_4]/[O_3]$ ratios 0.03-2.64. Reaction followed by ir absorption of C_2Cl_4 (10.9 μ), O_3(9.5 μ), $CCl_3CO.Cl$ (5.53 μ), CCl_2O (5.46 and 5.53 μ), and CCl_2CCl_2O (7.5 μ). MATHIAS, SANHUEZA, HISATSUNE and HEICKLEN 1974 (13)	Accepting the mechanism of HUYBRECHTS <u>et al</u>. (2) for the Cl initiated oxidation of C_2Cl_4, authors found that in presence of O_3, variation of quantum yield ratio $\{\Phi(CCl_3CO.Cl) + \frac{1}{2}\Phi(CCl_2O)\}/\Phi(CCl_2CCl_2O)$ with $[C_2Cl_4]/[O_3]$ gave ratio $k_2k_3/k_1k_{3a} = 6.7$ $Cl + O_3 \rightarrow ClO + O_2$ 1 $Cl + C_2Cl_4 \rightarrow C_2Cl_5$ 2 $ClO + C_2Cl_4 \rightarrow CCl_2CCl_2O + Cl$ 3a $\rightarrow CCl_3CO.Cl + Cl$ 3b $\rightarrow CCl_2O + CCl_3$ 3c $ClO + O_3 \rightarrow Cl + 2O_2$ 4a $\rightarrow ClO_2 + O_2$ 4b and $(k_{3a}+k_{3b})/k_{3a} + k_2k_4/k_1k_{3a} \simeq 0$. Authors thus derive $k_2/k_1 = 6.7$, using $k_2=1.3x10^{13}$ cm^3 mol^{-1} s^{-1} (4) to give $k_1=1.9x10^{12}$ cm^3 mol^{-1} s^{-1} at 305 K.

$Cl + O_3 \rightarrow ClO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
6.63×10^{12} 7.23×10^{12} 7.83×10^{12}	200 220 295	Cl_2 discharge flow system. Typical pressures 2-8 mm Hg (0.27-1.07 kPa), and total concentrations 1.7×10^{-12}-1.7×10^{-10} mol cm^{-3}. [Cl] measured by vacuum uv resonance fluorescence at 134.7 nm. ANDERSON, KAUFMAN and ZAHNISER 1975 (19)	Abstract only. Few details. k_1 determined from pseudo-first order decay of Cl. Expression $k_1 = 1.42 \times 10^{13} \exp(-170/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (200-360 K) attributed to these authors by (20), and used by (33). Average of these data and those of DAVIS used by (36).
$(8.01 \pm 1.6) \times 10^{12}$	298	Discharge flow system. Excess O_3 (8.3×10^{-13} to 5×10^{-11} mol cm^{-3}) added to Cl stream. Total concentrations 2.8×10^{-8} to 9.6×10^{-8} mol cm^{-3}. [Cl] determined by vacuum uv resonance absorption at 134.7 and 133.6 nm, and [O_3] by uv absorption at 253.7 nm. NIP and CLYNE 1975 (23)	H and O impurities generated in discharge removed by reaction with undissociated Cl_2. Small corrections for ozone consumption made to values of k_1 from pseudo first order decay of Cl. $Cl + O_3 \rightarrow ClO + O_2$ 1 Value quoted is that from studies using 134.7 nm wavelength. Results of 133.6 nm studies, giving $k_1 = (7.53 \pm 0.2) \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$, showed greater scatter due to small photon count signals. Authors favoured mean of this result and of CLYNE and WATSON (11), $k_1 = (9.58 \pm 0.2) \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ as reliable value. Reported by (20).
4.60×10^{12} 5.60×10^{12} $(8.01 \pm 1.6) \times 10^{12}$ 1.20×10^{13} 1.69×10^{13}	221 242 298 452 629	Cl_2-discharge flow system. Cl_2(∿7%)/Ar mixtures passed through discharge, and O_3 (8.3×10^{-13}-5×10^{-11} mol cm^{-3}) added downstream, giving total concentrations 2.8×10^{-8}-9.6×10^{-8} mol cm^{-3}. [Cl] monitored by vacuum uv absorption at 134.7 and 133.6 nm, and [O_3] by uv absorption at 253.7 nm. CLYNE and NIP 1976 (27)	Values of k_1 obtained from pseudo first order Cl decay. Small corrections (<6%) made for O_3 consumption. As for (23), greater scatter noted in data obtained by measuring [Cl] at 133.6 nm. Authors gave least squares fit to these data as $k_1 = (3.12 \pm 0.3) \times 10^{13} \exp\{-(420 \pm 30)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. Authors recommend mean value, $k_1 = 7.83 \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ at 298 K, of data of (11,27,28,32 and 34).

$Cl + O_3 \rightarrow ClO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.00 \pm 0.01) \times 10^{12}$	213	Flash photolysis study. CCl_4 (10-20 μ Hg; 1.3-2.7 Pa)/O_3(0.3-5.8 μ Hg; 4×10^{-2}-8×10^{-1} Pa)/Ar (10 and 20 mm Hg; 1.3 and 2.7 kPa) mixtures. Initial [Cl] range 1.7×10^{-14}-1.7×10^{-13} mol cm^{-3}. [O_3] measured by absorption at 253.7 nm, Cl decay monitored by resonance fluorescence. KURYLO and BRAUN 1976 (28)	From integrated pseudo first order decay of Cl, net Cl removal rate constant (allowing for presence of impurities) given by reciprocal 1/e time. k_1 given by slope of first order rate constant vs. [O_3]. Values presented here have been reduced by 7.5% to allow for error in [O_3], as reported by authors in erratum. Their revised Arrhenius expression is $k_1 = (1.64 \pm 0.27) \times 10^{13} \exp\{-(298 \pm 39)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ (213-298 K).
$(4.55 \pm 0.16) \times 10^{12}$	225		
$(4.89 \pm 0.11) \times 10^{12}$	251		
$(5.22 \pm 0.18) \times 10^{12}$	273		
$(5.91 \pm 0.17) \times 10^{12}$	297		
$(6.41 \pm 0.22) \times 10^{12}$	298		
$(7.83 \pm 0.18) \times 10^{12}$	295	Cl_2-discharge flow system. Cl_2(1%-5%)/He mixtures passed through discharge and added through moveable inlet to O_3, with Cl (2×10^{-10}-4.2×10^{-10} mol cm^3) in excess by factor >10. [O_3] decay followed by mass spectrometry, and [Cl] determined by (a) variation in [Cl_2] with activation of discharge, and (b) titration with NOCl. LEU and DE MORE 1976 (29 and 30)	Pseudo first order decay of O_3 gave k_1, after correction (20%-70%) for axial and radial diffusion.
$(5.16 \pm 0.37) \times 10^{12}$	220	Flash photolysis study. CCl_4(20-130 μ Hg; 2.7-17.3 Pa)/O_3(0-7.65 μ Hg; 1.0 Pa) /He (5 mm Hg; 667 Pa) or Ar (40 mm Hg; 5.3 kPa) mixtures. Cl atoms followed by resonance fluorescence. WATSON, MACHADO, FISCHER and DAVIS 1976 (32)	Initial conditions chosen so that [O_3]>[Cl], enabling pseudo first order decay of Cl atoms to be used in analysis. From these results, authors quote $k_1 = (1.86 \pm 0.2) \times 10^{13} \exp\{-(290 \pm 30)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ for the range 218-350 K. Data at 298 K for k_1 from this work and from (11,27,28 and 34) used to obtain mean value $k_1 = (7.95 \pm 1.87) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$. $Cl + O_3 \rightarrow ClO + O_2$ 1
$(5.39 \pm 0.71) \times 10^{12}$	239		
$(6.05 \pm 0.3\ ) \times 10^{12}$	259		
$(6.89 \pm 0.3\ ) \times 10^{12}$	298		
$(7.11 \pm 0.48) \times 10^{12}$	298		
$(7.84 \pm 0.6\ ) \times 10^{12}$	350		
5.43×10^{12}	204	Cl_2-discharge flow system. Cl_2(∿0.001%)/He mixtures passed through discharge and added through moveable inlet to O_3 at total pressures 2-5 mm Hg (267-666.5 Pa), such that 3.3×10^{-15}	Pseudo first order decay of Cl atoms gave k_1. Linear plots over 1.5 orders of magnitude in [Cl] showed absence of side reactions. Values presented here taken from graph and reduced by 7.5% following discovery of error in
6.24×10^{12}	222		
6.80×10^{12}	248		
$(7.24 \pm 0.7) \times 10^{12}$	296		
8.36×10^{12}	363		

$Cl + O_3 \rightarrow ClO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		$<[Cl]<3.3 \times 10^{-13}\ mol\ cm^{-3}$, $1.3 \times 10^{-11}<[O_3]<6.6 \times 10^{-11}\ mol\ cm^{-3}$. $[O_3]$ measured by absorption at 253.7 nm, and [Cl] decay followed by resonance fluorescence at 134.72 nm. ZAHNISER, KAUFMAN and ANDERSON 1976 (34)	$[O_3]$ calibration, as reported by authors in note. Corrected Arrhenius expression given by authors as $(1.31 \pm 0.3) \times 10^{13} \exp\{-(171 \pm 30)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Used by (31).
7.58×10^{12}	923	Shock tube study. HCl(10%)/O_2(19.5%)/O_3(0.019%)/Ar mixtures behind reflected shocks. Total pressures ∿9 atm (911.7 kPa). Reaction followed by absorption of ClO at 253.7 nm. PARK 1977 (37)	Computer modelling of results, according to mechanism $O_3 + M \rightarrow O + O_2 + M$ 5 $HCl + O \rightarrow OH + Cl$ $HCl + OH \rightarrow H_2O + Cl$ $Cl + O_3 \rightarrow ClO + O_2$ 1 $ClO + O \rightarrow Cl + O_2$ gave results in terms of ratio $k_1[O_3]/k_5[M]$. Approximate value for this ratio quoted as 0.2. Using k_5(M=Ar) determined in previous experiments described in this study, author quotes $k_1 = (8.13 \pm 2.4) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ over whole temperature range. Values presented here taken from author's Arrhenius plot.
8.21×10^{12}	981		
9.10×10^{12}	981		
8.08×10^{12}	1038		
7.29×10^{12}	1116		
8.89×10^{12}	1159		
7.52×10^{12}	1317		
$(1.28 \pm 0.07) \times 10^{13} \exp\{-(157 \pm 12)/T\}$	230-298	Cl_2-discharge flow study. Cl_2(∿0.01%)/He mixtures passed through discharge and added through moveable inlet to O_3. Method as for (28). ZAHNISER and KAUFMAN 1977 (39)	Experiments performed as check on temperature dependence of k_1 as determined previously (34). Authors found small contribution to Cl loss from walls, and gave expression presented here as fit to values of k_1 at 230, 260 and 298 K, as derived from pseudo first order Cl atom decay. Authors considered earlier values preferable as were based on larger set of data.

$Cl + O_3 \rightarrow ClO + O_2$

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.11 \pm 0.2) \times 10^{13}$	300	Review of reactions of atmosphere importance. Value is that of CLYNE and WATSON (11). WATSON 1974 (16)	Author's own value preferred. Listed by (20). Used by (21).
$(1.63 \pm 0.7) \times 10^{13}\ \exp\{-(257 \pm 110)/T\}$	205-298	Evaluation of reactions of atmospheric importance. WATSON 1977 (38)	Updating of author's previous review (16). Mean room temperature (300 K) value of $k_1 = (7.35 \pm 0.7) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ obtained from (27,28,29,32 and 34). Recommended Arrhenius expression derived from (27,28,32 and 34). Inclusion of data at higher temperatures (27,34) yielded expression $k_1 = (2.01 \pm 0.6) \times 10^{13}\ \exp\{-(310 \pm 80)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ (205-466 K). Used by (35).

Discussion

It has only recently been recognised that the release of man-made chlorofluoromethanes $CFCl_3$ (used as an aerosol propellant) and CF_2Cl_2 (aerosol propellant and refrigerant) into the atmosphere poses a possible risk of seriously reducing the earth's protective ozone layer [9,10,14,24].

The important mechanism is the chlorine atom catalysed removal of ozone:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

$$ClO + O \rightarrow Cl + O_2$$

following the photolysis of chlorofluoromethanes ("freons") in the stratosphere. (O atoms are present in the stratosphere to the extent of 10^{-17}-10^{-14} mol cm^{-3} [15,18,24] due to the photolysis of oxygen and ozone.) It would appear that there are no natural sinks for these "freons"—the $CFCl_3$ concentrations measured at stratospheric levels [8,17,24] are equivalent to the total world "freon" production up to 1974 [24]—and therefore the ozone-removing capabilities of these substances are very great.

Until the importance of the above reaction sequence was recognised, little experimental work had been made upon reaction 1. Since 1974 nine studies have produced room temperature values in the region $(8 \pm 0.9) \times 10^{12}$ cm^3 mol^{-1} s^{-1} [11,19,23,27,28,30,32,34,39]. Mathias et al. [13] measured the ratio k_1/k_2 at 305 K and used $k_2 = 1.3 \times 10^{13}$ cm^3 mol^{-1} s^{-1} [4], giving k_1 over a

$$Cl + C_2Cl_4 \rightarrow C_2Cl_5 \qquad (2)$$

factor of 4 below these other data. And even this value of k_1 would appear to be high, as there is general agreement on a lower value for k_2, e.g., 2.5×10^{12} cm^3 mol^{-1} s^{-1} at 400 K [1] and $(3.19 \pm 0.3) \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K [5], giving even lower values of k_1. Consequently we make no use of these results [13] in arriving at our recommended value for k_1.

Of the very recent data, good agreement has been reached at room temperature between discharge flow investigations [11,19,23,27,30,34,39] and flash photolysis studies [28,32]. It is interesting to observe that the discharge flow values for k_1 have been consistently falling, while those of the flash photolysis studies have been rising with successive determinations. At room temperature we recommended the value $k_1 = 7.27 \times 10^{12}$ cm^3 mol^{-1} s^{-1}.

The temperature dependence of k_1 is low, and values of the activation energy E_1 have been measured from 1305 J mol^{-1} (312 cal mol^{-1}) [39] to 3470 J mol^{-1} (830 cal mol^{-1}) [27]. There is no obvious justification for preferring any one measured value of E_1 over another, so we have taken a value of 1750 J mol^{-1} (420 cal mol^{-1}), lying between the most recent data of [32] (flash photolysis) and [34] (discharge flow). Our recommended expression is therefore

$$k_1 = 1.48 \times 10^{13} \exp(-210/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the temperature interval 200-400 K, with suggested error limits of ±40%.

The shock tube data of Park [37] at 920-1320 K are considerably lower than is given by extrapolating the above expression, and Park suggests this may be due to the reaction reaching a collision limit above ~500 K. We have found that his data have been somewhat incorrectly analysed, but this has only resulted in an error of ~4% in the author's temperatures and pressures.

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B11 $Cl + ClO_2 \rightarrow ClO + ClO$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-23.45	30.89	5.72
300	-23.45	30.89	5.70
500	-23.86	29.90	4.06
1000	-25.83	29.21	2.77
1500	-27.95	25.48	2.30
2000	-29.99	24.30	2.05
2500	-31.78	23.42	1.89
3000	-33.88	22.73	1.78
3500	-35.82	22.16	1.69
4000	-37.79	21.69	1.62
4500	-39.73	21.30	1.57
5000	-41.62	20.95	1.52

RECOMMENDED RATE CONSTANT

$k = 3.6 \times 10^{13}$ cm^3 mol^{-1} s^{-1}

$= 5.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

Temperature: 298 K.

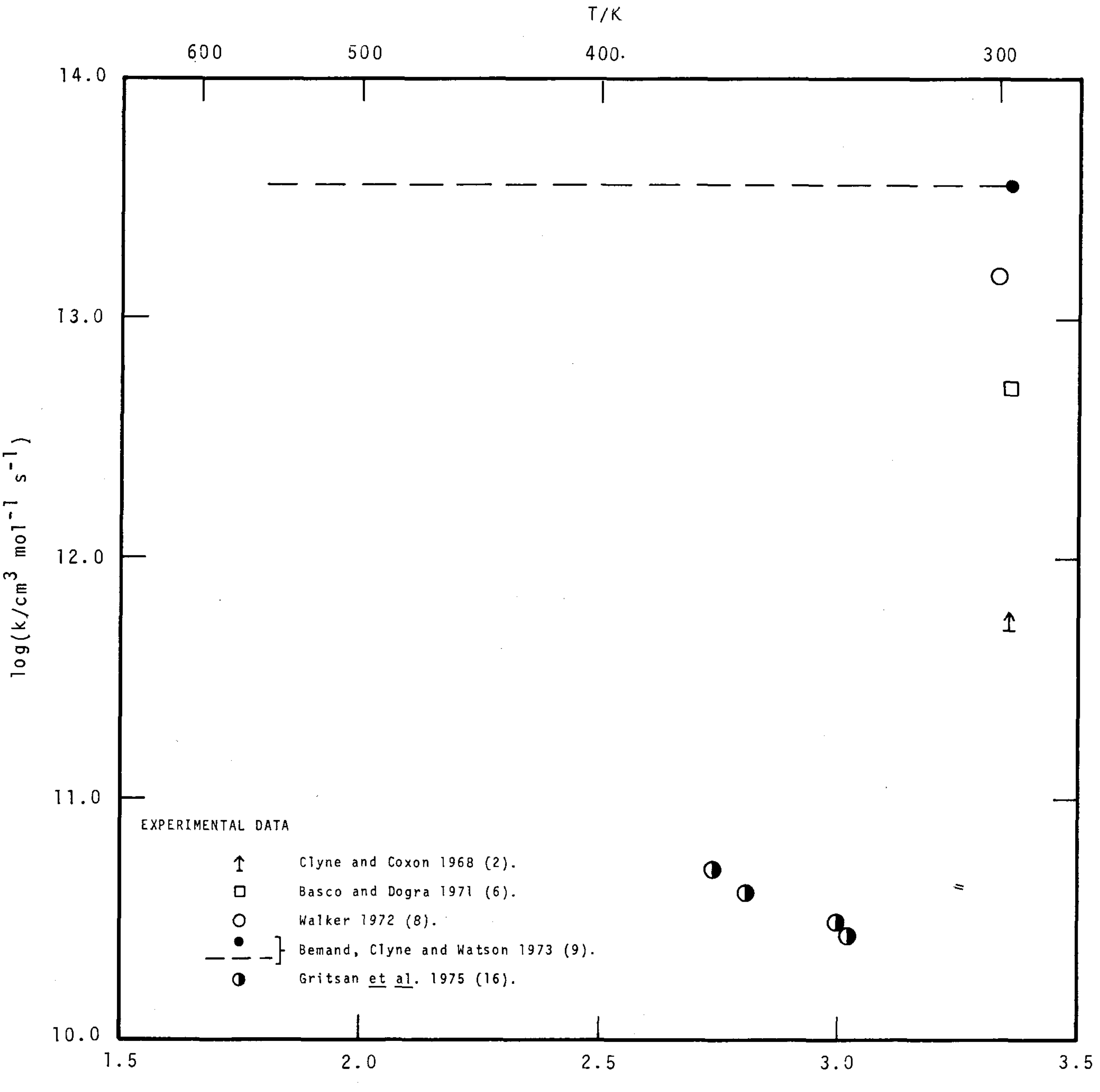
Suggested Error Limits: ±50%

Note: Recommended expression is that preferred by WATSON (14).

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$>5\times10^{11}$	298	Discharge flow study. ClO_2 added to flow of Cl (ca. 10^{-9} mol cm^{-3}) in Ar at total pressures between 137 and 307 Pa. [ClO] and [ClO_2] monitored by absorption spectroscopy at 277.2 and 351.5 nm respectively. CLYNE and COXON 1968 (2)	Stoichiometry ratio of reaction 1 ([ClO] formed/[ClO_2] removed) calculated as 1.9±0.1 from $Cl + ClO_2 \rightarrow ClO + ClO$ 1 $ClO + ClO \rightarrow$ products 2 observed [ClO], corrected for that decaying via reaction 2, using k_2 from this study. Estimate of k_1 evaluated from experiments where initial [Cl] and [ClO_2] were similar. Quoted by (4,5,6,7,14,25).

$Cl + ClO_2 \rightarrow ClO + ClO$



$Cl + ClO_2 \rightarrow ClO + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(5.1 \pm 0.74) \times 10^{12}$	298	*Flash photolysis study.* Mixtures of Cl_2(0.10-0.34 kPa), ClO_2(0.07-0.1 kPa) and Ar(26.7 kPa) photolysed at λ>310 nm with 160 or 260 J. [ClO] and [ClO_2] monitored by absorption spectroscopy at 277.2 and 351.5 nm respectively. BASCO and DOGRA 1971 (6)	Problem of overlapping Cl_2 and ClO_2 absorption spectra countered by measuring [ClO_2] decomposed and [ClO] produced in both presence and absence of Cl_2. Initial [ClO] obtained by extrapolation of decay plots to zero time. Initial [Cl] measured using Cl_2/NOCl/Ar mixtures and monitoring [NOCl] reduction. K_1 calculated assuming reactions 1, 1',3,4 and 5 to be important. Data $ClO_2 + h\nu \rightarrow O + ClO$ 3 $Cl_2 + h\nu \rightarrow Cl + Cl$ 4 $Cl + ClO_2 \rightarrow ClO + ClO$ 1 $Cl + ClO_2 \rightarrow Cl_2 + O_2$ 1' $O + ClO_2 \rightarrow ClO + O_2$ 5 $O + ClO \rightarrow Cl + O_2$ 6 $O + Cl_2 \rightarrow Cl + ClO$ 7 corrected for minor participation of reaction 7 using $k_7 = 4 \times 10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ from NIKI and WEINSTOCK (1). Reaction 6 considered negligible under these conditions. This postulate subsequently questioned by BEMAND, CLYNE and WATSON (9). Authors also assume difference in ClO_2 decomposition rate in presence and absence of Cl_2 due solely to reaction 1. [Cl] calculated from assumed stoichiometry. k_1 quoted is average of 47 determinations. Quoted by (5,11,14,25).
$(1.5 \pm 0.2) \times 10^{13}$	300	Discharge flow system. ClO_2 added to excess Cl (3×10^{-11} - 1×10^{-10} mol cm^{-3}) in Ar at 72 Pa total pressure. [ClO_2] monitored mass spectrometrically. [Cl] measured by titration with NOCl and monitoring Cl_2 afterglow emission at 520 nm. WALKER 1972 (8)	Pseudo-first order conditions. [ClO_2] monitored using m/e=67 peak. Data correction needed for appreciable background signal. k_1 value obtained is mean of eleven determinations.

$Cl + ClO_2 \rightarrow ClO + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(3.6\pm0.4)\times10^{13}$	298-588	Discharge flow systems. (a) Cl Atoms (typically 8×10^{-13} mol cm^{-3}) added to excess ClO_2(1.7×10^{-12}-1.2×10^{-11} mol cm^{-3}) in He or Ar. [Cl] monitored by atomic resonance fluorescence at 138 nm. (b) ClO_2(1.2×10^{-13} -7.0×10^{-13} mol cm^{-3}) added to excess Cl (1.8×10^{-12}-8.3×10^{-12} mol cm^{-3}) in He or Ar at 100 Pa total pressure. [ClO_2] monitored mass spectometrically. (c) ClO_2 (typically 3.4×10^{-12} mol cm^{-3}) added to excess NO (typically 8.1×10^{-11} mol cm^{-3}). [ClO_2] monitored by mass spectrometry. BEMAND, CLYNE and WATSON 1973 (9)	(a) Pseudo-first order conditions. 16,8 and 8 experiments carried out at 300, 431 and 588 K respectively giving temperature independent k_1 values. (b) Calibration of ClO_2 mass spectral sensitivity performed by 100% conversion to NO_2 with excess NO. Pseudo-first order conditions, 24 determinations carried out at 298 K. Data from (a) and (b) combined to give average k_1 value listed. (c) NO and ClO_2 react autocatalytically be reactions 8,9 and 1 $NO + ClO_2 \rightarrow ClO + NO_2$ 8 $NO + ClO \rightarrow Cl + NO_2$ 9 $Cl + ClO_2 \rightarrow ClO + ClO$ 1 because $k_1>k_9>>k_8$. Authors assumed that after 90% ClO_2 removal, [Cl] was approximately constant and equal to initial [ClO_2], and that pseudo-first order ClO_2 removal occurred by reaction 1. Value of k_1 thus obtained is an average of 26 determinations. Authors deduce $k_1=(3.6\pm1.8)\times10^{13}\exp((0\pm120)/T)$ $cm^3\ mol^{-1}\ s^{-1}$ in the temperature range 298-588 K. Quoted by (12, 13,14,17,18,19,22,25). Used by (23).
	335-365	Static photolysis study. ClO_2 (93.3 Pa) photolysed at 365.3 nm. [O_2] monitored by esr spectrometry. GRITSAN and PANFILOV 1975 (15)	Photodecomposition induction periods measured from rate of O_2 formation. Results interpreted in terms of dubious mechanism involving Cl_2O_3 intermediate. Authors assumed k_1' and k_{10} $Cl\ (wall) \rightarrow \frac{1}{2}Cl_2$ 10 were essentially temperature independent and thereby derived E_1=42 kJ mol^{-1} (10 kcal mol^{-1}).
2.7×10^{10} 3.10×10^{10} 4.07×10^{10} 5.1×10^{10}	328 334 356 365	Static photolysis study. ClO_2(5×10^{-9}-1.2×10^{-8} mol cm^{-3}), Cl_2 (0 and 247 Pa) and Ar(1.33 kPa) mixtures co-photolysed at 365.3 nm. Optical density of reaction mixture monitored photometrically at this wavelength.	Photodecomposition induction periods, typically a few minutes, measured in presence and absence of Cl_2. Results analysed in terms of previously proposed mechanism (15). k_1 values calculated using computed values for k_{10}, wall termination being assumed to be diffusion control-

$Cl + ClO_2 \rightarrow ClO + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		GRITSAN, PANFILOV and SUKHANOV 1975 (16)	led. Authors derived $k_1=(2.2\pm 0.2)x10^{14}$ $exp\{-(3020\pm 100)/T\}$ cm^3 mol^{-1} s^{-1}. Quoted by (25).
		REVIEW ARTICLE	
$(3.6\pm 0.5)x10^{13}$ $exp\{(0\pm 120)/T\}$	298-588	Preferred expression. WATSON 1974 (14) and 1977 (22)	Preferred expression is that of BEMAND, CLYNE and WATSON (9) but with smaller A-factor error limits. Quoted by (10,20). Also recommended by HUDSON (24) and ANDERSON (21).

Discussion

Measurements of the rate constant k_1 of the very fast reaction between chlorine atoms and chlorine dioxide have been

$$Cl + ClO_2 \rightarrow ClO + ClO \qquad (1)$$

carried out in discharge flow and both flash and static photolysis systems. All but one of the low pressure flow studies have used the technique of mixing the two reactants directly in an inert gas bath. In the first of these investigations Clyne and Coxon [2] could only obtain a lower limiting value of 5×10^{11} cm^3 mol^{-1} s^{-1} for k_1 by analysing the time dependences of the concentrations of ClO_2, ClO and the intensity of the chlorine afterglow emission spectrum. Walker [8] reinvestigated the reaction using a mass spectrometer to monitor the concentration of ClO_2. The Cl atom concentration was measured by titration with NOCl. Pseudo-first order conditions were employed with Cl in excess enabling a value for k_1 of $(1.5\pm 0.2)\times 10^{13}$ cm^3 mol^{-1} s^{-1} to be obtained. This result has not been published in the open literature. An identical method was used by Bemand, Clyne, and Watson [9] in one series of experiments, although the rate constant obtained was more than a factor of two greater than that found by Walker. They combined their data with that from a second experimental series in which ClO_2 was in excess and the Cl atom concentration was monitored by resonance fluorescence. The rate constant obtained, $k_1=(3.6\pm 0.4)\times 10^{13}$ cm^3 mol^{-1} s^{-1} was invariant with temperature over the range 298–588 K and was in excellent agreement with that measured in their third experimental series, which utilised the reaction between excess NO and ClO_2 as the Cl atom source. This latter reaction is initiated by reaction 8, the

$$NO + ClO_2 \rightarrow ClO + NO_2 \qquad (8)$$

$$NO + ClO \rightarrow Cl + NO_2 \qquad (9)$$

$$Cl + ClO_2 \rightarrow ClO + ClO \qquad (1)$$

oxidation of NO to NO_2 by ClO_2. The ClO formed reacts in turn with more NO by the faster oxidation 9 giving Cl atoms. These then react very rapidly with ClO_2 giving more ClO which re-fuels reaction 9. The overall reaction thus proceeds autocatalytically and results in a build up in Cl atom concentration which reaches a virtually constant level when most of the ClO_2 has been consumed, in the absence of any rapid reactions removing Cl. Thus at a high extent of conversion of ClO_2, e.g., >90%, the reaction becomes pseudo-first order with Cl in excess.

Basco and Dogra [6] investigated the kinetics of reaction 1 by flash photolysing $Cl_2/ClO_2/Ar$ mixtures at low energies with light of wavelength greater than 310 nm to avoid photolysis of the ClO radical. In analysing the data and deriving their k_1 value of $(5.1\pm 0.74)\times 10^{12}$ cm^3 mol^{-1} s^{-1} they considered that, as the flash energies were low, reaction 5 was of much greater importance than

$$O + ClO_2 \rightarrow ClO + ClO \qquad (5)$$

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

reaction 6, and that reaction 1 was negligible when Cl_2 was absent. Subsequent redeterminations of the rate constants for these reactions show these assumptions to be in error and throw doubt on the reliability of their value for k_1.

More recently Panfilov and co-workers have published two reports of studies of the variation of the induction period with temperature in the photolytically induced decomposition of ClO_2, both in the presence and absence of added Cl_2 [15,16]. At temperatures above ca. 333 K and pressures above ca. 130 Pa the reaction proceeds by a chain mechanism. The authors analysed their data in terms of a reaction scheme, originally proposed by McHale and von Elbe [3], involving the chain branching intermediate Cl_2O_3. Chain termination was assumed to be diffusion controlled Cl atom wall recombination. The values of k_1 derived are in extremely poor agreement with those obtained by other workers, probably as a result of a breakdown in the assumptions used and/or an incomplete understanding of the reaction mechanism. We do not therefore include them in our evaluation of k_1 for which the recommended value at 298 K is that also preferred by Watson [14], viz.

$$k_1 = 3.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

with an estimated error limit of ±50%. This rate constant appears to be temperature independent over the range 298–588 K and we feel that in view of the fact that it corresponds to a collision efficiency that is approximately only an order of magnitude lower than the theoretical collision rate at room temperature, it could be used with caution throughout this temperature range.

Rate of the Reverse Reaction

The sole determination of the rate of reaction −1 has been discussed elsewhere in this Volume (section B15). It gives

$$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2 \qquad (-1)$$

$k_{-1} = 6.5 \times 10^8$ cm^3 mol^{-1} s^{-1}. Combining this value with the recommended k_1 value results in $K_1 = 5.6 \times 10^4$ at 298 K giving $\Delta G_1^\circ = -27.1$ kJ mol^{-1} (-6.5 kcal mol^{-1}), in good agreement with $\Delta G_1^\circ = -27.6$ kJ mol^{-1} (6.6 kcal mol^{-1}) calculated from the thermochemical data recommended by Clyne, McKenney and Watson [17] for the participating species.

The Reaction $Cl + ClO_2 \rightarrow Cl_2 + O_2$

There appears to be no positive evidence to support the occurrence of

$$\text{Cl} + \text{ClO}_2 \rightarrow \text{Cl}_2 + \text{O}_2 \qquad (1')$$

reaction $1'$. Gritsan, Panfilov and Sukhanov [16] claim, however, to have measured a value for k_1' of $(9.09 \pm 0.24) \times 10^9$ cm^3 mol^{-1} s^{-1}, independent of temperature from 328–365 K, in their study of the photolysis of Cl_2/ClO_2 mixtures. In view of the extremely poor agreement between their values for k_1, obtained in the same investigation, and those of other workers we consider their k_1' value to be unreliable. Upper limits for k_1'/k_1 have been obtained by both Clyne and Coxon [2] and Basco and Dogra [6]. By measuring reaction stoichiometries they found $k_1'/k_1 < 0.1$ and 0.05, respectively.

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THERMODYNAMIC DATA

T (K)	ΔH^o (KJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-26.69	7.71	5.08
300	-26.69	7.69	5.05
500	-26.92	7.04	3.18
1000	-26.65	7.39	1.78
1500	-26.33	7.64	1.29
2000	-26.13	7.77	1.09
2500	-26.05	7.81	0.95
3000	-26.12	7.78	0.86
3500	-26.48	7.67	2.42
4000	-27.10	7.50	2.00
4500	-27.97	7.30	1.67
5000	-28.98	7.09	1.40

RECOMMENDED RATE CONSTANT

$$k = 2.51 \times 10^{12} \exp(-1368/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 4.17 \times 10^{-12} \exp(-1368/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 174-602 K.

Suggested Error Limits for Calculated Rate Constant: ±50% in the temperature range quoted.

Rate Parameters: $\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.40 \pm 0.32$

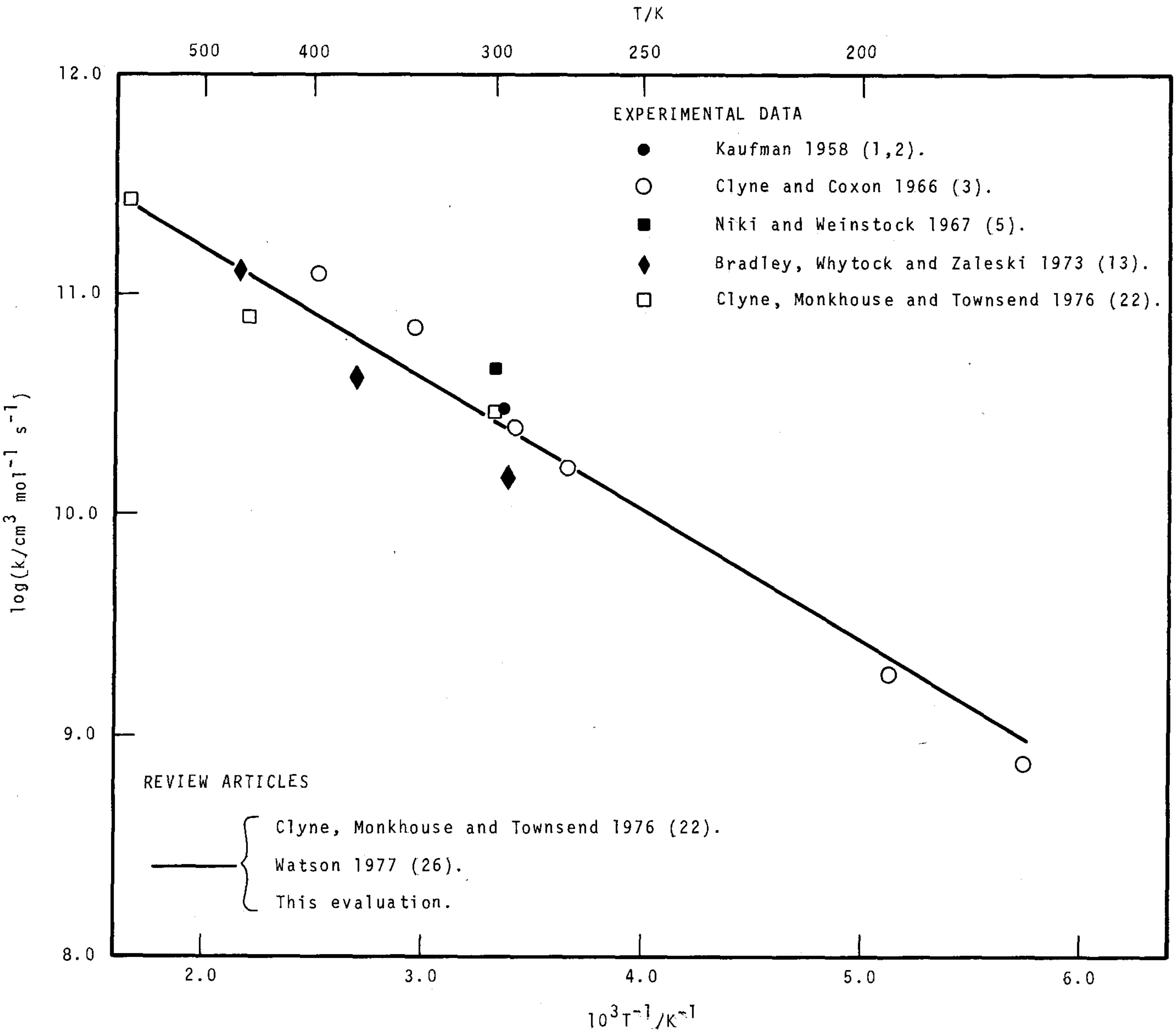
$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.38 \pm 0.32$

$E/\text{J mol}^{-1} = 11\ 374 \pm 1650$

$E/\text{cal mol}^{-1} = 2\ 718 \pm 400$

Note: Recommended expression is that suggested by CLYNE, MONKHOUSE and TOWNSEND (22).

$O + Cl_2 \rightarrow Cl + ClO$



$O + Cl_2 \rightarrow Cl + ClO$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
3.0×10^{10}	296	Discharge flow system. Cl_2 added to excess O in O_2 at 25-215 Pa. [O] monitored spectroscopically by titration with NO_2. KAUFMAN 1958 (1) and (2)	Flow tube walls "poisoned" with HF. Author reported Cl_2 catalysed O atom recombination with rate constant of 6.0×10^{10} $cm^3\ mol^{-1}\ s^{-1}$ (2), (preliminarily reported as $\sim5.0\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ (1)), and proposed the following scheme despite experimental first order rate dependence on [O] and [Cl_2]. $O + Cl_2 \rightarrow Cl + ClO$ 1 $O + ClO \rightarrow Cl + O_2$ 2 $Cl + O_2 + M \rightarrow ClOO + M$ 3 $O + ClOO \rightarrow ClO + O_2$ 4 Reactions 3 and 4 subsequently shown to be inoperative in this system (5), Cl_2 being reformed by fast wall recombination following rapid ClO removal by reaction 2. Thus k_1 is one-half measured Cl_2 catalysed O atom recombination rate constant. Quoted by (3, and 5).
$(7.4\ \pm1.5)\times10^{8}$	174	Discharge flow system. Excess Cl_2([Cl_2]>5[O]) added to flow of O (0.05-0.1% of total flow at pressures between 120-270 Pa) generated by reaction of N with excess NO in N_2. [O] monitored spectroscopically by air-afterglow from reaction with NO. CLYNE and COXON 1966 (3)	Pseudo-first order conditions. Reaction shown to be first order in [O] and [Cl_2]. k_1 independent of both pressure, in range 120-270 Pa, and nature of flow-tube surface, viz. clean vs. H_3PO_4 coated Pyrex. Authors recognised rate constant derived from [O] decrease equals $2k_1$ due to contribution from reaction 2. Suggested data could be fitted by either $k_1=(5.8\pm1.5)\times10^{12}\exp\{-(1560\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ or $k_1=(2.3\pm0.7)\times10^{11}T^{0.5}\exp\{-(1460\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (5,8,9,13, 16,21 and 22). Misquoted by (12 and 20). Listed by (11). Used by (10 and 24).
$(1.9\ \pm0.4)\times10^{9}$	195		
$(1.61\pm0.3)\times10^{10}$	273		
$(2.53\pm0.4)\times10^{10}$	292		
$(7.0\ \pm1.5)\times10^{10}$	337		
$(1.24\pm0.185)\times10^{11}$	396		
$(4.5\pm0.4)\times10^{10}$	300	Discharge flow system. (a) O-rich experiments. $O(^3P)$ produced by NO titration of N atoms in N_2 diluent. [O] $=9.1\times10^{-10}$ $mol\ cm^{-3}$, $N_2=1.38\times10^{-7}$ $mol\ cm^{-3}$, initial [Cl_2]$\leq3.5\times10^{-11}$ $mol\ cm^{-3}$ with HF treated flow-tube and [O]$=6.8\times10^{-10}$ $mol\ cm^{-3}$,	Pseudo-first order conditions. Experiments carried out with both (a) [O]>>[Cl_2] and (b) [O]<<[Cl_2]. In (a) upward curvature of [Cl_2] decay plots observed for HF treated reactor (but not for H_3PO_4 treated reactor), and ascribed to Cl wall recombination. Initial slope of plots gave $k_1=4.9\times10^{10}$

$O + Cl_2 \rightarrow Cl + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		N_2=1.13x10^{-7} mol cm^{-3}, initial $[Cl_2]$≤3.3x10^{-11} mol cm^{-3} with H_3PO_4 treated flow tube. $[Cl_2]$ monitored mass spectrometrically. (b) Cl_2-rich experiments. He or O_2 diluent. HF treated reactor. $O(^3P)$ from discharge in pure O_2. For [He]= 9.1x10^{-8} mol cm^{-3}, $[Cl_2]$=4.65x10^{-10} mol cm^{-3}, and for $[O_2]$= 8.5x10^{-8} mol cm^{-3}, $[Cl_2]$=6.5x10^{-10} mol cm^{-3}. [O] monitored mass spectrometrically. NIKI and WEINSTOCK 1967 (4) and (5).	cm^3 mol^{-1} s^{-1}. In H_3PO_4 reactor, k_1=4.3x10^{10} cm^3 mol^{-1} s^{-1}. In (b), $2k_1$=9.0x10^{10} and 8.4x10^{10} cm^3 mol^{-1} s^{-1} with He and O_2 diluents respectively. Authors combine data and suggest k_1=(4.5±0.4)x10^{10} cm^3 mol^{-1} s^{-1} (5). Preliminary report (4) gave k_1= 5.1x10^{10} cm^3 mol^{-1} s^{-1}. Quoted by (9,13,16,21,22). Listed by (7 and 11).
(1.48±0.78)x10^{10} (4.31±0.43)x10^{10} (1.29±0.84)x10^{11}	295 370 460	Discharge flow system. O atoms produced by NO titration of N in Ar diluent. Total pressure, 65-320 Pa. Reactant concentrations: $[Cl_2]$=1.88x10^{-10}-1.61x10^{-9} mol cm^{-3}, initial [O]=2.0x10^{-11}-9.3x10^{-11} mol cm^{-3}. 2.0x10^{-10}-1.65x10^{-9} mol cm^{-3} of NO added in some experiments. [O] and [Cl] monitored by esr spectroscopy. BRADLEY, WHYTOCK and ZALESKI 1973 (13)	Pseudo-first order conditions with $[Cl_2]$>[O]. No variation in k_1 observed when excess NO added. ClO not observed. Authors present no Arrhenius plot or individual rate constant data but give the expression $2k_1$=(1.23±0.54)x10^{13} exp{-(1805±130)/T} cm^3 mol^{-1} s^{-1} as summarising results from >30 experiments. CLYNE, MONKHOUSE and TOWNSEND (22) report k_1 values, as listed here, for this study however. Quoted by (18).
		Molecular beam study. Details not given. Mass spectrometric detection. PARRISH and HERSCHBACH 1973 (14)	Preliminary report. Long lived OCl_2 complex postulated. Authors report E_1≈13 kJ mol^{-1} (3 kcal mol^{-1}).
(2.91±0.32)x10^{10} (7.77±1.14)x10^{10} (2.66±0.16)x10^{11}	299 452 602	Discharge flow system. O atoms from titration of NO with N or by discharging slightly impure He, added to excess Cl_2(0.2-1.65 Pa). $[Cl_2]$/[O] ratio 200-1000, at total pressure of 170 Pa (low temperature) and 80 Pa (higher temperatures) in N_2 or He. [O] monitored by	Pseudo-first order conditions. Correction of data for effects of reaction 2 necessitated the use of computer modelling of observed concentration profiles due to non-achievement of steady state concentration of ClO. Authors used k_2=3.2x10^{13} cm^3 mol^{-1} s^{-1} (12), assumed temperature independent to derive k_1

$O + Cl_2 \rightarrow Cl + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		atomic resonance fluorescence at ca. 130.4 nm. CLYNE, MONKHOUSE and TOWNSEND 1976 (22)	values from which Arrhenius expression $\log(k_1/cm^3\ mol^{-1}\ s^{-1}) = (12.09\pm0.19)-(490\pm121)/T$ was calculated.
	306-425	Diffusional cloud flow system. O atoms ($\leqslant 3x10^{-11}$ mol cm^{-3}) from discharged O_2/Ar mixed with either Cl_2 ($1.7x10^{-9}$-$1.7x10^{-8}$ mol cm^{-3}) or Br_2, concentration approximately equivalent to [O], in Ar. [O] monitored by esr spectrometry. MOIN, YURKEVICH and DROGO'ITSKII 1976 (23)	Relative rate study. Cl_2 and Br_2 added alternately to O atoms and their flow rates adjusted to give equivalent decrease in [O]. $O + ClO \rightarrow Cl + O_2$ 2 $O + BrO \rightarrow Br + O_2$ 9 $O + Br_2 \rightarrow Br + BrO$ 10 Then as both reactions 2 and 9 are fast with $k_2 \approx k_9$, authors assumed k_1/k_{10} was given by ratio of Br_2 to Cl_2 flow rates. Results independent of an order of magnitude change in flow rates. Data only presented graphically from which we obtain the following k_1/k_{10} values: T/K k_1/k_{10} 306 $3.71x10^{-3}$ 335 $5.05x10^{-3}$ 355 $6.15x10^{-3}$ 373 $7.60x10^{-3}$ 400 $9.34x10^{-3}$ 425 $1.22x10^{-2}$ Authors derived $k_1/k_{10} = 10^{-0.600\pm0.53} \exp\{-(1310\pm45)/T\}$ and used incorrectly quoted expression for k_1 from CLYNE and COXON (3) to derive expression for k_{10}.
	950-1500	Shock tube study. Mixtures of O_3, Cl_2, O_2 and Ar, typically in ratio 1:5:25:500, at pressures behind reflected shock of 355-912 kPa. [ClO] monitored spectroscopically at 253.7 nm. PARK 1976 (24)	ClO absorption cross-section at 254 nm measured between 1660 and 2120 K. [ClO] decay curves computer modelled using reaction mechanism comprising reactions 1, -1,2,5,6,7 and 8. Values for $O + Cl_2 \rightleftharpoons Cl + ClO$ 1,-1 $O + ClO \rightarrow Cl + O_2$ 2 $Cl + O_3 \rightarrow ClO + O_2$ 5 $O_3 + M \rightarrow O + O_2 + M$ 6 $ClO + ClO \rightarrow Cl + ClOO$ 7 $ClO + ClO \rightarrow Cl_2 + O_2$ 8 (k_2+k_8) and the following k_1/k_2 values, presented in graphical form only, derived using k_6 from (6). Author used k_1 values k_1/k_2 T/K 0.026 950 0.025 976

$O + Cl_2 \rightarrow Cl + ClO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		PARK 1976 (24) continued.	0.026 1015 0.030 1036 0.034 1239 0.032 1270 0.036 1281 0.046 1281 0.043 1407 0.040 1417 0.042 1436 0.046 1436 0.042 1500 extrapolated from low temperature data of (3) to derive k_2 values.

REVIEW ARTICLES

3.79×10^{10}	300	Recommended value. WATSON 1974 (16)	Average of k_1 values from (3) and (5). Quoted by (19,21). Used by (25).
$(5.8\pm1.5)\times10^{12}\exp\{-(1560\pm50)/T\}$	174-396	Preferred value. ANDERSON 1976 (21)	Data from (3) favoured over that from (4) and (5), and the evaluation in (16).
$(2.51^{+1.38}_{-0.89})\times10^{12}\exp\{-(1368\pm134)/T\}$	174-602	Evaluation. CLYNE, MONKHOUSE and TOWNSEND 1976 (22)	Arrhenius expression is weighted least mean squares fit to data from (3,5,13 and 22). Quoted by (26).
$(2.50\pm1.14)\times10^{12}\exp\{-(1368\pm134)/T\}$	174-602	Preferred value. WATSON 1977 (26)	Adopted review expression of (22) after consideration of data from (3,5,13,22).

Discussion

The reaction between ground state atomic oxygen and

$$O + Cl_2 \rightarrow Cl + ClO \qquad (1)$$

molecular chlorine can sometimes occur in both inhibited combustion systems and polluted atmospheres containing chlorine compounds. Modelling such systems therefore requires an accurate assessment of its rate. A preliminary investigation of the dynamics of the reaction using a molecular beam technique [14] indicated that the reaction proceeds via a long lived OCl_2 complex and has an activation energy of ca. 13 kJ mol^{-1}.

Reaction 1 produces ClO molecules that can subsequently generate Cl atoms by reacting with oxygen atoms. As $k_2 >> k_1$, the

$$O + ClO \rightarrow Cl + O_2 \qquad (2)$$

steady state ClO concentration is low and the effective overall reaction becomes

$$2O + Cl_2 \rightarrow 2Cl + O_2 \qquad (11)$$

A resulting common feature of studies of reaction 1, in which the extent of reaction is measured by monitoring the oxygen atom concentration, is that under conditions where ClO reaches its steady state concentration the rate constant obtained for oxygen atom removal is $2k_1$. In the presence of NO reaction 12 competes with

$$ClO + NO \rightarrow Cl + NO_2 \qquad (12)$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (13)$$

reaction 2 for the consumption of ClO. The product NO_2 is, however, rapidly converted back to NO by O atoms, as in reaction 13, with the result that the overall stoichiometry is unaffected. Measurements of k_1 both with and without added NO confirm this hypothesis [13].

Only Niki and Weinstock [5] have followed the reaction by monitoring the decrease in both $[Cl_2]$ and [O]. Their k_1 values, obtained at 300 K using both methods, are self-consistent and in reasonable agreement with those derived by other workers [1,3,22]. The measured values of k_1 appear to be unaffected by the presence of molecular oxygen. This conclusion was first demonstrated by the agreement of the results from Clyne and Coxon's O_2-free experiments [3] with those of Kaufman [2]. Niki and Weinstock [5] obtained corroborating evidence in their study, and, in addition showed that reactor surfaces treated with HF, as in Kaufman's experiments, were much more efficient at catalysing Cl atom recombination than those washed with H_3PO_4.

The more recent studies of Bradley, Whytock and Zaleski [13] and Clyne, Monkhouse and Townsend [22] give k_1 values that are a factor of up to two lower than those of previous workers at equivalent temperatures. The reason for this discrepancy, which appears to increase at higher temperatures, is not apparent. Unfortunately the high temperature relative rate data of Park [24] cannot resolve this problem as there are no determinations of k_2 above room temperature. Similarly the relative rate data of Moin and co-workers [23] cannot be considered in our evaluation of k_1 as there are no rate data for reaction 10 above room temperature

$$O + Br_2 \rightarrow Br + BrO \qquad (10)$$

All the measurements of k_1 have relied on essentially the same discharge flow method, the only major differences being the various detection and reaction monitoring systems employed. An experimental study utilising an entirely different technique would be particularly appropriate, especially if rate measurements could be extended to higher temperatures.

We consider that the best expression currently available for k_1 is that derived by Clyne, Monkhouse and Townsend in their weighted evaluation of the available data [22]. While they omitted Kaufman's rate constant [2] its inclusion should not affect the Arrhenius parameters significantly, and we therefore recommend

$$k_1 = 2.51\times10^{12} \exp(-1368/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 174–602 K, with error limits of ±50%.

Rate of the Reverse Reaction

There are no experimental data for reaction -1.

$$Cl + ClO \rightarrow O + Cl_2 \qquad (-1)$$

Using our recommended expression for k_1 together with the equilibrium constant derived from the JANAF Tables, we obtain $k_{-1} = 1.05\times10^{12} \exp(-4590/T)$ cm^3 mol^{-1} s^{-1}.

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B13 $O + ClO \rightarrow Cl + O_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-229.12	-17.38	39.23
300	-229.13	-17.40	38.98
500	-229.55	-18.47	23.01
1000	-230.13	-19.33	11.28
1500	-230.36	-19.53	6.98
2000	-230.39	-19.54	5.00
2500	-230.13	-19.43	3.79
3000	-229.57	-19.23	2.99
3500	-228.76	-18.98	0.80
4000	-227.79	-18.72	0.75
4500	-226.78	-18.48	0.71
5000	-225.79	-18.28	0.67

RECOMMENDED RATE CONSTANT

$k_1 = 5.70 \times 10^{13} \exp(-183/T)$ cm^3 mol^{-1} s^{-1}

$= 9.47 \times 10^{-11} \exp(-183/T)$ cm^3 molecule^{-1} s^{-1}

Temperature Range: 200-500 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.

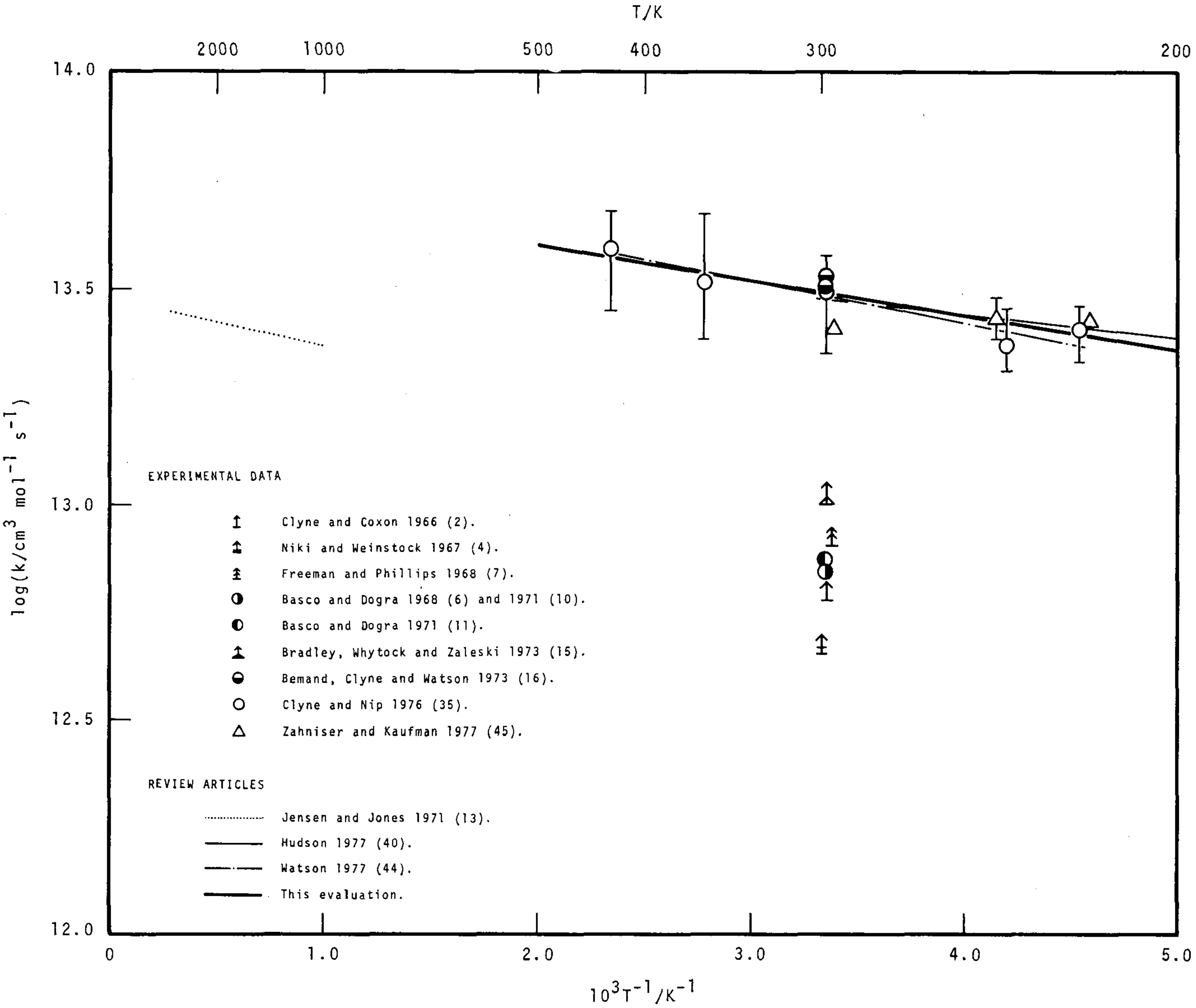
Rate Parameters: log(A/cm^3 mol^{-1} s^{-1}) = 13.756 ± 0.18

log(A/cm^3 molecule^{-1} s^{-1}) = -10.024 ± 0.18

E/J mol^{-1} = 1 520 ± 2300

E/cal mol^{-1} = 364 ± 550

$O + ClO \rightarrow Cl + O_2$



$O + ClO \rightarrow Cl + O_2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$\geq 6x10^{12}$	298	Discharge flow system. O-atoms (1%) in N_2 produced by NO titration of N at 85-430 Pa total pressure. ClO_2 in Ar added. [ClO] and $[ClO_2]$ monitored by absorption spectroscopy at 277.2 and 351.5 nm respectively. CLYNE and COXON 1966 (2)	Overall reaction stoichiometry of O plus ClO_2 measured as 1.98±0.03. Assumed that only reactions 1 and 2 were important under these conditions. Subsequent $O + ClO \rightarrow Cl + O_2$ 1 $O + ClO_2 \rightarrow ClO + O_2$ 2 determinations of the rate of the reaction of Cl with ClO_2 indicates that neglect of this reaction may be invalid. Data fitted to expression derived by integrating relevant differential equations applicable to this mechanism, to give $0.45 > k_1/k_2 > 0.15$. Minimum [O] decay rate indicated rate constant of rate controlling step $\geq 6x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$. Thus $k_1 \geq 6x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$. Data interpretation extended by these authors in subsequent report (3) suggesting $E_1 < 8.4$ kJ mol^{-1} (2.0 kcal mol^{-1}). Quoted by (4,6,7,10,14,35,44).
$\geq 4.5x10^{12}$	300	Discharge flow system. O atoms from discharge in pure O_2 added to excess Cl_2 in He or O_2. For $[H_2]$ =9.1x10^{-8} mol cm^{-3}, $[Cl_2]$ =4.65x10^{-10} mol cm^{-3}, and for $[O_2]$=8.5x10^{-8} mol cm^{-3}, $[Cl_2]$=6.5x10^{-10} mol cm^{-3}. [O], [ClO] and $[Cl_2]$ monitored mass spectrometrically. NIKI and WEINSTOCK 1967 (4)	Study of kinetics of reaction 3. Lower limit for $[Cl_2]/[ClO]$ $O + Cl_2 \rightarrow Cl + ClO$ 3 determined to be 100. From steady-state assumption for ClO, $k_1=k_3[Cl_2]/[ClO]$. Authors give $k_1 \geq 6.0x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$, but substituting their value, k_3=4.5 x10^{10} $cm^3\ mol^{-1}\ s^{-1}$ gives $k_1 \geq 4.5x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$. Using our k_3 value (this Volume, section B12) we calculate $k_1 \geq 2.6x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$.
$\geq 8x10^{12}$	296	Discharge flow system. 5 to 10-fold excess of Cl_2O in Ar added to O atoms from discharged O_2 in Ar at ca. 33 Pa total pressure. [O] measured by NO_2 titration; $[NO_2]$ and $[Cl_2O]$ monitored mass spectrometrically. FREEMAN and PHILLIPS 1968 (7)	Study of kinetics of reaction 4. Overall reaction stoichiometry $O + Cl_2O \rightarrow 2ClO$ 4 $O + ClO \rightarrow Cl + O_2$ 1 $Cl \rightarrow \frac{1}{2}Cl_2(wall)$ 5 determined to be 0.8 and constant for $[Cl_2O]/[O]$ ratios between 5 and 10. Authors therefore deduced reactions 1 and 5 were significant and computed $k_1 \geq 8x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ by assuming steady state approximation for $Cl + Cl_2O \rightarrow Cl_2 + ClO$ 6

$O + ClO \rightarrow Cl + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		FREEMAN and PHILLIPS 1968 (7) continued.	[Cl] and that $k_5 \approx k_6[Cl_2O]$, where $k_6 > 4x10^{11}$ cm^3 mol^{-1} s^{-1} (1). Quoted by (8,12,44). Used by (37). Misquoted by (38).
$(7.0\pm0.5)x10^{12}$	298	Flash photolysis system. (a) ClO_2 (8-33 Pa) plus Ar (10-26.7 kPa) mixtures at λ>315 nm with 1060 J. [ClO] monitored spectroscopically at 257.7, 277.2 and 292 nm. [ClO_2] measured spectroscopically at 351.5 nm. (b) Ar(10-26.7 kPa) with ClO_2 (6 or 10.9 Pa) plus Cl_2O (1.4,2.7,5.4,8.2 and 10.9 Pa) at λ>350 nm with 1060 and 1325 J. [ClO] and [ClO_2] analysis as in (a). BASCO and DOGRA 1968 (6) and 1971 (10)	(a) Essentially complete (>97%) photolytic decomposition of ClO_2. At delay times <250 μs, rapid ClO decay reaction observed to precede slower second order decay process. Authors suggested $ClO + ClO \rightarrow products$ 7 reactions 1 and 7 to be dominant. Calculated k_1 (average of 5 determinations) by subtracting ClO, estimated to be removed by reaction 7, from overall ClO loss. Preliminarily reported as $k_1=6x10^{12}$ cm^3 mol^{-1} s^{-1} (6). (b) ClO produced by reaction 4 offsets that lost in reaction 1. $O + Cl_2O \rightarrow 2ClO$ 4 Thus when $k_1[ClO]=2k_4[Cl_2O]$, decay of ClO becomes strictly second order, giving linear second order plots even at short delay times. Reactions of Cl with ClO_2 and Cl_2O considered negligible. After data correction for incomplete ClO_2 photolysis (ca. 7% remaining), authors found these conditions fulfilled for $[ClO]/[Cl_2O]=1.48\pm0.12$ giving $k_1/k_4=1.35\pm0.12$. Used by authors to derive k_4 value. Quoted by (11,34). Used by (37).
$(7.5\pm0.8)x10^{12}$	298	Flash photolysis system. ClO_2 (67-267 Pa) and Ar or N_2 (48 kPa) flashed with 1060 J; second flash (1330 J) fired after $2x10^{-4}$ s delay. [ClO] monitored spectroscopically at 277.2 and 292 nm. BASCO and DOGRA 1971 (11)	First flash photolyses >50% of ClO_2, the remainder being completely decomposed by reaction 2 within $2x10^{-4}$ s. Auxiliary flash partially decomposed ClO leading to further $O + ClO_2 \rightarrow ClO + O_2$ 2 [ClO] reduction over subsequent $2x10^{-4}$ s due to reaction 1 before slow bimolecular decay by reaction 6 resumed. $O_2^*(v \leq 14)$ observed after ClO photolysis. Authors assumed reactions other than 1 to be negligibly slow during $2x10^{-4}$ s following second

$O + ClO \rightarrow Cl + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BASCO and DOGRA 1971 (11) continued.	flash and hence calculated k_1. Quoted by (35,44).
$\geq 1 \times 10^{13}$	298	Discharge flow system. O atoms from NO titration of N in Ar diluent. Total pressure 65-320 Pa. Reactant concentrations: $[Cl_2]=1.88 \times 10^{-10}-1.61 \times 10^{-9}$ mol cm^{-3}, initial $[O]=2.0 \times 10^{-11}-9.3 \times 10^{-11}$ mol cm^{-3}. [O] and [Cl] monitored by esr spectroscopy. BRADLEY, WHYTOCK and ZALESKI 1973 (15)	Study under pseudo-first order conditions of kinetics of reaction 3. Authors use failure to detect ClO to estimate $k_1/k_3 \geq 10^3$, and from their value, $k_3=1.4 \times 10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$, derive $k_1 \geq 10^{13}$ at 298 K. $O + Cl_2 \rightarrow Cl + ClO$ 3
(a) $(3.2 \pm 0.5) \times 10^{13}$ (b) $(3.4 \pm 1.4) \times 10^{13}$	298 298	Discharge flow systems. (a) ClO_2 ($1.7 \times 10^{-13}-3.3 \times 10^{-10}$ mol cm^{-3}) added to Cl atom flow (3.3×10^{-10} mol cm^{-3}) in Ar containing O atom impurity (1.7×10^{-13} mol cm^{-3}). [O] monitored by resonance fluorescence at 130.6 nm. (b) As in (a) but with added O atom flow produced by either NO titration of N or discharged O_2 in He. [ClO] monitored mass spectrometrically. [O] measured by its diminution of the NO_2^+ ion current in the mass spectrometer, when added to NO_2 stream. BEMAND, CLYNE and WATSON 1973 (16)	(a) Authors reasoned that as $k_8 >> k_2$(16), ClO_2 would be quantitatively converted to ClO in $<10^{-3}$ s in excess Cl. $O + ClO_2 \rightarrow ClO + O_2$ 2 $Cl + ClO_2 \rightarrow 2ClO$ 8 Subsequent [O] decay due to reaction 1 alone. Pseudo first order conditions with [ClO]/2=initial $[ClO_2]$. Data correction incorporating side reactions 2,7, and 8, shown to be unnecessary. (b) Under experimental conditions reaction 9, used to measure [O], (in excess) calculated to be >99% complete. $O + NO_2 \rightarrow NO + O_2$ 9 Precision of study limited by ClO^+ formation in mass spectrometer ion source from absorbed Cl-containing compounds. Initial [O]/[ClO] ratios limited to range 1.5-5.5 in consequence. Quoted k_1 value is average of 15 determinations. Quoted by (17,19,21,24,25,28,30, 32,33,35,42,44). Used by (20,23, 26,29,36,37). Misquoted by (27).
$(2.54 \pm 0.40) \times 10^{13}$ $(2.33 \pm 0.50) \times 10^{13}$ $(3.14 \pm 0.90) \times 10^{13}$ $(3.29 \pm 1.40) \times 10^{13}$ $(3.91 \pm 1.10) \times 10^{13}$	220 238 298 358 426	Discharge flow system. O_3 added to mixture of Cl and O atoms in Ar at total pressure ca. 120 Pa. For excess O_3 ($\sim 8 \times 10^{-11}$ mol cm^{-3}) then $[Cl] \approx 2 \times 10^{-12}-1 \times 10^{-11}$ mol cm^{-3}, and for	Pseudo-first order conditions with [ClO]>>[O]. ClO produced by reaction 12, complete conversion of reactant of lower concentration being assumed. $Cl + O_3 \rightarrow ClO + O_2$ 12 $O + O_3 \rightarrow 2O_2$ 14 Reactions 10,11

$O + ClO \rightarrow Cl + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		excess Cl($\sim 8\times10^{-11}$ mol cm^{-3}) then $[O_3]\approx 4\times10^{-12}$-$2\times10^{-11}$ mol cm^{-3}. Initial [O] typically 5×10^{-13} mol cm^{-3}. [ClO] calculated from measurement of either $[O_3]$ by absorption at 253.7 nm, or [Cl] by absorption at 137.9 nm. [O] monitored by resonance fluorescence at 130.2 nm. CLYNE and NIP 1976 (35).	and 14 all negligibly slow. Linear dependence of fluorescence signal on [O] verified and first order dependence of rate on [ClO] demonstrated. $[O_3]>>[Cl]$ used at T$\geq$298 K and $[Cl]>>[O_3]$ used at T$\leq$298 K. 4,7,16,5 and 7 k_1 determinations performed at 220, 238,298,358 and 426 K respectively. Listed rate constant limits encompass all experimental values. Authors calculate $\log(k_1/cm^3\ mol^{-1}\ s^{-1}) = (13.81\pm0.12)-(97.2\pm32.8)/T$. Quoted by (44).
	950-1500	Shock tube study. Mixtures of O_3, Cl_2, O_2 and Ar, typically in ratio 1:5:25:500, at pressures behind reflected shock of 355-912 kPa. [ClO] monitored spectroscopically at 253.7 nm. PARK 1976 (37)	Absorption cross section for ClO at 253.7 nm measured between 1660 and 2120 K as $\varepsilon_{254}=\{1-\exp(-1236/T)\}\Sigma_{v=0}^{7}\sigma_v\exp(-1236v/T)$ $cm^2\ mol^{-1}$ where $\sigma_v=(2.62-0.33v)\times10^6$ $cm^2\ mol^{-1}$. [ClO] decay curves computer modelled using reaction mechanism comprising reactions 1,3,-3,10,11,12 and 13. Values for $(k_{10}+k_{11})$ and the following k_1/k_3 values derived using k_{13} expression from (9). Author then employed $k_3=5.6\times10^{12}\exp(-1560/T)$ $cm^3\ mol^{-1}\ s^{-1}$ from (3), measured over temperature range 174-396 K, to calculate k_1 values, from which the expression $k_1=2.1\times10^{13}(T/300)^{0.5} cm^3\ mol^{-1}\ s^{-1}$ was derived by including data from (7,10 and 16). Data presented in graphical form only. Quoted by $O + ClO \rightarrow Cl + O_2$ 1 $O + Cl_2 \rightleftarrows Cl + ClO$ 3,-3 $ClO + ClO \rightarrow Cl + ClOO$ 10 $ClO + ClO \rightarrow Cl_2 + O_2$ 11 $Cl + O_3 \rightarrow ClO + O_2$ 12 $O_3 + M \rightarrow O + O_2 + M$ 13 k_1/k_3 T/K 38.7 950 40.0 976 39.2 1015 33.8 1036 29.3 1239 30.9 1270 27.7 1281 21.7 1281 23.0 1407 25.3 1417 24.0 1436 21.7 1436 23.9 1500

$O + ClO \rightarrow Cl + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		PARK 1976 (37) continued.	(35,44).
	218-295	Discharge flow system. Cl_2(∼0.01%)/He mixtures passed through discharge, and added via moveable inlet to O_3/He stream. O atoms from O_2/He mixture, passed through second discharge, added further downstream, giving $1.33 \times 10^{-11} < [O_3] < 1.33 \times 10^{-10}$ mol cm^{-3}, $9.96 \times 10^{-13} < [O] < 1.33 \times 10^{-11}$ mol cm^{-3}, and $[Cl] \leqslant 1.66 \times 10^{-13}$ mol cm^{-3}. [Cl] monitored by resonance fluorescence at 134.7 nm. ZAHNISER and KAUFMAN 1977 (45)	Excess of both O_3 and O over Cl gives pseudo-first order conditions for reactions 1 and 12. $Cl + O_3 \rightarrow ClO + O_2$ 12 $O + ClO \rightarrow Cl + O_2$ 1 Increase of reaction time leads to steady state in [Cl] at which rates of 1 and 12 are equal. Steady state value of [Cl] therefore gave ratio k_1/k_{12}. Good linearity obtained for variation of $[O_3]$ by factor of ∼7, and by factor of 10 for [O]. T/K $k_1k_{12}^{-1}$ $k_1/cm^3mol^{-1}s^{-1}$ 218 4.73±0.24 $(2.67 \pm 0.1) \times 10^{13}$ 241 4.38±0.48 $(2.71 \pm 0.3) \times 10^{13}$ 295 3.54±0.16 $(2.57 \pm 0.1) \times 10^{13}$ These data expressed as $k_1/k_{12} = (1.55 \pm 0.17) \exp\{(246 \pm 30)/T\}$. Using their own expression $k_{12} = 1.31 \times 10^{13} \exp(-171/T)$ $cm^3\ mol^{-1}\ s^{-1}$, authors quote $k_1 = 2.83 \times 10^{13}$, 2.83×10^{13} and 2.59×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ (218,241 and 295 K), and $k_1 = (2.04 \pm 0.3) \times 10^{13} \exp\{(75 \pm 40)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (35 and 44). Values of k_1 above derived using our recommended expression for k_{12} (this Volume, section B10).
		REVIEW ARTICLES	
$3.0 \times 10^{13} \exp(-252/T)$	1000-3500	Estimated expression. JENSEN and JONES 1971 (13)	Authors modified the expression estimated by JENSEN and KURZIUS (5), $k_1 = 1.2 \times 10^{13} \exp(-1510/T)$ $cm^3\ mol^{-1}\ s^{-1}$, to accommodate the k_1 values at 298 K from (2) and (10).
$(3.2 \pm 0.5) \times 10^{13}$	298	Selected value. WATSON 1974 (22)	k_1 value from (16) selected in preference to those from (2,7 and 10). Quoted by (31). Used by (39 and 41).
$(3.2 \pm 0.5) \times 10^{13}$	298	Preferred value. ANDERSON 1976 (34)	Value from (16) favoured over that from (10).

$O + ClO \rightarrow Cl + O_2$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.64x10^{13}$ exp(-130/T)	200-300	Preferred expression. HUDSON 1977 (40)	Expression based on values k_1= $2.65x10^{13}$ (230 K) and $3.01x10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ (298 K), derived from data of (16,35 and 45). Used by (46).
$6.44x10^{13}$ exp(-224/T) $(3.13\pm0.3)x10^{13}$	220-425 298	Preferred expression and recommended value. WATSON 1977 (44)	Adopts expression of (37) and recommends k_1 value at 298 K, based on (16,37,39), after also considering data from (2,7,11, 34). Expression $6.62x10^{13}$ exp(-220/T) $cm^3\ mol^{-1}\ s^{-1}$ attributed to this review by (43).

Discussion

The reaction between oxygen atoms and ClO is fast even

$$O + ClO \rightarrow Cl + O_2 \qquad (1)$$

at room temperature, and as such it invariably plays an important role in systems where these two reactants are both present. Thus the ClO-forming reaction of O with Cl_2 is followed by reaction 1

$$O + Cl_2 \rightarrow Cl + ClO \qquad (3)$$

[3,4,15], as is the initial photodecomposition of ClO_2 [16]. Reaction 1 may also be important as the Cl atom regeneration step in the proposed Cl atom catalysed chain decomposition of O_3 in the stratosphere [18,20,21,23]. The ground $X^2\Pi$ state of ClO is split into two sub-states, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, with a splitting constant of 282±9 cm^{-1}. This small sub-state separation leads to the prediction that the upper sub-state is populated to an appreciable extent, 20% at 298 K, rising to 40% at 1000 K. Rate measurements of ClO reactions therefore presumably yield data referring to ClO molecules in a mixture of these two states. ΔH_f°(ClO) is tabulated in the JANAF tables for the $^2\Pi_{3/2}$ sub-state alone. These values should therefore be modified before calculating thermodynamic data for ClO reactions. At 298 K the corrected ΔH_f°(ClO) is 0.7 kJ mol^{-1} larger.

All of the attempts to measure k_1 except the most recent have been carried out at 298±2 K. Three of the determinations, giving lower limit values for k_1, have been deduced from semi-quantitative observations obtained in studies of the reactions of O atoms with Cl_2 [4,15], and with Cl_2O [7]. Clyne and Coxon [2] attempted to determine k_1 by studying the reaction of O with ClO_2. Subsequent work by Bemand, Clyne and Watson [16] shows however that the assumptions used in [2] to derive k_1, viz., that $k_2 > k_1 >> k_8$,

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (2)$$

$$Cl + ClO_2 \rightarrow 2ClO \qquad (8)$$

are incorrect and that the computed k_1 value is unreliable. They also reject that obtained by Basco and Dogra [10] from a study of ClO_2 flash photolysis on similar grounds, but show how both sets of experimental data can be rationalised using their more recent rate constant values. Bemand and coworkers' own measurements of k_1 have been performed using both resonance fluorescence and mass spectrometry to monitor oxygen atom concentrations. The two different methods give results that are in good agreement.

The most recent discharge flow studies of Clyne and Nip [35] and Zahniser and Kaufman [45] have covered the temperature range 200–500 K. Clyne's data (derived from pseudo first order O atom decay) show a more pronounced temperature effect, with $E_1 = 1.9$ kJ mol^{-1} (445 cal mol^{-1}), but the data of [45] (obtained under pseudo first order Cl atom removal conditions) are in good agreement with Clyne's absolute values.

Park has obtained the only available data concerning reaction 1 at temperatures greater than ca. 1000 K [37]. Unfortunately his measured k_1 values are expressed relative to k_3 and there are no data available for k_3 in the appropriate temperature range. We are therefore unable to use his data in evaluating k_1 but note that if the recommended low temperature Arrhenius expression of k_3 (section B12) is extrapolated to higher temperatures, then the k_1 values that can be calculated are in reasonable accord with those at ca. 298 K.

On the basis of the data of [16,35 and 45] we recommend for the temperature range 200–500 K the expression

$$k_1 = 5.70\times10^{13} \exp(-183/T)\ cm^3\ mol^{-1}\ s^{-1}$$

with error limits of ±50% over this range. Bearing in mind that this high value of k_1 indicates that the collision efficiency of reaction 1 is of the order of 0.1 at 298 K together with the apparent consistency of Park's relative rate data at high temperatures, it would seem that the activation energy, E_1, cannot be greater than ca. 8 kJ mol^{-1}.

Rate of the Reverse Reaction

There are no data available for the rate of the bimolecular reaction -1, Cl atoms normally reacting with O_2 via a termolecular

$$Cl + O_2 \rightarrow O + ClO \qquad (-1)$$

process to yield ClOO radicals (section B17). Using our recommended expression for k_1 and the equilibrium constant as given by the JANAF Tables, we derive $k_{-1}=8.76\times10^{14}$ exp(–27 700/T) cm^3 mol^{-1} s^{-1}, for temperatures 200–500 K.

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B14 $O + ClO_2 \rightarrow ClO + O_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-252.55	13.51	44.98
300	-252.55	13.49	44.68
500	-251.77	11.43	27.07
1000	-255.94	7.89	13.78
1500	-258.29	5.96	9.31
2000	-260.35	4.76	7.05
2500	-262.05	4.00	5.69
3000	-263.42	3.51	4.77
3500	-264.55	3.19	4.11
4000	-265.55	2.98	3.62
4500	-266.48	2.82	3.23
5000	-267.38	2.68	2.92

RECOMMENDED RATE CONSTANT

$k = 3.3 \times 10^{11}$ cm^3 mol^{-1} s^{-1}

$= 5.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}

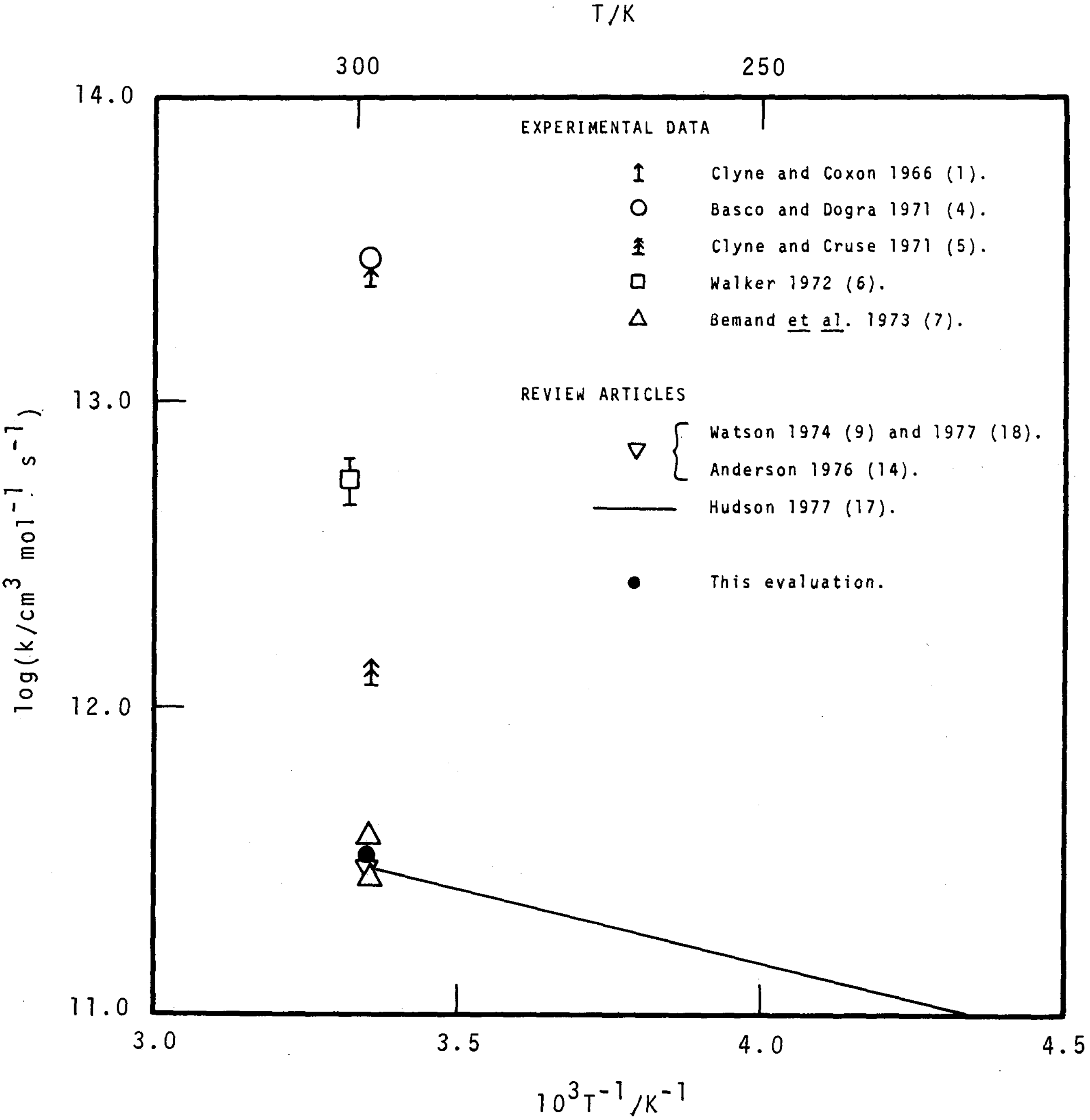
Temperature: 298 K.

Suggested Error Limits for Rate Constant: 75%.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$>2.4 \times 10^{13}$	298	Discharge flow system. ClO_2 in Ar added to O atoms (1%) in N_2 produced by titration of N with NO. Total pressure 85-430 Pa. [ClO] and $[ClO_2]$ monitored by absorption spectroscopy at 277.2 and 351.5 nm respectively. CLYNE and COXON 1966 (1)	Overall reaction stoichiometry measured as 1.98 ± 0.03. Assumed $O + ClO_2 \rightarrow ClO + O_2$ 1 $O + ClO \rightarrow Cl + O_2$ 2 $Cl + ClO_2 \rightarrow ClO + ClO$ 3 that only reactions 1 and 2 were important. Subsequent determination of k_3 indicate that neglect of reaction 3 is invalid (7). Data fitted to expression for $[ClO]/[ClO_2]$ derived from integrated rate expressions giving $0.45 > k_2/k_1 > 0.15$. Minimum [O] decay rate indicated rate constant for rate controlling step $\geqslant 6 \times 10^{12}$ cm^3 mol^{-1} s^{-1}. Thus $k_2 \geqslant 6 \times 10^{12}$ cm^3 mol^{-1} s^{-1} and k_1 as

$O + ClO_2 \rightarrow ClO + O_2$



$O + ClO_2 \rightarrow ClO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		CLYNE and COXON 1966 (1) continued.	listed. Quoted by (2,3,6,9 and 18).
	298	Flash photolysis study. Mixtures of ClO_2(10-12 Pa) Cl_2O(0 or 89-151 Pa) and Ar photolysed with 260 and 600 J at λ>340 nm. [ClO] monitored by absorption spectroscopy at 292 nm. Excited O_2 monitored at ∿310 nm (Schumann-Runge (0,12) band). BASCO and DOGRA 1971 (4)	Difference in ClO yields in presence and absence of Cl_2O measured. [Cl_2O] considered constant and [ClO_2] approximated to an average value for each run. Reaction 2 considered unimportant, an assumption subsequently rejected by BEMAND, CLYNE and WATSON (7). Derived $O + Cl_2O \rightarrow ClO + ClO$ 4 k_1/k_4=5.8±0.1 from [ClO] data and k_1/k_4=5.8±0.4 from depletion of O_2(v''=12) yield, produced in reaction 1, by added Cl_2O. Authors substituted k_4=5.2x10^{12} $cm^3\ mol^{-1}\ s^{-1}$ giving k_1=3.0x10^{13} $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (6,9, 14,18).
>1.2x10^{12}	298	Discharge flow study. ClO_2 in Ar added to excess O atoms from titration of N with NO. [O] monitored by O+NO chemiluminescence. Few details given. CLYNE and CRUSE 1971 (5)	Experiment performed to calibrate Cl atom resonance line absorption. Mechanism of CLYNE and COXON (1) adopted.
(5.6±1.0)x10^{12}	301	Discharge flow system. ClO_2 (0.007-0.01 Pa) added to excess O atoms (0.05-0.53 Pa) in N_2, produced by titration of N with NO. [ClO_2] monitored mass spectrometrically. WALKER 1972 (6)	Pseudo-first order conditions. NO flow rate carefully controlled to ensure its complete removal by N, thereby eliminating complications due to reaction of NO with ClO_2. k_1 is an average of 55 determinations.
2.83x10^{11}	298	Discharge flow studies. (a) ClO_2 (0.006-0.008 Pa) added to excess O atoms (0.20-0.73 Pa), formed either by titration of N with NO or by discharging O_2 in He, in the presence of NOCl. [ClO_2] monitored mass spectrometrically.	(a) Pseudo-first order conditions. Runs in absence of NOCl gave apparent k_1 values between 3x10^{12} and 1.2x10^{13} $cm^3\ mol^{-1}\ s^{-1}$. NOCl added as an efficient scavenger of Cl atoms in order to suppress reaction 3. Quoted k_1 is an average of four determinations.
3.82x10^{11}	298	(b) O atoms (0.002 and 0.003 Pa) produced as in (a) added to excess ClO_2	(b) Pseudo-first order conditions. Results independent of presence or absence of NOCl for

$O + ClO_2 \rightarrow ClO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		(0.3 and 0.8 Pa) in both presence and absence of NOCl. [O] monitored by resonance fluorescence. BEMAND, CLYNE and WATSON 1973 (7)	$[ClO_2]/[O]>100$. k_1 value is an average of four determinations. Authors combined results from both methods to give $k_1=3.3x10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$ at 298 K. Quoted by (8,9,10,11,12,14,15,18). Used by (16).
		REVIEW ARTICLES	
$3x10^{11}$	298	Preferred value. WATSON 1974 (9) and 1977 (18)	Based on (7). Data from (1) and (4) also considered. Quoted by (13).
$(3.0\pm0.3)x10^{11}$	298	Preferred value. ANDERSON 1976 (14)	k_1 value from (7) favoured over that from (4).
$1.2x10^{13}\ exp(-1100/T)$	200-300	Preferred expression. HUDSON 1977 (17)	Expression is estimated, based on value at 298 K.

Discussion

The reaction between oxygen atoms and chlorine dioxide has until recently been assumed to be very fast at room temperature,

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (1)$$

with a rate constant in excess of 10^{13} cm^3 mol^{-1} s^{-1}, and as such it was considered to play a major role in the flash photolysis of ClO_2. Early determinations of k_1 at 298 K appeared to substantiate these assumptions. Thus Clyne and Coxon [1], from discharge flow studies, and Basco and Dogra [4], using the flash photolysis of ClO_2, obtained values of $>2.4\times10^{13}$ and 3.0×10^{13} cm^3 mol^{-1} s^{-1}, respectively. Subsequently however, Bemand, Clyne and Watson [7] showed that the data interpretation of both of these previous studies was in error due to underestimation of the effects of Cl atoms formed by the very

$$O + ClO \rightarrow Cl + O_2 \qquad (2)$$

$$Cl + ClO_2 \rightarrow ClO + ClO \qquad (3)$$

fast reaction between O and ClO. They found that under conditions where the initial concentration ratio $[ClO_2]_o/[O]_o$ is less than approximately 5, reaction 3 becomes important resulting in autocatalytic chain removal of ClO_2. In this way spuriously high k_1 values are obtained with an observed stoichiometry similar to that for a simple $O+ClO_2$ elementary reaction. For $[ClO_2]_o/[O]_o>100$, Bemand and co-workers found $k_1=3.82\times10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K using resonance fluorescence to monitor O atom decay. For studies in which oxygen atoms were in excess, the rate of disappearance of ClO_2 was monitored mass spectrometrically. Under these conditions it was necessary to add NOCl to the reacting mixture as a Cl atom scavenger thereby suppressing autocatalytic ClO_2 destruction. In this way k_1 was reduced to a constant value of 2.83×10^{11} cm^3 mol^{-1} s^{-1} at 298 K. Although no other data are available to substantiate Bemand, Clyne and Watson's conclusions we consider that they are essentially reasonable. It would therefore appear that, contrary to earlier supposition, reaction 1 is of minimal importance in the flash photolysis of ClO_2, the initial photodissociation being followed by reactions 2 and 3. Furthermore a kinetic scheme based on this mechanism enables the experimental data of Basco and Dogra [4] to be simulated computationally [7]. We therefore recommend

$$k_1 = 3.3\times10^{11}\ cm^3\ mol^{-1}\ s^{-1}\ at\ 298\ K$$

with error limits of ±75%.

Rate of the Reverse Reaction

There appear to be no data on the rate of reaction of ClO with O_2 to give ClO_2 and oxygen atoms. Using our recommended k_1

$$ClO + O_2 \rightarrow O + ClO_2 \qquad (-1)$$

value at 298 K and the equilibrium constant value from the JANAF Tables gives $k_{-1}=3.5\times10^{-34}$ cm^3 mol^{-1} s^{-1}.

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B15 ClO + ClO → products

THERMODYNAMIC DATA

The reaction mechanism is uncertain and the primary reaction(s) is *not yet characterised*. No thermodynamic data can therefore be provided for this reaction.

RECOMMENDED RATE CONSTANT

$k = 1.5 \times 10^{10}$ cm^3 mol^{-1} s^{-1}

$= 2.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

Temperature: 298 K Pressure: <1.3 kPa (<9.8 mm Hg)

Suggested Error Limits for Rate Constant: ±15%

Rate Constant can be calculated from the empirical expression:

$k = 1.15 \times 10^{12} \exp(-1295/T)$ cm^3 mol^{-1} s^{-1}

$= 1.91 \times 10^{-12} \exp(-1295/T)$ cm^3 molecule^{-1} s^{-1}

Temperature Range: 295-600 K

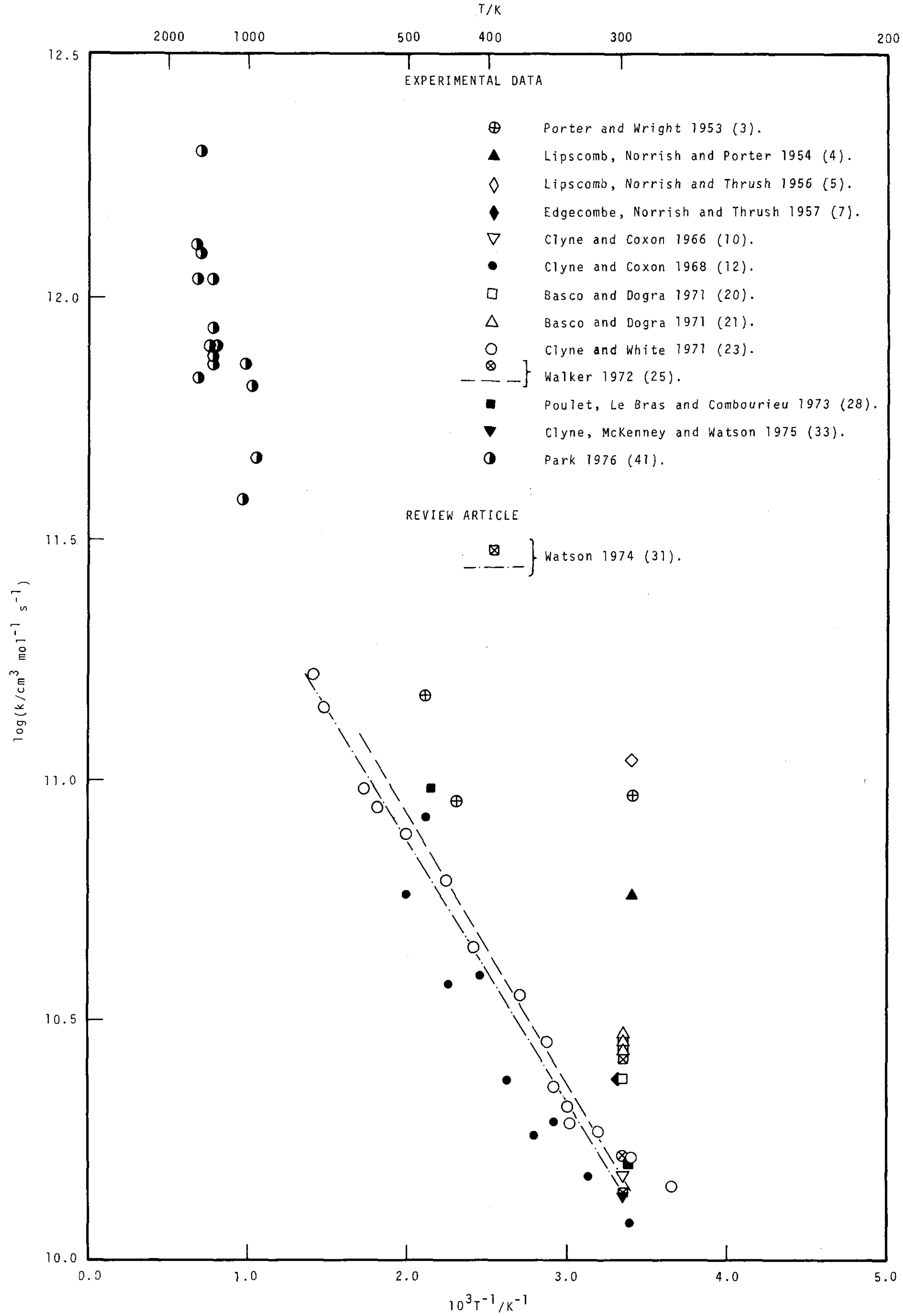
Suggested Error Limits for Rate Constant: 50%

Note: this expression is that of WALKER (25).

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$\geq 2.4\times10^{10}$ $\geq 2.3\times10^{10}$ $\geq 3.7\times10^{10}$	293 433 473	Flash photolysis study. Cl_2 (0.27-2.67 kPa; 2.0-20 mm Hg)/O_2(1.33-80.0 kPa; 10-600 mm Hg)/N_2(0-80 kPa; 0-600 mm Hg) mixtures, total pressure 7.33-81.3 kPa (55-610 mm Hg). [ClO] monitored spectroscopically at 277.3, 279.7, 282.4 and 257.7 nm. PORTER and WRIGHT 1953 (3)	Authors propose ClO produced by reactions 2 and 3. $Cl + O_2 \rightarrow ClOO$ 2 $Cl + ClOO \rightarrow 2ClO$ 3 Corrections for Cl absorption applied. Second order dependence of ClO disappearance and pressure independence of rate constant k_1 demonstrated. $ClO + ClO \rightarrow$ products 1 Authors apparently misconverted pressure units to concentration units and consequently quote $k_1 \geq 2.2\times10^{10}$ cm^3 mol^{-1} s^{-1} at 293 K. k_1 values calculated using ClO molar decadic extinction coefficient at 257.7 nm, $\varepsilon \geq 3.1\times10^5$ cm^2 mol^{-1}. Derived Arrhenius expression $k_1 \geq 2.2\times10^{10} \exp(0\pm330/T)$ cm^3 mol^{-1} s^{-1} for the temperature range 293-433 K, now corrected to $k_1 \geq 2.4\times10^{10} \exp(0\pm330/T)$ cm^3 mol^{-1} s^{-1}. Using $\varepsilon = 1.21\times10^6$ cm^3 mol^{-1} (see Discussion) gives $k_1 = 9.3\times10^{10}$, 9.1×10^{10} and 1.5×10^{11} cm^3 mol^{-1} s^{-1} at 293, 433 and 473 K respectively. Authors proposed

$ClO + ClO \rightarrow$ products



ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		PORTER and WRIGHT 1953 (3) continued.	ClO removal occurs via Cl_2O_2 dimer that subsequently decomposes to Cl_2 and O_2. Authors' k_1 expression quoted by (4,12 and 30), and rate constant by (5,8, 10,11 and 12). Misquoted by (24 and 33).
5.7x10^{10}	293	Flash photolysis study. Mixtures of ClO_2(⩽67 Pa; ⩽0.5 mm Hg) and either Ar, N_2 or CO_2 (⩽51 kPa; ⩽380 mm Hg) flashed with 250 J. [ClO] monitored spectroscopically at 257.7 nm. LIPSCOMB, NORRISH and PORTER 1954 (4)	Estimated that >90% ClO_2 decomposed per flash and that <1% ClO_3 present in reacting mixture. Measured ε=(1.19±0.1)x10^6 cm^2 mol^{-1} and used this value to calculate k_1. Using ε=1.21x10^6 cm^2 mol^{-1} gives k_1=5.8x10^{10} cm^3 mol^{-1} s^{-1}. Preliminary report of experiments described in (5).
6.2x10^{10}	293	Flash photolysis study. ClO_2/N_2 mixtures, typically at pressures of 67 Pa (0.5 mm Hg) and 77 kPa (580 mm Hg) respectively, photolysed at λ>300 nm with various flash energies between 240 and 1620 J. [ClO] monitored spectroscopically at 257.7 nm. LIPSCOMB, NORRISH and THRUSH 1956 (5)	ClO photolysis eliminated by filtering out light of λ<300 nm. Authors postulated ClO_3 formed as minor product and accordingly corrected absorption data which was interpreted in terms of reaction sequence 4,5,6,7 and 1 rather than the currently accepted sequence 4,8,9 and 1. $ClO_2 + h\nu \rightarrow ClO + O$ 4 $O + ClO_2 \rightarrow ClO + O_2$ 5 $O + ClO_2 \rightarrow ClO_3$ 6 $ClO_3 + h\nu \rightarrow ClO + O_2$ 7 $O + ClO \rightarrow Cl + O_2$ 8 $Cl + ClO_2 \rightarrow 2ClO$ 9 Authors' mechanism leads to assumption of equivalence of [ClO] (plus [ClO_3]) formed with [ClO_2] removed and thereby gives rise to an apparent dependence of ε, and hence of k_1, on flash energy. Authors nevertheless $k_1/10^{10}$ cm^{3}mol^{-1}s^{-1} — $\varepsilon/10^5$ cm^{2}mol^{-1} — Flash energy /J 1.9 — 11.4 — 240 2.7 — 10.6 — 320 4.1 — 11.1 — 400 5.5 — 8.5 — 1280 5.9 — 6.9 — 1620 recommend ε=6.8x10^5 cm^2 mol^{-1} and k_1=6.2x10^{10} cm^3 mol^{-1} s^{-1} at 293 K. Using ε=1.21x10^6 cm^2 mol^{-1} gives k_1=1.1x10^{11} cm^3 mol^{-1} s^{-1}. Compatability of

ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		LIPSCOMB, NORRISH and THRUSH 1956 (5) continued.	data with modern mechanism subsequently demonstrated by BEMAND, CLYNE and WATSON (27). Quoted by (8,10,11,12,20,24), misquoted by (31 and 33).
$(2.4\pm0.4)x10^{10}$	298	Flash photolysis study. Cl_2O (100,133 or 267 Pa; 0.75,1.0 or 2.0 mm Hg) plus SF_6 (8.0 kPa; 60 mm Hg) or occasionally N_2 or CO_2 (pressure unspecified) photolysed at $\lambda>281$ nm with 1120 J. [ClO] followed spectroscopically at 292 nm. EDGECOMBE, NORRISH and THRUSH 1957 (7)	[ClO] determined by assuming the extinction coefficient of Cl_2O at 292 and 291.2 nm to be equal and that optical densities difference at these wavelengths proportional to [ClO]. Also assumed [ClO] formed equivalent to [Cl_2O] removed for initial 2x10^{-4} s of reaction. Derived k_1 value is an average of six determinations and implies $\varepsilon(ClO)\approx5.0 x10^5\ cm^2\ mol^{-1}$ at 292 nm. Quoted by (8,10,11,12,20,21,24,31).
$(1.7\pm0.1)x10^{10}$	298	Discharge flow system. ClO produced by adding ClO_2 in Ar to Cl (2%) in Ar at total pressures between 173 and 400 Pa (1.3 and 3.0 mm Hg). [ClO] and [ClO_2] monitored spectroscopically at 277.2 and 351.2 nm respectively. CLYNE and COXON 1966 (10)	Rate observations limited to experimental conditions where $[ClO_2]/[ClO]\leq0.05$. Second order removal of ClO confirmed and maximum rate constant for first order removal estimated to be $<0.4\ s^{-1}$. Pressure independence of k_1 established. Addition of ClO + ClO → products 1 N_2 (72 or 88 Pa) or O_2 (63 or 73 Pa) to reaction mixture caused no significant variation in k_1 value. Experimentally an average of 26 determinations gave $k_1/\varepsilon=(1.26\pm0.05)x10^4\ cm\ s^{-1}$ from which authors calculated k_1 using $\varepsilon=(1.36\pm0.04)x10^6\ cm^2\ mol^{-1}$ also determined in this study. These authors subsequently report (12) pressure measurement errors due to incorrect McLeod gauge calibration resulting in revised ε (at $\lambda=257.7$ nm) and k_1 values of $(1.27\pm0.04)x10^6\ cm^2\ mol^{-1}$ and $(1.4\pm0.1)x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ respectively. Using $\varepsilon=1.21x10^6\ cm^2\ mol^{-1}$ we calculate $k_1=(1.5\pm0.1)x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$. Quoted by (11,12,14, 15,20,24,31 and 33).

ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1.20×10^{10}	294	Discharge flow system. ClO formed by reacting ClO_2 in Ar with Cl (ca. 1×10^{-9} mol cm^{-3}) in Ar at unspecified total pressures between 137 and 307 Pa (1.03 and 2.3 mm Hg). [ClO] monitored by absorption spectroscopy at 277.2 nm. Temperatures measured using both thermocouples and the nitrogen afterglow 'thermometer'. CLYNE and COXON 1968 (12)	Rate measurements delayed until ClO_2 completely consumed. Corrections applied for temperature differences between reaction zone and observation ports. Stoichiometry of reaction 9 demonstrated to be 1.9±0.1. $Cl + ClO_2 \rightarrow 2ClO$ 9 Variation of ε (ClO) at λ=277.2 nm with temperature in range 294-450 K shown to obey relationship $\varepsilon_{294}/\varepsilon_T=1+3.6\times10^{-3}(T-294)$ where $\varepsilon_{294}=(1.93\pm0.06)\times10^{6}\ cm^2\ mol^{-1}$ at T=294 K, and ε_T is the extinction coefficient at temperature T. This expression used by authors to derive k_1 values, subsequently tabulated by CLYNE and WHITE (23), to which they fitted both the expressions, $k_1=(7\pm2)\times10^{11}\exp\{-(1260\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ and $k_1=(1.4\pm0.4)\times10^{10}\ T^{0.5}\exp\{-(956\pm200)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Data was later corrected by CLYNE and WHITE (23) using $ClO + ClO + M \rightarrow Cl_2O_2 + M$ 1' $Cl_2O_2 + M \rightarrow ClO + ClO + M$ 10' $Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M$ 11' $k_1'k_{11}'/k_{10}'=1.2\times10^{16}\ cm^6\ mol^{-2}\ s^{-1}$ as derived by JOHNSTON, MORRIS and VAN DEN BOGAERDE (17) for M=Ar, to allow for third order ClO removal, by assuming experimental rate constant $k_{exp}\neq k_1$ but rather $k_{exp}=k_1+k_1'k_{11}'[M]/k_{10}'$ as previously suggested (17). Corrected k_1 values shown below. $k_1/cm^3mol^{-1}s^{-1}$ — T/K 1.10×10^{10} — 294 1.41×10^{10} — 318 1.78×10^{10} — 342 1.75×10^{10} — 357 2.31×10^{10} — 380 3.85×10^{10} — 406 3.69×10^{10} — 442 8.37×10^{10} — 472 5.74×10^{10} — 495 Uncorrected expression quoted by (11,13,16,17,18,19,20,24,30,31) and used by (36).
1.50×10^{10}	318		
1.95×10^{10}	342		
1.82×10^{10}	357		
2.38×10^{10}	380		
3.92×10^{10}	406		
3.75×10^{10}	442		
8.42×10^{10}	472		
5.79×10^{10}	495		

ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(2.65\pm0.3)\times10^{10}$	298	Flash photolysis studies. (a) ClO_2 (8.0-33 Pa; 0.06-0.25 mm Hg) plus Ar (10.0 or 26.7 kPa; 75-200 mm Hg) mixtures photolysed at $\lambda>310$ nm with energies varying from 0.16 to 1.06 kJ. [ClO_2] monitored at 351.5 nm.	Results of system (a) allowed $\varepsilon(ClO)$ to be calculated as $(1.15\pm0.06)\times10^6$, $(1.70\pm0.07)\times10^6$ and $(1.05\pm0.4)\times10^6$ $cm^2\ mol^{-1}$ at λ = 257.7, 277.2 and 292 nm respectively, by assuming that [ClO] produced = [ClO_2] removed and that [ClO] could be extrapolated back to zero time. Absorption due to ClO_3 considered negligible and its production dubious. Second order [ClO] decay observed at all time delays for low flash energies, but only at delays $>2.0\times10^{-4}$ s for high energies. Authors found k_1 pressure independent and derived its value (average of 57 determinations) using their measured ε. Using $\varepsilon=1.21\times10^6$ $cm^2\ mol^{-1}$ for λ =257.7 nm we calculate $k_1=(2.79\pm0.32)\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$. k_1 measured in system (b) is an average of 13 determinations. We calculate $k_1=(2.91\pm0.28)\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ for $\varepsilon=1.21\times10^6$ $cm^2\ mol^{-1}$. System (c) yielded k_1 from an average of eight determinations. Quoted by (21,22,30,31 and 33). Used by (41).
$(2.77\pm0.27)\times10^{10}$	298	(b) Mixtures of Cl_2 (0.67 and 1.0 kPa; 5.0 and 7.5 mm Hg), O_2 (6.7 kPa; 50 mm Hg) and Ar (20 kPa; 150 mm Hg) photolysed using flash energy of 1325 J. [ClO] monitored in both studies at 257.7 and 277.2 nm and additionally at 292 nm in (a).	
$(2.4\pm0.2)\times10^{10}$	298	(c) ClO_2 (6.0 and 11.8 Pa; 0.045 and .09 mm Hg) plus Cl_2O (1.36-15.4 Pa; 0.01-0.12 mm Hg) and Ar (26.7 kPa; 200 mm Hg) flash photolysed with energies of 260 and 1060 J at $\lambda>340$ nm. [ClO] measured at 292 nm. BASCO and DOGRA 1971 (20)	
$(2.77\pm0.22)\times10^{10}$	298	Flash photolysis studies. (a) Cl_2O (80 and 147 Pa; 0.6 and 1.1 mm Hg) and Ar (26.7 kPa; 200 mm Hg) photolysed at $\lambda>280$ nm using energies of 830, 1060 and 1325 J.	$\varepsilon(ClO)$ measured as $(1.61\pm0.05)\times10^6$ and $(9.9\pm0.7)\times10^5$ $cm^2\ mol^{-1}$ at 277 and 292 nm respectively, assuming [ClO] formed = [Cl_2O] removed and that [ClO] could be extrapolated to zero time. Authors obtained k_1 from averages of 7,4 and 6 determinations in systems (a), (b) and (c) respectively.
$(2.88\pm0.3)\times10^{10}$	298	(b) Mixtures of Cl_2O (80-160 Pa; 0.6-1.2 mm Hg), Cl_2 (173-333 Pa; 1.3-2.5 mm Hg) and Ar (26.7 kPa; 200 mm Hg) photolysed at $\lambda>310$ nm using energies of 260, 600 and 1060 J.	
$(3.0\pm0.5)\times10^{10}$	298	(c) Mixtures of Cl_2O (53-93 Pa; 0.4-0.7 mm Hg), Br_2 (53-334 Pa; 0.4-2.5 mm Hg) and Ar (26.7 kPa; 200 mm Hg) photolysed at either $\lambda>440$ nm or $\lambda>560$ nm using	

$ClO + ClO \rightarrow$ products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		flash energies of 600-1060 J. [ClO] monitored in all studies at 277.2 and 292 nm. [ClO_2] measured at 351.5 nm and [Cl_2O] between 250 and 257 nm or at 291.2 nm. BASCO and DOGRA 1971 (21)	
$1.43\mathrm{x}10^{10}$	273	Discharge flow system. ClO obtained from reaction of excess Cl atoms ($\leqslant 2\mathrm{x}10^{-9}$ mol cm^{-3}) in Ar plus SF_6 (0 and 35 mol %) with ClO_2 at total pressures between 0.06 and 1.1 kPa (0.45 and 8.25 mm Hg). [ClO] monitored spectroscopically at 277.2 nm. CLYNE and WHITE 1971 (23)	ClO concentrations calculated using extinction coefficient data of CLYNE and COXON (12). Second order plots of data were linear and gave values of experimental rate constant k_{exp} independent of pressure within experimental error. Following the mechanistic interpretation of JOHNSTON, MORRIS and VAN DEN BOGAERDE (17), authors assumed $k_{exp}=k_1+k_1'k_{11}'[M]/k_{10}'$ and using $k_1'k_{11}'/k_{10}'=1.2\mathrm{x}10^{16}$ $cm^6\ mol^{-2}\ s^{-1}$ for M=Ar (17) corrected k_{exp} values, as tabulated opposite, by assuming $k_1'k_{11}/k_{10}$ to be essentially temperature independent in the range 273-710 K, to give the following corrected k_1 values. $k_1/cm^3mol^{-1}s^{-1}$ — T/K $1.23\mathrm{x}10^{10}$ — 273 $1.45\mathrm{x}10^{10}$ — 293 $1.68\mathrm{x}10^{10}$ — 312 $1.76\mathrm{x}10^{10}$ — 330 $1.94\mathrm{x}10^{10}$ — 332 $2.15\mathrm{x}10^{10}$ — 342 $2.69\mathrm{x}10^{10}$ — 347 $3.43\mathrm{x}10^{10}$ — 369 $4.35\mathrm{x}10^{10}$ — 413 $6.08\mathrm{x}10^{10}$ — 444 $7.66\mathrm{x}10^{10}$ — 501 $8.71\mathrm{x}10^{10}$ — 550 $9.57\mathrm{x}10^{10}$ — 577 $1.41\mathrm{x}10^{11}$ — 675 $1.69\mathrm{x}10^{11}$ — 710 Authors combined these k_1 values with those of CLYNE and COXON (12) and calculated the expressions $k_1=(7.8\pm0.7)\mathrm{x}10^{11}\ \exp\{-(1150\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ and $k_1=3.14\mathrm{x}10^{13}T^{-0.5}\ \exp(-1420/T)$ $cm^3\ mol^{-1}\ s^{-1}$ as best representing the available data. Quoted by (30,31,33,34).
$1.64\mathrm{x}10^{10}$	293		
$1.86\mathrm{x}10^{10}$	312		
$1.93\mathrm{x}10^{10}$	330		
$2.11\mathrm{x}10^{10}$	332		
$2.31\mathrm{x}10^{10}$	342		
$2.85\mathrm{x}10^{10}$	347		
$3.58\mathrm{x}10^{10}$	369		
$4.49\mathrm{x}10^{10}$	413		
$6.21\mathrm{x}10^{10}$	444		
$7.77\mathrm{x}10^{10}$	501		
$8.81\mathrm{x}10^{10}$	550		
$9.66\mathrm{x}10^{10}$	577		
$1.42\mathrm{x}10^{11}$	675		
$1.70\mathrm{x}10^{11}$	710		

ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(1.67\pm0.20)\times10^{10}$ $(1.15\pm0.35)\times10^{12}\exp\{-(1295\pm155)/T\}$	298 294-587	Discharge flow system. ClO_2 added to excess Cl to generate ClO in large excess of Ar at total pressures in range 0.12-1.345 kPa (0.9-10.1 mm Hg) at 298 K, and 0.1-0.77 kPa (0.75-5.8 mm Hg) at 294, 383, 473 and 587 K. [ClO] monitored by absorption spectroscopy at 277.2 nm. WALKER 1972 (25)	k_1 value at 298 K is the average of 37 determinations. Within experimental error k_1 was independent of pressure. Results nevertheless analysed to determine third order rate constant (see below). Measurements at 294,383,473 and 587 K confined to unheated sections of flow tube. k_1 values computed from average $[ClO]^{-1}$ within furnace. Arrhenius expression calculated excluding data obtained at 298 K. Quoted by (31).
1.6×10^{10} 9.6×10^{10}	295 463	Discharge flow system. ClO formed by adding excess Cl_2O to Cl in He at total pressure of ca. 133 Pa (1 mm Hg). Few details given. [ClO] monitored mass spectrometrically. POULET, LE BRAS and COMBOURIEU 1973 (28)	ClO mass spectrometer signals calibrated by assuming [ClO] produced = [Cl] reacted and using reaction 12 to calibrate [Cl]. ClO + ClO → products 1 Cl + NOCl → NO + Cl_2 12 Second order [ClO] decay observed. Quoted by (34).
$(1.36\pm0.18)\times10^{10}$	298	Discharge flow system. ClO_2 added to excess Cl formed by discharging Cl_2 (1 mol %) in He at total pressure of 100-200 Pa (0.75-1.5 mm Hg) to produce ClO (1.7×10^{-11}-2.3×10^{-9} mol cm^3). [ClO] and [NO_2], from ClO titration with NO, monitored mass spectrometrically. CLYNE, McKENNEY and WATSON 1975 (33)	Mass spectrometer calibration achieved both by equating [ClO_2] Cl + ClO_2 → ClO + ClO 9 NO + ClO → Cl + NO_2 13 reacted with [ClO] produced in reaction 9, and by titrating ClO with NO giving NO_2, reaction 13. Rate measurements taken using the second method to determine [ClO]. Rate found to be strictly second order in [ClO] allowing k_1 to be obtained as an average of 12 determinations. Quoted by (31,39,43).
	298	Static photolysis system. Mixtures of $CFCl_3$ (1.44-6.33 kPa, 10.8-47.5 mm Hg) and O_3 (31.1-40.8 Pa, 0.233-0.306 mm Hg) photolysed at λ=213.9 nm using Zn lamp. [O_3] monitored spectrophotometrically at 253.7 nm. JAYANTY, SIMONAITIS and HEICKLEN 1975 (35)	Actinometry performed by measuring N_2 yield from N_2O photolysis and assuming $\Phi(N_2)$ = 1.41. Multi-step mechanism proposed in which ClO was formed by reaction 14 from Cl atoms Cl + O_3 → ClO + O_2 14 produced by $CFCl_3$ photodissociation. Quantum yield of O_3 removal, $\Phi(O_3)$ measured as 2.75 -4.56. Authors deduced $\Phi(O_3)$=

ClO + ClO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		JAYANTY, SIMONAITIS and HEICKLEN 1975 (35) continued.	4-4.5 at 1.3 kPa (10 mm Hg) total pressure, and by substitution in derived rate law $\Phi(O_3)=3+2k_{15}/k_{16}$, $ClO + ClO \rightarrow Cl + Cl + O_2$ 15 $ClO + ClO \rightarrow Cl_2 + O_2$ 16 obtained $k_{15}/k_{16}=0.5-0.75$.
4.67×10^{11}	950	Shock tube study. Mixtures of O_3, Cl_2, O_2 and Ar in ratio 1:5:25:500 typically, at pressures behind reflected shock of 355-912 kPa. [ClO] monitored spectroscopically at 253.7 nm. PARK 1976 (41)	Absorption cross section of ClO at 253.7 nm measured over temperature range 1660-2120 K by shocking Cl_2/O_2 mixtures, ratio 1:10, plus Ar, concentration 0-70 %. After correction for overlapping Cl_2 absorption and assuming that O_2, Cl_2, Cl, ClO and Ar were present in their equilibrium ratios at 2×10^{-5} s after shock, author combined data with that of JOHNSTON (17) at 257.7 nm to derive $\varepsilon_{254}=\{1-\exp(1-1236/T)\}\sum_{v=0}^{7}\sigma_v \exp(-1236v/T)$ cm^2 mol^{-1} where $\sigma_v=(2.62-0.33v) \times 10^6$ cm^2 mol^{-1}. ClO decay constant k_1, identified with $ClO + ClO \rightarrow Cl_2 + O_2$ 16 $ClO + ClO \rightarrow Cl + ClOO$ 17 $(k_{16}+k_{17})$. Values for both k_1 and k_8 derived by computer modelling ClO decay curves. $O + ClO \rightarrow Cl + O_2$ 8 Author estimates uncertainty factor of 2 in k_1 and combines data with that of BASCO and DOGRA (20) to calculate $k_1=2.5 \times 10^{12} \exp\{-1350/T\}$ cm^3 mol^{-1} s^{-1}. Data presented in graphical form only.
6.53×10^{11}	976		
7.31×10^{11}	1015		
3.84×10^{11}	1035		
7.94×10^{11}	1240		
7.31×10^{11}	1270		
8.63×10^{11}	1275		
7.58×10^{11}	1280		
1.09×10^{12}	1280		
7.94×10^{11}	1320		
1.23×10^{12}	1405		
1.99×10^{12}	1410		
6.83×10^{11}	1455		
1.09×10^{12}	1460		
1.28×10^{12}	1470		

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
(a) $(1.45 \pm 0.24) \times 10^{10}$	298	Recommended values. WATSON 1974 (31) and 1977 (47)	k_1 value (a) applicable to low pressure systems, e.g. discharge flow studies, based on (10,12, 23,25,33). Value (b) applies to high pressure studies e.g. flash photolysis, and is that found in the series (a) experiments of BASCO and DOGRA (21). Recommend $E_1=10.3 \pm 1.0$ kJ mol^{-1} under low pressure conditions. Combining authors' recommended low pressure
(b) 2.77×10^{10}	298		

$ClO + ClO \rightarrow$ products

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		WATSON 1974 (31) and 1977 (47) continued.	k_1 and E_1 gives $\log(k_1/cm^3\ mol^{-1}\ s^{-1}) = (11.97\pm0.25)-(538\pm52)/T$ for overall process. Quoted by (37). (a) used by (44) and re-recommended by HUDSON (45).
$7.83\times10^{11}\ \exp(-1150/T)$	Unspecified	Review. Expression reported as derived from (12,17 and 23). WOFSY and McELROY 1974 (32)	For use in modelling of ClO_x in atmosphere. A-factor is that of (12). Used by (42 and 46).
1.39×10^{10}	298	Evaluation. Value is that of (33) for sum of available routes for reaction 1. ANDERSON 1976 (38)	Available routes for reaction 1 given as $ClO + ClO \rightarrow Cl + OClO$ $\rightarrow Cl + ClO_2$ 17 $\rightarrow Cl_2 + O_2$ 16

THIRD ORDER REACTION: $ClO + ClO + M \rightarrow$ PRODUCTS

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Molecular modulation kinetic spectrometry study. Cl_2 (0.4 kPa), O_2 (3.6 kPa) and Ar (2.67-97.3 kPa) mixtures, and Cl_2 (0.16 kPa) plus O_2 (101.2 kPa) mixtures photolysed with square-wave excited lamps at flashing frequencies of 0.25, 0.5, 1,2,4,8,16 and 32 Hz. [ClO] and [ClOO] monitored by their phase shifted, modulated absorption signals at 257.7 and 250.0 nm respectively. JOHNSTON, MORRIS and VAN DEN BOGAERDE 1969 (17)	Observed phase of ClO indicated its formation as a secondary radical. Kinetic measurements carried out under conditions where ClOO phase shift $\approx 0^\circ$ and that of $ClO \approx -30^\circ$, i.e. at flashing frequency of 0.25 Hz, in order to minimise complications from ClOO signal. Ratio of phase to modulation amplitude gives factor, subsequently corrected for small ClOO signal contribution, from which second order experimental rate constant k_{exp} was derived using $\varepsilon = 1.27\times10^6\ cm^2\ mol^{-1}$ (12). Found strong dependence of k_{exp} on Ar pressure and interpreted k_{exp} as $(k_1 + k_1' k_{11}' [M]/k_{10}')$. $ClO + ClO \rightarrow$ products 1 $ClO + ClO + M \rightarrow Cl_2O_2 + M$ 1' $Cl_2O_2 + M \rightarrow ClO + ClO + M$ 10' $Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M$ 11' Due to experimental scatter authors could not extrapolate data to [M]=0 to obtain k_1. They demonstrated however that $k_1 \ll k_1' k_{11}' [M]/k_{10}'$ and thereby assumed $k_{exp} \approx k_1' k_{11}' [M]/k_{10}'$, from which they calculated for M=Ar, $k_1' k_{11}'/k_{10}' = 1.2\times10^{16}\ cm^6\ mol^{-2}\ s^{-1}$,

ClO + ClO → products

THIRD ORDER REACTION: CLO + CLO + M → PRODUCTS - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		JOHNSTON, MORRIS and VAN DEN BOGAERDE 1969 (17) continued.	and for $M=O_2$, $k'_1k'_{11}/k'_{10}=1.8x10^{16}$ cm^6 mol^{-1} s^{-1}. Quoted by (20 and 40). Used by (23).
$(7±7)x10^{15}$	298	Discharge flow system. ClO generated by adding ClO_2 to excess Cl in large excess of Ar at total pressures in range 0.12-1.345 kPa at 298 K. [ClO] monitored by absorption spectroscopy at 277.2 nm. WALKER 1972 (25)	Thirty-seven determinations of experimental second order rate constant k_{exp} carried out. Author interpreted k_{exp} as $(k_1 + k'_1[M])$ and, incorporating data of CLYNE and WHITE (23), plotted k_{exp} vs. [M]. Within experimental error plot had zero slope but least mean squares treatment gave $k_1=1.6x10^{10}$ cm^3 mol^{-1} s^{-1} and k'_1 (cm^6 mol^{-2} s^{-1}) as listed. Quoted by (31).

Discussion

Experimental determinations of the rate constant (defined by $-d[ClO]/dt=k_1[ClO]^2$) for the mutual self-interaction of ClO radicals have been largely confined to flash photolysis and discharge

$$ClO + ClO \rightarrow \text{products} \qquad (1)$$

flow studies. Most of these investigations have relied upon optical monitoring of ClO concentration by absorption spectroscopy as a means of measuring the extent of reaction. The now well known u.v. absorption spectrum of ClO was one of the first of any transient species to be characterised using the flash photolysis technique [1,2]. The use of an accurate value for the extinction coefficient ϵ_λ of ClO at the monitoring wavelength λ is fundamental to the conversion of optical density values into reactant concentrations needed in the calculation of k_1. Values obtained by early workers were in poor agreement due largely to an incomplete mechanistic understanding of the reaction systems used and in particular to a neglect of the fast reaction between ClO and O atoms.

$$O + ClO \rightarrow Cl + O_2 \qquad (8)$$

Consequently initial ClO concentrations, determined by extrapolation of second order ClO decay plots to zero time, were in error.

Two reliable measurements of ϵ at 257.7 nm and 298 K have been carried out. Clyne and Coxon [10] obtained $\epsilon=(1.27\pm0.04)\times10^6$ cm^2 mol^{-1}, after correction [12], from discharge flow studies. Basco and Dogra [20] subsequently measured $\epsilon=(1.15\pm0.06)\times10^6$ cm^2 mol^{-1} using the flash photolysis of ClO_2 in Ar as the ClO source. We have adopted the average value $\epsilon=(1.21\pm0.1)\times10^6$ cm^2 mol^{-1} as a basis for obtaining corrected k_1 values from the reported data. These values have then been used to construct our Arrhenius plot.

Using the flash photolysis of Cl_2/O_2 mixtures Porter and Wright [3] obtained the first kinetic data for reaction 1. They established that the reaction was second order in ClO, found k_1 to be both pressure and temperature independent within experimental error, and determined that the photolysis brought about no net overall composition change in the reaction mixture. Their proposed mechanism consisted of reactions 10, -10 and 11 with $k_{10} >> k_{11}$, and

$$Cl_2O_2 \rightleftharpoons ClO + ClO \qquad (10,-10)$$

$$Cl_2O_2 \rightarrow Cl_2 + O_2 \qquad (11)$$

they therefore identified k_1 with $k_{-10}k_{11}/k_{10}$. The results were subsequently criticised by Clyne and Coxon [12] who felt that a large adiabatic temperature rise probably occurred at lower experimental pressures, the effects of which were cancelled by a pressure dependence of the rate constant. Basco and Dogra disagreed with this criticism however, despite the poor agreement of Porter and Wright's data with their own.

The preliminary study of Lipscomb, Norrish and Porter [4] in which k_1 was measured using ClO_2 flash photolysis as the ClO source, was extended by Lipscomb, Norrish and Thrush [5]. Neglect of the fast reaction 8 led to their finding an apparent flash energy dependence of ϵ and k_1. Edgecombe, Norrish and Thrush [7] flash photolysed Cl_2O and obtained a k_1 value that is in agreement with the subsequent values of Basco and Dogra [20], although disagreement of the measured extinction coefficient indicates that this is fortuitous.

The first results of Clyne and Coxon were confined to 298 K and were subject to an error, later corrected, due to incorrect McLeod gauge calibration. These data were subsequently extended to cover the temperature range

294–495 K and the expression $k_1=(7\pm2)\times10^{11}$ $\exp\{-(1260\pm150)/T\}$ cm^3 mol^{-1} s^{-1} derived [12]. The introduction into the reaction mixture of potential Cl atom reaction partners such as ClO_2, O_3 and H_2 and their observed rapid removal led these authors to express a preference for a ClO decay mechanism comprising reactions 17,3,18 and 19, following a previous suggestion

$$ClO + ClO \rightarrow Cl + ClOO \qquad (17)$$

$$Cl + ClOO \rightarrow ClO + ClO \qquad (3)$$

$$Cl + ClOO \rightarrow Cl_2 + O_2 \qquad (18)$$

$$ClOO\ (+M) \rightarrow Cl + O_2(+M) \qquad (19)$$

of Benson and co-workers [6,9]. k_1 was therefore identified with k_{17}.

Further evidence for the participation of ClOO was obtained by Johnston, Morris and van den Bogaerde [17] who observed its absorption spectrum during the photolysis of gaseous $Cl_2/O_2/Ar$ mixtures. Using the then newly developed technique of molecular modulation kinetic spectrometry they found, in contrast to the results of previous workers, a pronounced linear dependence of k_1 on total pressure in the range 6.67–101.3 kPa, and interpreted their experimental second order rate constant k_{exp} as being approximately equivalent to $k_1'k_{11}'/k_{10}'$. Their mechanism therefore incorporated

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (1')$$

$$Cl_2O_2 + M \rightarrow ClO + ClO + M \qquad (10')$$

$$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M \qquad (11')$$

steps analogous to those proposed by Porter and Wright but with a pressure dependence included. Using molecular modulation mass spectrometry, Wu and Johnston continued these studies [26]. Their results are disappointing however as they failed to derive any rate constants from their data. They nevertheless demonstrated that their results were in poor quantitative agreement with those from the molecular modulation kinetic spectrometry study and in consequence concluded that either both studies involved a pressure dependent systematic error, or the simplifying assumptions used to treat the raw data were incorrect, or the reaction mechanism required revision. Whilst rejecting the first of these possibilities they decided that either or both of the other two could be valid and furthermore proposed that the observed pressure dependence under low light intensity conditions arises from reactions 19′, -19′ and 20, and not from 1′, 10′ and 11′. In view of the disagreement

$$Cl + O_2 + M \rightleftharpoons ClOO + M \qquad (-19',19')$$

$$Cl + Cl + M \rightarrow Cl_2 + M \qquad (20)$$

between these two investigations we approach conclusions based on the results with scepticism.

Clyne and White [23] in their investigation of reaction 1 over the temperature range 273–710 K, replaced the moveable detector used by Clyne and Coxon [12] with a fixed detector placed outside the heated portion of the flow tube. The results obtained were, within experimental error, independent of total pressure, in fair agreement with previous discharge flow studies and gave a reasonably linear Arrhenius plot. Westenberg [29] has however pointed out that the use of the fixed observation point technique to study the second order decay of a single labile species is theoretically invalid when the detector is placed outside the heated (or cooled) reaction zone. Despite the apparent consistency of the data we therefore view the results with reservation.

Basco and Dogra flash photolysed both ClO_2 [20] and Cl_2O [21] in the presence of various additives as well as repeating some of Porter and Wright's experiments with Cl_2/O_2 mixtures. The k_1 values obtained were found to be pressure independent and in good self-agreement, although higher by a factor of 1.8 than that of Clyne and Coxon [10] and approximately one-third that of Porter and Wright, measured at 293 K. No explanation was offered for this latter discrepancy. Basco and Dogra favoured a composite mechanism incorporating the major features of those previously discussed (reactions 10,-10,11′,18 and 21) and implying a dependence on pressure of the relative importance of the two routes 11′ and 18

$$Cl_2O_2 \rightarrow Cl + ClOO \qquad (21)$$

leading to products. This mechanism identifies k_1 with k_{-10}.

Walker [25] used an experimental method and apparatus similar to those employed by Clyne and Coxon [10,12]. An approximate method was used to calculate k_1 values from the average inverse ClO concentration within the heated section of the flow tube, obtained by measuring the rate of increase in $[ClO]^{-1}$ both in front of and behind the furnace. The results, presented only in Arrhenius form, give calculated rate constants that appear to be in good agreement with those from other discharge flow studies.

Unlike previous workers, Poulet, Le Bras and Combourieu [28] followed the reaction by sampling the reaction mixture in the flow tube using a mass spectrometer. The k_1 value obtained at 295 K is in good agreement with that from other discharge flow studies. That at 463 K is however somewhat higher than corresponding values (ca. ×1.4) and could well be in error, as the experimental technique is subject to Westenberg's criticism [29].

Clyne, McKenney and Watson [33] also used a mass spectrometer to follow the progress of reaction 1. Their rate constant $k_1=(1.36\pm0.18)\times10^{10}$ cm^3 mol^{-1} s^{-1}, measured at 298 K, agrees well with those from other discharge flow studies. In some experiments Cl atom concentration profiles were obtained thereby confirming the formation of Cl in parallel with the decay of ClO. ClO_2 was also observed as a reaction product, under conditions where Cl was not in excess and it was proposed that it arose via the minor reaction 22, the extent of which was estimated as $k_{22}/k_1=0.043^{+0.100}_{-0.026}$ at 298 K. Thermochemical agreements used by these authors indicated that the importance of reaction 22 should increase considerably at flame temperatures. In addition reaction 16 was considered; its role could not be assessed however.

$$\mathrm{ClO + ClO \rightarrow Cl_2 + O_2} \qquad (16)$$

$$\mathrm{ClO + ClO \rightarrow Cl + ClO_2} \qquad (22)$$

Park has obtained the only high temperature data for reaction 1 using the shock tube dissociation of ozone/chlorine mixtures [41]. Rate constants were derived by a computer modelling technique that matched the calculated and experimental ClO decay profiles. The computed rate constants are rather scattered and, on the authors admission, accurate to no more than a factor of two. It therefore seems to us pointless to attempt to draw any conclusions concerning the better or worse agreement of this data with that of either the low or higher pressure studies at lower temperatures.

Examination of all the available data reveals two immediately apparent inconsistencies. First the room temperature k_1 values obtained by Porter and Wright [3] and by Basco and Dogra [20] from similar flash photolysis studies of $\mathrm{Cl_2/O_2}$ mixtures are in complete disagreement. Of the two values only that of Basco and Dogra is substantiated by other data and we conclude that Porter and Wright's value is in error, as is their proposal that reaction 1 has a zero activation energy. Their k_1 values at 433 and 473 K are in much better agreement however with the data from discharge flow studies.

The second point of disagreement concerns the pressure dependence of k_1. Only Johnston and co-workers [17] using the molecular modulation technique have reported a marked effect of pressure on k_1. It is certainly true that the high pressure (ca. 27 kPa) flash photolysis results of Basco and Dogra give k_1 values larger than those obtained in low pressure discharge flow systems, but we remain as yet unconvinced that this finding is necessarily the result of a pressure dependent contribution to reaction 1, especially in view of the fact that such a conclusion depends on mechanistic interpretation. Furthermore Wu and Johnston's inability to satisfactorily resolve the quantitative discrepancies between their data and those of Johnston, Morris and van den Bogaerde together with their effective retraction of the previous postulate of pressure dependence of k_1, leads us to regard the evidence for such an effect as inconclusive. We are therefore unable to make any recommendation of the rate constant for reaction 1′, the alleged third order analogue of reaction 1.

$$\mathrm{ClO + ClO + M \rightarrow Cl_2O_2 + M} \qquad (1')$$

The mechanism of reaction 1 remains uncertain as does the role, if any, played by $\mathrm{Cl_2O_2}$. Cl atoms are however known to be present and it is probable that they are formed in parallel with ClOO radicals, though whether this reaction proceeds directly as in 17 and/or via a vibrationally excited $\mathrm{Cl_2O_2}$ intermediate as in -10 and 21 is not certain. Basco and Dogra failed to find any evidence for Cl atom formation. A possible explanation is that third order recombination, reaction 20, attenuated the concentration of Cl under their experimental conditions.

$$\mathrm{ClO + ClO \rightarrow Cl + ClOO} \qquad (17)$$

$$\mathrm{ClO + ClO \rightarrow Cl_2O_2^*} \qquad (-10)$$

$$\mathrm{Cl_2O_2^* \rightarrow Cl + ClOO} \qquad (21)$$

$$\mathrm{Cl + Cl + M \rightarrow Cl_2 + M} \qquad (20)$$

If $\mathrm{Cl_2O_2^*}$ is present, then it may also be able to decompose directly to $\mathrm{Cl_2}$ and $\mathrm{O_2}$. ClOO will decay by reactions 3, 18 and 19. Further minor reactions that should be considered include 22, proposed by Clyne and co-workers, and 16, which is equivalent to -10 followed by 11.

$$\mathrm{Cl_2O_2^* \rightarrow Cl_2 + O_2} \qquad (11)$$

$$\mathrm{Cl + ClOO \rightarrow ClO + ClO} \qquad (3)$$

$$\mathrm{Cl + ClOO \rightarrow Cl_2 + O_2} \qquad (18)$$

$$\mathrm{ClOO + M \rightarrow Cl + O_2 + M} \qquad (19)$$

$$\mathrm{ClO + ClO \rightarrow Cl + ClO_2} \qquad (22)$$

$$\mathrm{ClO + ClO \rightarrow Cl_2 + O_2} \qquad (16)$$

If two (or more) reactions, e.g., 17 and -10, are postulated to occur as primary reactions then unless both have identical activation energies, a curved Arrhenius plot should result. This curvature would only be apparent if the two activation energies were significantly different. Unfortunately the available data is sufficiently scattered to mask any curvature if it exists. Two pseudo-primary ClO decay paths could occur however if the reaction proceeded via a single vibrationally excited intermediate, such as $\mathrm{Cl_2O_2^*}$, which decomposed along two reaction channels. Under these circumstances when the intermediate-forming reaction is rate-determining a linear Arrhenius plot would be obtained.

It would seem that a detailed understanding of the mechanism will only be achieved after concentration vs time profiles of the species Cl, ClO, $\mathrm{Cl_2}$, $\mathrm{ClO_2}$ and possibly ClOO have been measured over extensive pressure and temperature ranges.

The rate constant of reaction 1 appears to be well characterised at room temperature in low pressure (<1.3 kPa) systems. We recommend

$$k_1 = 1.5 \times 10^{10}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}\ \text{at 298 K}$$

with error limits of ±15%. We prefer to make no recommendation at present for higher pressure systems. In view of the difficulties concerning the mechanism of the reaction we are reluctant to assign an activation energy and

Arrhenius *A*-factor. Nevertheless as the low pressure data give an apparently linear plot of $\log(k_1/\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$ vs T^{-1}, we suggest that k_1 values may be calculated for these experimental conditions from the following empirical equation of Arrhenius form over the temperature range 295–600 K with an error of ±50% in k_1.

$$k_1 = 1.15\times10^{12} \exp(-1295/T)\ \mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

This expression is that reported by Walker [25]. Its *recommendation here in no way implies* however that we specifically endorse the method used by that author in its measurement and derivation.

The Reaction $ClO + ClO \rightarrow Cl + ClO_2$

Only one study has been carried out that enables an

$$ClO + ClO \rightarrow Cl + ClO_2 \qquad (22)$$

estimate of k_{22} to be made. Clyne, McKenney and Watson [33] obtained $k_{22}/k_1 = 0.043^{+0.100}_{-0.026}$ at 298 K from a discharge flow system investigation, discussed above. The lack of comparative data precludes our commenting on the value of this ratio.

The Reactions $ClO + ClO \rightarrow 2Cl + O_2$ and $ClO + ClO \rightarrow Cl_2 + O_2$

Jayanty, Simonaitis and Heicklen [35] report the only available value for k_{15}/k_{16} from a study of the photolysis of

$$ClO + ClO \rightarrow 2Cl + O_2 \qquad (15)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (16)$$

$CFCl_3$ in the presence of O_3. Interpretation of their quantum yield data for O_3 removal required that a reaction mechanism be proposed. In view of the speculative nature of this scheme and the lack of any supporting evidence for reaction 15, we view the value obtained, $k_{15}/k_{16} = 0.5–0.75$ at 1.3 kPa, with scepticism.

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B16 $Cl + H_2O_2 \rightarrow HCl + HO_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-56.367	14.916	10.653
300	-56.367	14.908	10.592
500	-56.823	13.841	6.658
1000	-59.166	10.615	3.645
1500	-61.183	8.954	2.598
2000	-62.936	7.941	2.060
2500	-64.576	7.217	1.727
3000	-66.107	6.661	1.498

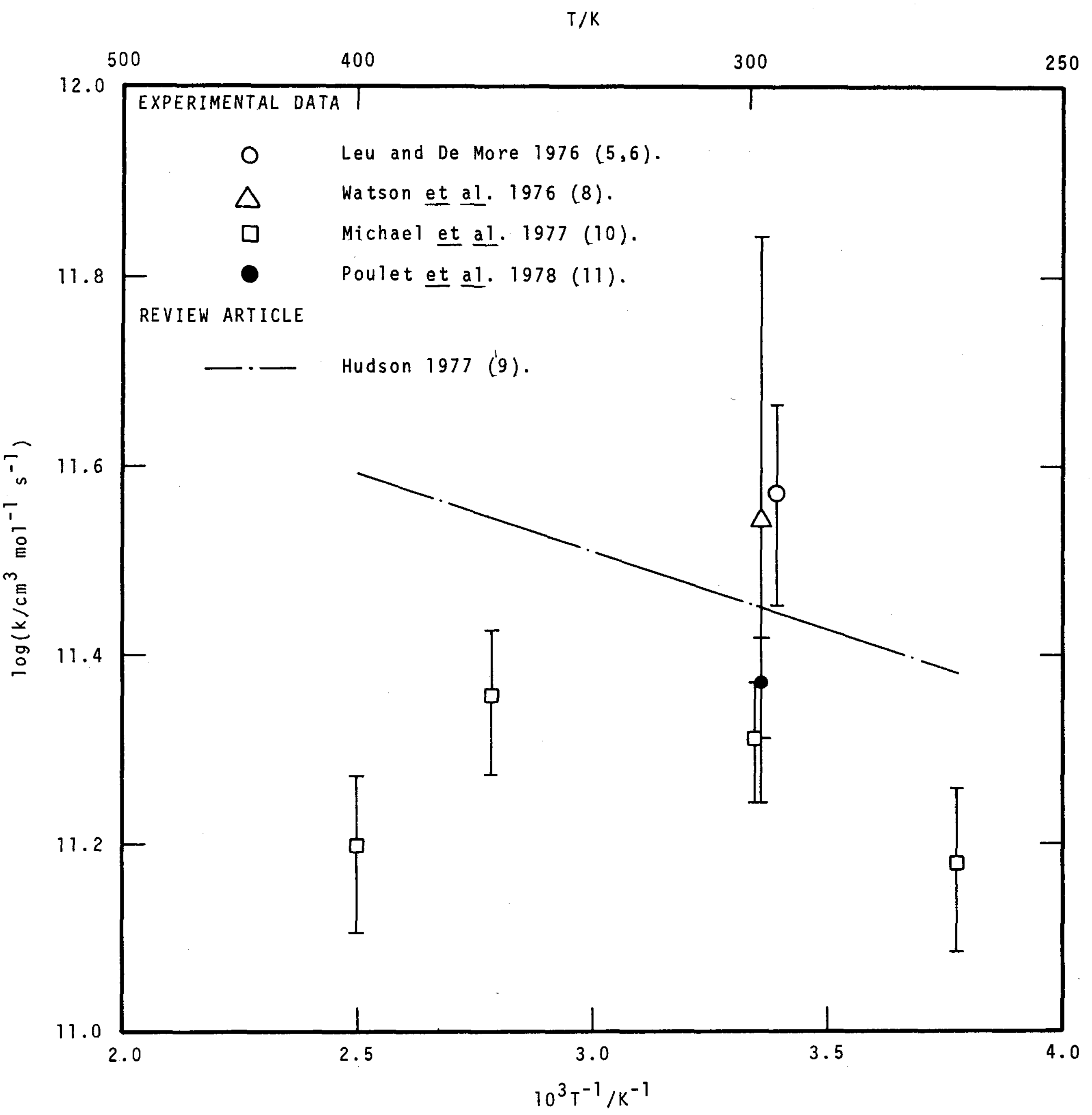
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(3.73 \pm 0.9) \times 10^{11}$	295	Discharge flow system. Cl_2 (1-5%)/He mixtures passed through discharge. H_2O_2 added through moveable inlet. [Cl] in excess by factor 10, varying over range 1.63×10^{-10}-8.00×10^{-10} mol cm^{-3}. Total pressures 1-2 mm Hg (133-267 Pa). Mass spectrometry used to monitor $[H_2O_2]$, and to determine [Cl], calibration being either by measuring $[Cl_2]$ both with and without microwave discharge in operation, or by titration with NOCl. LEU and DE MORE 1976 (5,6)	Good linear decay of $\log[H_2O_2]$ over more than order of magnitude variation in $[H_2O_2]$ indicated validity of pseudo first order kinetics. $[H_2O_2]$ remained constant in absence of Cl, showing negligible effect of heterogeneous H_2O_2 decomposition. $Cl + H_2O_2 \rightarrow HCl + HO_2$ 1

$Cl + H_2O_2 \rightarrow HCl + HO_2$



$Cl + H_2O_2 \rightarrow HCl + HO_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
3.49×10^{11}	298	Flash photolysis study. CCl_4 (65 μ Hg; 8.7 Pa)/ H_2O_2 (0-116.6 μ Hg; 15.5 Pa)/Ar (50 mm Hg; 6.7 kPa) mixtures. Initial $[H_2O_2]$/ [Cl] ratios varied 9×10^3-8×10^4. [Cl] decay followed by resonance fluorescence. WATSON, MACHADO, FISCHER and DAVIS 1976 (8)	Pseudo first order decay of [Cl] gave k_1 directly. Uncertainty in k_1 quoted as ± factor of 2. Quoted by (7). MICHAEL et al. (10) note that conversion from H_2O_2 partial pressure to $[H_2O_2]$ appears to be incorrect in this work, and quote their reworked value, obtained by least squares analysis of the original data, of $k_1 = (2.59 \pm 0.2) \times 10^{11}$.
$(1.51 \pm 0.3) \times 10^{11}$ $(2.05 \pm 0.3) \times 10^{11}$ $(2.27 \pm 0.4) \times 10^{11}$ $(1.57 \pm 0.3) \times 10^{11}$	265 299 359 400	Flash photolysis flow system. $COCl_2$ (120-300 μ Hg; 16-40 Pa)/H_2O_2 (86-234 μ Hg; 11.5-31 Pa)/Ar (30-80 mm Hg; 4.0-10.7 kPa) mixtures photolysed at $\lambda \geqslant$ 143 nm. [Cl] followed by resonance fluorescence in range 135-175 nm. MICHAEL, WHYTOCK, LEE, PAYNE and STIEF 1977 (10)	Flow rate of reactant mixtures required to be sufficiently fast to remove reaction products, which were found to contribute to Cl atom removal. Observed pseudo first order rate constants for [Cl] decay showed no variation with flash intensity or total pressure. Correction made for diffusional loss of Cl by performing experiments in absence of H_2O_2. Authors were unable to decide whether the value taken for $[H_2O_2]$ should be (a) the arithmetic mean of measurements taken before entry to, and after exit from, the reaction cell, or (b) the value measured at the cell exit. Due to this ambiguity two "equally acceptable" expressions were given: $k_1 = (1.89 \pm 0.3) \times 10^{11}\ cm^3\ mol^{-1}\ s^{-1}$, independent of T, and $k_1 = (7.47 \pm 0.2) \times 10^{11} \exp\{-(384 \pm 84)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
$(2.35 \pm 0.3) \times 10^{11}$	298	Discharge flow system. H_2O_2/Ar mixtures added via moveable inlet to Cl/He mixtures from Cl_2 discharge. Total pressures probably 0.24-0.36 mm Hg (32-48 Pa). Cl in excess. Reaction followed by mass spectrometry. POULET, LE BRAS, LAVERDET and COMBOURIEU 1978 (11)	Pseudo first order decay of H_2O_2 gave k_1 $Cl + H_2O_2 \rightarrow HCl + HO_2$ 1 Few details, results for k_1 not specifically described in this description of determination of k_2. $Cl + HO_2 \rightarrow HCl + O_2$ 2

$Cl + H_2O_2 \rightarrow HCl + HO_2$

REVIEW ARTICLE

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.02 \times 10^{12} \exp(-384/T)$	265-400	Review. Recommended expression based on value of k_1 at 298 K as average of values of (5 and 10), and activation energy of (10). HUDSON 1977 (9)	Mean value at 298 K quoted as being in good agreement with that of WATSON *et al.* (8).

Discussion

The reaction between chlorine atoms and hydrogen peroxide

$$Cl + H_2O_2 \rightarrow HCl + HO_2 \qquad (1)$$

is another of interest in the chemistry of the stratosphere. Maximum concentrations of stratospheric H_2O_2 have been calculated as $\sim 10^{-16}$ mol cm^{-3} (Crutzen, see [2,3]) and 10^{-15} mol cm^{-3} [1,2,7]. Prior to any experimental data, estimates of $k_1 \geqslant 10^{12}$ cm^3 mol^{-1} s^{-1} [4] gave Cl removal rates by reaction 1 of the same order as those by H_2 [2,3].

Room temperature values for k_1 determined in 1976 by Leu and De More [5,6] and by Watson et al. [8], using discharge flow and flash photolysis methods respectively, were in good agreement at $\sim 3.55 \times 10^{11}$ cm^3 mol^{-1} s^{-1}. But the most recent measurements, by Michael et al. [10], using a flash photolysis flow system, and Poulet et al. [11], by discharge flow methods, gave k_1 about 50% below this value. The only measurement of the temperature dependence of k_1, by [10], is irregular—either there is little temperature variation or their highest temperature value is too low.

Because of these uncertainties, we make no recommendation for the rate constant k_1.

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Miscellaneous Reactions Involving Cl/O Species

B17 $Cl + O_2 + M \rightarrow ClOO + M$

The termolecular reaction of Cl with O_2 constitutes the first step,

$$Cl + O_2 + M \rightarrow ClOO + M \qquad (1)$$

following Cl_2 photodissociation, in the reaction sequence occuring in flash photolysed Cl_2/O_2 mixtures [2,3,4,9]. Prior to flash photolysis many studies had been carried out on the influence of O_2 on the photochemical reaction between Cl_2 and H_2 [1]. Unfortunately none of these allowed rate constant data for reaction 1 to be unambiguously derived. The application of a steady state analysis to a mechanistic scheme, suggested in part by Benson and Buss [5], for Cl_2 catalysed O atom recombination, enabled Kaufman to obtain the first estimate for $k_1(M=O_2)$ as 7×10^{16} cm^6 mol^{-2} s^{-1} at 295 K [6]. Niki and Weinstock have rejected this value however as it is in conflict with their experimental data for the same reaction system [7].

The first direct experimental determinations of $k_1(M=Ar)$ were reported by Clyne and Coxon [8]. They noted a value obtained by Stedman in their laboratory, of 2×10^{14} cm^6 mol^{-2} s^{-1} over the temperature range 200-300 K, and themselves measured $k_1(M=Ar) < 2 \times 10^{15}$ cm^6 mol^{-2} s^{-1} at 300 K from flow studies at 270 Pa. Nicholas and Norrish reinvestigated the room temperature flash photolysis of Cl_2/O_2 mixtures in N_2 [9]. By monitoring the concentration of ClO by absorption spectroscopy and assuming that the half-life of the Cl atoms produced by the flash was equal to that for half-formation of ClO, they derived $k_1(M=N_2) = (6.2 \pm 1.1) \times 10^{14}$ cm^6 mol^{-2} s^{-1} at 293 K.

In view of the paucity of data for reaction 1 we have only been able to list the reported k_1 values and can make no recommendations. No data are available for the reverse reaction, -1, the decompositon of ClOO.

$$ClOO + M \rightarrow Cl + O_2 + M \qquad (-1)$$

and as the thermodynamic parameters for ClOO are not well established, k_{-1} values cannot be calculated with confidence.

Watson [10] however, has estimated his preferred expression $k_{-1}=1.14\times10^{15}\exp\{-(3581\pm11)/T\}$ cm^3 mol^{-1} s^{-1} using $\Delta H^\circ_{f,298}$(ClOO)=89.2 kJ mol^{-1} (21.3 kcal mol^{-1}) and k_1 from Stedman. If the proposed lower limit value $\Delta H^\circ_{f,298}$(ClOO)= 84.2 kJ mol^{-1} (20.1 kcal mol^{-1}) is used, then $k_{-1}=1.17\times10^{15}\exp\{-(4191\pm35)/T\}$ cm^3 mol^{-1} s^{-1} is obtained. Employing instead the k_1 value of Nicholas and Norrish increases the A-factor in both expressions by a factor of 3.04.

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B18 Cl + ClOO → products

The reaction of Cl atoms with the ClOO radical to give either Cl_2 and O_2

$$Cl + ClOO \rightarrow Cl_2 + O_2 \quad (1a)$$

$$Cl + ClOO \rightarrow ClO + ClO \quad (1b)$$

or ClO, plays a central role in the photooxidation of chlorine and in the decay of ClO radicals at low pressures. Despite its importance the only available measurements of k_{1a} and k_{1b} are those reported by Johnston, Morris, and van den Bogaerde [2] who used molecular modulation kinetic spectroscopy to study the photolysis of Cl_2/O_2 mixtures. The values obtained at 298 K, $k_{1a}=9.4\times10^{13}$ cm^3 mol^{-1} s^{-1} and $k_{1b}=8.7\times10^{11}$ cm^3 mol^{-1} s^{-1}, could only be derived by making several assumptions and by using an estimated value for ΔH°_f(ClOO) at 298 K of 95.4 kJ mol^{-1} (22.8 kcal mol^{-1}). This value is now thought to be some 6–11 kJ mol^{-1} too high [4]. Subsequently Wu and Johnston [3] have indicated that the assumptions may need to be reassessed. These results give $k_{1a}/k_{1b}=109$ in contrast to a previous estimate of 15 at the same temperature, calculated by Nicholas and Norrish [1] from a kinetic analysis of the rate of production of ClO in high energy flash photolysed $Cl_2/O_2/N_2$ mixtures. No absolute values of k_{1a} or k_{1b} were obtained in this latter study. Cox and Derwent [5] have recently reinvestigated the chlorine photosensitized oxidation of hydrogen using a stopped-flow method at 306 K and 1 atmosphere pressure, and have obtained a value for k_{1a} of $(1^{+1.0}_{-0.5})\times10^{13}$ cm^3 mol^{-1} s^{-1}. Cl_2 and H_2 pressures were typically in the ranges 0.8–4$\times10^{-4}$ atm and 0.2–20$\times10^{-3}$ atm, respectively, and mixtures were pressurised with either O_2 or O_2/N_2. Computer simulation of the experimental Cl_2 decay and H_2O_2 production rates, obtained by absorption spectroscopy, was employed to derive k_{1b}, using literature values for a series of 33 potentially participating reactions. It is noteworthy that unsatisfactory fits to the data were obtained when the k_{1b} value of Johnston and co-workers [2] was substituted.

At the time of writing the lack of data prevents our making a rate constant recommendation for reaction 1. We believe, however, that the data of Johnston et al. are the least reliable of those available.

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B19 O + Cl_2O → ClO + ClO

The fast reaction between oxygen atoms and chlorine monoxide

$$O + Cl_2O \rightarrow ClO + ClO \quad (1)$$

has been studied only at room temperature by discharge flow [1] and flash photolysis [2] techniques.

Freeman and Phillips [1] passed O$_2$/Ar mixtures through a discharge, and added Cl_2O/Ar downstream through a moveable inlet. The final mixture compositions were Ar(137–151 μm Hg; 18.3–20.1 Pa)/O_2 (5.4–31.8 μm Hg; 0.72–4.2 Pa)/O (0.48–2.19 μm Hg; 6.4$\times10^{-2}$–0.29 Pa)/Cl_2O (8.9$\times10^{-2}$–0.21 μm Hg; 1.2$\times10^{-2}$–2.8$\times10^{-2}$ Pa), with [O]/[Cl_2O] ratios 4.15–12.7. The stoichiometry of the reaction was determined with [Cl_2O]/[O] ratios 1.86–5.51, with O atom pressures 1–2 μm Hg (0.13–0.27 Pa). Mass spectrometry was used to follow Cl_2O and O. From the pseudo first order decay of Cl_2O, the rate constant k_1 was found from an average of 41 measurements to be $(8.3\pm1.4)\times10^{12}$ cm^3 mol^{-1} s^{-1}, at 298 K. The stoichiometry $\Delta[Cl_2O]/\Delta[O]$ was found to be ~0.8, which led these authors to consider the reaction mechanism to be

$$O + Cl_2O \rightarrow ClO + ClO \quad (1)$$

$$O + ClO \rightarrow Cl + O_2 \quad (2)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \quad (3)$$

$$Cl + \text{wall} \rightarrow 1/2Cl_2 \quad (w)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (4)$$

Under conditions of O atom excess, as in the rate constant measurement, the stoichiometry will be dependent upon the relative rates of reactions 3 and w.

Basco and Dogra [2] flash photolysed mixtures of ClO_2(45 and 82 μm Hg; 6 and 11 Pa)/Cl_2O (0, and 10.2–178 μm Hg; 1.4–23.8 Pa) at two different flash energies, 1.06 and 1.325 kJ. Filters were used to restrict photolysis to >340 nm, thereby preventing photolysis of Cl_2O. [ClO] was followed by plate photometry at 257.7, 277.2 and 292 nm. From the overall removal of ClO, according to

$$-d[\mathrm{ClO}]/dt = k_2[\mathrm{O}][\mathrm{ClO}] + k_4[\mathrm{ClO}]^2 - 2k_1[\mathrm{O}][\mathrm{Cl_2O}],$$

the authors were able to derive the ratio $k_1/k_2=(0.74\pm0.06)$ at 298 K. Using $k_2=7\times10^{12}$ cm^3 mol^{-1} s^{-1} (as measured in the same work) they derived $k_1=5.2\times10^{12}$ cm^3 mol^{-1} s^{-1}. Under their experimental conditions, with a high percentage of ClO_2 photodecomposition, they reasoned that unphotolysed ClO_2 would be rapidly consumed by excess oxygen atoms and that a competition between Cl_2O and ClO would ensue for the remaining O atoms. The reactions of ClO_2 and Cl_2O with Cl were considered negligible. Subsequent determinations of the rate of reaction 5 show that this assumption is probably unjustified under these experimental

$$\mathrm{Cl} + \mathrm{ClO_2} \rightarrow \mathrm{ClO} + \mathrm{ClO} \qquad (5)$$

conditions [3]. If our recommended value $k_2=3.2\times10^{13}$ cm^3 mol^{-1} s^{-1} (section B13) is substituted in the expression for k_1/k_2, one calculates $k_1=2.4\times10^{13}$ cm^3 mol^{-1} s^{-1}.

Although Freeman and Phillip's value [1] has been consistently recommended [4,5,6], because of the uncertainties in their stoichiometry, and in the absence of further, reliable, data, we make no recommendation for k_1.

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Note Added in Proof

A new measurement of the rate constant for the reaction

$$\mathrm{O} + \mathrm{Cl_2O} \rightarrow \mathrm{ClO} + \mathrm{ClO} \qquad (1)$$

has been reported by Miziolek and Molina [J. Phys. Chem. **82**, 1769 (1978)]. O atoms were generated by addition of NO to N atoms in an N_2-discharge flow system, and Cl_2O was added downstream through a moveable inlet. The total pressure was approximately 1 mm Hg (130 Pa). The pseudo-first-order decay of O atoms was monitored by measurement of the air afterflow intensity in presence of excess NO. The authors were concerned at the possible effects on the stoichiometry of the side-reactions (2) and (3) which were expected to be most important at low values of the ratio $[Cl_2O]/[O]$.

$$\mathrm{O} + \mathrm{ClO} \rightarrow \mathrm{Cl} + \mathrm{O_2} \qquad (2)$$

$$\mathrm{Cl} + \mathrm{Cl_2O} \rightarrow \mathrm{Cl_2} + \mathrm{ClO} \qquad (3)$$

They added C_2H_6 ($[C_2H_6]/[Cl_2O]=1$–12) to scavenge Cl atoms by the reaction

$$\mathrm{Cl} + \mathrm{C_2H_6} \rightarrow \mathrm{C_2H_5} + \mathrm{HCl} \qquad (6)$$

Under these conditions the apparent rate constant at 255 K was found to decrease to a limit as the initial $[Cl_2O]/[O]$ ratio increased to about 60. Rate constant measurements were made for initial $[Cl_2O]/[O]$ values in the range 58–230. The effects of (7) and (8) were also considered

$$\mathrm{NO} + \mathrm{ClO} \rightarrow \mathrm{NO_2} + \mathrm{Cl} \qquad (7)$$

$$\mathrm{NO_2} + \mathrm{O} \rightarrow \mathrm{NO} + \mathrm{O_2} \qquad (8)$$

and calculations by the authors suggested that under the conditions of measurement less than 1% of the O atoms reacted with species other than Cl_2O.

Values of k_1/cm^3 mol^{-1} s^{-1} were obtained as follows: 1.5×10^{12} (236 K), 1.8×10^{12} (254 K), 2.2×10^{12} (273 K) and 2.5×10^{12} (295 K). These data were expressed by the authors as $(1.6\pm0.2)\times10^{13}\exp[(-560\pm80)/T]$.

We consider these data to be the best so far available for this reaction.

B20 Cl + Cl_2O → ClO + Cl_2

The reaction between Cl and Cl_2O

$$\mathrm{Cl} + \mathrm{Cl_2O} \rightarrow \mathrm{ClO} + \mathrm{Cl_2} \qquad (1)$$

has been studied by Edgecombe, Norrish, and Thrush [1] and Basco and Dogra [2], both groups using the flash photolysis of chlorine in the presence of Cl_2O at wavelengths greater than 310 nm. Photolysis of ClO was therefore avoided and that of Cl_2O greatly reduced. By measuring the decrease in Cl_2O concentration and assuming that the total number of Cl_2O molecules removed was equivalent to the number of Cl atoms formed photochemically, Edgecombe and co-workers calculated $k_1>4\times10^{11}$ cm^3 mol^{-1} s^{-1}. Basco and Dogra assumed that the initial Cl concentration was equal to the total yield of ClO, and by monitoring the change in ClO concentration during the first 10^{-4}s of reaction, obtained from an average of six determinations, $k_1=(4.1\pm0.5)\times10^{11}$ cm^3 mol^{-1} s^{-1}. The reaction sequence occurring in the flash photolysis of Cl_2O has subsequently been discussed by Clyne, McKenney and Watson [3], and a comprehensive mechanism proposed.

There are no data for the reverse reaction of ClO with Cl_2. The value of the equilibrium constant calculated from the available thermodynamic data for the species in reaction 1, indicates, however, that k_{-1} should be smaller than k_1 by a factor of at least 10^{19}.

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B21 ClO + Cl_2O → ClO_2 + Cl_2

The ClO radical reacts with chlorine monoxide in two ways, producing either chlorine dioxide (reaction 1) or atomic chlorine, O_2 and Cl_2.

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2; \qquad (1)$$

$$\Delta H^\circ_{298} = -84.483 \text{ kJ mol}^{-1} \ (-20.192 \text{ kcal mol}^{-1})$$

Reaction 1 was first proposed by Finkelnburg et al. [1] as occurring following the photolysis of Cl_2O, to account for the production of ClO_2. Edgecombe et al. [2] flash photolysed Cl_2O (~1–3%)/SF_6 mixtures, at a total pressure of 8.0 kPa at room temperature. [Cl_2O], [ClO] and [ClO_2] were followed by absorption spectroscopy in the region 270–430 nm. [ClO_2] build-up was attributed entirely to reaction 1, the following reaction scheme being considered:

$$Cl_2O + h\nu \rightarrow Cl + ClO$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (2)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (3)$$

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \qquad (1)$$

Assuming $k_2 >> k_3$ they gave $k_1 = 1 \times 10^8$ cm^3 mol^{-1} s^{-1} at 298 K.

Basco and Dogra flash photolysed Cl_2O (~0.5%)/Cl_2 (~1%)/Ar mixtures at a total pressure of 26.7 kPa [3]. [Cl_2O], [ClO] and [ClO_2] were followed by absorption spectroscopy in the region 250–351.5 nm. The authors observed the same slow build-up of [ClO_2] as did Edgecombe et al. and attributed it to the same reaction mechanism. Making the same assumptions, they obtained $k_1 = 2.7 \times 10^8$ cm^3 mol^{-1} s^{-1} at 298 K.

Clyne et al. [4] have recently re-investigated the mechanism of Cl_2O flash photolysis. They come to the conclusion that there is no evidence for reaction 1 occurring, and produce evidence that reaction 3 is wrong, ClO_2 being produced directly by reaction 4 (see section B15).

$$ClO + ClO \rightarrow Cl + ClO_2 \qquad (4)$$

In view of the uncertainty in the mechanism of Cl_2O flash photolysis no recommendation is made for k_1.

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B22 $ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl$

The alternative path for the reaction between the ClO radical and chlorine monoxide was put forward by Edgecombe et al. [1] following the flash photolysis of Cl_2O.

$$ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl; \qquad (1)$$

$$\Delta H^\circ_{298} = -67.793 \text{ kJ mol}^{-1} \ (-16.203 \text{ kcal mol}^{-1})$$

In their study of the flash photolysis of Cl_2O (1–3%)/SF_6 mixtures at 8.0 kPa pressure, they followed [ClO], [Cl_2O], and [ClO_2] by absorption spectroscopy at 270–430 nm. They noted that during the [ClO] decay, the rate of disappearance of Cl_2O was much greater than the rate of formation of ClO_2, and attributed this to reaction 1:

$$Cl_2O + h\nu \rightarrow Cl + ClO$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (2)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (3)$$

$$ClO + Cl_2O \rightarrow Cl_2 + ClO_2 \qquad (4)$$

$$ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl \qquad (1)$$

Assuming $k_2 >> k_3$, and using their own value for k_4 obtained in the same study, they obtained $k_1 = 5.3 \times 10^7$ cm^3 mol^{-1} s^{-1} at 298 K.

Basco and Dogra [2], following the flash photolysis of Cl_2O (~0.5%)/Cl_2 (~1%)/Ar mixtures at a total pressure of 26.7 kPa, found $k_1 = 6.5 \times 10^8$ cm^3 mol^{-1} s^{-1}, using the same reaction mechanism as Edgecombe et al. The discrepancy in the results is considerable and Basco and Dogra point out that Edgecombe et al. found $-d[Cl_2O]/dt >> 2d[ClO_2]/dt$, implying $k_1 > k_4$.

Following the work of Clyne et al. [3] on Cl_2O flash photolysis, ClO_2 formation via reaction 4 has been rejected. The fast rate of removal of Cl_2O they attribute to reaction 2 followed by the fast reaction 5.

$$ClO + ClO \rightarrow Cl + ClOO \qquad (5)$$

In view of the uncertainty in the Cl_2O flash photolysis mechanism, no recommendation is made for k_1.

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B23 $ClO + O_3 \rightarrow$ products

The ClO radical is believed to be removed in the stratosphere by ozone [3] although the reaction is known to be slow. The exact mechanism is not clear, paths to ClOO and Cl atoms having been proposed [1,3,4].

In their study of the chlorine photosensitised decomposition of ozone [1], Norrish and Neville favoured reaction 1a.

$$ClO + O_3 \rightarrow Cl + 2O_2 \qquad (1a)$$

Cl_2(0.77–13.3 kPa) was photolysed at 365 nm in the presence of O_3 (50–90%)/O_2 mixtures at 2.0–11.5 kPa pressure. In some experiments O_2 (12.0–83.3 kPa), N_2 (25.1–73.5 kPa) or CO_2 (6.67–60.8 kPa) were added. The reaction was followed manometrically. For $[O_3] > [Cl_2]$, they found the following mechanism fitted the data:

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O_3 \rightarrow Cl + 2O_2 \quad (1a)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (2)$$

with $-d[O_3]/dt = 2I_a + 2(2/k_2)^{1/2} \cdot k_1[O_3](I_a)^{1/2}$.

Jayanty et al. [6] evaluated these data to give $k_1 = (2.8 \pm 1.4) \times 10^5$ cm^3 mol^{-1} s^{-1} at 298 K. They were in doubt as to the exact reaction path, accepting reaction 1b as an alternative.

$$ClO + O_3 \rightarrow ClO_2 + O_2 \quad (1b)$$

Clyne and Coxon [2] used O_3 as a scavenger for ClO radicals in a flow system, but found the reaction undetectably slow, with $k_1 < 3 \times 10^9$ cm^3 mol^{-1} s^{-1} at 294 K. In later work, Clyne et al. [5] favoured reaction 1b as the main path, and this has also been assumed by Stolarski and Cicerone [3] in their studies of stratospheric chlorine. Wofsy and McElroy [4] however, favour reaction 1c but believe it to be very slow.

$$ClO + O_3 \rightarrow ClOO + O_2 \quad (1c)$$

Recently, Birks et al. [7,8] obtained $k_{1b} = 9.0 \times 10^8$ cm^3 mol^{-1} s^{-1} at 297 K. Using a flow system, they produced Cl atoms in a discharge through Cl_2, and added O_3 further downstream. [ClO], [O_3], and [ClO_2] were monitored by mass spectrometry. The authors found [ClO_2] to be more than would be expected from disproportionation of ClO, and concluded that the excess was being produced by reaction 1b.

Although there remains controversy as to the exact reaction mechanism, it is clear that reaction 1 is indeed slow, and unimportant compared with other ClO-removing reactions.

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B24 $Cl + HO_2 \rightarrow HCl + O_2$

In order to model the effect of "odd chlorine" (derived from man-made chlorofluorocarbons) on the upper atmosphere, particularly the ozone layer, the rates of Cl removal by stratospheric constituents other than ozone must be known. HO_2 radicals have been calculated as having maximum concentrations of $\sim 10^{-17}$ mol cm^{-3} [2,5,6] and $\sim 10^{-16}$ mol cm^{-3} [10], and with an estimated rate constant $k_1 = 1.2 \times 10^{13}$ cm^3 mol^{-1} s^{-1} [1].

$$Cl + HO_2 \rightarrow HCl + O_2; \quad (1)$$

$$\Delta H^\circ_{298} = -234.5 \text{ kJ mol}^{-1} \ (-56.1 \text{ kcal mol}^{-1})$$

derived by comparison with the rate constant for

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

the rate of Cl atom removal by reaction 1 is comparable with that by the reaction

$$Cl + H_2 \rightarrow HCl + H$$

[5,6]. The above estimate for k_1 has been used by [6,7,10], and values of the same order of magnitude have been used by [3,5,11].

A value of k_1 was derived by Gavriliv et al. [4] from their determination of the reverse rate constant k_{-1}

$$HCl + O_2 \rightarrow Cl + HO_2 \quad (-1)$$

These authors quoted the temperature-independent value $k_1 = 2 \times 10^{12}$ cm^3 mol^{-1} s^{-1} for the range 853–1432 K.

The first direct experimental determination of k_1 was by Leu and De More [8,9], using a discharge flow system. Cl_2(1–5%)/He mixtures were passed through a discharge and added via a moveable injector to a stream of H_2O_2 at total pressures of 1–2 mm Hg (133–267 Pa). The initial conditions were given as $[Cl] = 6.8 \times 10^{-10}$ mol cm^{-3}, and $[Cl] \geqslant 10[H_2O_2]$. The reaction was followed by mass spectrometry. With HO_2 being produced by reaction 2

$$Cl + H_2O_2 \rightarrow HCl + HO_2 \quad (2)$$

(see section B16) the rate expression for [HO_2] reduced to $[HO_2] = k_2[H_2O_2]/k_1$, for $k_1 >> k_2$. Constant values of $[H_2O_2]/[HO_2]$ for reaction times between 5×10^{-4} and 3×10^{-3} s showed the approximations resulting from assuming $k_1 >> k_2$ to be valid. The average rate constant k_1 was quoted as $(1.81^{+1.81}_{-0.9}) \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 295 K. This value was used by Hudson [13].

Cox and Derwent [12] photolysed Cl_2 (3.3×10^{-9}–1.7×10^{-8} mol cm^{-3})/H_2 (8.3×10^{-9}–8.3×10^{-7} mol cm^{-3})/O_2 and O_2/N_2 mixtures at atmospheric pressure (101.3 kPa), using a stopped-flow technique. [Cl_2] was monitored by absorption at 310 nm, and [H_2O_2] by absorption at 220 nm. The authors found the [Cl_2] decay rate and the yield of H_2O_2 to be dependent upon the initial value of [H_2], contrary to steady state analysis of the simple mechanism

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$Cl + H_2 \rightarrow HCl + H$$

$$Cl + O_2 + M \rightarrow ClO_2 + M$$

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

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

The authors argued that reactions 1 and 3 were occurring simultaneously

$$Cl + HO_2 \rightarrow HCl + O_2 \quad (1)$$

$$Cl + ClO_2 \rightarrow Cl_2 + O_2 \quad (3)$$

under conditions of low $[H_2]/[Cl_2]$ ratios. Using computer simulation methods, the authors found the best value for k_1 to be $(1.51\pm0.6)\times10^{13}$ cm^3 mol^{-1} s^{-1} at 306 K.

The latest study, by Poulet et al. [14], used a discharge flow system to generate Cl atoms in He diluent. H_2O_2/Ar mixtures were added downstream via a moveable inlet, such that Cl atoms were in excess ($5.2\times10^{-10}<[Cl]<1.8\times10^{-9}$, and $2.0\times10^{-11}<[H_2O_2]<7.0\times10^{-10}$ mol cm^{-3}), at total pressures 0.25–0.36 mm Hg (32–48 Pa). Mass spectrometry was used to follow the reaction. As for the work of Leu and De More [8,9] the sequence of reactions 1 and 2 gave $[H_2O_2]/[HO_2]=k_1/k_2$. The resulting ratio was, however, found to be 170±45 at 298 K, compared with the value 48.5 obtained by [8,9]. Using their own value for k_2, Poulet et al. [14] quoted k_1 as $(3.98\pm1.6)\times10^{13}$ cm^3 mol^{-1} s^{-1} (298 K).

The error limits quoted for their values of k_1 and k_2 by Leu and De More give a range for k_1/k_2 of 20 to 128, this upper limit being within the error limits of Poulet et al. However, because of the good agreement between the values for k_1 at 300 K, derived by the different methods [8,12], we prefer the value $k_1=1.66\times10^{13}$ cm^3 mol^{-1} s^{-1} (300±5 K). The uncertainty limits on the ratio k_1/k_2 suggest that this value is subject to error limits of over a factor 3.

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B25 HCl + O$_2$ → HO$_2$ +Cl

Like the other hydrogen halides, hydrogen chloride acts as a flame inhibitor in hydrocarbon combustion. However, the reaction between HCl and O$_2$ has a high activation energy, and cannot be the reason, and in order to study the kinetics of (1) in a pyrolysis system, it is necessary to go to high temperatures, higher than those used for HBr and HI.

$$HCl + O_2 \rightarrow HO_2 + Cl; \qquad (1)$$

$$\Delta H^\circ_{298}=234.52 \text{ kJ mol}^{-1} \ (56.052 \text{ kcal mol}^{-1})$$

Gavriliv et al. [2] studied HCl oxidation in a flow pyrolysis system using HCl (10–90%)/O$_2$ (10–90%)/N$_2$ mixtures at 1 atm (101 kPa) pressure. [Cl$_2$] was determined iodometrically and [HCl] by titration with NaOH. An overall rate constant, based on the rate of disappearance of HCl, was obtained, $k_o=2.0\times10^{13}\exp(-26\,000/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 853–1423 K. The authors found the reaction to be first order in both [HCl] and [O$_2$], and thus reaction 1 was proposed as the initiation reaction, and an 8-step reaction scheme chosen similar to that for HBr [1]. On the basis of this mechanism the overall rate of HCl destruction is 4 times the rate of (1) so that k_1 was deduced to be $5.0\times10^{12}\exp(-26\,000/T)$ cm^3 mol^{-1} s^{-1}. Assuming the reverse reaction to have zero activation energy, they calculate $k_{-1}=2.0\times10^{12}$ cm^3 mol^{-1} s^{-1}. Using the equilibrium constant given by JANAF, we calculate $k_{-1}=3\times10^{13}$ cm^3 mol^{-1} s^{-1} over the temperature range 853–1423 K, possibly with a slight negative activation energy.

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B26 H + ClO$_2$ →ClO + OH

Broida et al. [1] believed that the reactions of H, N and O atoms with ClO$_2$ must be rapid on energetic grounds. Watson [4] found no evidence for the N+ClO$_2$ reaction, while O+ClO$_2$ has been shown to be moderately fast (section B14).

$$H + ClO_2 \rightarrow ClO + OH; \qquad (1)$$

$$\Delta H^\circ_{298}=-181.91 \text{ kJ mol}^{-1} \ (-43.479 \text{ kcal mol}^{-1})$$

The reaction of hydrogen atoms with chlorine dioxide has been studied in a flow system by Walker [2] and Bemand et al. [3]. Walker [2] produced H atoms by a discharge through H$_2$(<0.1%)/Ar mixtures at 70 Pa pressure. ClO$_2$ was added in excess downstream. [H] was determined by titration with NOCl, the [NOCl] decay being monitored mass spectroscopically. At 297 K, he found $k_1=(3.2\pm1.5)\times10^{13}$ cm^3 mol^{-1} s^{-1}. Bemand et al. [3] used a similar system, with H$_2$(<0.1%)/He mixtures at 100 Pa, detecting [H] by mass-spectrometric titration with NO$_2$. At 298 K, they found $k_1=3.4\times10^{13}$ cm^3 mol^{-1} s^{-1}, i.e., $k_1\cong100k_2$

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (2)$$

In view of the good results obtained for other ClO$_x$ reactions by Clyne's group, we recommend $k_1=3.4\times10^{13}$ cm^3 mol^{-1} s^{-1} at 298 K, with error limits of ±40%.

References

[1] Broida, H. P., Schiff, H. I., and Sugden, T. M., Nature **185**, 759 (1960).

[2] Walker, R. F., Ph. D. Thesis, London University (1972).

[3] Bemand, P. P., Clyne, M. A. A., and Watson, R. T., JCS Faraday I **69**, 1356 (1973).

[4] Watson, R. T., Ph. D. Thesis, London University (1973).

B27 H + Cl_2O → products

Hydrogen atoms react with chlorine monoxide by two different paths, both highly exothermic.

$$H + Cl_2O \rightarrow HClO + Cl; \qquad (1a)$$

$$\Delta H^\circ_{298} = -276.62 \text{ kJ mol}^{-1} \ (-66.114 \text{ kcal mol}^{-1})$$

$$H + Cl_2O \rightarrow HCl + ClO; \qquad (1b)$$

$$\Delta H^\circ_{298} = -296.96 \text{ kJ mol}^{-1} \ (-70.98 \text{ kcal mol}^{-1})$$

Freeman and Phillips investigated the reaction in a flow system [4], producing H atoms by a discharge through dilute H_2/Ar mixtures at ~20 Pa pressure. Cl_2O was added downstream in excess, and the reaction followed mass spectrometrically. They were only able to detect HClO as a product, from reaction 1a, but felt that reaction 1b was too exothermic to be ruled out as a possible route. They gave $k_1 = 1.3 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 296 K.

Perona et al. [7,8], studied the reaction by infra-red chemiluminescence, obtaining H atoms by a discharge through pure H_2 at 667 mPa pressure, and adding Cl_2O in excess downstream. [HCl] and [HClO] were monitored by i.r. emission spectroscopy at 1.7–2.1 and 2.75–2.90 μm, respectively. Both HCl and HClO were observed in vibrationally excited states, which led the authors to the conclusion that both reactions were occurring. A parallel study of reaction 2 showed that the HCl emission intensity from reaction 1b was twice that from reaction 2 under identical conditions, therefore $k_{1b} \cong 2k_2$.

$$H + Cl_2 \rightarrow HCl + Cl \qquad (2)$$

Taking k_2 from [2] gave $k_{1b} = 4 \times 10^{12}$ cm^3 mol^{-1} s^{-1} (7), i.e., $1/4k_1$ as determined in [4], giving $k_{1a} = 9 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 300 K. In a later paper [8] they take $k_2 = 1 \times 10^{13}$ cm^3 mol^{-1} s^{-1} [1,3,5,6] to give $k_{1b} = 2 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, i.e., greater than the value of Freeman and Phillips for $k_{1a} + k_{1b}$. Using our value for k_2, (section B6) we obtain $k_{1b} = 2.4 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 300 K.

More work is required on the individual reaction channels 1a and 1b. At this stage we can make no recommendation for k_1.

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Miscellaneous Reactions Involving Cl/N Species

B28 N + Cl_2 → NCl + Cl

Phillips [1,2] has twice investigated the reaction between nitrogen atoms and chlorine, in both cases assuming a straightforward mechanism of reaction 1 followed by reaction 2 and recombination of chlorine atoms heterogeneously.

$$N + Cl_2 \rightarrow NCl + Cl \qquad (1)$$

$$N + NCl \rightarrow N_2 + Cl \qquad (2)$$

In both cases active nitrogen was produced from a discharge through 100% N_2, a pressure of 400 Pa being quoted in [2]. Cl_2 was added downstream, and the nitrogen afterglow followed at 625 nm. No other emission was observed, and rate constants $k_1 = 1 \times 10^9$ (1) and 1.8×10^8 (2) cm^3 mol^{-1} s^{-1} were quoted at 293 K. In the later study, work was carried out over an extended temperature range to give $k_1 = 4.7 \times 10^9 \exp(-950/T)$ cm^3 mol^{-1} s^{-1} in the range 291–329 K. A correction was applied here to account for wall recombination of Cl atoms, which the authors believe accounts for the lower values of k_1.

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[1] Raxworthy, K. S., and Phillips, L. F., Can. J. Chem. **42**, 2928 (1964).

[2] Grigor, M. R., and Phillips, L. F., 11th Combustion Symp. 1171 (1967).

B29 NCl + Cl_2 → NCl_2 + Cl

There has been just one determination of the rate constant k_1, by Combourieu et al. [2].

$$NCl + Cl_2 \rightarrow NCl_2 + Cl \qquad (1)$$

They used a discharge flow system, producing Cl atoms in a discharge through dilute Cl_2/He mixtures at 26.7–133 Pa pressure, and adding N_3Cl downstream so that $[Cl] >> [N_3Cl]$. The reaction was followed mass spectrometrically. N_3Cl was consumed by the initial reaction 2, and N_3 by the subsequent reactions 3 and 4.

$$Cl + N_3Cl \rightarrow N_3 + Cl_2 \qquad (2)$$

$$Cl + N_3 \rightarrow NCl + N_2 \qquad (3)$$

$$N_3 + N_3 \rightarrow 3N_2 \qquad (4)$$

At this point, the decay of [NCl] could be followed, with NCl_2 detected as a product. Authors believed the initial second order decay to be due to reaction 5, followed by a first order decay at lower [NCl] due to reaction 1, from which k_1 could be determined.

$$NCl + NCl \rightarrow N_2 + Cl_2 \qquad (5)$$

They give $k_1=6.0\times10^{11}$ cm^3 mol^{-1} s^{-1} at 300 K. This may be compared with a value of $k_{-1}=2.3\times10^{10}$ cm^3 mol^{-1} s^{-1} at 300 K obtained by Clark and Clyne [1], who noted no complications due to reaction 1, suggesting that any NCl was rapidly removed by reaction 5, for which they gave $k_5\geqslant2.0\times10^{12}$ cm^3 mol^{-1} s^{-1}. In the absence of reliable thermodynamic data for NCl, it is not possible to comment further on these results.

References

[1] Clark, T. C., and Clyne, M. A. A., Trans. Faraday Soc. **66**, 372 (1970).

[2] Combourieu, J., Le Bras, G., Poulet, G., and Jourdain, J. L., 16th Combustion Symp. 863 (1977).

B30 $Cl + NCl_2 \rightarrow NCl + Cl_2$

In their initial study of NCl_2 decay, Clark and Clyne [1] noticed the apparent rate of decay was accelerated if excess Cl was produced in the initial discharge. This they claimed was consistent with the occurrence of reaction 1, and they performed experiments in which $[NCl_3]/[Cl]\sim0.1$, to obtain $k_1\cong3\times10^{10}$ cm^3 mol^{-1} s^{-1} at 298 K.

$$Cl + NCl_2 \rightarrow NCl + Cl_2; \quad (1)$$

thermodynamic data unavailable for NCl.

In the subsequent work using radical freezing [2,3] they were able to monitor $[NCl_2]$ more accurately, and made a more comprehensive study of reaction 1. Under similar conditions they obtained $k_1=4.0\times10^{12}\exp(-1550/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 259–373 K, agreeing well with the earlier work at 298 K.

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[1] Clark, T. C., and Clyne, M. A. A., Trans. Faraday Soc. **65**, 2994 (1969).

[2] Clark, T. C., and Clyne, M. A. A., 12th Combustion Symp. 333 (1969).

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B31 $NCl_2 + NCl_2 \rightarrow$ products

Dichloroamino radicals are produced during the decomposition of NCl_3, whether thermally [1] or during photolysis [2]. The mechanism of their decay is uncertain. Unlike NF_2 (section A15), they do not undergo a third order combination reaction [3].

Clark and Clyne [3,4,5], made an extensive study of the decay of NCl_2 radicals following their formation in a discharge flow system. In the initial study [3], a discharge was passed through a 5% Cl_2/Ar mixture at 133–420 Pa, and NCl_3/Ar mixtures added so that $[NCl_3]\cong[Cl]$. NCl_2 radicals were produced by the fast reaction 2. Their decay

$$Cl + NCl_3 \rightarrow NCl_2 + Cl_2 \quad (2)$$

was followed by u.v. absorption spectrometry at 299 nm, and also mass spectroscopically. It was found to be second order in NCl_2, giving $k_1=5.5\times10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K

$$NCl_2 + NCl_2 \rightarrow \text{products} \quad (1)$$

In a more extensive study [4,5], they employed the "radical freeze" method to measure smaller $[NCl_2]$ than before, by adding excess O atoms. These rapidly produce NO, which can be estimated from the air afterglow intensity.

$$O + NCl_2 \rightarrow NCl + ClO \quad (3)$$

$$O + NCl \rightarrow NO + Cl \quad (4)$$

A similar flow system was used to that in [3], with total pressures 80–307 Pa. Excess Cl atoms were removed by nickel wire downstream; this had no effect on reaction 1. $[NCl_2]$ decay was studied over the temperature range 259–373 K, giving the expression $k_1=5.0\times10^{11}\exp(0\pm200/T)$ cm^3 mol^{-1} s^{-1}, in good agreement with the earlier value at 298 K.

The mechanism of decomposition is still uncertain. Clark and Clyne [5] postulate an intermediate N_2Cl_x, decomposing to N_2 and Cl atoms, but no information is available on the value of x.

References

[1] Griffiths, J. G. A., and Norrish, R. G. W., Proc. Roy. Soc. **A130**, 591 (1931).

[2] Briggs, A. G., and Norrish, R. G. W., Proc. Roy. Soc. **A278**, 27 (1964).

[3] Clark, T. C., and Clyne, M. A. A., Trans. Faraday Soc. **65**, 2994 (1969).

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B32 $Cl + N_3Cl \rightarrow N_3 + Cl_2$

Chlorine atoms are readily abstracted from chlorine azide N_3Cl by a variety of attacking species. A preliminary measurement of k_1 was made by Clark and Clyne [1], using a discharge flow system. Cl atoms were produced in a discharge through Cl_2/Ar mixtures at 267–533 Pa pressure, N_3Cl added downstream so that $[Cl]\cong[N_3Cl]$. $[N_3]$ was monitored by u.v. absorption spectroscopy at 270 nm and a lower limit of $k_1>5.0\times10^{11}$ cm^3 mol^{-1} s^{-1} deduced at 300 K, implying $E_1<12.5$ kJ mol^{-1} (3 kcal mol^{-1}). Subsequent experiments with [Cl] increased gave little decrease in $[N_3]$, and the authors gave $k_1/k_2>10$.

$$Cl + N_3Cl \rightarrow N_3 + Cl_2; \quad (1)$$

thermodynamic data unavailable for N_3,N_3Cl.

$$Cl + N_3 \rightarrow NCl + N_2 \quad (2)$$

Recently the system has been re-investigated by Combourieu et al. [2], also using a discharge flow system. Cl atoms were produced in a discharge through a dilute Cl_2/He mixture at 26.7–133 Pa pressure, N_3Cl added downstream so that $[Cl]>>[N_3Cl]$. The reaction was monitored mass spectrometrically, and the rate constant k_1 derived from $[N_3Cl]$ disappearance. $[N_3]$ was not detected. Authors give $k_1=1.4\times10^{13}\exp(-550/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 300–657 K, above Clyne's lower limit at 298 K.

References

[1] Clark, T. C., and Clyne, M. A. A., Trans. Faraday Soc. **66**, 877 (1970).

[2] Combourieu, J., Le Bras, G., Poulet, G., and Jourdain, J. L., 16th Combustion Symp. 863 (1977).

B33 $NO + ClO \rightarrow Cl + NO_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-37.12	-32.20	4.821
300	-37.13	-32.21	4.781
500	-37.25	-32.60	2.188
1000	-35.86	-30.77	0.265
1500	-34.10	-29.34	-0.334
2000	-32.48	-28.40	-0.635
2500	-31.04	-27.76	-0.801
3000	-29.79	-27.31	-0.901
3500	-28.73	-26.97	-0.981
4000	-27.84	-26.74	-1.034
4500	-27.13	-26.57	-1.073
5000	-26.59	-26.45	-1.107

RECOMMENDED RATE CONSTANT

$k = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}

$= 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}

Temperature: 298 K

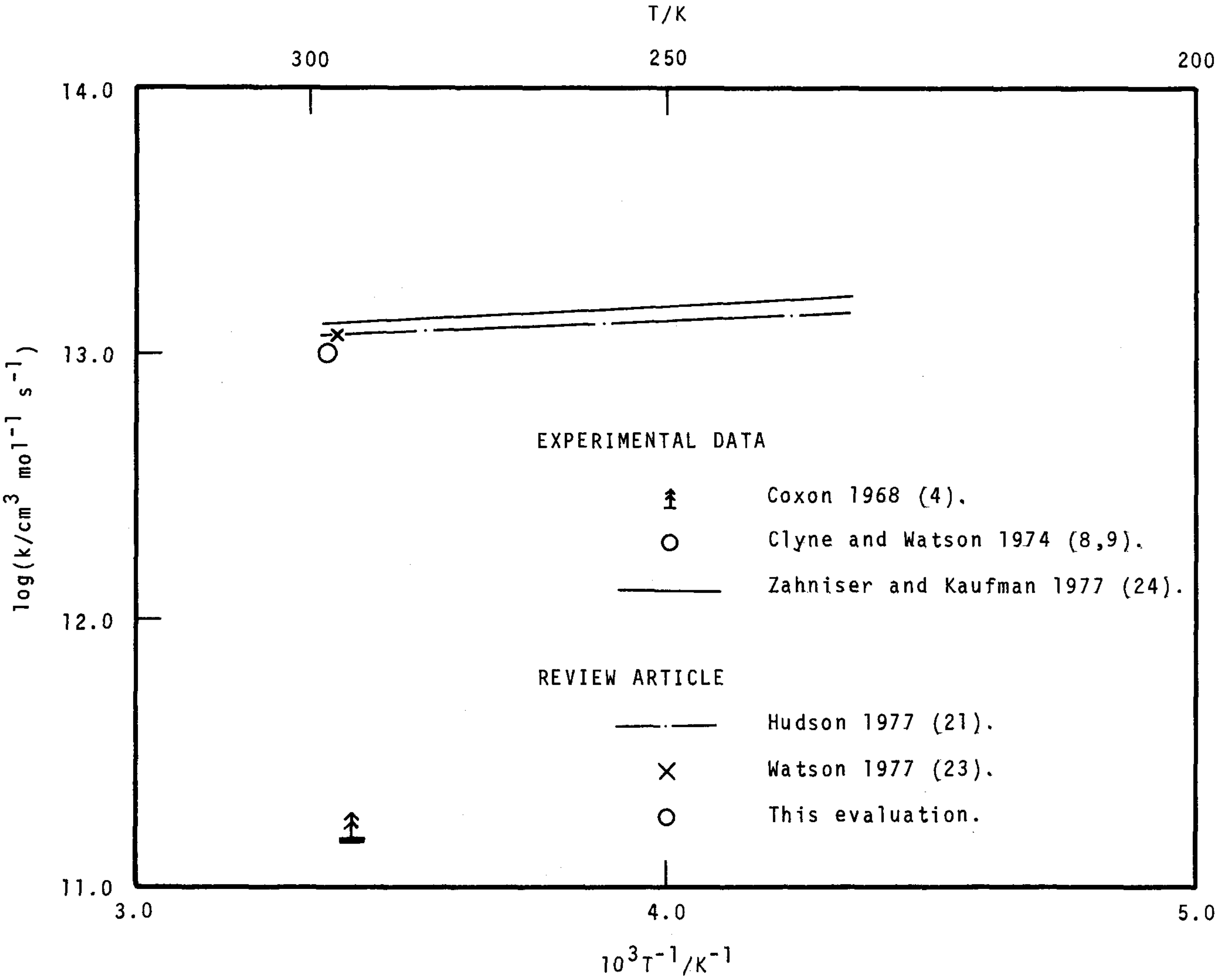
Suggested Error Limits for Calculated Rate Constant: A factor of 2.

Note: this value is that of CLYNE and WATSON (9).

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	298	Discharge flow system. Cl_2/Ar mixtures at total pressures of 111-148 Pa. ClO_2 added downstream so that $[Cl] \gg [ClO_2]$, NO/N_2 mixtures added further downstream at 72.0-261 Pa. [ClO] monitored by uv absorption spectroscopy at 277.2 nm. CLYNE and COXON 1966 (1)	Reaction 1 found to be fast and stoichiometric. Authors made a correction for the effects of reaction 2, using their own value of k_2 determined in the same study, but assumed all other reactions to be too slow to be important. $NO + ClO \rightarrow Cl + NO_2$ 1 $ClO + ClO \rightarrow$ products 2 However, they only determined ε_{ClO}, and no rate constant is reported.

$NO + ClO \rightarrow Cl + NO_2$



$NO + ClO \rightarrow Cl + NO_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$\geq 1.5 \times 10^{11}$	294	Flow system. ClO_2/Ar mixtures at a total pressure of 186 Pa. NO added in excess downstream. [ClO], [ClO_2] monitored by uv absorption spectroscopy at 277.6 and 351.5 nm respectively. COXON 1968 (4)	Under conditions of [NO] excess, reaction 1 rapidly follows reaction 3. $NO + ClO_2 \rightarrow ClO + NO_2$ 3 Reaction 4 proved to be a complicating factor, and a piece of nickel wire was inserted around the mixing jet to remove Cl atoms. $Cl + ClO_2 \rightarrow ClO + ClO$ 4 From the variation in the [ClO_2]:[ClO] ratio along the flow tube, author obtained $k_1/k_3=0.30$ at 294 K. Using his own lower limit for k_3 determined in the same study under conditions of [ClO_2] excess, he obtained the quoted lower limit for k_1. Quoted by (3,5,6,11,23).
1.0×10^{13}	298	Discharge flow system. Cl_2/Ar mixtures, no details of pressures given. Trace amounts of ClO_2 added downstream, NO added in excess further downstream. [ClO] monitored by mass spectrometry. WATSON 1973 (8) and CLYNE and WATSON 1974 (9)	Small quantities of ClO radicals ($\sim 10^{-12}$ mol cm^{-3}) produced by reaction 4, and reaction 1 studied under normal pseudo-first order conditions. Quoted by (7, 10,11,12,13,14,15,16,17,19,22). Used by (23).
$6.81 \times 10^{12} exp(200/T)$	230-298	Discharge flow system. Cl_2 (<0.01%)/He mixtures at total pressures of 267-533 Pa. O_3 added downstream, NO further downstream. [Cl], [ClO] monitored by resonance fluorescence. No further details available. ZAHNISER and KAUFMAN 1977 (24)	ClO radicals produced by reaction 5, rapidly decaying via reaction 1. $Cl + O_3 \rightarrow ClO + O_2$ 5 $ClO + NO \rightarrow Cl + NO_2$ 1 Authors obtained ratio $k_1/k_5=0.52 exp(373/T)$ over the quoted temperature range, and used their own expression for k_5 (20) to give the quoted expression for k_1. Using our expression for k_5 (This Vol., section B10) we obtain $k_1= 7.7 \times 10^{12} exp(163/T)$ cm^3 mol^{-1} s^{-1}, in reasonable agreement with KAUFMAN. Original data used by (23).

$NO + ClO \rightarrow Cl + NO_2$

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		Review of rate constants of ClO_x of atmospheric interest. WATSON 1974 (11)	Quotes (4 and 9).
$6.02x10^{12}exp(200/T)$	230-298	Review. Recommended value, with k_1 at 298 K as average of values of (9 and 24), and temperature dependence of (24). HUDSON 1977 (21)	Earlier, tentative value of 1.33 $x10^{13}$ cm^3 mol^{-1} s^{-1} (298 K) also quoted.
$1.1x10^{13}$	298	Preferred value. WATSON 1977 (23)	Combines results of (9 and 24). Also quotes (4).

Discussion

Reaction 1 has been shown to be fast and stoichiometric [1] and like reaction 6, is a useful titration reaction for ClO radicals [2,3].

$$NO + ClO \rightarrow Cl + NO_2 \qquad (1)$$

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

It is important in stratospheric chemistry, where it provides the link between the NO_x and ClO_x cycles for removal of ozone [9,10,12,14].

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (5)$$

$$NO + ClO \rightarrow Cl + NO_2 \qquad (1)$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (7)$$

However, it is believed that the importance is limited to altitudes <15 km [10], where [O] is small, since reaction 7 is rate controlling and $k_7 << k_6$. Another complication could be reaction 8, whose importance in stratospheric chemistry has not yet been clearly established, but there is evidence to suggest that it may play a key role in ClO removal [18].

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (8)$$

The rate of reaction 1 is little better known than its exact role in stratospheric chemistry. It is certainly fast, too fast for accurate measurements using conventional absorption spectrocopy [1,4]. The two recent determinations of k_1, detecting [ClO] by mass spectrometry [9] and resonance fluorescence [24] agree well at room temperature and the small negative activation energy suggested by Kaufman [24] is compatible with the fast rate.

In the absence of further data over an extended temperature range, we can only recommend the value $k_1 = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 298 K, with error limits of a factor of 2.

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Note Added in Proof

In a recently published paper Leu and De More [J. Phys. Chem. **82**, 2049 (1978)] report new measurements of the rate constant for reaction (1).

$$NO + ClO \rightarrow Cl + NO_2 \qquad (1)$$

ClO was produced by the addition of trace amounts of O_3 to Cl atoms generated in a Cl_2-discharge flow system, and NO was introduced through a moveable inlet downstream. The carrier gas was He and the total pressure was probably in the range 1–3 mm Hg (130–400 Pa). The pseudo-first-order decay of ClO was followed by mass spectrometry for various initial [NO]/[ClO] ratios greater than 10. Interference from secondary reactions was thought to be negligible on the basis of their published rate constants. Values of k_1 were obtained as follows:

$k_1/cm^3\ mol^{-1}\ s^{-1}$	T/K
$(1.23\pm0.04)\times10^{13}$	226.7
$(1.17\pm0.04)\times10^{13}$	231.0
$(1.26\pm0.06)\times10^{13}$	234.7
$(1.10\pm0.11)\times10^{13}$	265.6
$(9.2\pm0.6)\times10^{12}$	299.0
$(7.9\pm0.4)\times10^{12}$	360.7
$(7.5\pm0.4)\times10^{12}$	392.0
$(6.9\pm0.2)\times10^{12}$	415.4

This set of data was expressed as $k_1=(3.45\pm0.11)\times10^{12}\ \exp[(296\pm20)/T]$.

This work is in good agreement with that of [9] and the expression agrees within a factor of 1.4 with that of [24]. It also confirms the negative temperature dependence observed by the latter. In view of this we feel able to make the revised recommendation, $k_1=4.9\times10^{12}\ \exp(250/T)\ cm^3\ mol^{-1}\ s^{-1}$ with error limits of ±50% over the temperature range 220–420 K.

B34 $NOCl + M \rightarrow NO + Cl + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	159.83	114.11	-22.040	-26.429
300	159.84	113.98	-21.867	-26.258
500	160.88	116.89	-10.701	-15.314
1000	161.91	118.45	- 2.271	- 7.185
1500	161.82	118.39	0.549	- 4.542
2000	161.09	117.98	1.955	- 3.260
2500	159.87	117.44	2.793	- 2.519
3000	158.23	116.84	3.348	- 2.043
3500	156.21	116.22	3.739	- 1.719
4000	153.83	115.58	4.029	- 1.487
4500	151.08	114.90	4.250	- 1.318
5000	147.99	114.29	4.423	- 1.190

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$
$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 1.3 \times 10^{15} \exp(-16\,100/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)
$= 2.2 \times 10^{-9} \exp(-16\,100/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar)

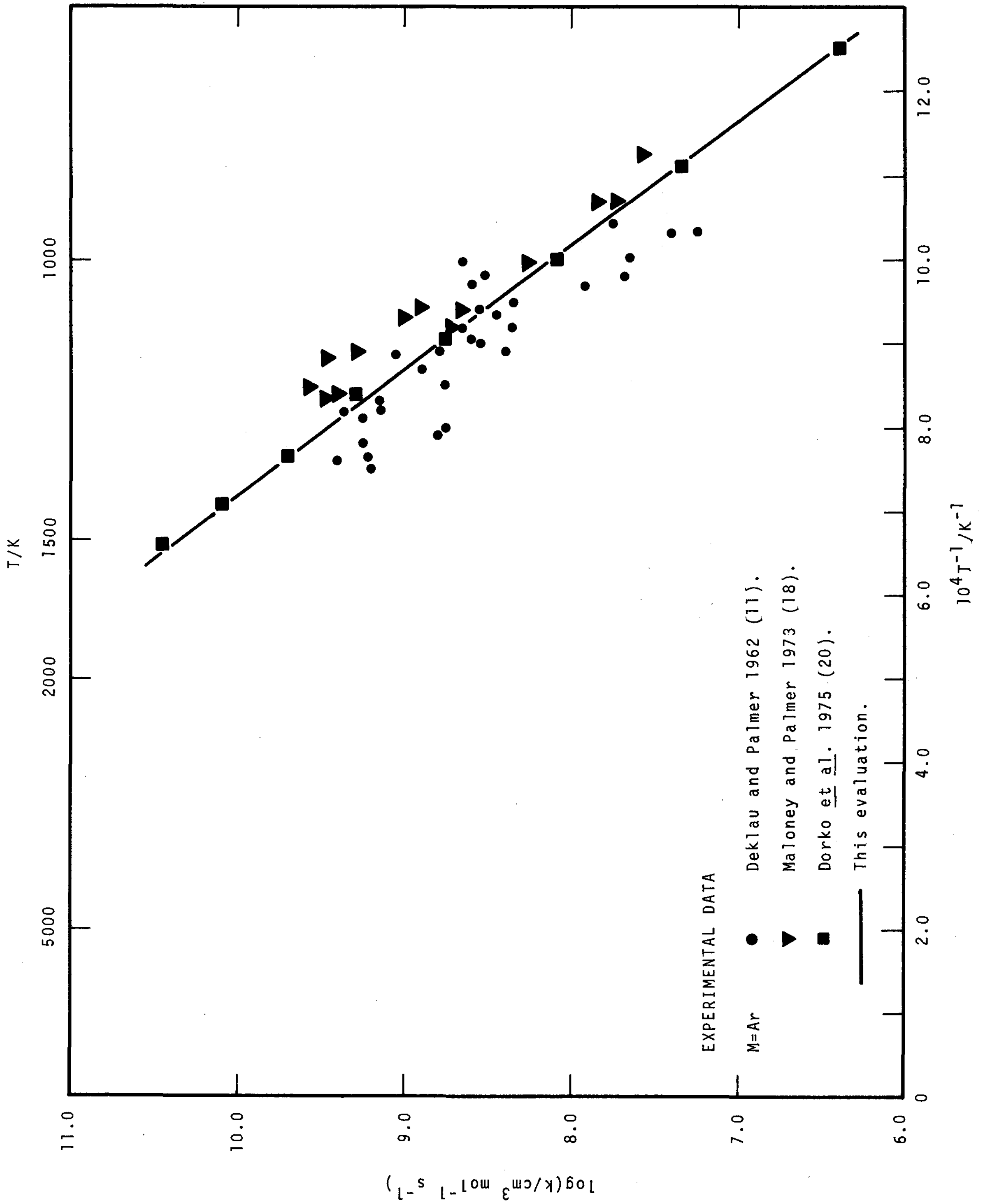
Temperature Range: 800-1500 K.

Suggested Error Limits for Calculated Rate Constant: a factor of two over the entire temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 15.11 \pm 0.30$
$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -8.66 \pm 0.30$
$E/J\ mol^{-1} = 134\ 000 \pm 6\ 000$
$E/cal\ mol^{-1} = 32\ 000 \pm 1\ 500$

Note: Expression is that of DORKO et al. (20). Expression for k^o (M=NOCl) given in the Discussion.

$NOCl + M \rightarrow NO + Cl + M$

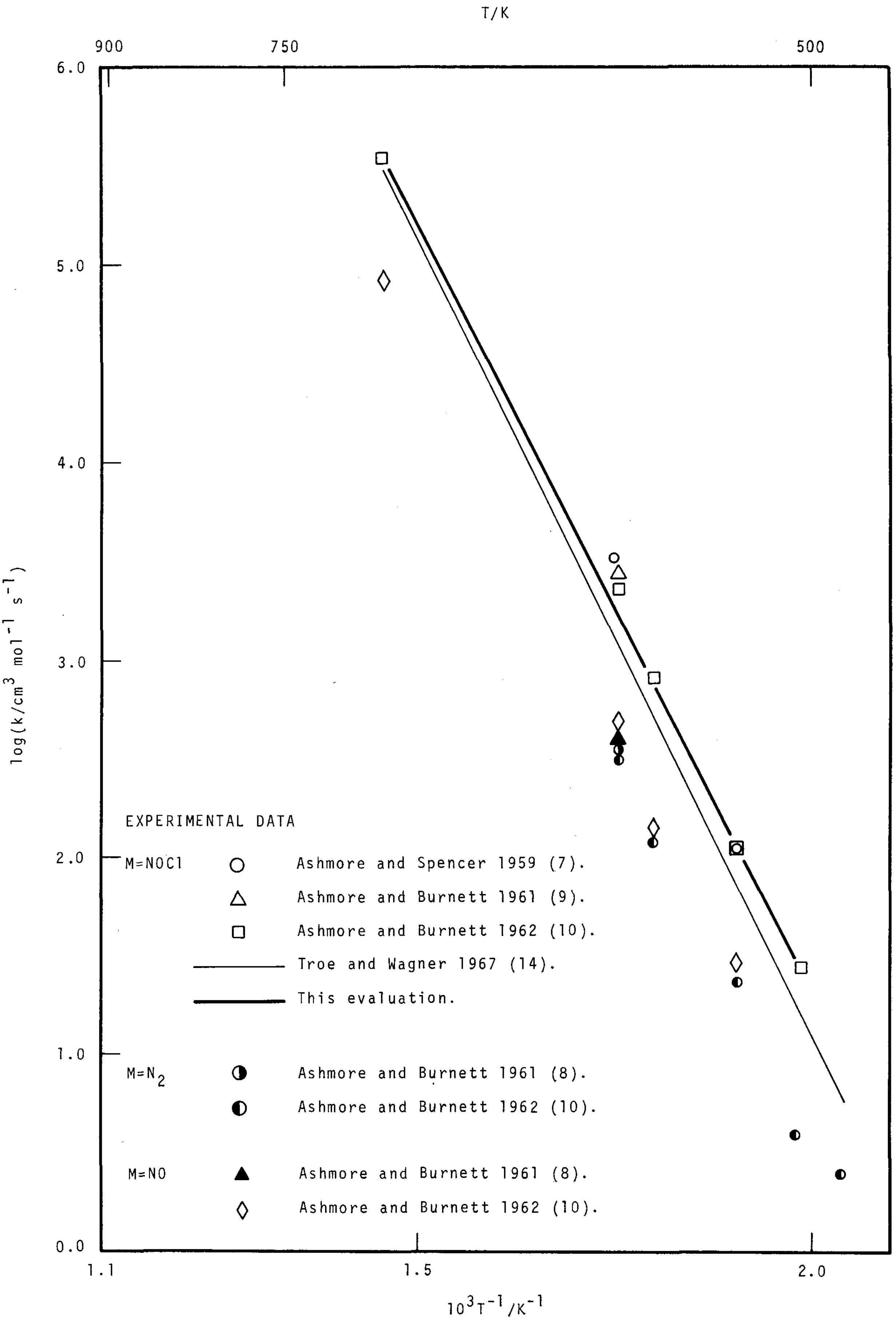


$NOCl + M \rightarrow NO + Cl + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o			
$(6.5\ \pm1.0\ )\times10^1$ M=CO_2	523	Static system. NOCl (0.53 -6.67 kPa) alone and with CO_2, Cl_2 or N_2O (0.53-30.7 kPa). Reaction followed manometrically. ASHMORE and SPENCER 1959 (7)	An overall rate constant for decomposition, k_o, was obtained, with $k_o = 2k_2+2k_1$. $NOCl + M \rightarrow NO + Cl + M$ 1 $2NOCl \rightleftharpoons 2NO + Cl_2$ 2,-2 After correcting for wall loss, authors used their own value of k_{-2} from this work to obtain values of k_1. They obtained the expressions $k_1(M{=}NOCl)=7.9\times10^{17}\exp(-19\ 100/T)$, $k_1(M{=}CO_2) = 2.0\times10^{17}\exp(-18\ 600/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (523-573 K). Used by (14). General expression for all third bodies $k_1 \approx 10^{17}\exp(-19\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$ quoted by (9).
$(1.46\pm0.15)\times10^3$ M=CO_2	573		
$(1.1\ \pm0.2\ )\times10^2$ M=NOCl	523		
$(3.2\ \pm0.2\ )\times10^3$ M=NOCl	573		
$(3.0\ \pm2.0\ )\times10^1$ M=Cl_2	523		
$(6.0\ \pm2.0\ )\times10^2$ M=Cl_2	573		
$(1.36\pm0.13)\times10^3$ M=N_2O	573		
$(2.75\pm0.27)\times10^3$ M=NOCl	573	Static system. NOCl (0.67 -11.9 kPa)/NO(0.26-9.53 kPa)/NO_2 (56.1-317.9 Pa)/N_2 (0.34-3.17 kPa) mixtures. Reaction followed manometrically, $[NO_2]$ monitored by absorption of light at 445-500 nm. ASHMORE and BURNETT 1961 (8)	When NO_2 was present, reaction 3 occurred, initiating a reaction chain involving NO_2Cl. $NOCl + NO_2 \rightarrow NO_2Cl + NO$ 3 It was thus not possible to determine $k_1(M{=}NO_2)$ directly and the value given is an upper limit determined by the authors from the expression $k_1(M{=}NO_2)+2k_3k_4(M{=}NO)/k_{-3}=(2.13\pm0.43)\times10^4$ $cm^3\ mol^{-1}\ s^{-1}$ at 573 K. $NO_2Cl + M \rightarrow NO_2 + Cl + M$ 4 In experiments involving pure NOCl, some deviation from second-order kinetics was noted at pressures above 2.5 kPa, believed due to the reaction entering its first-order region. The value of $k_1(M{=}NOCl)$ given here is the limiting second-order rate constant.
$(4.0\ \pm0.6\ )\times10^2$ M=NO	573		
$(3.6\ \pm0.4\ )\times10^2$ M=N_2	573		
$\leqslant 10^4$ M=NO_2	573		
2.5×10^0 M=N_2	493	Static system. NOCl alone, or with NO, N_2 or H_2. No details of pressures given. Reaction followed as in (8). ASHMORE and BURNETT 1962 (10)	The overall rate constant $k_o=2k_1+2k_2$ was first measured, and the value of k_1 (M=NOCl) determined using k_2 from (1). Values of k_1 (M=others) were then determined by comparison. Transition from first to second order kinetics was noted for M=NOCl at pressures of about 6 kPa.
4.0×10^0 M=N_2	503		
2.5×10^1 M=N_2	523		
1.4×10^2 M=N_2	553		
3.2×10^2 M=N_2	573		
3.0×10^1 M=NO	523		
1.5×10^2 M=NO	553		
4.3×10^2 M=NO	573		
9.1×10^4 M=NO	684		
$1.0\times10^{16}\exp(-17\ 550/T)$ M=H_2	573-684		

$NOCl + M \rightarrow NO + Cl + M$



$NOCl + M \rightarrow NO + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
2.8×10^{1}	M=NOCl	503	ASHMORE and BURNETT 1962 (10) continued.	The following expressions were derived for k_1 from the data given:- $k_1(M=N_2)=1.8\times10^{16}\exp(-18\ 000/T)$ cm^3 mol^{-1} s^{-1} (T=473-573 K), $k_1(M=NO)=2.8\times10^{16}\exp(-18\ 100/T)$ cm^3 mol^{-1} s^{-1} (T=523-684 K), and $k_1(M=NOCl)=6.9\times10^{16}\exp(-17\ 800/T)$ cm^3 mol^{-1} s^{-1} (T=523-684 K). Quoted by (12,13,18). Misquoted by (19). Used by (14).
1.2×10^{2}		523		
7.9×10^{2}		553		
2.4×10^{3}		573		
3.6×10^{5}		684		
6.0×10^{7}	M=Ar	964	Shock tube study. NOCl (1.33-4.0 kPa) alone and diluted with Ar to a total pressure of 6.67-26.7 kPa. [NOCl] followed by absorption at 385, 436 and 546 nm. DEKLAU and PALMER 1962 (11)	Authors found that simple Arrhenius expression gave poor agreement between low and high temperature data, and applied Hinshelwood theory instead. This gave good results for k_1 (M=Ar), but there were still discrepancies in k_1(M=NOCl), $NOCl + M \rightarrow NO + Cl + M$ 1 E_1 was assumed to be the bond dissociation energy = 155.5 kJ mol^{-1} (37.2 kcal mol^{-1}). Taking one point from this study, and one from (7), Hinshelwood theory gives $k_1(M=NOCl)=1.1\times10^{9}T^{0.5}(18\ 700/T)^{7.01}(1/\Gamma(8.01))\exp(-18\ 700/T)$ cm^3 mol^{-1} s^{-1}, $k_1(M=Ar)=1.5\times10^{11}T^{0.5}(18\ 700/T)^{3.43}(1/\Gamma(4.43))\exp(-18\ 700/T)$ cm^3 mol^{-1} s^{-1}. Applying an Arrhenius expression to the results for M=Ar, we obtain $k_1=3.8\times10^{17}\exp(-23\ 100/T)$ cm^3 mol^{-1} s^{-1}. Quoted by (10,12,13,15,18,19). Value of k_1 at 1100 K given as 4×10^{8} cm^3 mol^{-1} s^{-1} by (14).
1.8×10^{7}		967		
2.4×10^{7}		975		
4.5×10^{7}		1000		
4.7×10^{8}		1003		
3.4×10^{8}		1018		
4.6×10^{7}		1025		
3.8×10^{8}		1029		
8.5×10^{7}		1035		
2.3×10^{8}		1058		
3.9×10^{8}		1063		
2.8×10^{8}		1066		
2.3×10^{8}		1088		
4.5×10^{8}		1090		
4.2×10^{8}		1098		
3.6×10^{8}		1110		
2.5×10^{8}		1119		
6.0×10^{8}		1125		
1.2×10^{9}		1131		
8.0×10^{8}		1144		
5.5×10^{8}		1171		
1.4×10^{9}		1205		
1.4×10^{9}		1212		
2.3×10^{9}		1215		
1.8×10^{9}		1242		
5.5×10^{9}		1250		
6.0×10^{8}		1269		
1.8×10^{9}		1282		
1.7×10^{9}		1312		
2.4×10^{9}		1325		
1.6×10^{9}		1332		
3.7×10^{7}	M=Ar	890	Shock tube study. NOCl (0.51-2.0%)/Ar mixtures at 53.7-92.9 kPa pressure. Incident shocks. [NOCl] monitored by uv spectroscopy at 270 nm.	Bimolecular decomposition ignored. Over the given temperature range, authors obtain $k_1 = 8.9\times10^{15}\exp(-17\ 500/T)$ cm^3 mol^{-1} s^{-1}. Combining their results with those of (7) they obtain
5.0×10^{7}		932		
5.9×10^{7}		935		
1.8×10^{8}		1007		
4.6×10^{8}		1065		
8.0×10^{8}		1065		
1.0×10^{9}		1074		
5.4×10^{8}		1081		
2.0×10^{9}		1123		

$NOCl + M \rightarrow NO + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.8×10^{9}	1134	MALONEY and PALMER 1973 (18)	$k_1=1.8\times10^{16}\exp(-18\ 300/T)\ cm^3\ mol^{-1}\ s^{-1}$. Using both sets of data, they also produced an RRK calculation which gives a good fit to both, $k_1=1.5\times10^{13}T^{0.5}(1/(1.5)!)(18\ 800/T)^{1.5}\exp(-18\ 800/T)\ cm^3\ mol^{-1}\ s^{-1}$, where the N-Cl bond dissociation energy is 156 kJ mol^{-1} (37.3 kcal mol^{-1}) (16). Used by (21).
3.8×10^{9}	1176		
2.7×10^{9}	1188		
3.1×10^{9}	1193		
2.3×10^{6} M=Ar	800	Shock tube study. NOCl (0.1 and 1%)/Ar mixtures at 1-10 atm. (101-1010 kPa) total pressure. Reflected shocks. Ir emission from NOCl followed at 4.69 μm. DORKO, GRIMM, SCHELLER and MUELLER 1975 (20)	Authors found no dependence of the unimolecular rate constant on [NOCl] and thus ignored any contribution from reaction 2, considering only reactions 1 and 5. $NOCl + M \rightarrow NO + Cl + M$ 1 $NOCl + NOCl \rightarrow 2NO + Cl_2$ 2 $NOCl + Cl \rightarrow NO + Cl_2$ 5 Reaction 1 was found to be occurring in its low pressure region, in good agreement with theory (2,17). Using a Lindemann-Hinshelwood approximation, they calculated $k_1=1.8\times10^{17}T^{-0.5}\exp(-19\ 000/T)\ cm^3\ mol^{-1}\ s^{-1}$, giving good agreement with the experimental data, particularly at higher temperatures. From the experimental data they obtained $k_1=1.3\times10^{15}\exp(-16\ 100/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the quoted temperature range. Used by (21).
2.2×10^{7}	900		
1.3×10^{8}	1000		
5.6×10^{8}	1100		
1.9×10^{9}	1200		
5.4×10^{9}	1300		
1.3×10^{10}	1400		
2.8×10^{10}	1500		
	1000	Theoretical study. TROE 1975 (21)	A value for the activation energy E_1=142 kJ mol^{-1} (34 kcal mol^{-1}) obtained at 1000 K by the author, using his own unimolecular reaction rate theory. Compared favourably with the average of (18 and 20).

$NOCl + M \rightarrow NO + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (s^{-1})	Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^∞			
$6.0\times10^{11}\exp(-19\ 000/T)$	523-593	Static system. H_2(6.67-9.33 kPa)/Cl_2(6.67-9.33 kPa)/NOCl (10.7-1330 Pa) /NO (13.3-133 Pa) mixtures alone or diluted with N_2, Ar (6.67-26.7 kPa). Reaction followed manometrically. ASHMORE and CHANMUGAM 1953 (4,5)	Authors found overall rate of removal of NOCl too fast to be accounted for by reaction 2. $NOCl + NOCl \rightarrow 2NO + Cl_2$ 2 They proposed reaction 1 as an initiation reaction in the combustion of H_2/Cl_2 mixtures, believing the reaction to be first order because the rate was unaffected by additions of inert gases. $NOCl \rightarrow NO + Cl$ 1 Allowing for the effects of reaction 2 by using the data of WADDINGTON and TOLMAN (1), and assuming E_1=159 kJ mol^{-1} (38 kcal mol^{-1}), the Cl-N= bond dissociation energy, they obtained the expression given, which gives at 573 K, $k_1=2.3\times10^{-3}$ s^{-1}. Quoted by (6). ASHMORE later questioned the validity of the results (7).
$2.3\times10^{10}\exp(-16\ 600/T)$	All	Theoretical study, based on statistical reaction rate theory. KECK and KALELKAR 1968 (15)	Activation energy low for first order reaction, as with same authors' determination of the activation energy for NO_2Cl decomposition (This Vol., section B47) $k_1^\infty=6.3\times10^3$ s^{-1} at 1100 K, in good agreement with first order rate constant derived from data of (11).

REVIEW ARTICLES

Rate Constant k (s^{-1})	Temperature (K)	Method and Reference	Comments
$6.3\times10^{16}\exp(-17\ 800/T)$ M=NOCl		Review of unimolecular thermal decomposition reactions. TROE and WAGNER 1967 (14)	Quoted expression is the average of data from (7 and 10). Authors also quote k_1 (M=Ar)=4×10^8 cm^3 mol^{-1} s^{-1} at 1100 K from data of (11), and relative third body efficiencies from (7 and 10). High collision efficiency of NOCl noted.
		Review of dissociation of triatomic molecules. TROE and WAGNER 1973 (19)	Authors quote (11), and attribute the expression $k_1(M=Ar)=6.9\times10^{15}\exp(-17\ 800/T)$ cm^3 mol^{-1} s^{-1} to (10) over the temperature range 473-684 K.

Discussion

The decomposition of nitrosyl chloride may proceed either by the atomic or molecular mechanisms (section B36).

$$NOCl + M \rightarrow NO + Cl + M \quad (1)$$

$$NOCl + Cl \rightarrow NO + Cl_2 \quad (5)$$

$$NOCl + NOCl \rightarrow 2NO + Cl_2 \quad (2)$$

Reaction 2 is important only at low temperatures and high concentrations of NOCl [4,18]. Under the conditions of the atomic mechanism, reaction 5 follows immediately after reaction 1 and then acts in competition. Reaction 5 is fast, but there is an early determination of k_5 [3] which has been used by most authors to correct apparent values of k_1 obtained.

The earliest studies of reaction 1 were made in static systems by Ashmore et al. [7,8,10]. Ashmore and Chanmugam [4] had already proposed that reaction 1 accounted for anomalous values in the study of the molecular decomposition at higher temperatures [1]. The results of all three determinations of k_1 are in good agreement for a range of third bodies, but there are insufficient data for $M = N_2$ or NO to make recommendations. However, for M=NOCl we recommend the expression of Ashmore and Burnett [10], $k_1 = 6.9 \times 10^{16} \exp(-17\,800/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 500–700 K, with error limits of ±50%.

The remaining determinations of k_1 [11,18,20] are all shock tube studies at ~1000 K with Ar as third body. The agreement is generally very good, and expressions derived extrapolate well back to the lower temperature data. Deklau and Palmer [11] also produced an expression for M=NOCl using Lindemann-Hinshelwood theory, but no details of experimental results are given. All authors made some attempt to fit unimolecular reaction rate theory to the results, with a reasonable degree of success, but not consistently over the whole temperature range. We recommend the expression of Dorko et al. $k_1 = 1.3 \times 10^{15} \exp(-16\,100/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 800–1500 K, with error limits of a factor of two.

Ashmore and Chanmugam [4,5] claimed to have measured the first-order rate constant at pressures as low as 6 kPa, but Ashmore and Spencer [7] later questioned the validity of the results obtained on the grounds that the effect of added N_2 had not been studied sufficiently, and showed that the reaction was second order at these pressures. Dorko et al. [20] found no evidence of a first-order contribution even at 10 atm. The case of NO_2Cl (section B47) suggests much higher pressures are required.

Relative Efficiencies of Third Bodies

M=NOCl	Cl_2	CO_2	NO_2	NO	N_2	H_2	N_2O	Temp. (K)	Ref.
1	0.19	0.46					0.42	573	(7)
1			≤3.64	0.15	0.13			573	(8)
1				0.18	0.13	0.21		573	(10)

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B35 $NO + Cl + M \rightarrow NOCl + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-159.83	-114.11	22.040	26.429
300	-159.84	-113.98	21.867	26.258
500	-160.88	-116.89	10.701	15.314
1000	-161.91	-118.45	2.271	7.185
1500	-161.82	-118.39	-0.549	4.542
2000	-161.09	-117.98	-1.955	3.260
2500	-159.87	-117.44	-2.793	2.519
3000	-158.23	-116.84	-3.348	2.043
3500	-156.21	-116.22	-3.739	1.719
4000	-153.83	-115.58	-4.029	1.487
4500	-151.08	-114.90	-4.250	1.318
5000	-147.99	-114.29	-4.423	1.190

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.006$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 5.3 \times 10^{15} \exp(520/T)\ cm^6\ mol^{-2}\ s^{-1}$ $(M=Cl_2)$

$= 1.5 \times 10^{-32} \exp(520/T)\ cm^6\ molecule^{-2}\ s^{-1}$ $(M=Cl_2)$

Temperature Range: 200-670 K.

Suggested Error Limits for Calculated Rate Constant: ±75% over the whole temperature range.

Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 15.72$ ±0.25

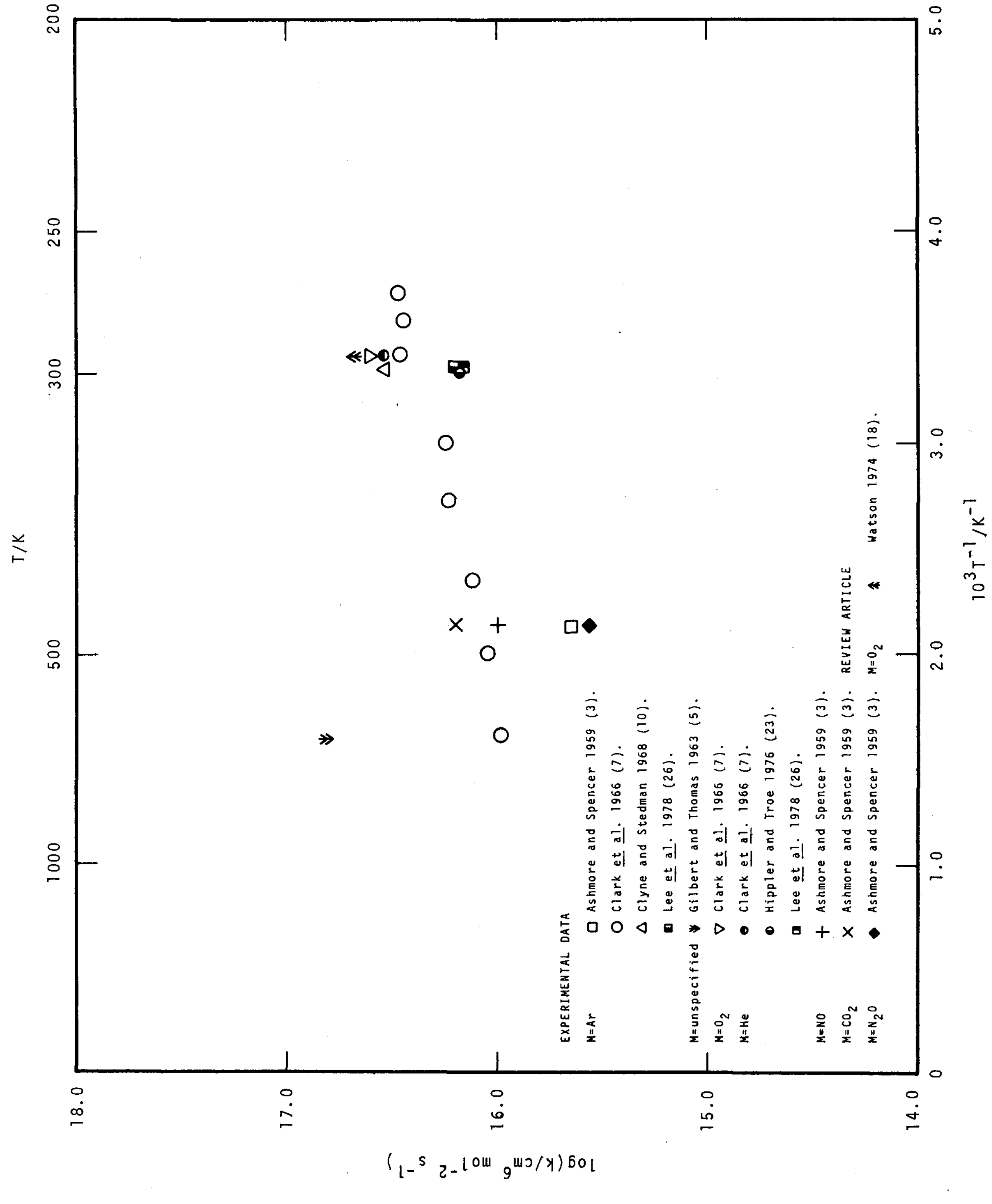
$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -31.82$ ±0.25

$E/J\ mol^{-1} = -4300$ ±620

$E/cal\ mol^{-1} = -1030$ ±150

Note: Expression is that of KONDRATIEV (14), re-stated in Arrhenius form.

NO + Cl + M → NOCl + M

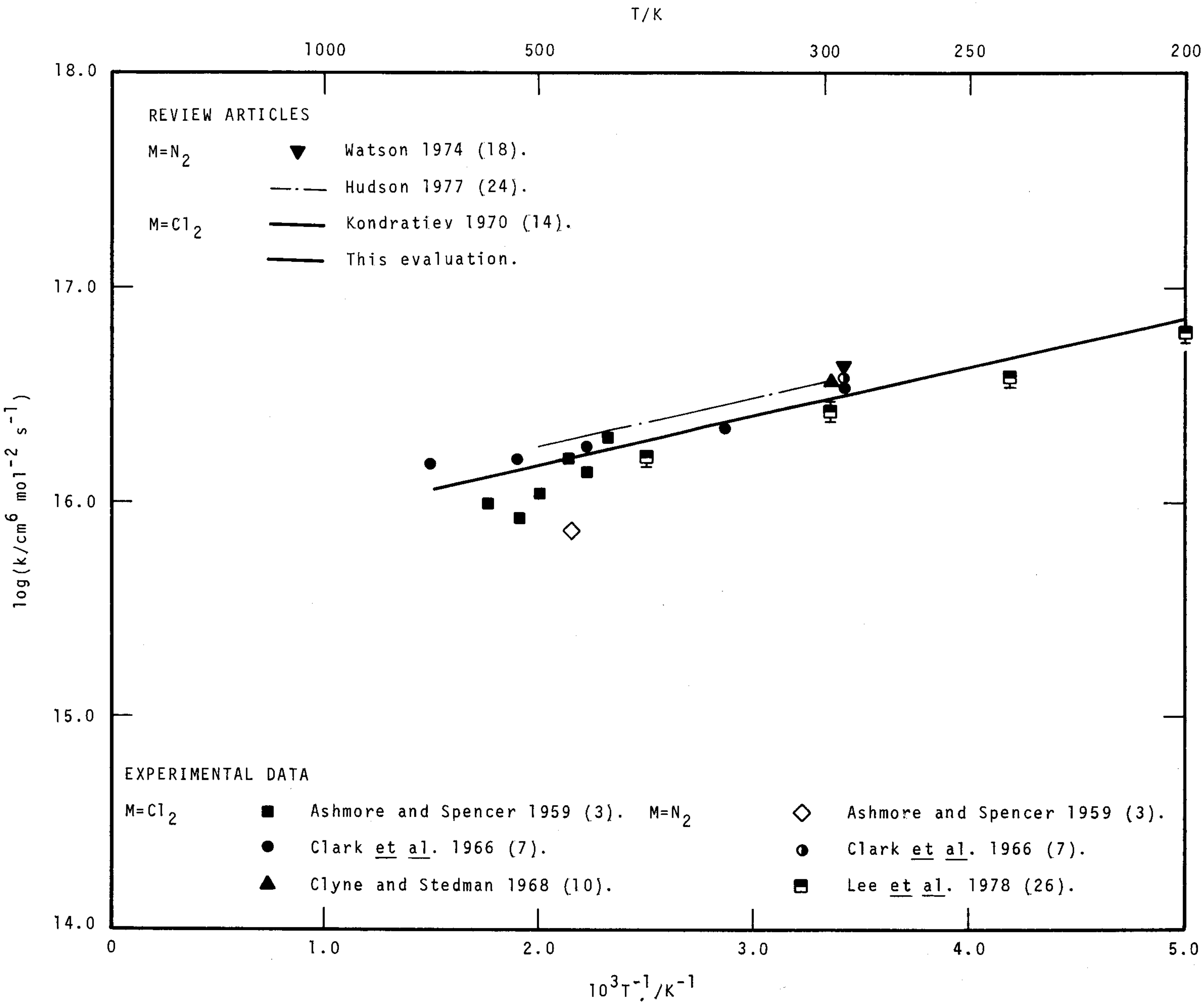

T/K
200
250
300
500
1000
$\log(k/\mathrm{cm^6\ mol^{-2}\ s^{-1}})$
18.0
17.0
16.0
15.0
14.0
$10^3T^{-1}/K^{-1}$
0
1.0
2.0
3.0
4.0
5.0
EXPERIMENTAL DATA
M=Ar □ Ashmore and Spencer 1959 (3).
○ Clark et al. 1966 (7).
△ Clyne and Stedman 1968 (10).
■ Lee et al. 1978 (26).
M=unspecified ⪢ Gilbert and Thomas 1963 (5).
M=O$_2$ ▽ Clark et al. 1966 (7).
M=He ● Clark et al. 1966 (7).
◐ Hippler and Troe 1976 (23).
■ Lee et al. 1978 (26).
M=NO + Ashmore and Spencer 1959 (3).
M=CO$_2$ × Ashmore and Spencer 1959 (3).
M=N$_2$O ◆ Ashmore and Spencer 1959 (3).
REVIEW ARTICLE
M=O$_2$ ⪡ Watson 1974 (18).

$NO + Cl + M \rightarrow NOCl + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.0×10^{16} 1.4×10^{16} 1.6×10^{16} 1.1×10^{16} 8.7×10^{15} 9.9×10^{15} } $M=Cl_2$ $(1.6\pm0.4)\times10^{16}$ $M=CO_2$ $(1.0\pm0.2)\times10^{16}$ $M=NO^2$ $(7.4\pm2.0)\times10^{15}$ $M=N_2$ $(4.5\pm1.0)\times10^{15}$ $M=Ar$ $(3.7\pm1.0)\times10^{15}$ $M=N_2O$	430 450 470 500 523 573 470 470 470 470 470	Static system. NO(0.80-6.67 kPa)/Cl_2 (0.53-13.3 kPa) mixtures alone and diluted with Ar, N_2, CO_2 or N_2O at 6.67-40.0 kPa pressure. Reaction followed manometrically. ASHMORE and SPENCER 1959 (3)	To obtain k_1, authors corrected for the effect of reactions 2 and -3 and the initiation reaction 3. $NO + NO + Cl_2 \rightarrow 2NOCl$ 2 $NO + Cl_2 \rightleftharpoons NOCl + Cl$ 3,-3 k_2, k_3 and k_{-3} were all taken from values determined by the authors in the same work. The values of k_1 ($M=Cl_2$) showed a large scatter with $[Cl_2]$, but no dependence on $[Cl_2]$. The errors were considered due to the approximations made in the calculations. Authors derived the expression k_1 ($M=Cl_2$) = 9.0×10^{14} exp(1320/T) $cm^6\ mol^{-2}\ s^{-1}$ over the temperature range 430-573 K. Quoted by (7,14,18,25).
$(6.6\pm2.0)\times10^{16}$ $M=NO+HCl+NOCl+NO_2$	627	Static system. HCl(29.4%)/NO_2 (21.6)%/NO mixture at total pressure of 73.6 kPa. Reaction followed manometrically. GILBERT and THOMAS 1963 (5)	System designed to study rate of reaction 4. Authors postulated that reactions 5,-3 and 1 would occur rapidly afterwards, reaction 1 leading to the pressure change in the system. $HCl + NO_2 \rightarrow HNO_2 + Cl$ 4 $HCl + HNO_2 \rightarrow H_2O + NOCl$ 5 $NOCl + Cl \rightarrow NO + Cl_2$ -3 $NO + Cl + M \rightarrow NOCl + M$ 1 Taking k_{-3} from (1) and k_4 from (4) they obtained a value of k_1, which they considered reasonable in view of the simple mechanism assumed.
3.0×10^{16} 2.8×10^{16} 2.9×10^{16} 1.8×10^{16} 1.7×10^{16} 1.3×10^{16} 1.1×10^{16} 9.8×10^{15} } $M=Ar$ 3.4×10^{16} 2.2×10^{16} 1.8×10^{16} 1.6×10^{16} 1.5×10^{16} } $M=Cl_2$ 3.5×10^{16} $M=N_2$ $(3.5\pm0.5)\times10^{16}$ $M=He$ $(3.9\pm0.5)\times10^{16}$ $M=O_2$ $(3.5\pm0.5)\times10^{16}$ $M=SF_6$	270 280 293 333 366 425 500 620 293 350 450 525 670 293 293 293 293	Discharge flow system. Cl_2 (0.02-100%)/He(Ar) mixtures at a total pressure of 133-667 Pa. NO and SF_6 added downstream. Cl/O_2 mixtures produced by adding Cl_2 to the products of an O_2 discharge, and Cl/N_2 mixtures by adding first NO and then Cl_2 to an N_2 discharge. Flow tube treated with H_3PO_4. [Cl] followed by monitoring the chlorine afterglow. CLARK and CLYNE 1966 (6) and	Flow tube H_3PO_4-coated to avoid catalytic recombination of Cl atoms by NOCl. Reaction 1 was assumed to be followed by the fast reaction -3. No evidence was found for the reverse reaction -1. $NO + Cl + M \rightleftharpoons NOCl + M$ 1,-1 Intensity of radiation from chlorine afterglow assumed $\propto[Cl]^2$ Authors obtained the following activation energies E_1=-4.6±0.4 kJ mol^{-1} (-1.1±0.1 kcal mol^{-1})(M=Ar),

$NO + Cl + M \rightarrow NOCl + M$



NO + Cl + M → NOCl + M

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature	Method and Reference	Comments
			CLARK, CLYNE and STEDMAN 1966 (7)	$E_1=-3.0\pm0.8$ kJ mol^{-1} (-0.7 ± 0.2 kcal mol^{-1}) (M=Cl_2), and -5.0 ± 0.8 kJ mol^{-1} (-1.2 ± 0.2 kcal mol^{-1}) (M=SF_6). From these data we obtain the following expressions:- $k_1(M=Ar)=3.6\times10^{15}\exp(550/T)$ $cm^6\ mol^{-2}\ s^{-1}$; $k_1(M=Cl_2)=1.0\times10^{16}\exp(350/T)$ $cm^6\ mol^{-2}\ s^{-1}$; $k_1(M=SF_6)=4.5\times10^{15}\exp(600/T)$ $cm^6\ mol^{-2}\ s^{-1}$, all over the temperature range 270-620 K. Used by (15,18). Quoted by (11, 14,17,20,21,25).
$(3.5\pm0.5)\times10^{16}$ $(3.4\pm0.5)\times10^{16}$	M=Cl_2 M=Ar	298 298	Discharge flow system. Cl_2, or Cl_2/Ar mixtures at 133-667 Pa pressure. NO added downstream. Flow tube H_3PO_4 coated. [Cl] followed by monitoring chlorine afterglow at 520 nm. CLYNE and STEDMAN 1968 (10)	Following work by the same authors on Cl atom recombination (9), it was found that the intensity of emission in the chlorine afterglow was not always $\propto[Cl]^2$, that in fact $I\propto[Cl]^n$ where n varied with wavelength. At 520 nm, n=2 for M=Cl_2 and 1.7 for M=Ar, hence the increase in the value k_1(M=Ar) over that in (7). Authors also suspect that the values given there for k_1(M=He, N_2, O_2 and SF_6) are all slightly too low. Quoted by (8, 13,16). Used by (25).
		298	Static photolysis of NOCl (38.7-143 Pa) in the presence of NO(77.4-1140 Pa) and inert gases (N_2 at 13.3-40.0 kPa, CF_4 at 16.0-80.0 kPa and He at 10.7-101 kPa). NOCl and Cl_2 frozen at 88 K, [Cl_2] determined by treatment with KI and ir analysis of I_3^- complex at 295 nm. TIMMONS and DARWENT 1969 (12)	At the high pressures used, authors found reaction 1 to be in its second-order region, and obtained the rate constant ratio k_{-3}/k_1. No details are given of the results for individual inert gases, but the results are averaged to give $k_{-3}/k_1=0.26\pm0.10$ at 298 K. NO + Cl + M → NOCl + M 1 NOCl + Cl → NO + Cl_2 -3
1.5×10^{16}	M=He	300	Flash photolysis study. Cl_2/He mixtures at total pressures of 1-100 atm. (0.10-10.1 MPa) in the presence of NO. [Cl_2] monitored by u.v. absorp-	Authors found rate of Cl_2 formation catalysed by NO, and attributed this to the rate determining reaction 1 and the fast reaction -3. Reaction third order up to 10 atm, when

$NO + Cl + M \rightarrow NOCl + M$

EXPERIMENTAL DATA -CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature	Method and Reference	Comments
		tion at 313 nm. HIPPLER and TROE 1976 (23)	fall off to second order began. Second order limit $k_1^{\infty}=3.0\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ obtained. Quoted by (22).
$\left.\begin{array}{l}(6.17\pm1.0)\times10^{16}\\(3.81\pm0.4)\times10^{16}\\(2.64\pm0.3)\times10^{16}\\(1.59\pm0.1)\times10^{16}\end{array}\right\}M=N_2$ $(1.60\pm0.1)\times10^{16}$ M=Ar $(1.49\pm0.1)\times10^{16}$ M=He	200 239 298 400 298 298	Flash photolysis flow study. $COCl_2/NO$ (18.3-800 μm Hg; 2.4-106.6 Pa)/N_2 (15-120 mm Hg; 2-16 kPa), or Ar (15-75 mm Hg; 2-10 kPa), or He (15-90 mm Hg; 2-12 kPa) mixtures photolysed at λ> 143 nm. Resonance fluorescence used to follow [Cl]. LEE, MICHAEL, PAYNE and STIEF 1978 (26)	Linear pseudo first order decays of [Cl], together with absence of dependence upon flash energy, indicated negligible contributions from secondary reactions. Data for $k_1(M=N_2)$ expressed as $(4.28\pm0.4)\times10^{15}\exp\{(532\pm20)/T\}$ $cm^6\ mol^{-2}\ s^{-1}$, or, equally acceptable, $1.40\times10^{21}\ T^{-1.91}$ $cm^6\ mol^{-2}\ s^{-1}$.

REVIEW ARTICLES

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature	Method and Reference	Comments
		Review of reactions of atoms and small free radicals. CLYNE 1968 (8).	Quotes (10) as updating the results in (7).
$4.8\times10^{19}T^{-(1.29\pm0.70)}$ $M=Cl_2$	290-620	Evaluation. KONDRATIEV 1970 (14)	Based on least-squares calculation of data from (3 and 7). Author gives error limits of two orders of magnitude.
4.0×10^{16} $M=N_2$ 4.7×10^{16} $M=O_2$	293 293	Estimated value. WATSON 1974 (18) and 1977 (25)	Author quotes (3) for $M=N_2$, and (7) for $M=N_2$ and O_2 as well as E_1 (M=Ar). The estimations are derived from the work of CLYNE and STEDMAN (10) who claimed that the values of k_1 given in (7) were underestimated. The estimated values given here are the values from (7) increased by 15%. Recommended by (19,21).
4.0×10^{16} $M=N_2$	298	Selected value for use in atmospheric chemistry. ANDERSON 1976 (21)	Selected value is that of (18). Also quotes (7). No criteria for selection given.
$6.17\times10^{15}\exp(530/T)$ $M=N_2$	Unspecified	Recommended expression for use in modelling effects of ClO_x in atmosphere. HUDSON 1977 (24)	

Discussion

Nitric oxide and chlorine may combine by both "molecular" and "atomic" routes. The molecular path (section B36) is important only at low temperatures and in the absence of Cl atoms [2]. In the presence of Cl atoms, reaction 1 is considerably faster than reaction 2.

$$NO + Cl + M \rightarrow NOCl + M \qquad (1)$$

$$NO + NO + Cl_2 \rightarrow 2NOCl \qquad (2)$$

Reaction 1 has been observed both in its third and second order regions, and has been studied in a variety of systems. In the early determinations in static systems, [3,5] it could only be inferred that reaction 1 took place, and k_1 could only be deduced after making allowances for reactions such as reaction 2, and approximations in both the calculations and mechanism assumed. In view of this, the values of k_1 determined in these studies must be considered only with wide error limits.

Clark et al. [6,7] studied the reaction in a flow system, where reaction 2 could be discounted and no evidence was found for the reverse reaction. Reaction 1 was now followed by the fast reaction –3, producing in effect an NO-catalysed chlorine recombination.

$$NOCl + Cl \rightarrow NO + Cl_2 \qquad (-3)$$

Subsequent work by Clyne and Stedman [10] showed that the assumption that the radiation intensity followed in this study $\propto [Cl]^2$ was true only for $M = Cl_2$, and the results for other third bodies had to be revised on the basis $I_0 \propto [Cl]^n$ where n varied with the third body chosen.

In a static photolysis study of NOCl, Timmons and Darwent [12] found reaction 1 operating in its second-order high pressure region, using pressures up to 1 atm. In this system they were only able to produce the ratio k_{-3}/k_1, and this is given only as an average value for all inert gases used. If a value of $\sim 10^{13}$ cm^3 mol^{-1} s^{-1} is assumed for k_{-3} at 298 K, this gives $k_1^\infty \cong 4 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, in good agreement with the value quoted in [22] for unpublished work by Hippler and Troe [23]. Hippler and Troe themselves used flash photolysis, and produced a value of $k_1(M = He)$ quite a bit below the value in [7].

Only the results for $M = Cl_2$ are in sufficient agreement to allow a recommendation, and here we recommend $k_1 = 5.3 \times 10^{15} \exp(520/T)$ cm^6 mol^{-2} s^{-1} over the temperature range 200–670 K, with error limits of ±75%. This is the expression of Kondratiev [14], rearranged in Arrhenius form, extended to 200 K as it appears from the recent work of Lee et al. [26] that there is no great change in E_1 with M.

Relative Efficiencies of Third Bodies

M=Ar	Cl_2	N_2	O_2	NO	N_2O	He	CO_2	SF_6	Temp. (K)	Ref.
1	3.56	1.64		2.22	0.82		3.56		470	(3)
1	1.17	1.20	1.35			1.20		1.20	293	(7)
1	1.03								298	(9)
		1[a]	1.18[a]						293	(14)

[a] Efficiency relative to N_2.

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B36 $NOCl + NOCl \rightarrow 2NO + Cl_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	77.074	121.04	-7.180	-11.569
300	77.078	121.07	-7.096	-11.487
500	77.239	121.61	-1.716	- 6.329
1000	75.200	118.93	2.284	- 2.630
1500	71.969	116.33	3.570	- 1.520
2000	68.078	114.11	4.182	- 1.033
2500	63.630	112.12	4.526	- 0.786
3000	58.708	110.33	4.740	- 0.651
3500	53.402	108.70	4.880	- 0.578
4000	47.717	107.18	4.976	- 0.540
4500	41.577	105.73	5.040	- 0.528
5000	34.893	104.33	5.084	- 0.529

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$
$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

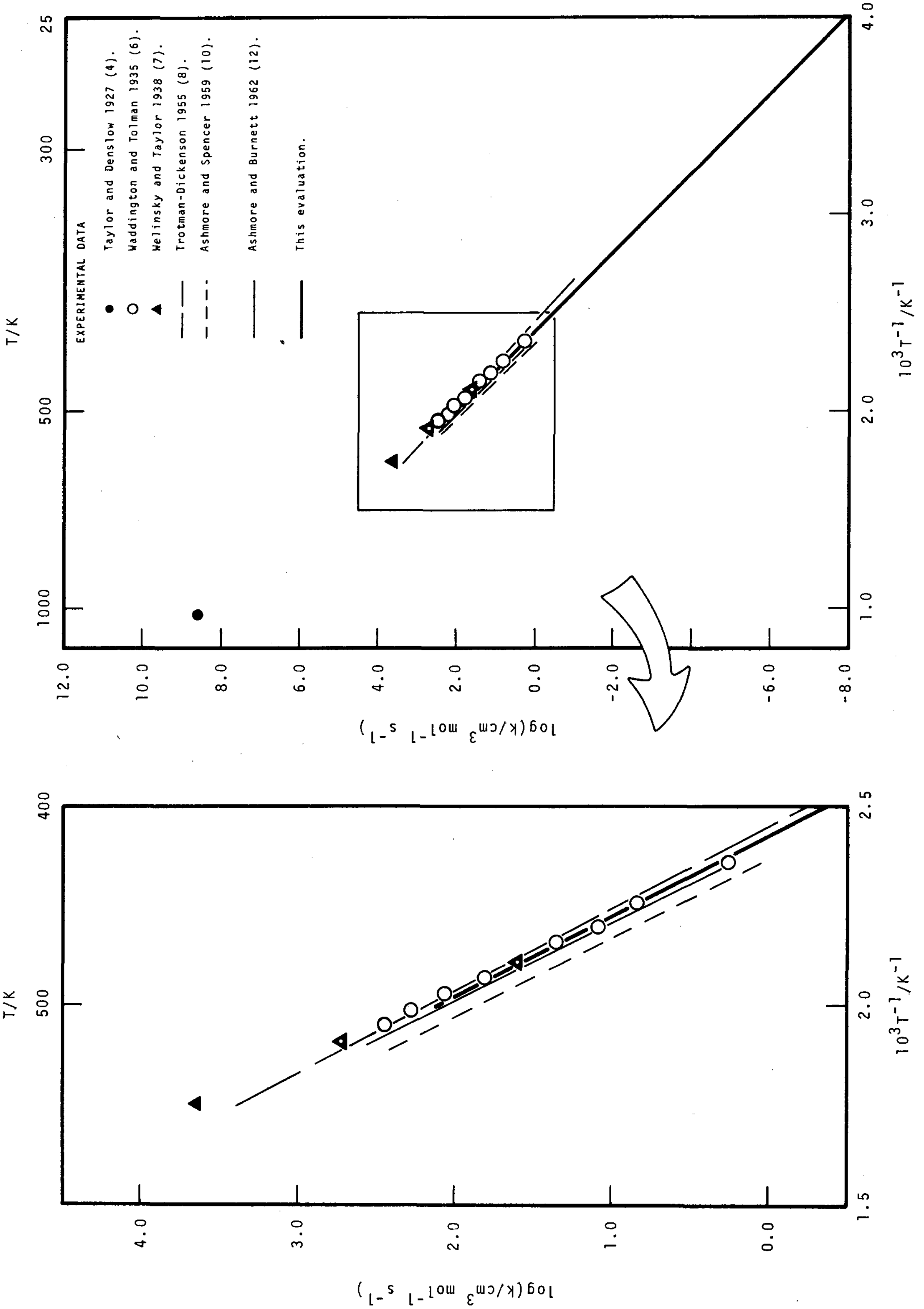
$k_1 = 1.0 \times 10^{12} \exp(-11\ 400/T)$ cm^3 mol^{-1} s^{-1}
$= 1.7 \times 10^{-12} \exp(-11\ 400/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 250-500 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over the whole temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1})$ = 12.00 ±0.18
$\log(A/cm^3\ molecule^{-1}\ s^{-1})$ = -11.77 ±0.18
$E/J\ mol^{-1}$ = 94 800 ±12 000
$E/cal\ mol^{-1}$ = 22 650 ± 3 000

NOCl + NOCl → NO + NO + Cl_2



$NOCl + NOCl \rightarrow 2NO + Cl_2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
4.0×10^8	1020	Flow system. $NOCl/N_2$ mixtures flowing at 0.3 $cm^3\ s^{-1}$. No details of pressures given. [NOCl] determined by absorption in $AgNO_3$, [Cl_2] by absorption in Na_3AsO_3. TAYLOR and DENSLOW 1927 (4)	Rate constant calculated using the bimolecular theory of TRAUTZ (1). No attempt was made to consider the possible effect of the reverse reaction -1 or of reaction 2. The rate constant obtained was assumed to be k_1. $NOCl + NOCl \rightleftharpoons 2NO + Cl_2$ 1 $NOCl + M \rightarrow NO + Cl + M$ 2 Quoted by (16).
1.9×10^0 6.2×10^0 1.2×10^1 2.2×10^1 3.8×10^1 6.1×10^1 1.1×10^2 1.9×10^2 2.8×10^2 5.3×10^2	423 443 453 463 473 483 493 503 513 523	Static system. NOCl at 1.80-29.7 kPa pressure. Reaction followed manometrically. WADDINGTON and TOLMAN 1935 (6)	Effect of reverse reaction considered. Authors derive expression $k_1=2.2\times10^{11}T^{0.5}\exp(-12\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the given temperature range, but note a slight increase in E_1 with temperature. Data recalculated by ASHMORE and SPENCER (10) allowing for the effect of reaction 2 above 450 K to give $k_1=1.6\times10^{12}\exp(-11\ 800/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the given temperature range. ASHMORE and BURNETT (12) redetermined k_2, and derived $k_1=2.4\times10^{12}\exp(-11\ 840/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the same temperature range. Original expression quoted by (7, 9,10,16). Expression of (10) quoted by (13,14,15,16,17,18). Expression of (12) quoted by (14, 15,16).
3.8×10^1 5.4×10^2 5.0×10^3	473 523 573	Static system. NOCl at 2.67-21.1 kPa pressure. Reaction followed manometrically. WELINSKY and TAYLOR 1938 (7)	No expression determined for k_1, as authors claim activation energy increases with temperature. They give E_1=95.0 kJ mol^{-1} (22.7 kcal mol^{-1}) at 473 K and 118.4 kJ mol^{-1} (28.3 kcal mol^{-1}) at 573 K using these data. TROTMAN-DICKENSON (8) derives the expression $k_1=6.3\times10^{11}\exp(-11\ 100/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 373-574 K, and BENSON (11) gives $k_1=1.7\times10^{12}T^{0.5}\exp(-13\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$. (7,8)quoted by (16).

$NOCl + NOCl \rightarrow 2NO + Cl_2$

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2.4\times10^{12}\exp(-11\ 840/T)$	423-524	Review. KONDRATIEV 1970 (16)	Recommended expression is that of (12). Also quotes (4,6,7,8 10), and value from TRAUTZ and WACHENHEIM derived from K_1k_{-1} (3).
		Review of reactions of halogen, nitrogen and sulphur compounds. WHITE 1972 (17)	Quotes (10). Refers also to (6 and 7).

Discussion

The bimolecular decomposition of nitrosyl chloride has not received the same amount of attention as the termolecular reverse reaction. Trautz [2] considered it unimportant in the study of the termolecular reaction under the low temperature conditions he used, and it was not until the 1930's that any rate data became available over an extended temperature range.

$$NOCl + NOCl \rightarrow 2NO + Cl_2 \qquad (1)$$

In the evaluation, the rate constant k_1 is defined by the expression:

$$-d[NOCl]/dt = 2k_1\ [NOCl]^2$$

All of the rate data quoted in the table were divided by two to conform with this definition.

Apart from the early work of Taylor and Denslow [4], all of the experimental studies of reaction 1 have been made by following pressure changes in the reaction vessel, and carried out at temperatures comparable to those used in the study of reaction –1. Taylor and Denslow obtained a rate constant for NOCl disappearance at 1020 K which they called k_1, but did not take into account the effects of the reverse reaction, and of reaction 2.

$$NOCl + M \rightarrow NO + Cl + M \qquad (2)$$

The other studies give results which agree well among themselves, and extrapolate to a value not much below that of Taylor and Denslow, even when the effect of the reverse reaction is considered [6,7]. Ashmore and co-workers [10,12] recalculated the results of Waddington and Tolman [6] taking into account reaction 2, k_1 being $\cong 10k_2$ at 500 K. If the expression of Ashmore and Burnett [12] is extrapolated to 1000 K, it gives a value of k_1 lower by a factor of 50 than that determined by Taylor and Denslow. If we reject the high temperature value, and consider the expression of Ashmore and Burnett, we obtain good agreement with the expression derived from our value of k_{-1} (section B37) and the equilibrium constant over the range 400–500 K. However, at 300 K, there is as much as a factor of 2 difference between the two expressions. In view of the more extensive data on reaction –1, and the good agreement between several studies, we recommend the expression derived from k_{-1} and K_1:

$$k_1 = 1.0 \times 10^{12} \exp(-11\ 400/T)\ cm^3\ mol^{-1}\ s^{-1}$$

with error limits of ±50% over the temperature range 250–500 K. This agrees well with the expression $k_1 = 6.3\times10^{11}$ $\exp(-11\ 100/T)$ $cm^3\ mol^{-1}\ s^{-1}$ derived by Trotman-Dickenson [8] from his expression for k_{-1} and K_1 as determined by Dixon [5].

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B37 $NO + NO + Cl_2 \rightarrow 2NOCl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-77.074	-121.04	7.180	11.569
300	-77.078	-121.07	7.096	11.487
500	-77.239	-121.61	1.716	6.329
1000	-75.200	-118.93	-2.284	2.630
1500	-71.969	-116.33	-3.570	1.520
2000	-68.078	-114.11	-4.182	1.033
2500	-63.630	-112.12	-4.526	0.786
3000	-58.708	-110.33	-4.740	0.651
3500	-53.402	-108.70	-4.880	0.578
4000	-47.717	-107.18	-4.976	0.540
4500	-41.577	-105.73	-5.040	0.528
5000	-34.893	-104.33	-5.084	0.529

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.006$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 4.1 \times 10^{10} \exp(-2500/T)\ cm^6\ mol^{-2}\ s^{-1}$

$= 1.1 \times 10^{-37} \exp(-2500/T)\ cm^6\ molecule^{-2}\ s^{-1}$

Temperature Range: 250-500 K.

Suggested Error Limits for Calculated Rate Constant: ±30% over the whole temperature range.

Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 10.61 \pm 0.15$

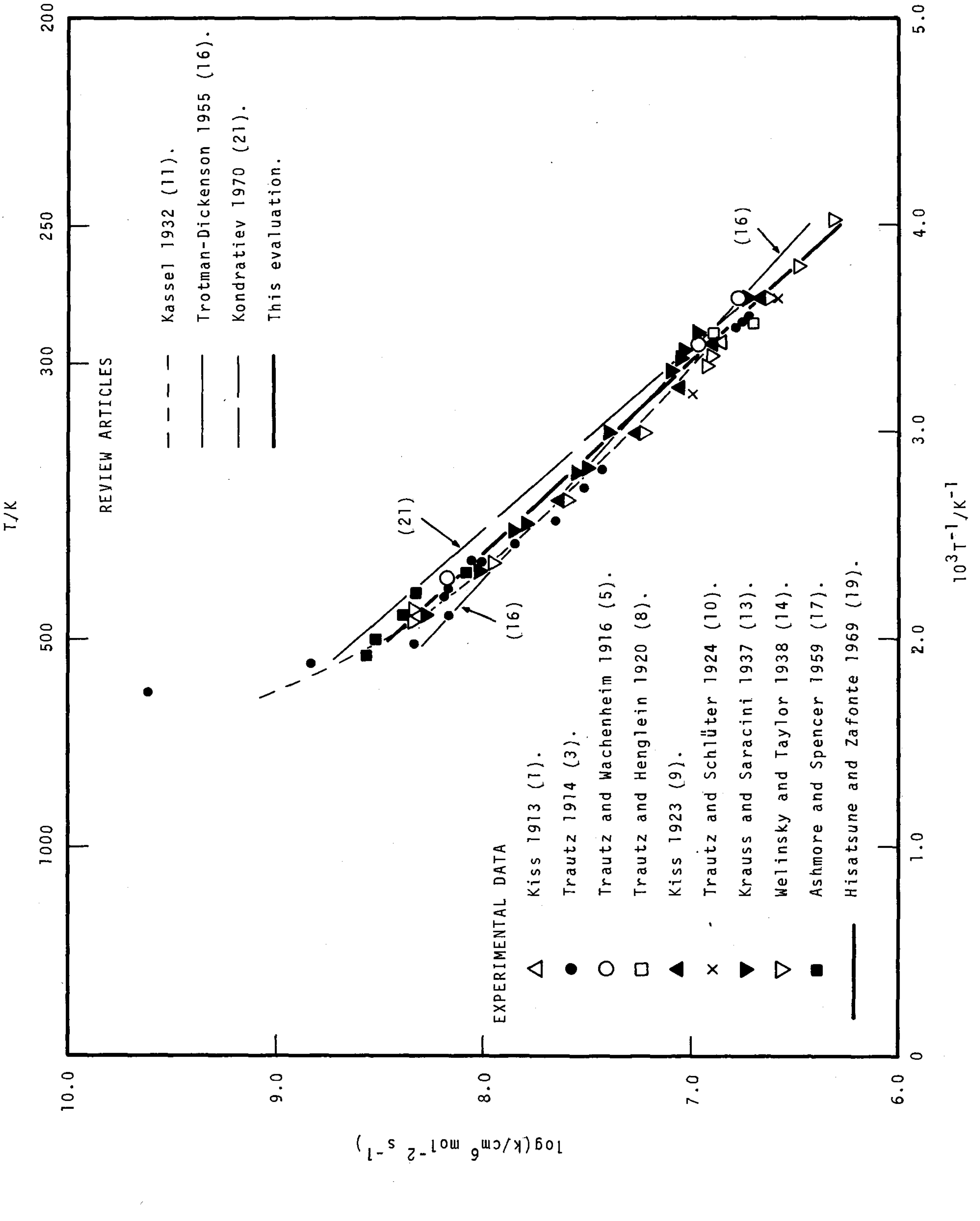
$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -36.96 \pm 0.15$

$E/J\ mol^{-1} = 20\ 800 \pm 3100$

$E/cal\ mol^{-1} = 4970 \pm 750$

Note: Expression corresponds to that of HISATSUNE and ZAFONTE (19) over the temperature range 278-338 K.

$NO + NO + Cl_2 \rightarrow NOCl + NOCl$



$NO + NO + Cl_2 \rightarrow 2NOCl$

EXPERIMENTAL DATA

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
$7.2x10^6$	291	Static system. No quantitative details available. Reaction followed manometrically. KISS 1913 (2)	Details taken from (3 and 9). Used by (3). Reaction found to be third order. $NO + NO + Cl_2 \rightarrow 2NOCl$ 1 Quoted by (8,9,11).
$5.27x10^6$ 5.6 $x10^6$ $5.88x10^6$ $1.95x10^7$ $2.73x10^7$ $3.38x10^7$ $4.18x10^7$ $4.45x10^7$ $7.23x10^7$ $1.07x10^8$ $1.01x10^8$ $1.48x10^8$ $1.55x10^8$ $1.53x10^8$ $2.19x10^8$ $6.65x10^8$ $1.13x10^9$	281.7 282.6 284.4 333.4 355.1 365.2 374.7 386.2 401.4 419.3 419.7 441.6 451.1 473.9 505.8 528.4 566.4	Static system. NO at 5.55-17.3 kPa and Cl_2 at 4.23-28.6 kPa pressure. Reaction followed manometrically. TRAUTZ 1914 (3)	Author calculated values of k_1 from thermodynamic data, and found good agreement between theory and experiment up to 400 K. At higher temperatures he attributed the apparently rapid increase in rate to the increased importance of the reverse reaction, and also the onset of reaction 2 $NOCl + NO \rightarrow (NO)_2Cl$ 2 Using thermodynamic data and k_1 from KISS (2) he calculated the activation energy E_1=9.27 kcal mol^{-1} over the temperature range 281.7-386.2 K, using the method described in his own reaction rate theory (1). From the rate data given, we obtain E_1=4.5 kcal mol^{-1} over that temperature range. Data re-expressed in (4) as $k_1=1.4x10^{14}T^{-1}exp(-2950/T)$ cm^6 mol^{-2} s^{-1}. Quoted by (3,5,9,11,12,14,16,21). E_1 quoted by (6).
6.0 $x10^6$ $9.53x10^6$ $1.47x10^8$	273 291.2 434	Static system. NO at 3.84-12.90 kPa and Cl_2 at 6.05-100.7 kPa pressure. Reaction followed manometrically. TRAUTZ and WACHENHEIM 1916 (5)	Authors note results in good agreement with those of (3), and obtain $k_1=(1.1\pm0.1)x10^{14}T^{-1}$ $exp(-2740\pm200/T)$ cm^6 mol^{-2} s^{-1}, over the quoted temperature range. Quoted by (8,9,11,12,14,16,21). E_1 quoted by (6).
$5.08x10^6$ $7.38x10^6$	280.8 288.9	Static system. NO at 9.41-61.3 kPa and Cl_2 at 9.28-29.8 kPa pressure. Reaction followed manometrically. TRAUTZ and HENGLEIN 1920 (8)	TRAUTZ's revised molecular reaction rate theory is used (4) to give $k_1=1.02x10^{14}T^{-1}exp(-2800/T)$ cm^6 mol^{-2} s^{-1} between 280.8 and 288.9 K. Quoted by (9,11,14,16,21).

$NO + NO + Cl_2 \rightarrow 2NOCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.6\ x10^6$ $7.53x10^6$ $1.22x10^7$ $1.88x10^7$ $4.18x10^7$	273 291 311 333.5 373.3	Static system. NO at 13.6 -42.3 kPa and Cl_2 at 6.55-32.3 kPa pressure. In some experiments Br_2 (0.51-2.15 kPa), CO_2 (4.70-54.5 kPa), H_2O (0.40-1.6 kPa), H_2 (54.6 kPa) or HCl (57.3 kPa) were added. Reaction followed manometrically. KISS 1923 (9)	The catalytic effect of additives on reaction 1 was studied. Of the additives used only Br_2 was found to have a slight catalytic effect, the author proposing two reaction schemes to account for this:- $NO + NO + Br_2 \rightarrow 2NOBr$ $2NOBr + Cl_2 \rightarrow 2NOCl + Br_2$ or $Cl_2 + Br_2 \rightarrow 2BrCl$ $2BrCl + 2NO \rightarrow 2NOCl + Br_2$ No attempt was made to investigate intermediate products. Quoted by (10,14,16,21).
$4.13x10^6$ $1.13x10^7$	273 313	Static system. NO at 5.33 -27.0 kPa and Cl_2 at 5.27-89.1 kPa pressure. Reaction followed manometrically. TRAUTZ and SCHLÜTER 1924 (10)	Authors attempted to show that reaction proceeded via a two stage mechanism, by using extreme concentration ratios of [NO]:[Cl_2] $NO + Cl_2 \rightarrow NOCl_2$ $NOCl_2 + NO \rightarrow 2NOCl$ They claimed that k_1 fell when excess NO was used, and rose when excess Cl_2 was used. Their data are recalculated in (14), where it is shown that no such trend occurs.
$1.58x10^{10}T^{0.5}exp(-3450/T)$	423-523	Calculated value, from their value of k_{-1} and the equilibrium constant K. WADDINGTON and TOLMAN 1935 (12)	From their results for k_{-1}, authors noted that E_1 increases with temperature over the range considered, and thus the value used in the expression is only an approximate one. Quoted by (13,14,16,20,21).
$5.55x10^6$ $5.78x10^6$ $9.05x10^6$ $1.07x10^7$ $1.08x10^7$ $1.26x10^7$ $2.49x10^7$ $3.18x10^7$ $3.60x10^7$ $6.20x10^7$ $7.30x10^7$ $1.05x10^8$ $1.91x10^8$	273.2 273.8 292.0 294.2 296.0 303.2 333.2 350.0 353.0 388.4 394.0 423.0 470.0	Static system. NO at 14.5 -46.2 kPa and Cl_2 at 10.3-107.6 kPa pressure. Reaction followed manometrically. KRAUSS and SARACINI 1937 (13)	No deviation from third order relationship over all [NO]:[Cl_2] ratios. Again, slight increase in E_1 noted at higher temperatures. $NO + NO + Cl_2 \rightarrow 2NOCl$ 1 Quoted by (14,16). Used by (21).

$NO + NO + Cl_2 \rightarrow 2NOCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
2.02×10^6	248	Static system. NO at 7.0-21.1 kPa and Cl_2 at 5.80-13.6 kPa pressure. Reaction followed manometrically. WELINSKY and TAYLOR 1938 (14)	Authors agree with findings in (13), and criticise the conclusions of (3 and 10), that the reaction proceeds in two stages via the formation of $NOCl_2$. E_1 found to increase with temperature, assuming a $T^{\frac{1}{2}}$ dependence of A factor, from 15.6 kJ mol^{-1} (3.7 kcal mol^{-1}) at 248 K to 41.3 kJ mol^{-1} (9.9 kcal mol^{-1}) at 573 K, using data derived from the authors' determination of k_{-1} and K_1 in the same work. Used by (16,17,18, 21).
3.16×10^6	263		
4.49×10^6	273		
7.99×10^6	295		
8.50×10^6	300.5		
1.78×10^7	333.5		
4.18×10^7	373		
9.18×10^7	419		
2.29×10^8	469		
2.27×10^8	476		
$(1.23\pm0.2)\times10^8$	430.5	Static system. NO at 0.8-6.67 kPa and Cl_2 at 0.53-13.3 kPa pressure. Some experiments at 470.5 K carried out with 6.67-40 kPa Ar, N_2, CO_2 or N_2O added. Reaction followed manometrically. ASHMORE and SPENCER 1959 (17)	Authors were first to consider the alternative method of combination, reaction 3, whose reverse had been shown to be important in NOCl decomposition. $NO + Cl + M \rightarrow NOCl + M$ 3 By introducing this reaction into the scheme, they found that E_1 no longer increased with temperature. Combining their results with those of (14), they obtained $k_1=1.26\times10^{11}\exp(-3000/T)$ cm^6 mol^{-2} s^{-1} over the temperature range 373-523 K. Quoted by (23). Used by (21).
$(2.12\pm0.4)\times10^8$	450.5		
$(2.27\pm0.4)\times10^8$	470.5		
$(3.40\pm0.6)\times10^8$	500		
$(3.63\pm1.0)\times10^8$	523		
$(2.1\pm0.1)\times10^{10}\exp(-2280/T)$	278-338	Static system. NO (0.64-64.0 kPa)/Cl_2 (0.57-57.0 kPa) mixtures. [NOCl] followed by i.r. absorption at 16.7 μm. HISATSUNE and ZAFONTE 1969 (19)	No variation in rate of reaction 1 with pressure. $NO + NO + Cl_2 \rightarrow 2NOCl$ 1 In an attempt to determine the precise mechanism of the reaction O_2 or Br_2 were added in some runs as competitors for the NO. With added O_2 there was no change in reaction rate, but addition of Br_2 lead to a complex series of reactions forming first NOBr then NOCl, giving an overall $k_1=4.8\times10^9$ cm^6 mol^{-2} s^{-1} at 303 K, compared with $k_1=1.1\times10^7$ cm^6 mol^{-2} s^{-1} from the original experiments, probably due to reaction 5 $NO + NO + BrCl \rightarrow NOCl + NOBr$ 5 Quoted by (22,23).

$NO + NO + Cl_2 \rightarrow 2NOCl$

REVIEW ARTICLES

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2x10^{(-21+430/T)}T^{10.5}$	273-566	Empirical value. KASSEL 1932 (11)	Expression chosen to fit data of (3,8,9,10). Data of (5) also quoted. Author claims this gives an activation energy E_I increasing with temperature from 14.5 kJ mol^{-1} (3.5 kcal mol^{-1}) at 273 K to 40.0 kJ mol^{-1} (9.6 kcal mol^{-1}) at 566 K. $NO + NO + Cl_2 \rightarrow 2NOCl$ 1
$1.3x10^{10}exp(-2110/T)$		Preferred value. TROTMAN-DICKENSON 1955 (16)	Quotes (3,5,8,9,12,13,14). Preferred value based on data of (14). Quoted by (18 and 21).
$8.31x10^{10}exp(-2650/T)$	273-523	Evaluation. KONDRATIEV 1970 (21)	Based on (13,14,17). When (12) is taken into account the expression becomes k_1=1.38x10^{11} exp(-2800/T) $cm^6\ mol^{-2}\ s^{-1}$. Expression is not recommended due to possibility of side reactions.
		Review of reactions of halogen, nitrogen and sulphur compounds. WHITE 1972 (23)	Quotes (17 and 19). Notes apparent discrepancy between them, but makes no attempt to resolve this. Refers also to (5,9,12,13,14).

Discussion

Reaction 1 is one of the series of classic termolecular reactions as described by Kassel [11]

$$NO + NO + Cl_2 \rightarrow 2NOCl \qquad (1)$$

The reaction was studied initially by Trautz in 1906, although he published no data for a further eight years. By 1924, over the course of several studies [3,5,8,10], he established the value of the rate constant k_1 over a temperature range of 300°, a value which has been confirmed by subsequent workers.

We define the rate constant discussed in this evaluation by the expression:

$$-d[NO]/dt = -2d[Cl_2]/dt = d[NOCl]/dt = 2k_1[NO]^2[Cl_2].$$

Trautz and co-workers, and Krauss [13] followed Bodenstein's practice and defined k_1 according to the expression

$$-d[Cl_2]/dt = k_1\ (\text{Bodenstein})\ (\tfrac{1}{2}[NO])^2[Cl_2]$$

and their figures have thus been divided by four to comply with our definition. All other authors have defined k_1 in terms of the rate of removal of nitric oxide, or of the rate of production of NOCl, and these rate constants have thus been divided by two to comply.

All studies except one [19] of reaction 1 have been performed by monitoring the pressure changes in a reaction vessel. This made it difficult to assess the reaction mechanism accurately. Initially, a straight three-body collision was assumed [1,3,5,8], but Trautz later considered the probability of this to be too low [7] and proposed a two-step mechanism involving the formation of $NOCl_2$ as an intermediate [10].

$$NO + Cl_2 \rightarrow NOCl_2$$

$$NOCl_2 + NO \rightarrow 2NOCl$$

This theory was later discredited by Kassel's work on ternary collisions [11] and by Welinsky and Taylor's recalculation of the data in [10] to show that they were commensurate with a single step, three-body collision [14].

One problem facing all early workers was the apparent increase in E_1 with temperature above 400 K, leading to a slightly curved plot in this region. Trautz [3] ignored these data in calculating an Arrhenius expression but Welinsky and Taylor claimed E_1 increased from 15.6 kJ mol^{-1} (3.7 kcal mol^{-1}) at 248 K to 41.3 kJ mol^{-1} (9.9 kcal mol^{-1}) at 573 K, assuming also a $T^{-1/2}$ temperature dependence. The problem was first resolved by Ashmore and Chanmugam [15], who postulated the simpler atomic recombination route 3, a few Cl atoms being formed by reaction 4 above 500 K, k_3 being $>>k_1$.

$$NO + Cl + M \rightarrow NOCl + M \quad (3)$$

$$NO + Cl_2 \rightarrow NOCl + Cl \quad (4)$$

Subsequently, Ashmore and Spencer [17] used low temperature data from Waddington and Tolman [12] to obtain corrected values of k_1 up to 523 K.

If the data of Trautz above 500 K are ignored, there is good agreement between all the remaining experimental data. We therefore recommend the following expression:

$$k_1 = 4.1 \times 10^{10} \exp(-2500/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

with error limits of ±30% over the temperature range 250–500 K. Care is advised if extrapolating to higher temperatures, as the behaviour of the reaction above 500 K is still by no means fully understood.

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Note Added in Proof

The authors would like to thank the referees for bringing to their attention the work of Stoddart [J. Chem. Soc. 823 (1940); 388 (1944)]. In this work the pressure change associated with the reaction of NO(300 mm Hg; 40 kPa)/Cl_2 (200 mm Hg; 27 kPa) mixtures was followed up to Cl_2 conversions of about 50%. In the first four or five runs in each new reaction vessel the reaction displayed good third order kinetics, and rate constants of 5.7×10^6 and 6.9×10^6 cm^6 mol^{-2} s^{-1} were obtained at 288 and 298 K, respectively. These values are in reasonable agreement with the data of other workers at these temperatures. However, in more aged vessels the reaction showed a puzzling dependence on the vessel history which the authors attributed to a heterogeneous step in the overall process. Briefly, the observed third order rate constant decreased during the course of each experiment, recovering, although never completely, between experiments if the time interval between successive experiments was relatively long, but remaining very low if the reaction vessel was quickly evacuated and refilled. The rate constant was also affected by various treatments of the vessel surface including drying, and baking under vacuum, but did not depend on the surface to volume ratio. In view of this last fact, and the fact that no other workers observed any departure from simple third order kinetics at low temperatures, we see no reason to change our recommendation in the light of this work.

B38 $Cl + NOCl \rightarrow NO + Cl_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-82.755	6.925	14.860
300	-82.760	6.908	14.771
500	-83.642	4.724	8.985
1000	-86.713	0.485	4.555
1500	-89.856	-2.059	3.021
2000	-93.006	-3.870	2.227
2500	-96.236	-5.314	1.733
3000	-99.520	-6.510	1.392
3500	-102.801	-7.523	1.141
4000	-106.110	-8.406	0.947
4500	-109.508	-9.209	0.790
5000	-113.094	-9.962	0.661

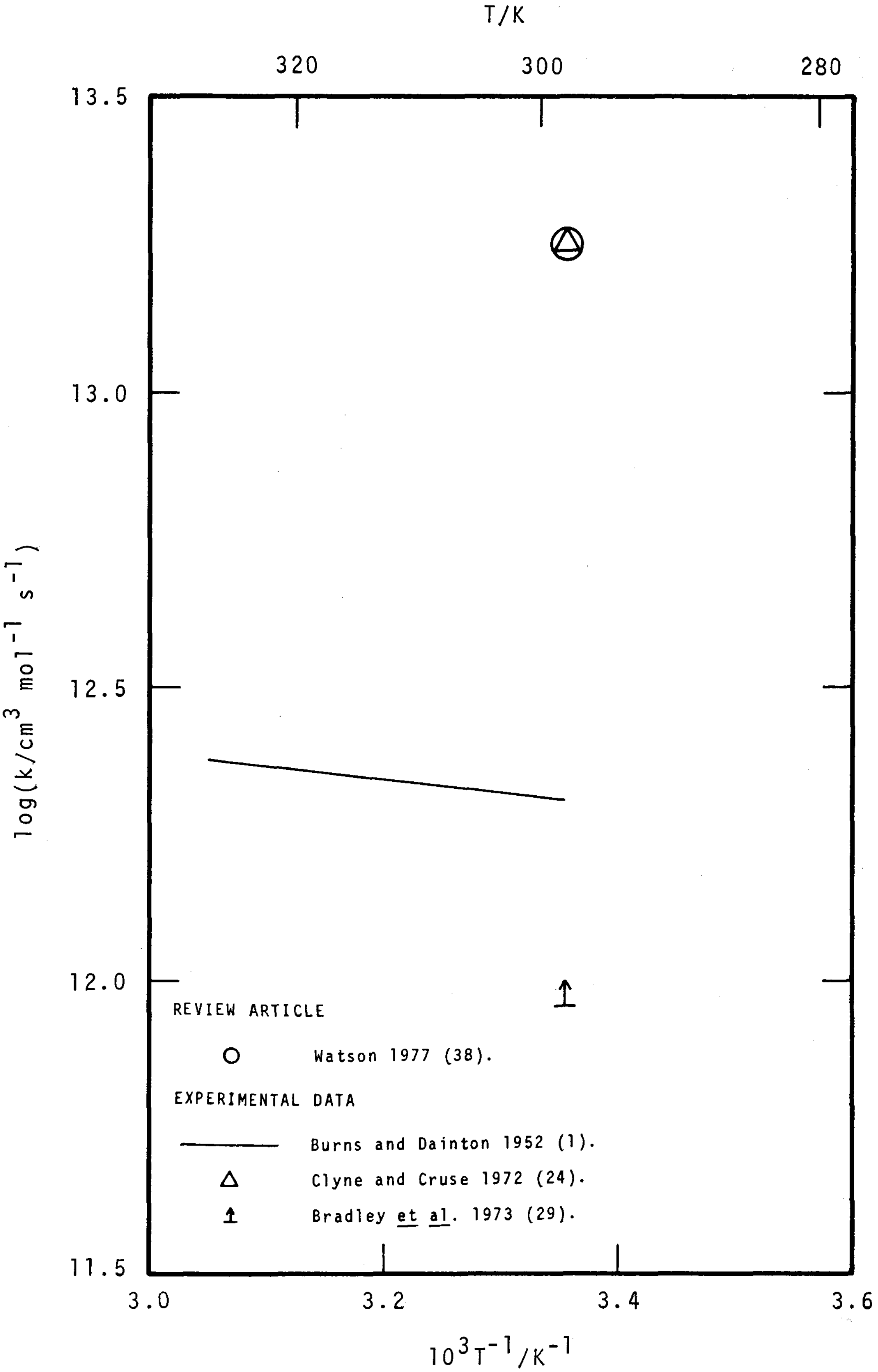
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.2 \times 10^{13} \exp(-530/T)$	298-328	Static system. Photolysis of Cl_2(6.67-40.0 kPa) at 365 nm in the presence of CO (6.67-40.0 kPa) and NOCl (0.19-2.67 Pa). Reaction followed manometrically, and by monitoring absorption of light at 365 nm. *BURNS and DAINTON 1952 (1)*	Authors observed inhibition of phosgene formation when NOCl was present in the photolysis cell, attributing this to reaction 1 and 2. $Cl + NOCl \rightarrow NO + Cl_2$ 1 $NOCl + COCl \rightarrow$ products 2 From pressure measurements they deduced that reaction 1 predominated at low CO pressures and reaction 2 at high CO pressures. Value obtained for k_1 based on authors' own value for k_6 determined in same study.

$Cl + NOCl \rightarrow NO + Cl_2$



EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BURNS and DAINTON 1952 (1) continued.	$COCl + Cl_2 \rightarrow COCl_2 + Cl$ 6 Quoted by (4,5,8,9,10,12,14,16, 17,20,27,33,38). E_1 quoted by (18). At 298 K, authors obtain k_1=2.2x10^{12} $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (15,17,19,21,22,23). Expression extended to higher temperatures by (2,3). BENSON (7) gives expression as k_1=3.9x$10^{11}T^{\frac{1}{2}}$exp(-380/T) $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (20). Authors also derive a theoretical expression k_1=3.35x10^{15}exp(-1000/T) $cm^3\ mol^{-1}\ s^{-1}$, disagreeing considerably with the experimentally determined expression.
	298	Static photolysis of NOCl (38.7-143 Pa) in the presence of NO (77.4-1140 Pa) and inert gases (N_2 at 13.3-40.0 kPa, CF_4 at 16.0 -80.0 kPa and He at 10.7-101 kPa). NOCl and Cl_2 frozen down at 88 K, Cl_2 treated with KI, and $[I_3]$ determined by i.r. spectroscopy at 295 μm. TIMMONS and DARWENT 1969 (18)	Rate constant ratio k_1/k_3 determined, with reaction 3 in its second-order region. $NO + Cl + M \rightarrow NOCl + M$ 3 Ratio averaged for all M, no individual details given. k_1/k_3 = 0.26±0.10 at 298 K. Assuming E_3=0, and A_1=A_3, authors obtained E_1=3.4kJ mol^{-1} (0.8 kcal mol^{-1}). Quoted by (26).
1.8x10^{13}	298	Discharge flow system. Cl (<1%)/Ar mixtures at a total pressure ∿150 Pa. NOCl added in excess downstream at 0.30-2.24 Pa pressure [Cl] monitored by resonance fluorescence at 138 nm. CLYNE and CRUSE 1972 (24)	Discrepancy with the data from (1) noted. The low value of k_1 given there attributed to absorption of NOCl on the vessel walls at the relatively high concentrations used there, and also the complicated nature of the CO/Cl_2/NOCl system. Quoted by (25,28,30,31,32,33,35, 36,38).
>9x10^{11}	298	Discharge flow system. N_2 (<1%)/Ar mixtures at total pressures of 184-349 Pa. O atoms produced by N+NO titration, NOCl added downstream at 0.19-2.25 Pa so that [NOCl]>[O]. Reaction	Cl atoms were not detected in the mass spectrometer, but ClO was, and thus the following mechanism was postulated. $NOCl + O \rightarrow NO + ClO$ 4 $ClO + O \rightarrow O_2 + Cl$ 5 $Cl + NOCl \rightarrow NO + Cl_2$ 1

$Cl + NOCl \rightarrow NO + Cl_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		followed mass spectrometrically. BRADLEY, WHYTOCK and ZALESKI 1973 (29)	Even if [O] were increased, the detection limit for Cl atoms was never reached, and the authors could only give a lower limit for k_1.
		REVIEW ARTICLES	
		Review of reactions of halogen, nitrogen and sulphur compounds. WHITE 1972 (27)	Quotes (1).
	300	Review of Cl atom reactions. CLYNE 1973 (30)	CLYNE's own work (24) quoted.
$1.8x10^{13}$	298	Preferred value. WATSON 1977 (38)	Preferred value is that of (24). (1) also quoted. Used by HUDSON (37).

Discussion

The fast reaction 1 has been assumed responsible for removal of chlorine atoms in the decomposition of nitrosyl chloride [2,6] and other NOCl/Cl systems [28], and has frequently been used as a titration reaction for Cl atoms [e.g., 11,13,17,28,29].

$$Cl + NOCl \rightarrow NO + Cl_2 \qquad (1)$$

Its rapid rate has made study difficult, and there has has been relatively little work done on obtaining a rate constant. The first value of k_1 was obtained by Burns and Dainton [1], working on the photochemical formation of phosgene from CO/Cl_2 mixtures. They added trace amounts of NOCl to the photolysis mixture and found the rate of $COCl_2$ formation inhibited. Assuming this due to reaction 1 they obtained a value of k_1 making use of their value of k_6. It is difficult to comment on the accuracy of this determination, there being no other data on the rate of reaction 6.

$$COCl + Cl_2 \rightarrow COCl_2 + Cl \qquad (6)$$

Their value of k_1 remained the only one available until the more recent work of Clyne et al. [24,25]. Using a discharge flow system at low [NOCl] they obtained first an estimated lower limit for $k_1 \geqslant 6 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K [25] in a preliminary study of the stoichiometry of reaction 1, and then in a more detailed study [24], the value in the table, an order of magnitude higher than that obtained by Burns and Dainton.

No further detailed studies have been undertaken. Bradley et al. [29] were unable to clear the controversy in their study of the reaction of O atoms with NOCl. They were unable to detect Cl atoms by mass-spectrometry and were thus able only to put a lower limit on k_1.

In view of the limited data available, no recommendation is made for k_1.

Rate of the Reverse Reaction

Ashmore et al. considered the reverse reaction –1 in their studies of NOCl dissociation [2,4,6].

$$NO + Cl_2 \rightarrow NOCl + Cl \qquad (-1)$$

In the $H_2/Cl_2/NO/NOCl$ system, Ashmore and Chanmugam postulated reaction –1 as a chain initiation reaction [2]. They used the expression for k_1 of Burns and Dainton extrapolated to 573 K and the equilibrium constant to calculate a value of $k_{-1} = 6.35 \times 10^4$ cm^3 mol^{-1} s^{-1} at 573 K, and giving an expression $k_{-1} = 4 \times 10^{12} \exp(-10\,200/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 523–673 K.

Ashmore and Spencer [6] studied the reaction of nitric oxide and chlorine directly, incorporating reaction –1 into their scheme. By observing the formation of NOCl, they obtained values for $k_{-1} = 2.7 \times 10^2$ (430.5 K), 8.3×10^2

(450.5 K) and 1.0×10^3 (470.5 K) $cm^3\ mol^{-1}\ s^{-1}$. This leads to the overall expression $4.1 \times 10^8 \exp(-6000/T)$ $cm^3\ mol^{-1}\ s^{-1}$, in poor agreement with any value of k_{-1} determined from k_1 and the equilibrium constant.

The data available on reaction −1 appear to show even less agreement than those on reaction 1, and no recommendation is made.

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B39 $H + NOCl \rightarrow NO + HCl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-271.73	21.272	48.718
300	-271.75	21.234	48.425
500	-273.48	16.903	29.453
1000	-278.75	9.590	15.061
1500	-283.32	5.849	10.171
2000	-287.21	3.607	7.690
2500	-290.76	2.025	6.181
3000	-294.17	0.782	5.163
3500	-297.45	-0.272	4.427
4000	-301.06	-1.205	3.869
4500	-304.70	-2.063	3.430
5000	-308.54	-2.867	3.073

RECOMMENDED RATE CONSTANT

$k = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}

$= 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

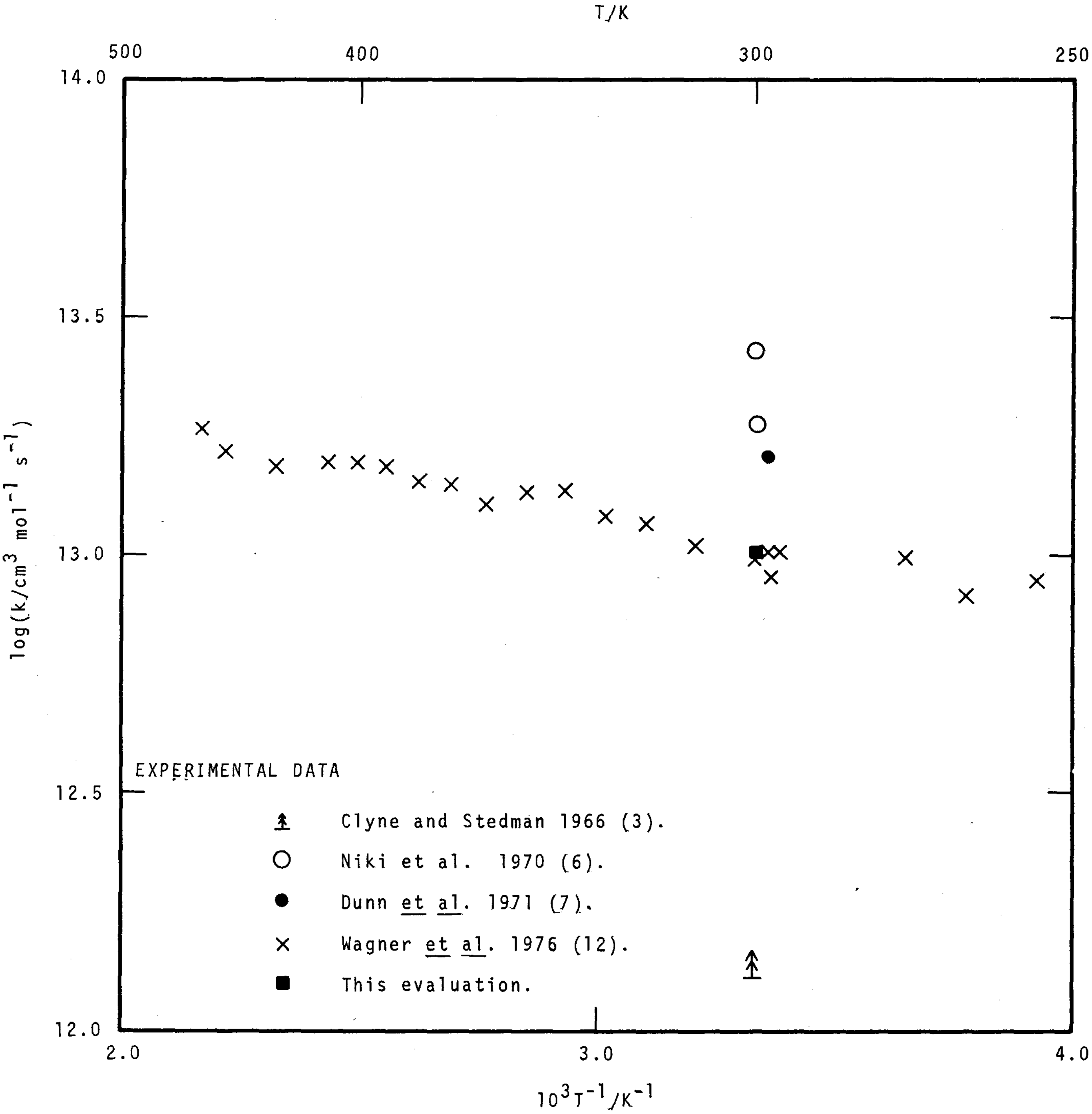
Temperature: 300 K.

Suggested Error Limits for Calculated Rate Constant: A factor of two.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$>1.3 \times 10^{12}$	300	Discharge flow system. 100% H_2 at 140-404 Pa pressure, NOCl added downstream so that [NOCl]< [H]. Flow tube walls phosphoric acid coated. [H] removed by metal foil, products condensed at 77 K, and [HCl], [NOCl] determined by i.r. spectroscopy. CLYNE and STEDMAN 1966 (3)	Stoichiometry of the reaction observed to be 1, and a lower limit for k_1 determined from the minimum contact time for the reactants between the NOCl inlet and the metal foil. $H + NOCl \rightarrow NO + HCl$ 1 Use of an isothermal-wire calorimeter (2) showed that recombination of H atoms in this region was negligible.

$H + NOCl \rightarrow NO + HCl$



$H + NOCl \rightarrow NO + HCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant K ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (k)	Method and Reference	Comments
		CLYNE and STEDMAN 1966 (3) continued.	Quoted by (4,5,6,7,12).
$2.7x10^{13}$	300	Discharge flow system. 100%H_2, NOCl added downstream. Reaction followed mass spectrometrically. No further details available. NIKI, STEDMAN and STEFFERSON 1970 (6)	Authors note presence of large amounts of vibrationally excited H_2, but make no comment on its possible effect on reaction 1. Quoted by (7), where the value $k_1 = 1.9x10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ is also attributed to these authors as having been given by them at the 160th ACS Meeting.
$1.6x10^{13}$	298	Discharge flow system. H_2 (1-10%)/Ar mixtures at 13.3 Pa pressure. NOCl added downstream over a wide range of [H]:[NOCl] ratios. Flow tube wall phosphoric acid coated. [NOCl] monitored mass spectrometrically. DUNN, SUTTON, FREEMAN, McEWAN and PHILLIPS 1971 (7)	Stoichiometry of 1 obtained. Authors found [NOCl] very difficult to monitor mass spectrometrically, due to the low sensitivity of the instrument, and had to follow the NCl^+ fragment. Value of k_1 given is the average of 12 values obtained under "optimum conditions". Vibrationally excited HCl produced was concluded not to affect the stoichiometry, as $k_1 > 10k_2$. $H + HCl(v=1) \rightarrow H_2 + Cl$ 2 Quoted by (8,9,12).
$8.8x10^{12}$	255	Discharge flow system. H_2/He mixtures at 313-373 Pa pressure. NOCl added downstream at 0.1-0.5 Pa, giving [NOCl]:[H] ≈100. [H] monitored by Lyman-α fluorescence at 121.6 nm. WAGNER, WELZBACHER and ZELLNER 1976 (12)	Under the conditions used, authors considered secondary reactions to be unimportant, taking $k_1/k_2 > 200$. From a least squares treatment of their data they obtain $k_1 = 4.6x10^{13}\exp(-450/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 255-461 K.
$8.3x10^{12}$	265		
$9.8x10^{12}$	274		
$1.01x10^{13}$	296		
$9.1x10^{12}$	297		
$1.01x10^{13}$	298		
$9.7x10^{12}$	300		
$1.05x10^{13}$	312		
$1.17x10^{13}$	322		
$1.21x10^{13}$	332		
$1.36x10^{13}$	341		
$1.34x10^{13}$	351		
$1.28x10^{13}$	361		
$1.42x10^{13}$	371		
$1.42x10^{13}$	381		
$1.53x10^{13}$	391		
$1.56x10^{13}$	401		
$1.55x10^{13}$	411		
$1.53x10^{13}$	431		
$1.70x10^{13}$	451		
$1.83x10^{13}$	461		

REVIEW ARTICLE

Review of elementary gas reactions. KAUFMAN 1969 (4)	Quotes (3). Discusses use of reaction 1 as a titration for H atoms. $H + NOCl \rightarrow NO + HCl$ 1

Discussion

The rapid reaction between hydrogen atoms and nitrosyl chloride has been used as a source of vibrationally excited HCl [11], and for H atom scavenging [9]. It can also be used as a titration reaction for estimating H atom concentrations [3,12].

$$H + NOCl \rightarrow NO + HCl \quad (1)$$

The analogous reaction 3 is preferred in this latter respect however, as it is nearly an order of magnitude faster at room temperature [12,13]. The advantage of reaction 1 is that it does not produce OH radicals, which can interfere with the titration in some systems [4].

$$H + NO_2 \rightarrow NO + OH \quad (3)$$

All investigations of reaction 1 have used discharge flow methods. Clyne and Stedman [3], more interested in the stoichiometry of the reaction were able only to give a lower limit for k_1, assuming minimum contact time for the reactants before quenching the reaction. Dunn et al. [7] followed [NOCl] mass spectrometrically, but found this difficult, and selected only the results they considered most reliable to give a value of k_1. In both studies, the flow tubes were coated with phosphoric acid to preserve unit stoichiometry by reactions 1, 2, and 4 rather than lose Cl atoms by wall recombination.

$$H + HCl \rightarrow H_2 + Cl \quad (2)$$

$$Cl + NOCl \rightarrow NO + Cl_2 \quad (4)$$

The HCl molecule is known to be vibrationally excited [1]. Clyne and Stedman determined $E_2 \cong 12.5$ kJ mol^{-1} (3 kcal mol^{-1}) [3], which energy Dunn et al. assumed to be contained by HCl^v, and on this basis derived $k_2 \sim 0.05\ k_1$. This relationship has been confirmed by more recent work on k_2 for HCl ($v=1$) [10]. However, if [NOCl]> >[H], reaction 2 becomes unimportant, and it was under such conditions that Wagner et al. [12] studied reaction 1, over an extended temperature range, monitoring [H] decay rather than [NOCl] disappearance. At room temperature their value of k_1 is up to a factor of two lower than in earlier studies, but is to be preferred in view of the absence of complicating secondary reactions and the accurate measurements of [H].

In the absence of further data we prefer not to recommend any expression for k_1 over an extended temperature range, but give $k_1 = 1 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 300 K, based on [12], with error limits of a factor of two.

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Miscellaneous Reactions Involving NOCl

B40 N + NOCl → NO + NCl

The first two studies of the reaction between nitrogen atoms and nitrosyl chloride produced quite different conclusions on its rate and mechanism.

$$NOCl + N \rightarrow NO + NCl; \quad (1)$$

thermodynamic data unavailable for NCl.

Biordi [1] studied the reaction in a flow discharge system, passing pure N_2 (260–780 Pa) through a discharge, and adding NOCl downstream so that [NOCl] < [N]. The reaction was followed by monitoring the NO β and N_2 first positive emissions. The flow tube walls were not treated in any way, and so no Cl atoms were assumed present downstream. Assuming reaction 1 to be fast, Biordi postulated reactions 1 to 4 to fit the observed stoichiometry of two N atoms consumed per NOCl molecule destroyed, followed by reactions 5 and 6 to account for the slow decay of N and O atoms.

$$NOCl + N \rightarrow NO + NCl \quad (1)$$

$$N + NO \rightarrow N_2 + O \quad (2)$$

$$N + NCl \rightarrow N_2 + Cl \quad (3)$$

$$NOCl + Cl \rightarrow NO + Cl_2 \quad (4)$$

$$O + Cl_2 \rightarrow ClO + Cl \quad (5)$$

$$N + Cl_2 \rightarrow NCl + Cl \quad (6)$$

This mechanism excluded the possibility of determining k_1 from the measurements made, but this was achieved later by Dunn et al. [2], in a flow system where the tube walls were coated with phosphoric acid, preventing Cl atom recombination. They obtained an overall stoichiometry of 1:1, and, assuming the extra NOCl to be removed by reactions with O atoms, obtained a value of $k_1 = 1.1 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at room temperature, three orders of magnitude less than that assumed by Biordi, and three orders of magnitude less than the corresponding NO_2 reaction:

$$NO_2 + N \rightarrow \text{products} \qquad (7)$$

Warnatz et al. [3] also used an N_2-discharge flow system, following the pseudo first order decay of N atoms in excess NOCl by mass spectrometry. Assuming the stoichiometry to be 1:1, these authors quote an approximate value at room temperature for k_1 of $\sim 10^{10}$ cm^3 mol^{-1} s^{-1}.

Despite the agreement between this value and that of Dunn et al. [2], the uncertainties over the reaction mechanism lead us to make no recommendation for k_1.

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B41 O + NOCl → NO + ClO

The reaction between oxygen atoms and nitrosyl chloride appears to be approximately three orders of magnitude slower than the corresponding reaction with hydrogen atoms.

$$NOCl + O \rightarrow NO + ClO; \qquad (1)$$

$$\Delta H^\circ_{298} = -109.44 \text{ kJ mol}^{-1} \text{ } (-26.16 \text{ kcal mol}^{-1})$$

$$NOCl + H \rightarrow NO + HCl \qquad (2)$$

The reaction path was first deduced by Dunn et al. [1] in a mass-spectrometric study of the products following the addition of NOCl to O atoms produced in a discharge. O atoms were produced either by passing O_2(31–38%)/Ar mixtures at 46.3–84.2 Pa pressure through the discharge, or by an N+NO titration. The flow tube walls were poisoned with phosphoric acid. Under these conditions ClO radicals were observed, but no evidence was found for NO_2 or NCl, ruling out reactions 3 and 4.

$$NOCl + O \rightarrow NO_2 + Cl \qquad (3)$$

$$NOCl + O \rightarrow O_2 + NCl \qquad (4)$$

A value of $k_1 = 2.0 \times 10^{10}$ cm^3 mol^{-1} s^{-1} was obtained at room temperature by measuring the rate of disappearance of NOCl in excess of O atoms, and taking into consideration the fast reactions

$$ClO + O \rightarrow O_2 + Cl \qquad (5)$$

$$NOCl + Cl \rightarrow NO + Cl_2 \qquad (6)$$

Bradley et al. [2] also used the discharge flow method but over an extended temperature range. O atoms were produced by N + NO titration in Ar (184–249 Pa) and NOCl added downstream so that [NOCl] > [O]. The reaction was followed both mass spectrometrically and by e.s.r. spectroscopy. The former method showed ClO radicals to be among the products, but neither they nor Cl atoms could be observed by e.s.r. due to the fast reactions 5 and 6. No details are given of individual determinations of k_1, the authors giving only the Arrhenius expression $k_1 = 4.5 \times 10^{12} \exp(-1500/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 298–406 K. At 298 K this gives $k_1 = 2.9 \times 10^{10}$ cm^3 mol^{-1} s^{-1}, in good agreement with the value of Dunn et al.

However, Warnatz et al. [3] also followed the pseudo first order decay of O atoms in an excess of NOCl, using a discharge flow system and mass spectrometry, and obtained a higher value for k_1 at room temperature of $\sim 10^{11}$ cm^3 mol^{-1} s^{-1}. No consideration was made for the stoichiometry being different from 1:1.

Although the data from Göttingen are usually reliable, we consider that the agreement between the data of Dunn et al. [1] and of Bradley et al. [2], derived under conditions of O atom and NOCl excess, respectively, is sufficient to give an interim value $k_1 = 2.5 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 298 K, with error limits of ±50%.

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B42 NO_2 + NOCl → NO_2Cl + NO

In the reaction between nitrosyl chloride and chlorine dioxide, reaction 1 occurs as part of the reaction scheme, but has a long induction period. This can be eliminated by adding NO_2 to the initial mixture [3].

$$NO_2 + NOCl \rightarrow NO_2Cl + NO; \qquad (1)$$

$$\Delta H^\circ_{298} = 17.57 \text{ kJ mol}^{-1} \text{ } (4.20 \text{ kcal mol}^{-1})$$

Initial studies of the NOCl/ClO_2 reaction with added NO_2 at a total pressure of 13.3 kPa [2] showed that the rate of disappearance of ClO_2 was dependent solely on [NOCl] and [NO_2], and a rate constant $k_1 = 3.12 \times 10^2$ cm^3 mol^{-1} s^{-1} was obtained at 273 K. A more exhaustive study by Martin and Köhnlein [3] showed that the parallel reaction 2 was also important in the system and that the disappearance of ClO_2 depended on both reactions 1 and 2.

$$NO_2 + ClO_2 \rightarrow NO_3 + ClO \qquad (2)$$

Mixtures of NOCl (0.67–13.3 kPa)/NO_2 (0.53–2.67 kPa)/ClO_2 (0.67–8.0 kPa) were allowed to react over a temperature range 253–281 K, and the reaction followed manometrically. The reaction products were analysed by wet chemical methods to establish the overall stoichiometry, and hence the proportion of NO_2 reacting via paths 1 and 2. An overall expression was obtained for $k_1 = 1.9 \times 10^{10} \exp(-5000/T)$ cm^3 mol^{-1} s^{-1}.

Ashmore and Burnett [5] obtained a value for $k_1 = 6.6 \times 10^6$ cm^3 mol^{-1} s^{-1} at 573 K from the thermodynamic data of Ray and Ogg [4], taking k_{-1} from [1]. This compares with a value of 2.9×10^6 cm^3 mol^{-1} s^{-1} at this temperature using the expression of Martin and Köhnlein. A more recent determination of k_{-1} [6] leads to an even greater discrepancy, and no recommendation is made for k_1.

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B43 $NO_2Cl + NO \rightarrow NOCl + NO_2$

The reaction between nitryl chloride and nitric oxide is important in the $NOCl/NO_2$ system.

$$NO_2Cl + NO \rightarrow NOCl + NO_2; \qquad (1)$$

$$\Delta H^\circ_{298} = -17.57 \text{ kJ mol}^{-1} \ (-4.20 \text{ kcal mol}^{-1})$$

The rate constant k_1 was determined by Freiling et al. [1] in a static system from 300–344 K and in a flow system over the temperature range 274–302 K. In the static method, low reactant pressures were used (NO, NO_2Cl both at 16.0–147.0 Pa), while in the flow system higher pressures were used (NO, NO_2Cl both 0.38–2.51 kPa, 1:1 mixtures, in N_2, total pressure 7.60–51.2 kPa). In both methods the reaction was followed by monitoring absorption of light at 436 nm. Authors assumed a simple bimolecular mechanism, and obtained $k_1 = 8.3 \times 10^{11} \exp(-3500/T)$ cm^3 mol^{-1} s^{-1} over the whole temperature range. k_1 requoted by Benson [3] as $5.4 \times 10^{10} T^{1/2} \exp(-3300/T)$ cm^3 mol^{-1} s^{-1}.

Ashmore and Burnett [4] used this value, and the value of K_1 determined by Ray and Ogg [2] to give $k_{-1} = 6.6 \times 10^6$ cm^3 mol^{-1} s^{-1} at 573 K.

More recently, Wilkins et al. [5] studied reaction 1 in a static system, following [NO_2], [NOCl] and [NO_2Cl] by rapid scan i.r. spectroscopy at 5.5–6.3 μm. The reaction mixture contained NO (0.3–5%), NO_2Cl (0.3–2.0%) and N_2 at a total pressure of 63.5–68.1 kPa. They obtained the expression $k_1 = 1.4 \times 10^{12} \exp(-3470/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 265–324 K, almost a factor of two higher than the expression of Freiling et al.

Although the activation energy E_1 seems established at about 29 kJ mol^{-1} (7 kcal mol^{-1}), there is considerable disagreement in the A factor between the two studies, and no recommendation is made.

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B44 $NO_3 + NOCl \rightarrow NO_2Cl + NO_2$

This reaction is believed to be responsible for the rapid formation of nitryl chloride during the reaction of ozonised oxygen with nitrosyl chloride [3].

$$NOCl + NO_3 \rightarrow NO_2Cl + NO_2; \qquad (1)$$

$$\Delta H^\circ_{298} = -77.655 \text{ kJ mol}^{-1} \ (-18.560 \text{ kcal mol}^{-1})$$

Schumacher and Sprenger [1] postulated a direct reaction between nitrosyl chloride and ozone, but Johnston and Leighton [3] failed to reproduce this and claimed that there must have been traces of nitrogen in Schumacher's oxygen stream, leading to N_2O_5 formation. They repeated the experiments, in a flow tube, adding N_2O_5 to the ozone flow and following [NOCl] by absorption of light at 405 nm, obtaining NO_2Cl and oxygen as the products. They assumed the following reaction scheme:

$$N_2O_5 + M \rightleftharpoons NO_2 + NO_3 + M \qquad (2,-2)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (3)$$

$$NOCl + NO_3 \rightarrow NO_2Cl + NO_2 \qquad (1)$$

Using their own values for k_2, k_{-2} and k_3 [2], they obtained $k_1 = 7 \times 10^7$ cm^3 mol^{-1} s^{-1} at 313 K. Assuming $A_1 = 10^{12}$ cm^3 mol^{-1} s^{-1}, this gave $E_1 = 25$ kJ mol^{-1} (6 kcal mol^{-1}).

Following their experiments on the pyrolysis of N_2O_5, and their determination of k_2, k_{-2}, and k_3, Schott and Davidson [4] recalculated k_1 as 2.3×10^7 cm^3 mol^{-1} s^{-1} at 313 K.

In the absence of further experimental data, no recommendation is made for k_1.

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B45 $NOCl + NO_2Cl \rightarrow NO + NO_2 + Cl_2$

Reaction 1 occurs during the thermal decomposition of nitrosyl chloride in the presence of added NO_2, a system studied by Ashmore and Burnett [3,4].

$$NOCl + NO_2Cl \rightarrow NO + NO_2 + Cl_2; \qquad (1)$$

$$\Delta H^\circ_{298} = 59.58 \text{ kJ mol}^{-1} \ (14.24 \text{ kcal mol}^{-1})$$

Both studies used a static system. In the earlier work [3], the reaction vessel contained NOCl (0.67–11.9 kPa)/NO

(0.26–9.53 kPa)/NO_2 (56.1–317.9 Pa)/N_2 (0.34–3.17 kPa) mixtures, and the reaction was followed manometrically. $[NO_2]$ was monitored by absorption of light between 445 and 500 nm. A four reaction mechanism was assumed for consumption and production of NO_2 in the absence of N_2:

$$NOCl + NO_2 \rightleftharpoons NO_2Cl + NO \qquad (2,-2)$$

$$NO_2Cl + M \rightarrow NO_2 + Cl + M \qquad (3)$$

$$NOCl + NO_2Cl \rightarrow NO_2 + NO + Cl_2 \qquad (1)$$

Taking k_{-2} from [1] and K_2 from [2], the authors were able to obtain k_1+k_3 (M=NOCl)$=1.5\times10^6$ cm^3 mol^{-1} s^{-1} at 573 K, from which they gave $k_1\leqslant1.5\times10^6$ cm^3 mol^{-1} s^{-1}.

In the second study [4], these experiments were repeated and gave k_1+k_3 (M=NOCl)$=2.1\times10^{16}$ exp(−13 250/T) cm^3 mol^{-1} s^{-1} over the temperature range 473–573 K. No details of individual rate constant determinations are given.

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B46 NOCl + COCl → products

There has been only one study of reaction 1, by Burns and Dainton [2], while investigating the photochemical formation of phosgene

$$NOCl + COCl \rightarrow \text{products} \qquad (1)$$

They used a static photolysis system, photolysing Cl_2 (6.67–40.0 kPa), at 365 nm in the presence of CO (6.67–40.0 kPa) and NOCl (0.19–2.67 Pa). The reaction was followed both manometrically and by absorption of light at 365 nm. Reaction 1 only became important at high CO pressures. From data on the formation of phosgene without added NOCl [1] and from data on CO consumption, the authors found $k_1=4.8\times10^{13}$ exp(−570/T) cm^3 mol^{-1} s^{-1} (T=298–328 K). No details are available of k_1 at individual temperatures. No investigation of the products of reaction 1 was made, the authors postulating two paths, but giving preference to neither.

$$NOCl + COCl \rightarrow CO + Cl_2 + NO \qquad (1a)$$

$$NOCl + COCl \rightarrow COCl_2 + NO \qquad (1b)$$

In the absence of confirmatory data, no recommendation is made for k_1.

References

[1] Burns, W. G., and Dainton, F. S., Trans. Faraday Soc. **48**, 39 (1952).
[2] Burns, W. G., and Dainton, F. S., Trans. Faraday Soc. **48**, 52 (1952).

B47 $NO_2Cl + M \rightarrow NO_2 + Cl + M$

THERMODYNAMIC DATA

T (K)	ΔH^o ($kJ\ mol^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	$\log K_p$ (K_p in atm)	$\log K_c$ (K_c in mol cm^{-3})
298	142.25	132.91	-17.890	-22.279
300	142.26	132.96	-17.826	-22.217
500	142.90	134.66	- 7.895	-12.508
1000	142.66	134.46	- 0.429	- 5.343
1500	141.47	133.51	2.048	- 3.043
2000	139.90	132.61	3.273	- 1.942
2500	138.14	131.83	3.999	- 1.313
3000	136.30	131.15	4.478	- 0.913
3500	134.39	130.57	4.814	- 0.644
4000	132.44	130.05	5.063	- 0.453
4500	130.45	129.58	5.254	- 0.314
5000	128.45	129.16	5.404	- 0.209

SI Units: $\log(Kp/Pa) = \log(K_p/atm) + 5.006$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 5.5 \times 10^{14} \exp(-12\ 700/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)

$= 9.1 \times 10^{-10} \exp(-12\ 700/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)

Temperature Range: 450-1000 K.

Suggested Error Limits for Calculated Rate Constant: ±75% over the whole temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.74 \pm 0.25$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.04 \pm 0.25$

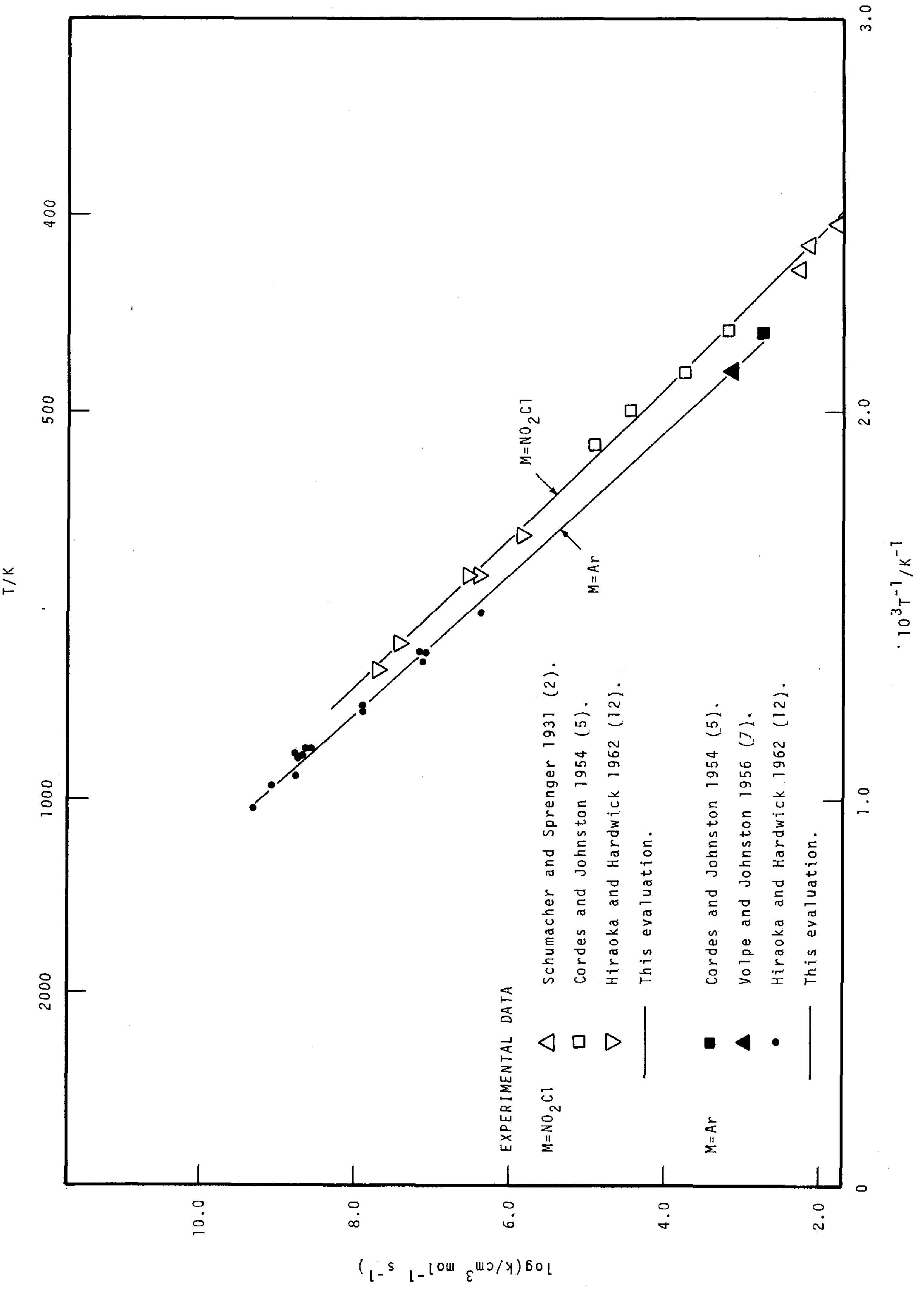
$E/J\ mol^{-1} = 105\ 900 \pm 21\ 000$

$E/cal\ mol^{-1} = 25\ 300 \pm 5\ 000$

Note: Expressions for $k^o(M=NO_2Cl)$, $k^o(M=N_2)$ and $k^o(M=NO_2)$ are given in the Discussion.

$NO_2Cl + M \rightarrow NO_2 + Cl + M$

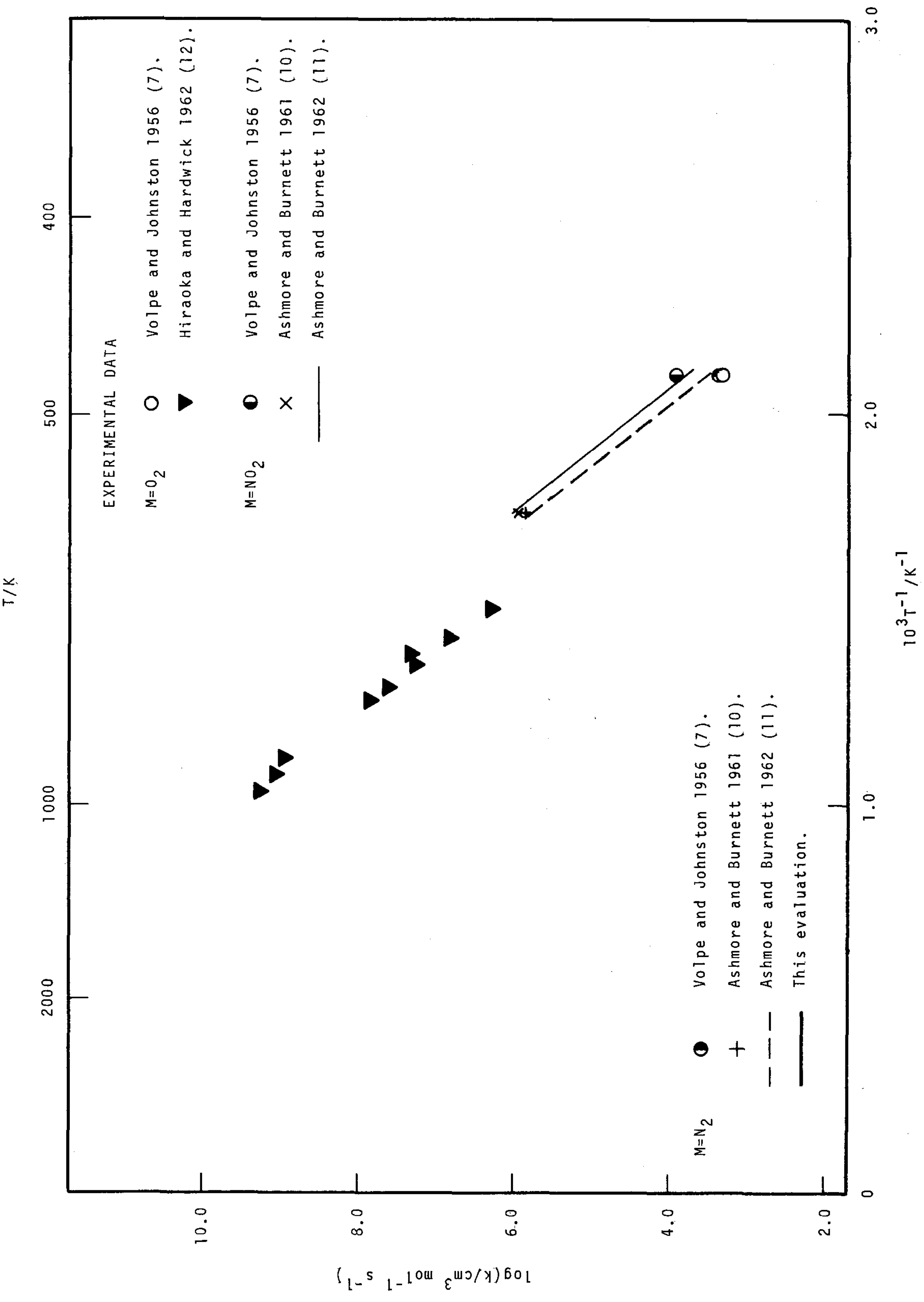
SECOND ORDER PLOT



$NO_2Cl + M \rightarrow NO_2 + Cl + M$

EXPERIMENTAL DATA

Rate Constant k (cm mol$^-$ s^{-1})		Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o				
0.6×10^2	$M = NO_2Cl$	403	Static system. NO_2Cl alone at 1.33-792 kPa pressure and in NO_2Cl (14-62.5%)/M mixtures at total pressures of 17.7-67.6 kPa, where M= H_2, N_2, O_2, Cl_2, NO_2, CO_2 or CO. Reaction followed manometrically. SCHUMACHER and SPRENGER 1929 (1) SCHUMACHER and SPRENGER 1931 (2)	Authors found that the rate constant associated with the disappearance of NO_2Cl increased with pressure, both for pure NO_2Cl and in NO_2Cl/M mixtures. They concluded that the rate determining step was a unimolecular reaction occurring in its transition region from first to second order kinetics, but were unable to go to high or low enough pressures to obtain limiting values of k_1. $NO_2Cl + M \rightarrow NO_2 + Cl + M$ 1 The quoted second-order rate constants for $M = NO_2Cl$ were plotted by CORDES and JOHNSTON (5), and used by (12,16). We obtain the expression $2.0 \times 10^{16} \exp(-13\,700/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the given temperature range.
1.3×10^2		413		
1.9×10^2		423		
1.7×10^3	$M = NO_2Cl$	453	Static system. NO_2Cl alone at 62.4-1507 Pa pressure and in NO_2Cl (10%)/Ar mixtures at 0.75-8.0 kPa and in NO_2Cl (32-59%)/NO_2 mixtures, no pressures given. $[NO_2]$ monitored by i.r. absorption at 4.36 μm. CORDES and JOHNSTON 1954 (5)	For experiments involving pure NO_2Cl, authors used much lower pressures than SCHUMACHER and SPRENGER, to obtain the limiting second order rate constant. They obtained the expression $k_1 = (2.9 \pm 0.2) \times 10^{16} \exp(-13\,850/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the quoted temperature range. Used by (12, 16,17,20,21). Quoted by (10,18,19). E_1 quoted by (11). A_1 quoted by (9). In the experiments with Ar as third body only the low pressure results were used in evaluating k_1 as a transition to first order kinetics began above about 2 kPa. NO_2 was found to give similar results as a third body as NO_2Cl.
6.0×10^3		476		
2.8×10^4		500		
8.5×10^4		521		
5.5×10^2	M=Ar	453		



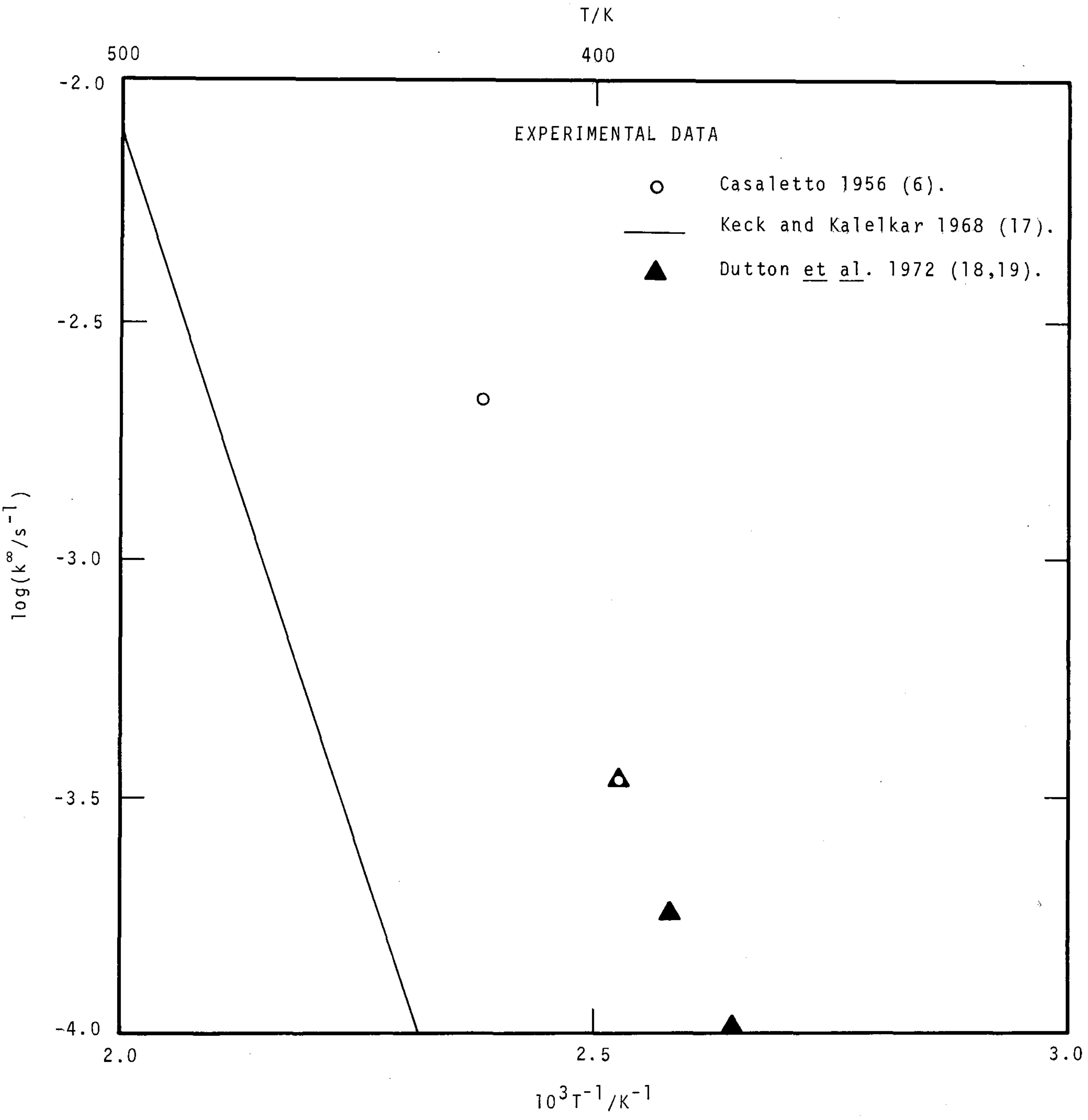
$NO_2Cl + M \rightarrow NO_2 + Cl + M$
SECOND ORDER PLOT

$NO_2Cl + M \rightarrow NO_2 + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
8.0×10^3 M=NO_2 2.6×10^3 M=CO_2 2.4×10^3 M=SF_6 2.7×10^3 M=N_2O 1.4×10^3 M=Ar 3.1×10^3 M=SiF_4 2.3×10^3 M=Cl_2 1.4×10^3 M=Kr 1.8×10^3 M=O_2 1.9×10^3 M=He 2.1×10^3 M=N_2 1.9×10^3 M=Xe 1.3×10^3 M=Ne 2.5×10^3 M=H_2 3.3×10^3 M=CCl_2F_2	476 476 476 476 476 476 476 476 476 476 476 476 476 476 476	Static system, as in (5). NO_2Cl/M mixtures, with $[NO_2Cl]$ constant at 368 Pa, and [M]=19.8-1021 Pa, where M=NO_2,CO_2,SF_6,N_2O,Ar,SiF_4, Cl_2,Kr,O_2,He,N_2,Xe,Ne or CCl_2F_2. $[NO_2]$ monitored by i.r. absorption at 4.36 μm. VOLPE and JOHNSTON 1956 (7)	Decomposition found to predominate over any possible reaction with the third body. All decompositions found to be second order. k_1(M=NO_2) and k_1(M=N_2) quoted by (11), used by (10). k_1(M=Ar) used by (12,17,20). k_1(M=O_2) quoted by (12).
		Theoretical study. SLATER 1959 (9)	A_1 derived from KASSEL theory (3), to be 7.2×10^{16} cm^3 mol^{-1} s^{-1}. Also some work done on the ratio k_1/k_1^∞ at various pressures, but no absolute value of k_1^∞ given.
$(8.3\pm1.1)\times10^5$ M=NO_2 $(6.9\pm1.8)\times10^5$ M=N_2 $\leqslant1.5\times10^6$ M=NOCl	573 573 573	Static system. NOCl(0.67-1.9 kPa)/NO(0.26-9.53 kPa) /NO_2 (56.1-317.9 Pa)/N_2 (0.34-3.17 kPa) mixtures. Reaction followed manometrically. $[NO_2]$ monitored by absorption of light at 445-500 nm. ASHMORE and BURNETT 1961 (10)	The following scheme was proposed for production and consumption of NO_2: $NOCl + NO_2 \rightleftharpoons NO_2Cl + NO$ 2,-2 $NO_2Cl + M \rightarrow NO_2 + Cl + M$ 1 $NO_2Cl + NOCl \rightarrow NO_2 + NO + Cl_2$ 3 Taking k_2 and k_{-2} from (4) and (8) and k_3+k_1(M=NOCl) from runs made in the absence of N_2, authors obtained the quoted values of k_1. The upper limit for k_1(M=NOCl) is in fact the value of k_3+k_1(M=NOCl).
$1.4\times10^{17}\exp(-14\ 670/T)$ M=NO_2 $1.3\times10^{17}\exp(-14\ 970/T)$ M=N_2	473-573 473-573	Static system. NOCl alone, or with NO, N_2 and NO_2 added. No details of pressures given. Reaction followed as in (10). ASHMORE and BURNETT 1962 (11).	Extension of work, in (10) to lower temperatures. Authors give the following values at 476 K: k_1(M=N_2)=2.8×10^3 cm^3 mol^{-1} s^{-1}; k_1(M=NO_2)=5.9×10^3 cm^3 mol^{-1} s^{-1}. They also give the following expression for k_1(M=NOCl)+k_3=$2.1\times10^{16}\exp(-13\ 250/T)$ cm^3 mol^{-1} s^{-1} (T=473-573 K). No upper limit for k_1(M=NOCl) was given. k_1(M=N_2) quoted by (14,16). k_1(M=NO_2) quoted by (14).

$NO_2Cl + M \rightarrow NO_2 + Cl + M$
FIRST ORDER PLOT



$NO_2Cl + M \rightarrow NO_2 + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
$2.5x10^6$	M=Ar	678	Shock tube study. NO_2Cl (100%), NO_2Cl(1.9-5.1%)/Ar and NO_2Cl(2%)/O_2 mixtures at total pressures of 9.28 -78.6 kPa. $[NO_2]$ monitored by absorption of light at 434 nm. HIRAOKA and HARDWICK 1962 (12)	The following expressions were derived from these data: $k_1(M=Ar)=2.8x10^{13}T^{0.5}exp(-13\ 000/T)$ cm^3 mol^{-1} s^{-1} (used by (15,21)). $k_1(M=O_2)=3.7x10^{13}T^{0.5}exp(-13\ 500/T)$ cm^3 mol^{-1} s^{-1}, $k_1(M=NO_2Cl)=1.7x10^{13}T^{0.5}exp(-11\ 900/T)$ cm^3 mol^{-1} s^{-1}. The authors used the results from (7) to give $k_1(M=Ar)=1.3x10^{13}T^{0.5}exp(-12\ 430/T)$ cm^3 mol^{-1} s^{-1} and those from (2 and 5) to give $k_1(M=NO_2Cl)=8.0x10^{13}T^{0.5}exp(-11\ 700/T)$ cm^3 mol^{-1} s^{-1}.
$1.5x10^7$		727		
$1.2x10^7$		730		
$1.4x10^7$		739		
$8.0x10^7$		816		
$8.0x10^7$		819		
$4.0x10^8$		882		
$4.4x10^8$		888		
$6.0x10^8$		891		
$9.6x10^8$		899		
$5.5x10^8$		911		
$5.5x10^8$		941		
$1.2x10^9$		965		
$2.0x10^9$		1032		
$2.2x10^6$	$M=O_2$	666		
$7.0x10^6$		700		
$2.3x10^7$		721		
$1.9x10^7$		737		
$4.6x10^7$		768		
$7.0x10^7$		790		
$9.0x10^8$		899		
$1.2x10^9$		936		
$1.7x10^9$		967		
$7.0x10^5$	$M=NO_2Cl$	596		
$3.3x10^6$		634		
$3.0x10^6$		634		
$2.6x10^7$		712		
$5.0x10^7$		753		

1st ORDER RATE CONSTANT k_1^∞ (s^{-1})

$3.5x10^{-4}$	396	Static system. No details given. CASALETTO 1956 (6)	Data obtained at "moderate" and "high" pressures (19). The lack of a smooth transition between the two sets of results is attributed to a grease-catalysed contribution to the moderate pressure data. Values of k_1 given are from high pressure data. Quoted by (9,19).
$2.2x10^{-3}$	420		
$9.1x10^9exp(-13\ 900/T)$	All	Theoretical study based on statistical reaction rate theory. KECK and KALELKAR 1968 (17)	Authors obtain a first order rate constant $k_1^\infty(M=Ar)=2.0x10^{-4}$ s^{-1} at 460 K from the results of (5 and 7), and compare this with their own value $k_1^\infty=6.3x10^{-4}$ s^{-1} at that temperature. No further details given.

$NO_2Cl + M \rightarrow NO_2 + Cl + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (s^{-1})	Temperature (K)	Method and Reference	Comments
1.0×10^{-4} 1.8×10^{-4} 3.5×10^{-4}	378 388 396	Static system. NO_2Cl/N_2 mixtures (proportion not given) at total pressures of 0.97-29.2 MPa. $[NO_2]$ monitored by absorption of light at 436 nm. DUTTON 1971 (18) DUTTON, BUNKER and HARRIS 1972 (19)	At the high pressures used, authors noted only a small pressure effect was observed, and reaction 1 was taken as being in its first-order region. $NO_2Cl + M \rightarrow NO_2 + Cl + M$ 1 Combining their results with those of (6), they obtained an activation energy of ∿105 kJ mol^{-1} (25 kcal mol^{-1}). From their results alone we obtain the expression $k_1^{\infty} = 7.0 \times 10^7 \exp(-10\ 300/T)$ s^{-1} over the quoted temperature range. Used by (21, 24).

REVIEW ARTICLES

Review of dissociation of tetratomic molecules. TROE and WAGNER 1967 (16)	Quote results of (5,11) ($M=N_2$), also the liquid phase work of BEGGS et al. (13). Expression from (12) (M=Ar) recalculated in Arrhenius form to give $k_1 = 1.3 \times 10^{15} \exp(-13\ 400/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 600-1000 K.
Review of dissociation of tetratomic molecules. TROE and WAGNER 1973 (20)	Results quoted from (5) for $M=NO_2Cl$ converted to M=Ar by using the relative third body efficiencies from (7). Expression for M=Ar from (12) extended over the temperature range 400-1000 K.

RELATIVE THIRD BODY COLLISION EFFICIENCIES

M=Ar	NO_2Cl	NO_2	CO_2	SF_6	SiF_4	N_2O	He	Ne	Kr	Xe	H_2	N_2	O_2	CCl_2F_2	Cl_2	T K	Ref
1	3.09															453	(5)
1		5.7	1.86	1.7	2.2	1.92	1.36	0.93	1.0	1.36	1.79	1.5	1.29	2.36	1.64	476	(7)
	1.2[a]											1[a]				573	(10)
	1.82[a]											1[a]				573	(11)
1													0.94			899	(12)

a = Efficiency relative to N_2

Discussion

The decomposition of nitryl chloride has received much attention, both theoretical and experimental. Because of its size, first order decomposition is only observed at very high pressures [6,19,20,23]. The bimolecular decomposition reaction 4 is unknown, no evidence having been found in any decomposition studies. In this respect it differs from nitrosyl chloride. It also shows the typical nitryl/nitrosyl relationship in that its decomposition is approximately four orders of magnitude faster at 500 K.

$$NO_2Cl + M \rightarrow NO_2 + Cl + M \qquad (1)$$

$$NO_2Cl + NO_2Cl \rightarrow 2NO_2 + Cl_2 \qquad (4)$$

Most of the studies of k_1 have involved monitoring either the disappearance of NO_2Cl or the appearance of NO_2, but changes in total pressure have also been used [1,2]. In some cases it has been necessary to halve the values of k_1 obtained by the former methods, to take into account the rapid reaction 5 which follows after reaction 1.

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2 \qquad (5)$$

Watson [22] estimates $k_5 >> 2\times10^{10}$ cm^3 mol^{-1} s^{-1} following preliminary work by Clyne and White [25].

Second Order Rate Constant k_1°

The majority of studies of reaction 1 have been in the relatively low pressure, second-order region [1,2,5,7,10,11,12]. With the exception of the shock tube work of Hiraoka and Hardwick [12], all work has been in static systems. Over the temperature range studied (400–1000 K), the agreement is reasonable for each of the wide range of third bodies considered. With NO_2Cl itself as third body, three studies show good agreement over the whole temperature range from 400–753 K [1,5,12]. Schumacher and Sprenger [1,2] were not able to obtain a limiting low pressure rate constant, but the values of k_1 given, as recalculated by Cordes and Johnston [5] give good enough agreement to be considered in our evaluation. We recommend the expression $k_1^\circ(M=NO_2Cl)=4.0\times10^{14}$ $\exp(-11\,800/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 400–750 K, with error limits of a factor of two.

The data for $k_1(M=Ar)$ consist of that of Hiraoka and Hardwick [12] coupled with two low temperature determinations [5,7].

The agreement is good, and despite the absence of any medium temperature results we recommend the expression $k_1^\circ(M=Ar)=5.5\times10^{14}$ $\exp(-12\,700/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 450–1000 K, with error limits of ±75%.

The remaining high temperature data are for $M=O_2$, for which there is only one low temperature point, and we consequently make no recommendation here. Of the other third bodies, only NO_2 and N_2 have been considered in any detail. The three studies for $M=N_2$ and $M=NO_2$ [7,10,11] are in good agreement, and we recommend the expressions of Ashmore and Burnett [11] over the temperature range 450–600 K, with error limits of ±50%, i.e., $k_1^\circ(M=N_2)=1.3\times10^{17}$ $\exp(-14\,970/T)$ cm^3 mol^{-1} s^{-1}, and $k_1^\circ(M=NO_2)=1.4\times10^{17}$ $\exp(-14\,670/T)$ cm^3 mol^{-1} s^{-1}.

Volpe and Johnston [7] have investigated the effect of a wide range of third bodies at 476 K. The relative efficiencies are given in the table following this Discussion.

1st Order Rate Constant k_1^∞

There have been only two investigations of reaction 1 conducted at pressures sufficiently high to put the reaction in its first order region. No details are available of Casaletto's work [6], but his value of k_1 at 396 K agrees with that of Dutton et al. [18,19] at the same temperature, their results being obtained at pressures of up to 300 atm, where no second order contribution would be expected [20,23]. In a theoretical study, Keck and Kalelkar [17] found $E_1^\infty=115$ kJ mol^{-1} (27.5 kcal mol^{-1}). A least squares fit to the data of [6 and 18,19] gives $k_1^\infty=4.1\times10^9$ $\exp(-11\,900/T)$ s^{-1} over the temperature range 370–420 K. However, this expression is unreliable as (a) the activation energy E_1^∞ is smaller than ΔH° for reaction 1, and indeed smaller than E_1° for the low pressure limit, and (b) the pre-exponential factor is far too small for a first order unimolecular decomposition. We feel, therefore, that there are aspects of the reaction mechanism as yet not fully understood, and make no recommendation.

Rate of the Reverse Reaction

There is only one reported value for k_{-1}, by Clark and Clyne [15].

$$NO_2 + Cl + M \rightarrow NO_2Cl + M \qquad (-1)$$

In a discharge flow system at 293 K, they obtained $k_{-1} = 1 \times 10^{17}$ cm^6 mol^{-2} s^{-1} (M=Ar) as a preliminary value, but no further details are recorded. As expected, this is faster than the corresponding NO reaction, and the NO_2Cl itself is rapidly removed by the titration reaction 5.

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2 \qquad (5)$$

Watson [22,26] attributes a preliminary value of k_{-1} (M=Ar)$=2.6 \times 10^{17}$ cm^6 mol^{-2} s^{-1} at 398 K to Clyne and White [25], but no further details are available.

A value of $k_{-1} = 3.5 \times 10^{18}$ cm^6 mol^{-2} s^{-1} is obtained from the expression for the reverse reaction and the equilibrium constant, but in view of the lack of firm data on k_1 at 293 K we cannot recommend this value either.

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B48 $ClO + NO_2 + M \rightarrow ClONO_2 + M$

THERMODYNAMIC DATA

Thermodynamic data are unavailable for $ClONO_2$.

RECOMMENDED RATE CONSTANT

$k^o = 1.68 \times 10^{15} \exp(1070/T)$ $cm^6\ mol^{-2}\ s^{-1}$ $(M=N_2)$
$= 4.63 \times 10^{-33} \exp(1070/T)$ $cm^6\ molecule^{-2}\ s^{-1}$ $(M=N_2)$

Temperature Range: 240-500 K.

Suggested Error Limits for Calculated Rate Constant: ±20% over quoted temperature interval.

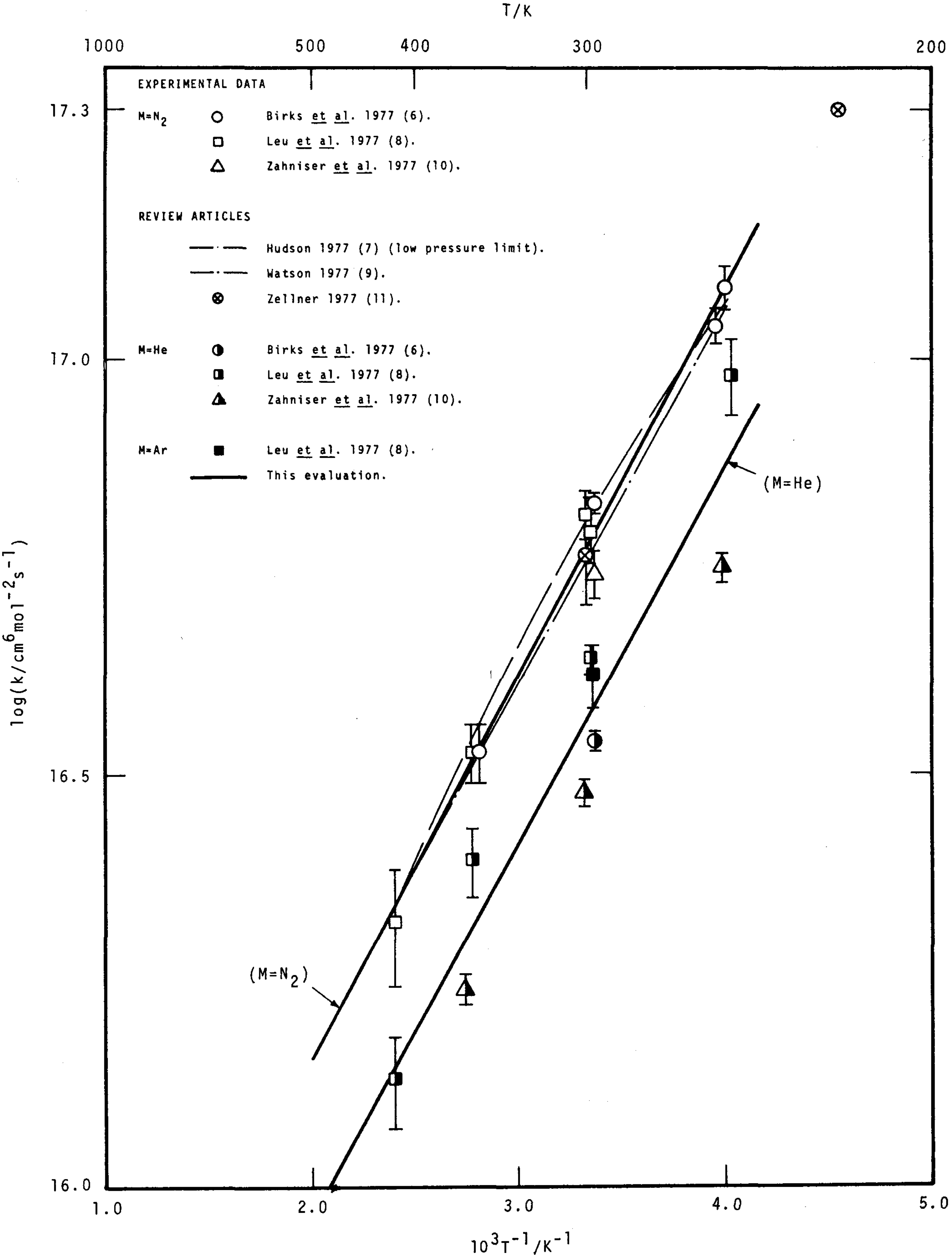
Note: an expression for k^o (M=He) is also given in the Discussion.

Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 15.225 \pm 0.08$
$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -32.334 \pm 0.08$
$E/J\ mol^{-1} = -8\ 900 \pm 1\ 420$
$E/cal\ mol^{-1} = -2\ 130 \pm 340$

EXPERIMENTAL DATA

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.22\pm0.07)\times10^{17}$ M=N_2	250	Discharge flow system. Cl_2 (0.25%)/He mixtures passed through discharge. O_3 added in large excess downstream, and NO_2(1-5%)/He or N_2 mixtures added further downstream, such that $[NO_2]/[ClO] \geq 20$. Total pressures 1-5 mm Hg (133.3-666.5 Pa). Reaction followed by decay of [ClO], using mass spectrometry. BIRKS, SHOEMAKER, LECK, BORDERS and HART 1976 (3) and 1977 (6)	ClO decay corrected for contribution from cracking of $ClONO_2$ product. Reappearance of ClO characterised by parameter α, and authors found that 20% error in α (α varied over range 0.1-0.15) gave ±5% error in k_1. $ClO + NO_2 + M \rightarrow ClONO_2 + M$ 1 No significant variation with pressure. Least squares fit to these data given as $k_1=(1.60\pm0.2)\times10^{15} \exp\{(1090\pm70)/T\}$ $cm^6\ mol^{-2}\ s^{-1}$ $(M=N_2)$.
$(1.10\pm0.05)\times10^{17}$ M=N_2	253		
$(6.71\pm0.2\ )\times10^{16}$ M=N_2	297		
$(3.37\pm0.3\ )\times10^{16}$ M=N_2	356		
$(3.47\pm0.1\ )\times10^{16}$ M=He	297		
$(9.57\pm1.02)\times10^{16}$ M=He	248	Discharge flow system. Cl_2 (0.01%)/He mixtures passed through discharge. O_3 and He, Ar or N_2 added downstream. NO_2 added through moveable inlet. Total pressures 1-9 mm Hg (133.3-1200 Pa). [ClO] range 1.7×10^{-13}-8.3×10^{-12} mol cm^{-3}, and $6.6\times10^{-10} \leq [NO_2] \leq 1.0\times10^{-8}$ mol cm^{-3}. Mass spectrometry used to monitor [ClO]. LEU, LIN and DE MORE 1977 (8)	Pseudo first order decay of ClO used to derive k_1. Linear plots of second order rate constant indicated purely third order process. These data expressed as $k_1(M=He)=(9.65\pm1.2)\times10^{14} \exp\{(1140\pm40)/T\}$ $cm^6\ mol^{-2}\ s^{-1}$, $k_1(M=N_2)=(1.34\pm0.1)\times10^{15} \exp\{(1150\pm20)/T\}$ $cm^6\ mol^{-2}\ s^{-1}$.
$(4.35\pm0.2\ )\times10^{16}$ M=He	299		
$(2.48\pm0.2\ )\times10^{16}$ M=He	360		
$(1.35\pm0.2\ )\times10^{16}$ M=He	417		
$(4.17\pm0.4\ )\times10^{16}$ M=Ar	298		
$(6.24\pm0.6\ )\times10^{16}$ M=N_2	299		
$(6.53\pm0.4\ )\times10^{16}$ M=N_2	300		
$(3.36\pm0.3\ )\times10^{16}$ M=N_2	360		
$(2.10\pm0.3\ )\times10^{16}$ M=N_2	417		

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



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

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(5.62\pm0.2)\times10^{16}$ M=He $(3.01\pm0.1)\times10^{16}$ M=He $(1.74\pm0.1)\times10^{16}$ M=He $(5.51\pm0.4)\times10^{16}$ M=N_2	251 301 365 297	Discharge flow system. Cl_2/He mixtures passed through discharge, and O_3 added downstream. NO_2 added through sliding inlet, giving $[NO_2]/[ClO]>10^3$. Total pressures 1.1-6.5 mm Hg (146.6-866.5 Pa). Some O_3 added to NO_2 to scavenge NO impurities. [ClO] determined by titration with NO, and monitoring [Cl] by resonance fluorescence at 134.7 nm. ZAHNISER, CHANG and KAUFMAN 1977 (10)	Titration of ClO by NO gave Cl atoms via reaction $ClO + NO \rightarrow Cl + NO_2$ NO impurities in NO_2, at level of ∿0.1%, gave overestimation of k_1 by factor 2.5, due to ClO removal by sequence $ClO + NO \rightarrow Cl + NO_2$ $Cl + NO_2 + M \rightarrow ClNO_2 + M$ Purification of NO_2 to $NO\approx10^{-2}\%$ gave values of k_1 20% higher than those obtained upon addition of O_3 traces to NO_2, reducing NO to $<2\times10^{-3}\%$ by mechanism $NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + O_3 \rightarrow NO_3 + O_2$ $NO_3 + NO \rightarrow 2NO_2$ Values for k_1(M=He) expressed as $2.01\times10^{24}T^{-3.15}$ or $(1.28\pm0.02)\times10^{15}\exp\{(950\pm10)/T\}$ $cm^6\ mol^{-2}\ s^{-1}$.

REVIEW ARTICLES

$\frac{1.20\times10^{25}T^{-3.34}}{1+6.75\times10^{3}\ T^{-0.6}[M]^{0.5}}$ M=N_2	250-417	Review. Recommended expression for use in stratospheric modelling. HUDSON 1977 (7)	Expression is that proposed by ZAHNISER et al. (10), with denominator giving pressure dependence based on theoretical RRKM model. [M] in this expression is in mol cm^{-3}. Expression shown on Arrhenius plot is with [M]=0.
$1.85\times10^{15}\exp(1030/T)$ M=N_2	250-417	Review. Preferred expression, derived from least squares fit to all available data (3,8,10). WATSON 1977 (9)	Author comments that slight fall-off is to be expected at ∿50 mm Hg (6.7 kPa) from theoretical RRKM predictions. None of available data obtained in this pressure range (relevant to stratosphere at 20-25 km).
2.0×10^{17} M=N_2 $(5.8\pm0.7)\times10^{16}$ M=N_2	220 300	Theoretical application of Kassel fall-off curves to experimental data. ZELLNER 1977 (11)	k_1 data of (6,8 and 10) considered. Value at 300 K from all data and at 220 K from extrapolation of (6 and 8), plus assumption of same temperature dependence for M=N_2 as for M=He in work of (10).

Discussion

Chlorine nitrate has been postulated [4,5] as a possible sink for both ClO and NO_x pollutants in the stratosphere. Several investigations have since been made of the rate of $ClONO_2$ formation, all using discharge flow systems [3,8,10]. ClO was produced by adding O_3 to Cl_2/carrier gas that had been passed through a discharge:

$$Cl + O_3 \rightarrow ClO + O_2$$

All these studies followed the pseudo first order decay of ClO in excess NO_2, using mass spectrometry [3,8] or by titration with NO

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

followed by determination of [Cl] by resonance fluorescence [10]. There is good agreement between the data of [3 and 8] for $k_1(M=N_2)$, but the single value determined by Zahniser et al. [10] is somewhat lower, by ~15%. There is more scatter over the data for $k_1(M=He)$, with a difference of ~40% between [10] and [8].

On the basis of all the available data, we recommend the expressions

$$k_1^\circ = 1.68\times10^{15} \exp(1070/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \ (M=N_2)$$

with uncertainty limits of ±20%, and

$$k_1^\circ = 1.15\times10^{15} \exp(1040/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \ (M=He)$$

to ±50%. Both these expressions are valid over the temperature range 240–500 K.

Rate of the Reverse Reaction

It is believed that chlorine nitrate does not decompose by the same path as the fluoride, reaction –1 being energetically favourable to the route leading to NO_3+Cl [1]

$$ClONO_2 + M \rightarrow ClO + NO_2 + M \qquad (-1)$$

The decomposition was first studied in a static system by Cafferata et al. [1]. Mixtures of $ClONO_2$ (14.9–182.1 mm Hg; 2.0–24.3 kPa)/NO_2 (0.3–31.2 mm Hg; 40 Pa–4.2 kPa), $ClONO_2$ (42.2 mm Hg; 5.6 kPa)/NO_2 (1 mm Hg; 133.3 Pa)/Cl_2 (204.8 mm Hg; 27.3 kPa), and $ClONO_2$ (51.4 mm Hg; 6.9 kPa)/NO_2 (0.5 mm Hg; 66.7 Pa)/CO_2 (386.5 mm Hg; 51.5 kPa) were pyrolysed at temperatures 363–403 K. From the pressure profiles, with corrections for the reformation of $ClONO_2$ by reaction 1, and removal by reaction 2

$$ClO + ClONO_2 \rightarrow NO_2 + O_2 + Cl_2 \qquad (2)$$

these authors obtained pressure-dependent values of k_{-1}. Plotting $1/k_{-1}$ vs. $1/p$ they extrapolated to infinte pressure, and obtained $k_{-1}^\infty=1.5\times10^{14} \exp(-15\ 100/T)$ s^{-1}.

The reaction was further studied by Knauth et al. [2], both in the gas phase and in solution, in order to establish the mechanism more accurately. The gas phase study was a calorimetric one, at 373 K, to measure the dissociation energy of NO_3Cl over a pressure range 8.12–23.4 kPa. Assuming $(\Delta H_{298}^\circ)_{-1} \leqslant E_{-1}$, and $A_{-1}=10^{14}$ s^{-1}, this gave $k_{-1}^\infty > 10^{14} \exp(-12\ 500/T)$ s^{-1}, at and around 373 K. This lower limit is in fact four orders of magnitude greater than the value of Cafferata et al. at 373 K. Knauth et al. attribute this difference to the contribution of reaction 1, which was underestimated by Cafferata et al.

Note Added in Proof

In a recent study [12] Knauth has followed the decomposition of $ClONO_2$ in a static system by measurement of [$ClONO_2$] by i.r. spectrophotometry, over pressure and temperature ranges of 20–375 mm Hg(2.7–50 kPa) and 333–363 K. Studies in N_2 yielded the expression

$$k^\circ_{-1}(M=N_2) = 7.9\times10^{18} \exp(-12\ 000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The experimental method is simple and direct, and the reactions of the product radicals are sufficiently well understood to suggest that the measured values of k_{-1} are reasonably reliable, but confirmatory studies are needed before any recommendation can be made.

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B49 $O + ClONO_2 \rightarrow$ products

THERMODYNAMIC DATA

Thermodynamic data for $ClONO_2$ are unavailable.

RECOMMENDED RATE CONSTANT

$k = 1.83 \times 10^{12} \exp(-810/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$

$\ \ = 3.03 \times 10^{-12} \exp(-810/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$

Temperature Range: 213-295 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over quoted temperature range.

Note: this expression is that given by KURYLO 1977 (3).

Rate Parameters:

$\log(A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 12.261 \pm 0.18$

$\log(A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = -11.519 \pm 0.18$

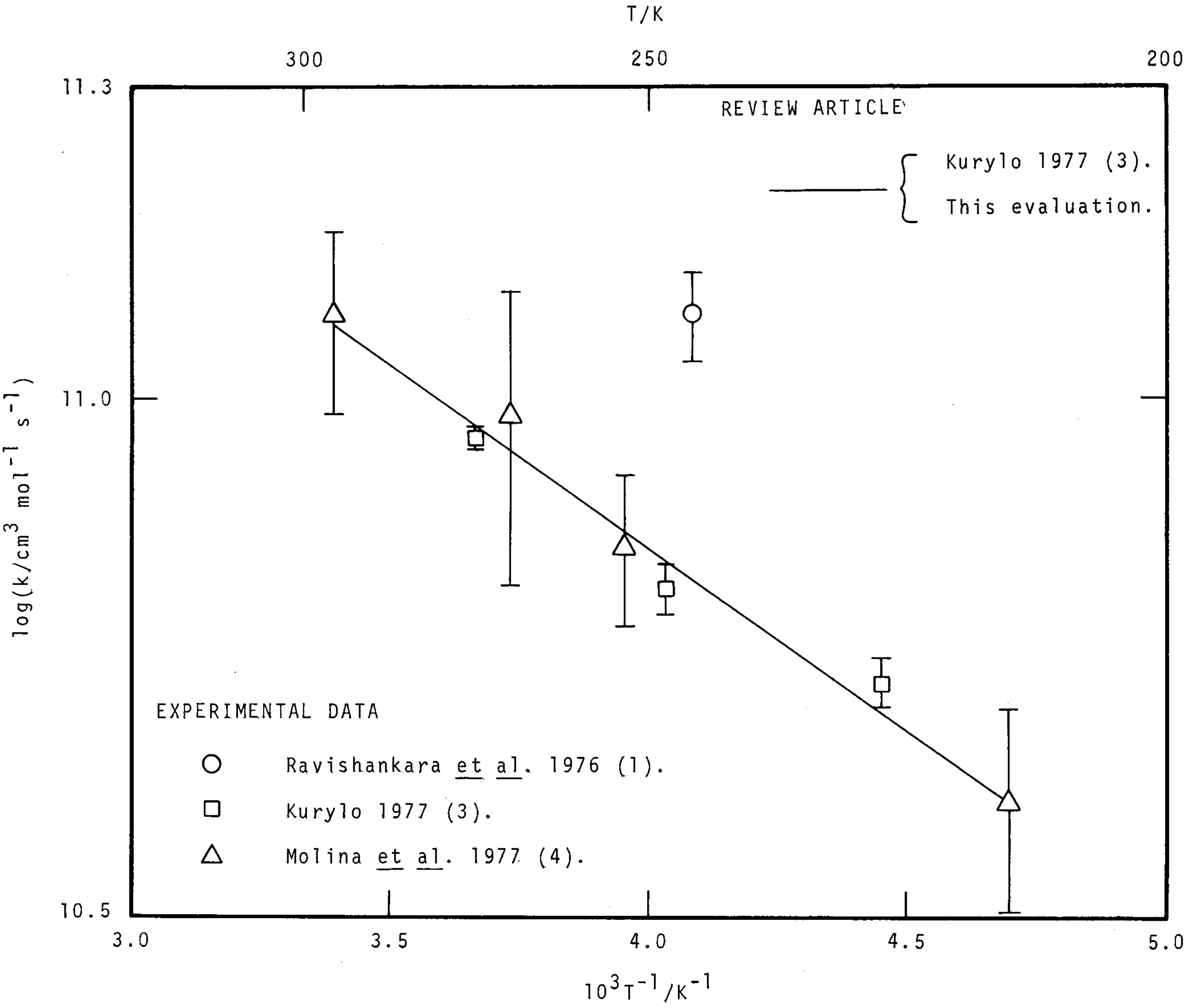
$E/\mathrm{J\ mol^{-1}} = 6\ 720 \pm 5\ 280$

$E/\mathrm{cal\ mol^{-1}} = 1\ 610 \pm 1\ 260$

EXPERIMENTAL DATA

Rate Constant k ($\mathrm{cm^3\ mol^{-1}\ s^{-1}}$)	Temperature (K)	Method and Reference	Comments
$(1.20\pm0.1)\times10^{11}$	245	Flash photolysis study. O_2 (150 μm Hg; 20 Pa)/$ClONO_2$ (0-16 μm Hg; 2.1 Pa)/Ar (20 mm Hg; 2.7 kPa) mixtures. [O] followed by resonance fluorescence. RAVISHANKARA, DAVIS, SMITH, TESI and SPENCER 1976 (1) and 1977 (5)	$[ClONO_2]/[O] > 10^3$ suggested secondary reactions as negligible. No dependence of pseudo first order rate constants on flash energy.
$(5.32\pm0.3)\times10^{10}$ $(6.56\pm0.4)\times10^{10}$ $(9.15\pm0.2)\times10^{10}$	225 248 273	Flash photolysis flow system. $ClONO_2$/Ar mixtures at 10 mm Hg (1.3 kPa) total pressure, with $8.34\times10^{-10} \leqslant [ClONO_2] \leqslant 5.52\times10^{-9}$ mol $\mathrm{cm^{-3}}$. O atom resonance fluorescence monitored. KURYLO 1977 (3)	As $[ClONO_2]/[O] \geqslant 100$, pseudo first order decay of [O] analysed. No variation in first order rate constants with flash energy, i.e. [O], indicating unimportant secondary reactions. These data expressed as $k_1=(1.13 \pm0.8)\times10^{12}\exp\{-(690\pm170)/T\}$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$. Combination of these results with those of MOLINA <u>et al</u>. (4) gave $k_1=(1.83\pm0.9)\times10^{12} \exp\{-(810\pm130)/T\}$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$ (213-295 K). Used by (2).

$O + ClONO_2 \rightarrow$ products



O + $ClONO_2 \rightarrow$ products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.10\pm0.9)\times10^{10}$	213	N_2-discharge flow system. NO added to N atoms, and $ClONO_2$ added downstream through moveable inlet. Total pressures 1-2 mm Hg (133.3-266.6 Pa). [O] determined by titration with NO, and air afterglow. MOLINA, SPENCER and MOLINA 1977 (4)	$O + ClONO_2 \rightarrow$ products 1 Values of k_1 from pseudo first order decay of [O]. k_1 found to vary with both $[ClONO_2]/[O]$ and [NO]/[O], limiting values obtained at $[ClONO_2]/[O] > 1500$ and $[NO]/[O] > 100$, at 295 K. Results considered consistent with reaction path $O + ClONO_2 \rightarrow ClO + NO_3$ 1a with suppression of subsequent reaction 2 $O + ClO \rightarrow Cl + O_2$ 2 by NO according to $NO + ClO \rightarrow Cl + NO_2$ Authors expressed these data as $k_1=(2.05\pm0.4)\times10^{12}\exp\{-(840\pm60)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
$(7.23\pm1.2)\times10^{10}$	253		
$(9.64\pm3.0)\times10^{10}$	268		
$(1.20\pm0.2)\times10^{11}$	295		

Discussion

Recent concern over the effects of Cl and NO_x on the Earth's ozone layer has led to investigations of the reactions of chlorine nitrate, possibly formed in the stratosphere by the reaction

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

and a possible common sink for both ClO_x and NO_x. Although the primary removal of $ClONO_2$ is believed to be solar photolysis, the possibility that removal by O atoms is important has prompted studies of reaction 1

$$O + ClONO_2 \rightarrow \text{products} \qquad (1)$$

The three investigations reported so far have all used different techniques. The flash photolysis flow results of Kurylo [3] are in good agreement with the discharge flow data of Molina et al. [4], while the static flash photolysis results of Ravishankara et al. [1,5] are nearly a factor of 2 higher at 245 K. Kurylo attributed this difference to possible NO_2 traces or $ClONO_2$ desorption in the static system [1,5], these effects being minimised by his flow technique [3]. The high values of k_1 of [1] and [5] could alternatively be due to their use of O_2 as the source of O atoms: we have estimated that the rate of O atom removal by reaction 1 is less than an order of magnitude above that by reaction with the O_2 parent molecule.

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

We therefore recommend the estimate of Kurylo [3] of k_1 from his own data and those of Molina et al. [4], i.e.,

$$k_1 = 1.83\times10^{12} \exp(-810/T)\ cm^3\ mol^{-1}\ s^{-1}$$

within error limits of ±50% over the temperature range 213–295 K.

The mechanism of reaction 1 is unconfirmed at present. Molina et al. [4] considered the stoichiometry of 2 at low [NO]/[O] ratios, and the stoichiometry of more than 3 at both low [NO]/[O] and $[ClONO_2]/[O]$, to be consistent with the initiation reaction 1a

$$O + ClONO_2 \rightarrow ClO + NO_3 \qquad (1a)$$

followed by the reaction sequence

$$O + ClO \rightarrow Cl + O_2$$

$$O + NO_3 \rightarrow NO_2 + O_2$$

$$O + NO_2 \rightarrow NO + O_2$$

In the presence of NO, ClO is removed by the reaction

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

Kurylo [3] preferred the reaction sequence suggested by Smith et al. [6]

$$O + ClONO_2 \rightarrow ClONO + O_2$$

$$O + ClONO \rightarrow ClO + NO_2$$

$$O + ClO \rightarrow Cl + O_2$$

$$O + NO_2 \rightarrow NO + O_2$$

which also gives stoichiometries >3 at low $[ClONO_2]/[O]$ ratios. However the latter sequence does not give the same variation in stoichiometry, with addition of NO, as that observed by Molina et al. [4].

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Miscellaneous Reactions Involving Cl, N, and O Species

B50 $Cl + ClONO_2 \rightarrow$ products

Speculation that stratospheric $ClONO_2$ might act as a sink for both NO_x and ClO_x [1,2,3,4] has prompted studies of the reactions of $ClONO_2$. Reaction 1

$$Cl + ClONO_2 \rightarrow \text{products} \qquad (1)$$

has been studied by Kurylo and Manning [6] using flash photolysis. $ClONO_2$ (6.7–67 μm Hg; 0.9–9.0 Pa)/Ar mixtures at total pressures 10 and 20 mm Hg (1.3 and 2.7 kPa), at 250 K, and $ClONO_2$ (0–67 μm Hg; 9.0 Pa)/CCl_4 (6.7–33.5 μm Hg; 0.9–4.5 Pa)/Ar mixtures, also at 10 and 20 mm Hg (1.3 and 2.7 kPa) total pressures, at 224, 250 and 273 K, were flash photolysed in a flow system. The resonance fluorescence of Cl atoms, was used to follow the reaction, giving pseudo first order rate constants (as $30 \leqslant [ClONO_2]/[Cl] \leqslant 300$). The authors obtained the values of $k_1 = (6.93 \pm 1.2) \times 10^{10}$ cm^3 mol^{-1} s^{-1} (224 K), $(8.37 \pm 0.7) \times 10^{10}$ (250 K), and $(1.14 \pm 0.2) \times 10^{11}$ (273 K). No pressure effect was found for these results, which the authors fitted by expression $k = (1.01^{+3.9}_{-0.8}) \times 10^{12} \exp\{-(607 \pm 388)/T\}$ cm^3 mol^{-1} s^{-1}. They were unable to identify the reaction route. Possibilities are

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3$$

or

$$Cl + ClONO_2 \rightarrow Cl_2O + NO_2.$$

The only other data available for k_1 is a preliminary result by Ravishankara et al. [5,7] who quote $k_1 \cong 6.02 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 245 K, obtained in a static flash photolysis study. Kurylo and Manning [6] quote $k_1 \cong 4.82 \times 10^{10}$ cm^3 mol^{-1} s^{-1} for this work.

Without further data, we make no recommendation for k_1.

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B51 $OH + ClONO_2 \rightarrow$ products

Another conceivably important reaction for stratospheric $ClONO_2$ removal is its reaction with OH radicals

$$OH + ClONO_2 \rightarrow \text{products} \qquad (1)$$

Ravishankara et al. [1,2] used flash photolysis of O_3 (25 μm Hg; 3.3 Pa)/H_2 (100 μm Hg; 13.3 Pa)/Ar (20 mm Hg; 2.7 kPa) mixtures, in the presence of 0–13 mm Hg (1.7 kPa) $ClONO_2$, to study this reaction. [OH] was followed by u.v. resonance fluorescence, in an excess of $ClONO_2$, and k_1 determined as $(2.23 \pm 0.1) \times 10^{11}$ cm^3 mol^{-1} s^{-1} (at 245 K) from pseudo first order kinetics. By varying the flash intensity (and hence [OH]), the authors found no variation in k_1, indicating that secondary reactions were negligible.

A discharge flow system was used by Zahniser et al. [3] in which H_2/He mixtures were passed through a discharge, and NO_2 added downstream, giving OH via

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

at concentrations of 1.7×10^{-13} mol cm^{-3}. $ClONO_2$ was added through a moveable inlet, giving total pressures of 2.3–5.0 mm Hg (306.6–666.5 Pa). By using resonance fluorescence to monitor the pseudo first order decay of OH, these authors found $k_1 = (1.84 \pm 0.04) \times 10^{11}$ (246 K), $(2.10 \pm 0.06) \times 10^{11}$ (271 K), $(2.37 \pm 0.07) \times 10^{11}$ (295 K), $(2.64 \pm 0.02) \times 10^{11}$ (347 K), and $(3.09 \pm 0.07) \times 10^{11}$ cm^3 mol^{-1} s^{-1} (387 K). These values were expressed as $k_1 = (7.17 \pm 0.6) \times 10^{11} \exp\{-(333 \pm 22)/T\}$ cm^3 mol^{-1} s^{-1}.

In the absence of further data, we make no recommendation for k_1.

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B52 $N + Cl_2O \rightarrow NCl + ClO$

There has been just one determination of the rate of reaction 1, by Freeman and Phillips [1]

$$N + Cl_2O \rightarrow NCl + ClO; \qquad (1)$$

thermodynamic data unavailable for NCl.

They used a discharge flow system, passing a discharge through pure N_2 at 40 Pa pressure, and a Cl_2O (0.1%)/Ar mixture added downstream at the same pressure so that $[N] \approx 10[Cl_2O]$. The reaction was followed mass spectrometrically, and a 1:1 stoichiometry was found.

Assuming reaction 1 to be the primary reaction, the authors found at 296 K that $k_1=(9.1\pm1.5)\times10^{11}$ cm^3 mol^{-1} s^{-1}.

No recommendation is made.

Reference

[1] Freeman, C. G., and Phillips, L. F., J. Phys. Chem. **72**, 3028 (1968).

B53 $NO_2 + Cl_2O \rightarrow NO_2Cl + ClO$

The reactions of nitrogen dioxide with Cl-containing compounds have been studied by Martin et al. [1,2,3]. They postulated reaction 1 as the rate determining step in the reaction between NO_2 and Cl_2O [3].

$$NO_2 + Cl_2O \rightarrow NO_2Cl + ClO; \qquad (1)$$

$$\Delta H^\circ_{298}=-7.623 \text{ kJ mol}^{-1} \ (-1.822 \text{ kcal mol}^{-1})$$

It is followed by the rapid reaction 2 to give nitroxy chloride and nitryl chloride as the overall products.

$$NO_2 + ClO + M \rightarrow NO_3Cl + M \qquad (2)$$

They used a static system with both NO_2 and Cl_2O at pressures between 1.33 and 13.3 kPa, the reaction being followed manometrically. Over the temperature range 293–333 K they obtained $k_1=4.35\times10^{10}\exp(-5800/T)$ cm^3 mol^{-1} s^{-1}. The low A factor they found to be similar to the value for the reactions of NO_2 with other Cl-containing compounds.

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B54 $NO + ClO_2 \rightarrow NO_2 + ClO$

There have been just two estimations of the rate of reaction 1, important as a source of Cl atoms in the ClO_x chain [2].

$$NO + ClO_2 \rightarrow NO_2 + ClO; \qquad (1)$$

$$\Delta H^\circ_{298}=-60.576 \text{ kJ mol}^{-1} \ (-14.478 \text{ kcal mol}^{-1})$$

Coxon [1] studied the reaction directly in a flow system, adding NO to a ClO_2/Ar mixture at 186 Pa pressure. To avoid complications from the subsequent fast reaction 2, only the initial reaction rate was measured, by following [ClO_2] and [ClO] by u.v. absorption at 351.5 and 277.6 nm, respectively.

$$NO + ClO \rightarrow NO_2 + Cl \qquad (2)$$

From the rate of disappearance of ClO_2, a value of $k_1 \geqslant 5\times10^{11}$ cm^3 mol^{-1} s^{-1} at 294 K was estimated. Later $k_2/k_1=0.30\pm0.05$ was obtained in a competitive study, in which Cl atoms were removed on nickel wire to eliminate the complicating reaction 3

$$Cl + ClO_2 \rightarrow 2ClO. \qquad (3)$$

Bemand et al. [2] studied reaction 1 in a flow system using both mass spectrometry (for ClO and ClO_2) and atomic resonance fluorescence to follow [Cl]. In this way they were able to detect concentrations at least two orders of magnitude lower than was Coxon, and to follow the disappearance of [Cl] more accurately. To obtain a rate constant they flowed NO (82.3–1190 mPa) with ClO_2 (7.41–30.1 mPa) and added NOCl or Br_2 as a scavenger to remove Cl atoms by the fast reactions 4 and 5

$$NOCl + Cl \rightarrow NO + Cl_2 \qquad (4)$$

$$Br_2 + Cl \rightarrow Br + BrCl \qquad (5)$$

This gave $k_1=(2.1\pm0.3)\times10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K, i.e., below Coxon's lower limit.

It has been suggested that Coxon's value is high due to neglect of Cl atom removal by surfaces in his experiments. Surface effects are now known to be important in such flow systems, and it is likely that the result of Bemand et al. is more likely to be correct, but until further results confirm it no recommendation is made.

References

[1] Coxon, J. A., Trans. Faraday Soc. **64**, 2118 (1968).
[2] Bemand, P. P., Clyne, M. A. A., and Watson, R. T., JCS Faraday I **69**, 1356 (1973).

B55 $NO_2 + ClO_2 \rightarrow NO_3 + ClO$

The reaction between nitrogen dioxide and chlorine dioxide has been studied in NO_2/ClO_2 [1] and in $NO_2/ClO_2/NOCl$ [2] systems.

$$NO_2 + ClO_2 \rightarrow NO_3 + ClO; \qquad (1)$$

$$\Delta H^\circ_{298}=34.652 \text{ kJ mol}^{-1} \ (8.282 \text{ kcal mol}^{-1})$$

Storjohann [1] found that a simple bimolecular reaction took place between NO_2 and ClO_2, and obtained $k_1=3.5\times10^1$ cm^3 mol^{-1} s^{-1} at 273 K. Subsequently, Martin and Köhnlein [2] studied the reaction in mixtures of NOCl (0.67–13.3 kPa)/NO_2 (0.53–2.67 kPa) and ClO_2 (0.67–8.0 kPa), also at 273 K, the reaction being followed manometrically. NO_2 was assumed to disappear by reaction 1 and by reaction with NOCl. From analysis of the products, they obtained $k_1=4.2\times10^1$ cm^3 mol^{-1} s^{-1} at 273 K, in good agreement with the earlier work.

References

[1] Storjohann, A., Ph. D. Dissertation, Kiel University (1953).
[2] Martin, H., and Köhnlein, E., Z. Phys. Chem. **17**, 375 (1958).

B56 $N_2O + Cl \rightarrow N_2 + ClO$

The reactions of halogen atoms with nitrous oxide were studied following the discovery of the strong catalytic effect of halogens on the dissociation of N_2O [12].

$$N_2O + Cl \rightarrow N_2 + ClO; \qquad (1)$$

$$\Delta H^\circ_{298} = -102.12 \text{ kJ mol}^{-1} \ (-24.407 \text{ kcal mol}^{-1})$$

Musgrave and Hinshelwood [2] added Cl_2 (0–34.8 kPa) to N_2O (26.7–40.0 kPa) in a static system, and followed the reaction manometrically. They found that the rate of disappearance of N_2O increased linearly with the amount of Cl_2 added, with no indication of a limiting first order rate being found. Recalculation of the results, using both contemporary [1] and more recent JANAF data for the Cl_2/Cl equilibrium, yields no satisfactory value for a second order rate constant. The experiments were carried out over the temperature range 953–1017 K, and from the pseudo-first order rate constant an activation energy $E_1 = 195$ kJ mol^{-1} (46.5 kcal mol^{-1}) was obtained.

This high activation energy was questioned by Kaufman et al. [3] who studied the reaction over the temperature range 927–1031 K, using a similar method, with Cl_2 at 0.13–2.13 kPa and N_2O at 2.67 kPa pressure. They obtained the expression $k_1 = 1.3 \times 10^{14} \exp(-16\,900/T)$ cm^3 mol^{-1} s^{-1}, giving a rate constant approximately one order of magnitude smaller than that of Musgrave and Hinshelwood at 1000 K.

Both the high A factor, and the assumption that most of the Cl atoms produced recombine to form Cl_2, have been criticised by Benson and Buss [4]. Kaufman et al. calculated that $(-d[N_2O]/dt)/(d[Cl]/dt) = 5.5$ at 927 K. Benson and Buss, however, claim that unless $(-d[N_2O]/dt)/(d[Cl]/dt \leqslant 0.1$, then reaction 2 becomes important as a means of removing N_2O, explaining the large catalytic effect of Cl_2 in the N_2O decomposition

$$ClO + N_2O \rightarrow N_2 + ClOO. \qquad (2)$$

Thus, they claim, Kaufman's k_1 should be halved to allow for reaction 2.

References

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[3] Kaufman, F., Gerri, N. J., and Pascale, D. A., J. Chem. Phys. **24**, 32, (1956).

[4] Benson, S. W., and Buss, J. H., J. Chem. Phys. **27**, 1382 (1957).

B57 $NO_2 + HCl \rightarrow HNO_2 + Cl$

There have been two studies of this reaction which is very slow at 300 K but proceeds at a readily measurable rate at around 600 K [1,2].

$$NO_2 + HCl \rightarrow HNO_2 + Cl; \qquad (1)$$

$$\Delta H^\circ_{298} = 102.81 \text{ kJ mol}^{-1} \ (24.572 \text{ kcal mol}^{-1})$$

Rosser and Wise [1] measured the rate in a static system, monitoring $[NO_2]$ by absorption of light at 420 and 500 nm, correcting at the former wavelength for absorption by Cl_2, a reaction product. They used a mixture containing 0.1–10% NO_2 in HCl at total pressures of 4.39–58.2 kPa, and over the temperature range 523–693 K. It was assumed that reaction 1 was the initiating step. However, the reaction mechanism is complex and by no means well-established. Rosser and Wise obtained an expression $k_1 = 4.0 \times 10^{11} \exp(-11\,800/T)$ cm^3 mol^{-1} s^{-1}, and by comparison of E_1 with $(\Delta H^\circ)_1$, inferred that E_{-1} must be very small.

Gilbert and Thomas [2], also using a static system, followed the reaction manometrically and photometrically. They used much higher concentrations of NO_2, the pressures of both NO_2 and HCl varying over the range 2.67–13.3 kPa. Under these conditions, working between 573 and 673 K, they found a stoichiometry different from that obtained by Rosser and Wise, leading to an overall pressure drop not observed by the latter authors. At 633 K, they gave $k_1 = 3.8 \times 10^3$ cm^3 mol^{-1} s^{-1}, in reasonable agreement with the value of Rosser and Wise at this temperature. They observed an overall activation energy of 74.1 kJ mol^{-1} (17.7 kcal mol^{-1}).

Further work is required on the reaction before any recommendation for k_1 can be made.

References

[1] Rosser, W. A., Jr., and Wise, H., J. Amer. Chem. Soc. **64**, 602 (1959).

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B58 $Cl + HNO_3 \rightarrow$ products

There has been only one experimental determination of the rate constant k_1 for the reaction between chlorine atoms and nitric acid, by Leu and DeMore [2].

$$Cl + HNO_3 \rightarrow \text{products} \qquad (1)$$

They used a discharge flow system, producing Cl atoms in a discharge through Cl_2(1–5%)/He mixtures at 133–267 Pa pressures. HNO_3 was added downstream so that $[Cl] > 10[HNO_3]$. $[HNO_3]$ was monitored by mass spectrometry, [Cl] by NOCl titration, the $[Cl_2]$ produced again being determined by mass spectrometry. The flow tube was coated with phosphoric acid to minimise Cl atom recombination at the walls. A rate constant $k_1 = 4.1 \times 10^9$ cm^3 mol^{-1} s^{-1} was obtained at 295 K, the authors setting error limits of ±50% to account for the effect of diffusion on such a slow reaction.

Reaction 1 is believed to occur in the stratosphere [1], where it would be a sink for Cl atoms, presumably producing HCl as a product. From a knowledge of $[HNO_3]$ in the stratosphere, and by comparison with reaction 2, Rowland and Molina [1] estimated $k_1 = 4 \times 10^{12} \exp(-400/T)$ cm^3 mol^{-1} s^{-1}, but in view of the low rate constant determined experimentally, the importance of reaction 1 may have been overestimated.

$$OH + HNO_3 \rightarrow NO_3 + H_2O \qquad (2)$$

References

[1] Rowland, F. S., and Molina, M. J., Rev. Geophys. Space Phys. **13**, 1 (1975).
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Note added in Proof

There is a large discrepancy between the previously reported value of k_1 and that recently measured by Poulet, Le Bras and Combourieu (J. Chem. Phys. **69**, 767 (1978)).

$$Cl + HNO_3 \rightarrow \text{products} \qquad (1)$$

Essentially the same experimental method as that of Leu and De More [2] was used, except that $[HNO_3]$ and [Cl] were a factor of 10 greater in the more recent study. Results over the temperature range 439–633 K yielded the expression

$$k_1 = 9.0 \times 10^{12} \exp(-4400/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

At 295 K this gives $k_1 = 3 \times 10^6$ cm^3 mol^{-1} s^{-1} compared with 4.1×10^9 cm^3 mol^{-1} s^{-1} obtained by Leu and De More. Poulet et al. attribute the difference to the occurrence of wall reactions in the other study.

Further studies are needed before any recommendation can be made.

B59 $NO_2 + COCl \rightarrow NO + Cl + CO_2$

This reaction has been postulated to be responsible for the production of CO_2 from attack on chloroform by NO_2 [2,3].

$$NO_2 + COCl \rightarrow NO + Cl + CO_2; \qquad (1)$$

$$\Delta H^\circ_{298} = -152.28 \text{ kJ mol}^{-1} \ (-36.395 \text{ kcal mol}^{-1})$$

George and Thomas [2] believed that NOCl and CO_2 were the products following the reaction of NO_2 and $CHCl_3$. Thomas and Woodman [3] attempted to verify this by producing COCl radicals by the thermal reaction between CO and Cl_2, (1:1 mixtures, total pressure 28 kPa) with added NO_2 (2 kPa). The reaction was followed manometrically and $[NO_2]$ by absorption of light at 470 nm. NOCl and CO_2 were found in the products analysed at room temperature although the NOCl would be dissociated at the temperatures of the experiments, 654–746 K. After making allowances for the equilibria in reactions 2 and 3, they obtained $k_1 = 6.9 \times 10^{11}$ $\exp(80/T)$ cm^3 mol^{-1} s^{-1}.

$$Cl_2 + M \rightleftharpoons Cl + Cl + M \qquad (2)$$

$$CO + Cl + M \rightleftharpoons COCl + M \qquad (3)$$

Due to uncertainties in K_3 [1] however, an error of ±1050 J mol^{-1} (±250 cal mol^{-1}) was introduced into the activation energy E_1, and the authors recommend only a small activation energy.

References

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[2] George, D. V., and Thomas, J. H., Trans. Faraday Soc. **57**, 266 (1961).
[3] Thomas, J. H., and Woodman, G. R., Trans. Faraday Soc. **63**, 2728 (1967).

B60 $Cl + COCl \rightarrow CO + Cl_2$

THERMODYNAMIC DATA

(Thermodynamic data are not available for COCl.)

RECOMMENDED RATE CONSTANT

$$k_1 = 1.30 \times 10^{15} \exp(-1670/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$
$$= 2.16 \times 10^{-9} \exp(-1670/T) \ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Temperature Range: 300-600 K.

Rate Parameters: $\log(A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 15.114$

$\log(A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = -8.666$

$E/\mathrm{J\ mol^{-1}} = 13\ 890$

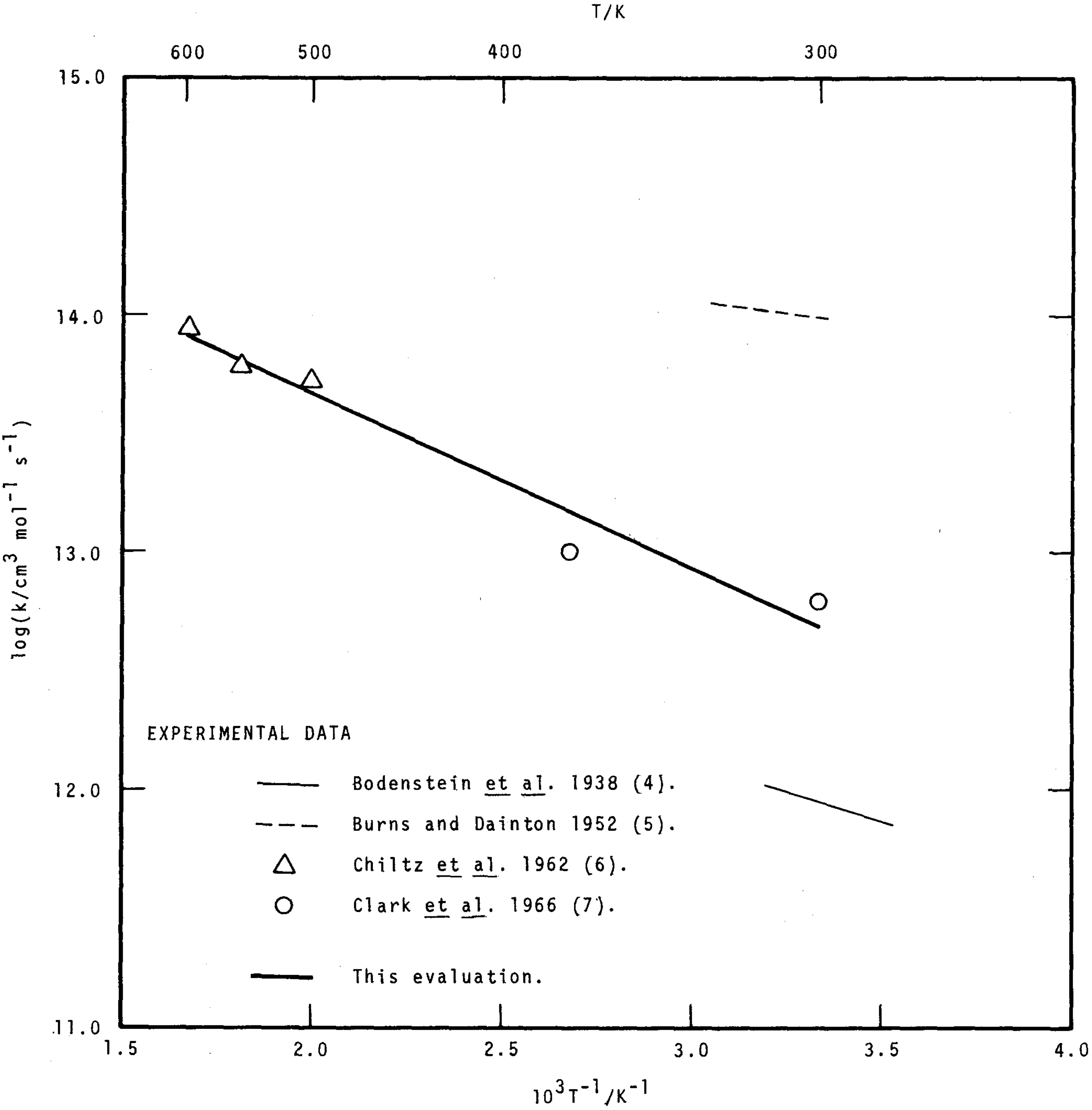
$E/\mathrm{cal\ mol^{-1}} = 3320$

Note: this expression is probably an upper limit, see Discussion.

EXPERIMENTAL DATA

Rate Constant k ($\mathrm{cm^3\ mol^{-1}\ s^{-1}}$)	Temperature (K)	Method and Reference	Comments
	283-313	Static system. CO(∼200 mm Hg; 26.7 kPa)/Cl_2 (∼300 mm Hg; 40 kPa) mixtures photolysed using rotating sector. Reaction monitored by changes in pressure. BODENSTEIN, BRENSCHEDE and SCHUMACHER 1938 (4)	Mechanism for photosynthesis of $COCl_2$ proposed as $Cl_2 + h\nu \rightarrow 2Cl$ $CO + Cl + M \rightleftarrows COCl + M$ 2,-2 $COCl + Cl_2 \rightarrow COCl_2 + Cl$ 3 $Cl + COCl \rightarrow CO + Cl_2$ 1 and used to analyse data from earlier studies by BODENSTEIN et al. (e.g. 1,3), giving ratios $k_3(K_2/k_1)^{\frac{1}{2}}$ and $k_3K_2/K_4^{\frac{1}{2}}$ $Cl_2 + M \rightleftarrows Cl + Cl + M$ 4,-4 Using expressions for K_2 and k_3 determined in this work, authors' abstract gives $k_1 = 1.35 \times 10^{12} T^{\frac{1}{2}} \exp(-980/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$, although the pre-exponential value quoted in the text of the paper is 1.12×10^{12}. If we use BURNS and DAINTON's (5) expression for K_2, we derive $k_1 = 2.75 \times 10^{11} T^{\frac{1}{2}} \exp(-660/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$.

$Cl + COCl \rightarrow CO + Cl_2$



$Cl + COCl \rightarrow CO + Cl_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4 \times 10^{14}\ \exp(-420/T)$	298-328	Static system. CO(50-500 mm Hg; 6.7-66.7 kPa)/Cl_2 (50-350 mm Hg) mixtures photolysed at ∿365 nm, using rotating sector. Pressure and transmitted light intensity monitored. BURNS and DAINTON 1952 (5)	Corrections made for scattered light and non-uniformity of absorption. Using BODENSTEIN mechanism, authors obtained both K_2 and k_1K_2. Elimination of K_2 gave k_1. Authors believed errors in pre-exponential constants ∿10% and in activation energies ∿30%.
	500-600	Static system. CO(17.9-299.8 mm Hg; 2.39-40 kPa)/Cl_2 (188.3-503.4 mm Hg; 25.1-67.1 kPa) mixtures, with $[Cl_2]/[CO]$ ratios 0.96-19.72, photolysed. Pressure and incident light intensity monitored, and $[Cl_2]$ measured by absorption at 366 nm. CHILTZ, ECKLING, GOLDFINGER, HUYBRECHTS, MARTENS and SIMOENS 1962 (6)	Initial slopes of pressure profiles gave ratios $k_3(K_2/k_1)^{\frac{1}{2}}$ $CO + Cl\ (+M) \rightleftharpoons COCl\ (+M)$ 2,-2 $COCl + Cl_2 \rightarrow COCl_2 + Cl$ 3 $Cl + Cl + M \rightarrow Cl_2 + M$ -4 $Cl + COCl \rightarrow CO + Cl_2$ 1 and k_{-4}/k_1K_2. Good agreement (within 50%) found for values of $k_3(K_2/k_1)^{\frac{1}{2}}$ with those of BODENSTEIN *et al*. (4) but almost an order of magnitude below those of BURNS and DAINTON (5). T (K) — $k_3(K_2/k_1)^{\frac{1}{2}}$ ($cm^3 mol^{-1} s^{-\frac{1}{2}}$) — k_{-4}/k_1K_2 — k_1 ($cm^3 mol^{-1} s^{-1}$) 502.4 — 7.76×10^4 — 0.138 — 5.34×10^{13} 552.3 — 7.08×10^4 — 0.186 — 6.05×10^{13} 598.9 — 6.76×10^4 — 0.174 — 9.01×10^{13} Using our recommendation for k_{-4} ($M=Cl_2$), and BURNS and DAINTON's (5) expression for K_2, we obtain the values of k_1 tabulated above.
	300,373	Discharge flow system. Cl_2 (0.02-1%)/Ar or He passed through discharge and CO added downstream. Total pressures 2-4 mm Hg (266.7-533.2 Pa). [Cl] calibrated by titration with NOCl and relative [Cl] determined by monitoring red chlorine afterglow. Reaction tube coated with H_3PO_4. CLARK, CLYNE and STEDMAN 1966 (7)	Homogeneous recombination of Cl atoms suppressed by low values of [Cl]. Assuming mechanism $CO + Cl + M \rightleftharpoons COCl + M$ 2,-2 $Cl + COCl \rightarrow CO + Cl_2$ 1 variation of apparent second-order rate constant with $[Cl]_0$ gave values of k_2 and $1/k_1K_2$. At 300 K $1/k_1K_2 = (3.8 \pm 1.0) \times 10^{-18}$ and at 373 K $1/k_1K_2 = (1.8 \pm 0.4) \times 10^{-17}\ mol^2\ s\ cm^{-6}$. Using BURNS and DAINTON's (5) expression for K_2 authors give $k_1 = 6.3 \times 10^{12}$ and $10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ at 300 and 373 K respectively, within limits of ±50%.

Discussion

There are few reported data on the rate of reaction of Cl atoms with COCl

$$\mathrm{Cl} + \mathrm{COCl} \rightarrow \mathrm{CO} + \mathrm{Cl_2} \qquad (1)$$

Static photolysis has been used by all the studies [4,5,6] except one [7], which used a discharge flow system to generate Cl atoms.

The mechanism for the photosynthesis of phosgene is generally accepted as being that described by Bodenstein [4]

$$\mathrm{Cl_2} + h\nu \rightarrow \mathrm{Cl} + \mathrm{Cl}$$

$$\mathrm{CO} + \mathrm{Cl} + \mathrm{M} \rightleftharpoons \mathrm{COCl} + \mathrm{M} \qquad (2,-2)$$

$$\mathrm{COCl} + \mathrm{Cl_2} \rightarrow \mathrm{COCl_2} + \mathrm{Cl} \qquad (3)$$

$$\mathrm{Cl} + \mathrm{COCl} \rightarrow \mathrm{CO} + \mathrm{Cl_2} \qquad (1)$$

An alternative mechanism proposed by Rollefson [2], involving the formation of the complex Cl_3 following the primary photolysis, was found to predict experimental behaviour other than that observed by Burns and Dainton [5].

Steady state analysis of the Bodenstein mechanism gives the variation of the experimentally observed variable (e.g., pressure [4,5], $[Cl_2]$ [6], [Cl] [7]) in terms of the ratio $k_3(K_2/k_1)^{1/2}$. Bodenstein et al. [4] and Chiltz et al. [6] included reaction –4 in their interpretation

$$\mathrm{Cl} + \mathrm{Cl} + \mathrm{M} \rightarrow \mathrm{Cl_2} + \mathrm{M}, \qquad (-4)$$

and also obtained ratios $K_2k_3/K_4^{1/2}$ [4] and k_{-4}/k_1K_2 [6]. Following Clark et al. [7] we have used the expression for K_2 derived by Burns and Dainton [5] to convert the results of [4] and [6] so that direct comparison may be made between all the available data. We find that a reasonable Arrhenius fit may be made to the data of [6] and [7], i.e., the latest sets of results, whereas the earlier studies [4,5] lie considerably above [5] and below [4] this line.

The data are in rough agreement [6,7] and were determined by two totally different techniques. The Arrhenius fit

$$k_1 = 1.30\times10^{15} \exp(-1670/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

satisfactorily describes the data, over the temperature range 300–600 K, but the exceptionally high pre-exponential factor suggests that the above expression is probably an upper limit to k_1.

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Miscellaneous Reactions Involving Cl Atoms

B61 $CH_3 + Cl_2 \rightarrow Cl + CH_3Cl$

There have been only two determinations of the rate of the reaction between molecular chlorine and methyl radicals

$$\mathrm{CH_3} + \mathrm{Cl_2} \rightarrow \mathrm{Cl} + \mathrm{CH_3Cl}; \qquad (1)$$

$$\Delta H^\circ_{298} = 108.1 \ \mathrm{kJ\ mol^{-1}}\ (25.83\ \mathrm{kcal\ mol^{-1}})$$

an important step in the chlorination of CH_4.

The first study was conducted by Eckling et al. [2] in a static photolysis system. The photo-initiated chlorination of CH_4 was followed manometrically, and the ratios k_1k_2/k_3 and

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{CH_3} + \mathrm{HCl} \qquad (2)$$

$$\mathrm{Cl} + \mathrm{CH_3} \rightarrow \mathrm{CH_3Cl} \qquad (3)$$

$$\mathrm{CH_3} + \mathrm{CH_3} \rightarrow \mathrm{C_2H_6} \qquad (4)$$

k_1k_3/k_2k_4 were reported as 5.4×10^7 cm^3 mol^{-1} s^{-1} and 30, respectively, at 303 K. From these ratios and $k_4 = 3.16\times10^{13}$ cm^3 mol^{-1} s^{-1} [1] as quoted by the authors we obtain $k_1 = 2.26\times10^{11}$ cm^3 mol^{-1} s^{-1} (303 K). Using their quoted expression $k_1 = 7.94\times10^{12} \exp(-1160/T)$ cm^3 mol^{-1} s^{-1} we derive $k_1 = 1.74\times10^{11}$ cm^3 mol^{-1} s^{-1} at 303 K, a difference of 25%. Using our value $k_4 = 2.41\times10^{13}$ cm^3 mol^{-1} s^{-1} (Volume 5, to be published) with the above ratios we obtain $k_1 = 1.97\times10^{11}$ cm^3 mol^{-1} s^{-1}.

These values are in accordance with the value of k_1 determined at 298 K by Combourieu et al. [3,4]. Using a discharge flow system, in which H_2/He mixtures were passed through the discharge, CH_2N_2 added to produce CH_3 radicals via the reaction

$$\mathrm{H} + \mathrm{CH_2N_2} \rightarrow \mathrm{CH_3} + \mathrm{N_2}$$

and finally excess Cl_2 in He added downstream, giving total pressures 0.45–0.7 mm Hg (60–93.3 Pa), the authors followed the decay of CH_3. Assuming CH_3 to be removed solely by reactions 1 and 4, they determined k_1 as $(2.35\pm0.7)\times10^{11}$ cm^3 mol^{-1} s^{-1} (298 K).

Because of the good agreement between the latter result and the value $k_1 = 1.97\times10^{11}$ cm^3 mol^{-1} s^{-1}, which were obtained in totally different systems, we recommend the value $k_1 = (2.16\pm0.36)\times10^{11}$ cm^3 mol^{-1} s^{-1} (300±3 K).

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B62 $S + Cl_2 \rightarrow SCl + Cl$

Sulphur atoms undergo a fast reaction at room temperature with chlorine, the only data available being those of Clyne and Townsend [1].

$$S + Cl_2 \rightarrow SCl + Cl; \qquad (1)$$

thermodynamic data unavailable for SCl

S atoms were produced in an SO_2 ($\sim$0.1%)/Ar discharge, and Cl_2 added downstream so that $[Cl_2] \sim 50[S]$. Total pressure $\sim$20 Pa. [S] was monitored by resonance fluorescence at 182.04 nm, calibrated by titration with O_2, [O] being monitored at 130 nm.

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

In some experiments [Cl] was also followed at 138 nm. Impurity species such as SO and O were at too low concentration to interfere with the main reaction. At 298 K they found from the pseudo first order decay of [S], $k_1 = (6.62 \pm 0.6) \times 10^{12}$ cm^3 mol^{-1} s^{-1}. From further experiments at temperatures up to 514 K, they obtained $k_1 = (1.69 \pm 0.06) \times 10^{13} \exp\{-(290 \pm 60)/T\}$ cm^3 mol^{-1} s^{-1}, an expression in good agreement with transition state theory, assuming a nonlinear S-Cl-Cl complex.

Reference

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C1 $Br_2 + M \rightarrow Br + Br + M$

THERMODYNAMIC DATA

T (K)	ΔH^o ($kJ\ mol^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	192.811	104.429	-28.325	-32.713
300	192.824	104.466	-28.116	-32.507
500	193.803	106.997	-14.658	-19.271
1000	196.079	110.135	- 4.490	- 9.404
1500	198.991	112.470	- 1.054	- 6.144
2000	202.447	114.458	0.692	- 4.523
2500	206.037	116.056	1.758	- 3.554
3000	209.476	117.315	2.480	- 2.911
3500	212.656	118.294	3.006	- 2.452
4000	215.535	119.068	3.404	- 2.112
4500	218.120	119.675	3.720	- 1.847
5000	220.430	120.160	3.974	- 1.639

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.0056$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 2.35 \times 10^{14} \exp(-21\ 630/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)

$= 3.90 \times 10^{-10} \exp(-21\ 630/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)

(k is defined by $-d[Br_2]/dt = k[Br_2][M]$)

Temperature Range: 1300-2500 K

Suggested Error Limits for Calculated Rate Constant: factor of 3 over whole temperature range.

Rate Parameters:

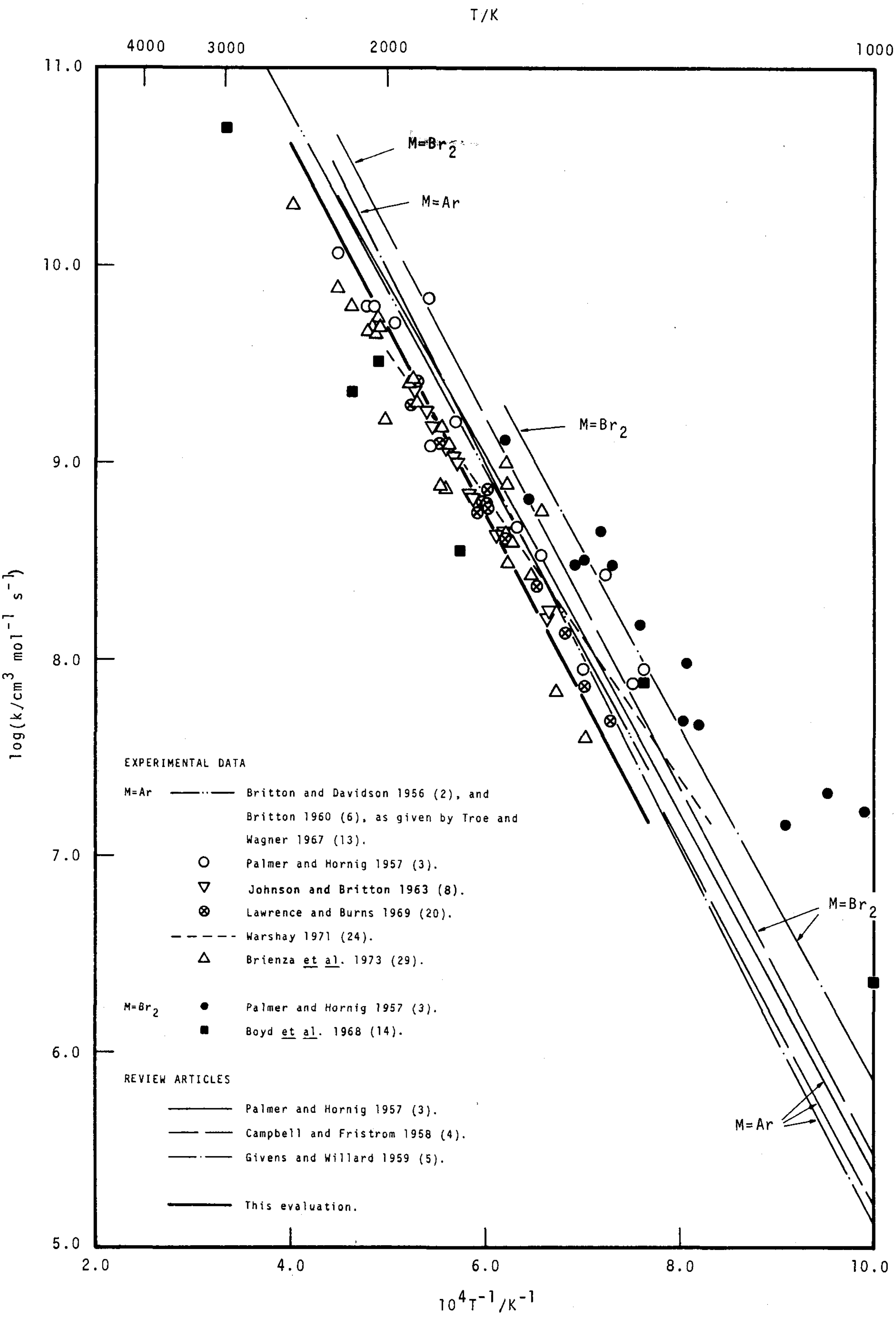
$\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.371 \pm 0.5$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.409 \pm 0.5$

$E/J\ mol^{-1} = 179\ 810 \pm 51\ 880$

$E/cal\ mol^{-1} = 42\ 980 \pm 12\ 400$

$Br_2 + M \rightarrow Br + Br + M$



$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
		1400-2700	Shock tube study. Br_2(1%, 2%, 4%, 6% and 10%)/Ar mixtures. Incident shocks. Br_2 followed by absorption at 487 or 436 nm. BRITTON and DAVIDSON 1956 (2)	Br_2 dissociation data analysed in terms of k_{-1} $Br + Br + M \rightarrow Br_2 + M$ -1 Results from Br_2-rich mixtures less certain due to larger temperature change during reaction: uncertainty in extinction coefficient behaviour gives error limits of factor 2. Data given as $k_1(M=Ar)=2.5\times10^{14}\exp(-20\ 830/T)$ $cm^3\ mol^{-1}\ s^{-1}$ by (13), although original gives no correction for $M=Br_2$.
8.9×10^7	M=Ar	1310	Shock tube study. Pure Br_2 and 1:10 Br_2/Ar mixtures under incident shock conditions. Br_2 decay followed by absorption at 439 nm. PALMER and HORNIG 1957 (3)	Authors considered 5-20 μm Hg (0.67-2.67 Pa) air impurities in initial gas mixtures (typically 10-40 mm Hg; 1.3-5.3 kPa) to have negligible effects. Rate constants k_1 $Br_2 + M \rightarrow Br + Br + M$ 1 determined from initial slope of absorption profile, corrected for change in Br_2 absorption coefficient with temperature during dissociation, and, at high temperatures, for emission. Values of k_1 in Br_2/Ar mixtures corrected for $k_1(M=Br_2)$ to give $k_1(M=Ar)$. Authors give as simple least squares fits $k_1(M=Ar)=2.52\times10^{11}T^{\frac{1}{2}}\exp(-15\ 440/T)$ and $k_1(M=Br_2)=2.70\times10^{11}T^{\frac{1}{2}}\exp(-14\ 700/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over ranges 1310-2225 K and 1010-1610 K respectively. Alternative forms, using D(Br-Br) = 190.4 kJ mol^{-1} (45.5 kcal mol^{-1}) given as $k_1(M=Ar)=5.54\times10^{27}T^{-3.96}\exp(-22\ 900/T)$ and $k_1(M=Br_2)=2.88\times10^{23}T^{-2.7}\exp(-22\ 900/T)$ $cm^3\ mol^{-1}\ s^{-1}$. TROE and WAGNER (13) give $k_1(M=Ar)$ as $1.7\times10^{13}\exp(-16\ 300/T)$ $cm^3\ mol^{-1}\ s^{-1}$, for 1200-2200 K. CAMPBELL and FRISTROM (4) used these data to derive expressions for k_{-1} $Br + Br + M \rightarrow Br_2 + M$ -1
7.5×10^7		1330		
2.7×10^8		1380		
9.0×10^7		1425		
3.4×10^8		1520		
4.7×10^8		1580		
1.6×10^9		1750		
1.2×10^9		1840		
6.8×10^9		1840		
5.1×10^9		1965		
6.2×10^9		2050		
6.2×10^9		2080		
1.15×10^{10}		2225		
1.7×10^7	$M=Br_2$	1010		
2.1×10^7		1050		
1.8×10^7		1100		
4.6×10^7		1220		
9.7×10^7		1240		
4.8×10^7		1245		
1.5×10^8		1320		
3.0×10^8		1370		
4.5×10^8		1390		
3.2×10^8		1425		
2.9×10^8		1445		
6.4×10^8		1550		
1.3×10^9		1610		

$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
		1300-1900	Shock tube study. Br_2(2% and 5%)/Ar, 5%Br_2/He, 2%Br_2/N_2, 2%Br_2/CO, Br_2(2% and 5%)/O_2, and 2% Br_2/CO_2 mixtures behind incident shocks. Decay of Br_2 followed by absorption at 500 nm. BRITTON 1960 (6)	Dissociation rate determined from initial slope of absorption profile and analysed in terms of k_{-1}. Small corrections for emission found to be negligible below 1900 K. Corrections made to data from Br_2/N_2, CO and O_2 mixtures to allow for vibrational-relaxation. No corrections for M $=Br_2$. Data expressed as $k_1(M=Ar) = 2.5x10^{14}\ exp(-20\ 830/T)\ cm^3\ mol^{-1}\ s^{-1}$ by (13).
$2.8x10^8$	M=Ar+Br_2	1470	Shock tube study. Br_2(5.34 -20.2%)/Ar mixtures behind incident shocks. Absorption at 436 nm used to follow [Br_2]. HIRAOKA and HARDWICK 1962 (7)	Authors define k_1 as $([Br_2]k_1(M=Br_2)+[Ar]k_1(M=Ar))/[M]$. Using those values at 1470 K we obtain $k_1(M=Ar)=2.17x10^8$ and $k_1(M=Br_2)= 1.40x10^9\ cm^3\ mol^{-1}\ s^{-1}$. $Br_2 + M \rightarrow Br + Br + M$ 1
$3.3x10^8$		1470		
$8.0x10^8$		1610		
$7.1x10^8$		1660		
$8.0x10^8$		1680		
$5.7x10^8$		1690		
$1.3x10^9$		1800		
$1.3x10^9$		1810		
$1.5x10^{11}$		1990		
$1.78x10^8$	M=Ar+Br_2	1502	Shock tube study. Br_2(5%)/Ar mixtures behind incident shocks and Br_2(5% and 2%)/Ar mixtures behind reflected shocks. Br_2 decay monitored by absorption at 500 nm. JOHNSON and BRITTON 1963 (8)	Authors made no distinction between Ar or Br_2 as third body, giving overall k_1 40% below previous evaluations (2,3,6). Values of k_1 are those from incident shock study, taken from graph. Values obtained behind reflected shocks dependent upon reflecting surface and position of measurement. KONDRATIEV (26) gives expression $k_1=5.12x10^{10}exp(-18\ 920/T)\ cm^3\ mol^{-1}\ s^{-1}$ (1500-1900 K) for this work.
$1.67x10^8$		1504		
$4.18x10^8$		1609		
$4.58x10^8$		1618		
$4.36x10^8$		1635		
$6.57x10^8$		1701		
$6.96x10^8$		1709		
$1.00x10^9$		1746		
$1.09x10^9$		1759		
$1.22x10^9$		1782		
$1.52x10^9$		1829		
$1.81x10^9$		1898		
$2.58x10^9$		1898		
		1200-1900	Shock tube study. 1%Br_2 mixtures in Ar, Ne and Kr. Incident shocks. Br_2 followed by absorption at 440 nm. WARSHAY 1965 (9)	Corrections due to change in absorption coefficient during dissociation eliminated by use of low Br_2 percentage. Values of k_1 $Br_2 + M \rightarrow Br + Br + M$ 1 obtained from initial slope of absorption profile. Least squares fits made assuming simple collision form (i.e. $T^{\frac{1}{2}}$ dependence) for pre-exponential factor, but are not specified. Data (presented graphically) appear to be same as those displayed in (11 and 24) but scaling is different by a factor close to ln10.

$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1.32×10^{7} M=Ar+Br_2	1214	Shock tube study. 1% Br_2 mixtures in Ar, Ne and Kr. Incident shock conditions. Absorption of Br_2 at 440 nm used to follow dissociation. WARSHAY 1966 (11)	No metal surfaces allowed to contaminate Br_2. Low Br_2 percentages used to minimise temperature drop during dissociation. Values presented here are taken from (23), being uncorrected for boundary layer effects or for influence of Br_2 as third body. Least squares fits given as $k_1(M{=}Ar)=2.18\times10^{11}T^{\frac{1}{2}}\exp(-15\ 850/T)$, $k_1(M{=}Ne)=1.82\times10^{11}T^{\frac{1}{2}}\exp(-15\ 750/T)$, and $k_1(M{=}Kr)=4.32\times10^{11}T^{\frac{1}{2}}\exp(-16\ 910/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (1200-1900 K). $k_1(M{=}Ar)$ used by (16, 17,30), and by author (25) in study of effects of boundary layers. Boundary layer-corrected fits given (24) as $k_1(M{=}Ar)=(2.14\pm0.78)\times10^{11}T^{\frac{1}{2}}\exp\{-(15\ 750\pm550)/T\}$, $k_1(M{=}Ne)=(1.04\pm0.5)\times10^{11}T^{\frac{1}{2}}\exp\{-(14\ 640\pm705)/T\}$, and $k_1(M{=}Kr)=(3.32\pm0.6)\times10^{11}T^{\frac{1}{2}}\exp\{-(16\ 510\pm250)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ (1200-2000 K). $k_1(M{=}Ar)$ used by (33). Empirical forms of these data presented by WAGNER (23) as $k_1(M{=}Ar)=2.09\times10^{28}T^{-4.2}\exp(-22\ 900/T)$, $k_1(M{=}Ne)=7.25\times10^{30}T^{-5}\exp(-22\ 900/T)$, and $k_1(M{=}Kr)=5.03\times10^{26}T^{-3.7}\exp(-22\ 900/T)$ $cm^3\ mol^{-1}\ s^{-1}$ for the range 1200-2000 K. TROE and WAGNER (31) give empirical form for $k_1(M{=}Ar)$ as $9.47\times10^{27}T^{-4.1}\exp(-22\ 900/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (1200-1900 K), as compared with simple Arrhenius fit to these data, $k_1(M{=}Ar)=1.4\times10^{13}\exp(-16\ 710/T)$ $cm^3\ mol^{-1}\ s^{-1}$, for the same temperature interval.
2.77×10^{7}	1264		
5.93×10^{7}	1315		
9.91×10^{7}	1367		
8.52×10^{7}	1368		
5.79×10^{7}	1370		
1.21×10^{8}	1421		
2.23×10^{8}	1496		
2.20×10^{8}	1526		
4.37×10^{8}	1575		
4.26×10^{8}	1599		
9.07×10^{8}	1718		
1.48×10^{9}	1820		
1.80×10^{9}	1828		
1.98×10^{7} M=Ne+Br_2	1255		
3.18×10^{7}	1316		
6.68×10^{7}	1353		
5.14×10^{7}	1360		
8.25×10^{7}	1380		
1.17×10^{8}	1420		
1.41×10^{8}	1446		
2.43×10^{8}	1532		
2.45×10^{8}	1554		
3.77×10^{8}	1580		
1.12×10^{9}	1793		
8.70×10^{6} M=Kr+Br_2	1177		
2.22×10^{7}	1245		
1.99×10^{7}	1256		
7.74×10^{7}	1379		
2.45×10^{8}	1525		
9.33×10^{8}	1697		
1.76×10^{9}	1806		
1.66×10^{9}	1843		
2.15×10^{9}	1867		
3.73×10^{9}	2008		
2.29×10^{6} M=Br_2	1000	Shock tube study. Pure Br_2 behind incident shocks. Two-body emission at 598 nm used to monitor Br atoms. BOYD, BROWN, BURNS and LIPPIATT 1968 (14)	Analysis of data as for (15). Data believed reliable by authors presented in form of k_1/K_1: we have interpolated thermodynamic data to convert to values of k_1 given here.
7.63×10^{7}	1313		
3.55×10^{8}	1742		
3.26×10^{9}	2042		
2.29×10^{9}	2157		
4.96×10^{10}	2985		

$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
1.99×10^7	M=Ar+Br_2	1346	Shock tube study. 1:10 Br_2/Ar mixtures under incident shock conditions. Growth of [Br] followed by two-body emission at 598 nm. BOYD, BURNS, LAWRENCE and LIPPIATT 1968 (15)	Values of k_1 determined assuming effectively instantaneous electronic equilibration of Br atoms, and vibrational relaxation of Br_2 to have negligible effect. Uncertainties in emission calibration, evaluation of initial slope of emission profile, impurity level, and boundary layer effects considered insignificant compared to quoted overall precision of ±40%. For $k_1(M=Br)/k_1(M=Ar)=2.0$ (3) difference between $k_1(M=Ar+Br_2)$ and $k_1(M=Ar)$ only 9%. Computational matching of whole emission profiles used to evaluate $k_{-1}(M=Br)$. $Br + Br + M \rightarrow Br_2 + M$ -1 (see this Volume, section C2).
3.27×10^7		1398		
4.58×10^7		1437		
4.13×10^7		1445		
1.03×10^8		1446		
4.85×10^8		1465		
3.55×10^8		1548		
2.28×10^8		1548		
3.21×10^8		1558		
2.09×10^8		1580		
1.81×10^8		1602		
4.13×10^8		1608		
7.40×10^8		1620		
8.61×10^8		1620		
3.77×10^8		1630		
7.35×10^8		1681		
7.81×10^8		1681		
7.83×10^8		1681		
1.05×10^9		1696		
6.57×10^8		1713		
7.80×10^8		1731		
5.95×10^8		1739		
1.45×10^9		1749		
9.91×10^8		1769		
1.14×10^9		1779		
1.16×10^9		1782		
1.35×10^9		1808		
1.40×10^9		1808		
1.85×10^9		1820		
1.69×10^9		1841		
2.26×10^9		1852		
2.35×10^9		1852		
1.25×10^9		1857		
1.85×10^9		1857		
1.04×10^9		1860		
1.36×10^9		1861		
1.38×10^9		1861		
1.63×10^9		1874		
1.96×10^9		1884		
1.70×10^9		1886		
2.55×10^9		1889		
1.87×10^9		1891		
1.82×10^9		1893		
2.08×10^9		1902		
1.90×10^9		1912		
2.13×10^9		1914		
2.84×10^9		1920		
2.16×10^9		1921		
1.98×10^9		1926		
2.01×10^9		1926		
2.10×10^9		1926		
2.79×10^9		1931		
2.73×10^9		1939		
3.91×10^9		2081		
5.99×10^9		2085		
3.18×10^9		2119		
5.46×10^9		2138		
5.45×10^9		2144		
3.58×10^9		2170		
3.73×10^9		2179		
7.82×10^9		2230		
6.54×10^9		2244		
8.58×10^9		2360		
1.21×10^{10}		2387		

$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature	Method and Reference	Comments
4.83×10^7	M=Ar+Br_2	1374	Shock tube study. Br_2/Ar mixtures in ratios 1:10 and 1:99. Incident shocks. Br atoms followed by two-body recombination radiation at 598 nm. LAWRENCE and BURNS 1969 (20)	Data presented graphically in form k_1/K_1. "Fair" agreement with previous data (3,6,10) leads authors to believe Br_2 vibrationally frozen during first few μs behind shock. Values of k_1 in 1%Br_2/Ar mixtures tabulated in (15), the values for 1:10 mixtures cannot be separated from those for equal mixtures obtained in (15).
7.23×10^7		1425		
1.38×10^8		1467		
2.34×10^8		1527		
4.20×10^8		1609		
5.86×10^8		1659		
6.23×10^8		1659		
7.24×10^8		1659		
6.21×10^8		1666		
5.68×10^8		1688		
1.25×10^9		1813		
2.62×10^9		1883		
1.95×10^9		1898		
1.12×10^7	M=Xe+Br_2(a)	1212	Shock tube study. (a) 1%Br_2/Xe, (b) 3%Br_2/Xe, and 1%Br_2/20%Xe/He mixtures behind incident shocks. Br_2 decay followed by absorption at 440 nm. WARSHAY 1970 (22)	k_1 determined from initial slope of Br_2 absorption profile $Br_2 + M \rightarrow Br + Br + M$ 1 Values presented here are those tabulated in (24), uncorrected for boundary layer effects or for contribution from Br_2-Br_2 collisions. Effect of ignoring latter in 1%Br_2/ noble gas mixtures is <3% error. Boundary layer correction applied (24) to least squares fits to these data, giving $k_1(M{=}He)=(2.15\pm0.86)\times10^{11}T^{\frac{1}{2}}\exp\{-(16\ 050\pm600)/T\}$ and $k_1(M{=}Xe)=(6.92\pm1.73)\times10^{11}T^{\frac{1}{2}}\exp\{-(17\ 860\pm350)/T\}$ cm^3 mol^{-1} s^{-1} (1200-1950 K). Comparison between results from mixtures (a) and (b) gives Br_2 <4 times as effective as Xe over this temperature range. These data, together with those from (11) corrected for boundary layer effects, used by author in discussion of Br_2 dissociation mechanism (21). Data presented in empirical form by WAGNER (23): $k_1(M{=}He)=3.93\times10^{27}T^{-4}\exp(-22\ 900/T)$ and $k_1(M{=}Xe)=6.07\times10^{23}T^{-2.8}\exp(-22\ 900/T)$ cm^3 mol^{-1} s^{-1} (1200-2000 K).
1.40×10^7		1246		
3.14×10^7		1305		
4.47×10^7		1351		
5.77×10^7		1398		
9.91×10^7		1445		
2.70×10^8		1550		
2.93×10^8		1557		
8.66×10^8		1689		
8.06×10^8		1715		
2.94×10^8		1924		
3.30×10^8		1937		
7.39×10^6	M=Xe+Br_2(b)	1184		
4.19×10^7		1338		
7.03×10^7		1393		
2.98×10^8		1569		
7.95×10^8		1680		
1.37×10^9		1789		
4.31×10^9		1980		
1.60×10^7	M=Xe+He+Br_2	1221		
2.11×10^7		1261		
1.81×10^7		1306		
4.75×10^7		1363		
7.96×10^7		1398		
1.20×10^8		1475		
1.80×10^8		1507		
2.24×10^8		1538		
2.40×10^8		1541		
6.52×10^8		1633		
8.27×10^8		1722		
9.33×10^8		1764		
1.25×10^9		1795		
1.67×10^9		1874		
$9.0\ \times10^6$	M=CO_2	1183	Shock tube study. 1.911% Br_2/70.613%CO_2/Xe mixture behind incident shocks. Br_2 monitored as in (22).. WARSHAY 1972 (27)	Contributions of Xe-Br_2 and Br_2-Br_2 collisions taken into account, and boundary layer correction applied to least squares fit, given as $k_1(M{=}CO_2)=4.78\times10^{11}T^{\frac{1}{2}}\exp(-16\ 660/T)$ cm^3 mol^{-1} s^{-1} (1200-1800 K), with 20% rms error. Values presented here taken from graph.
1.46×10^7		1207		
4.57×10^7		1279		
3.59×10^7		1306		
7.50×10^7		1356		
3.11×10^8		1477		
3.04×10^8		1487		
8.25×10^8		1621		
6.49×10^8		1651		
1.26×10^9		1703		
1.75×10^9		1767		

$Br_2 + M \rightarrow Br + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$\sim 2\ \times10^{9}$ $\sim 2.5\times10^{9}$ } M=He+Br_2	1940 1960	Shock tube study. Br_2(5% and 9.5%)/Ar and Br_2(15%)/He mixtures. Incident shocks. Emission at 620, 595 and 620 nm used to follow Br. WESTBERG and GREENE 1972 (28)	Small correction ($\leqslant$8%) for self-absorption of emission considered in analysis of initial slope. Boundary layer corrections also made. Emission profiles at 3 wavelengths analysed at 3 points, assuming $k_1(M=Br_2)/k_1(M=Ar)=2$ (3, 14, 24). If $k_1(M=Br)/k_1(M=Ar)$ taken as 10, results agree "fairly well" with those of (8, 15 and 24). Data from M=He mixtures subject to severe boundary layer growth: values presented here are from close behind shock front.
8.69×10^{7} (a) M=Ar, Br_2	1602	Shock tube study. (a) Br_2 (7.25%, 8.1% and 8.68%)/Ar and (b) Br_2(4.95%, 5.95%)/CO(4.95% and 1.95% respectively)/Ar mixtures behind incident shocks. $[Br_2]$ followed by absorption at 435.8 nm. BRIENZA, KRUGH and PALMER 1973 (29)	Rate constants determined from initial slopes of absorption profiles, corrected for variation in gas density and in absorption coefficient during dissociation. No increase in dissociation rate observed in Br_2/CO/Ar mixtures indicated no rapid route via $Br_2 + CO \rightarrow COBr + Br$ $COBr + M \rightarrow CO + Br + M$ Authors considered data from mixtures (b) to be of better precision, and fitted by expression $k_1(M=Ar,Br_2)=1.59\times10^{21}T^{-2}\exp(-22\ 870/T)\ cm^3\ mol^{-1}\ s^{-1}$ (1400-2500 K). Absorption profiles also analysed over whole of initial period to show variation of k_1 (corrected for reverse reaction) with temperature (corrected for boundary layer formation) during each particular run. Comparison made between this variation and rate constant expression. Authors also used data of WARSHAY (24) together with their own Br_2/CO/Ar data to give $k_1(M=Ar,Br_2)=1.91\times10^{13}\exp(-17\ 210/T)\ cm^3\ mol^{-1}\ s^{-1}$. $Br_2 + M \rightarrow Br + Br + M$ 1 Only values from mixtures (b) appear on our Arrhenius plot.
4.15×10^{8}	1631		
7.15×10^{8}	1639		
5.48×10^{8}	1647		
1.31×10^{9}	1663		
1.60×10^{8}	1675		
4.73×10^{8}	1695		
6.14×10^{8}	1702		
1.25×10^{9}	1713		
5.42×10^{8}	1714		
2.59×10^{8}	1715		
2.85×10^{8}	1743		
3.24×10^{9}	1793		
5.48×10^{8}	1820		
2.98×10^{9}	1945		
1.14×10^{9}	1947		
4.38×10^{9}	1950		
4.92×10^{9}	1981		
5.57×10^{9}	2024		
6.38×10^{9}	2055		
5.42×10^{9}	2083		
5.78×10^{9}	2104		
1.74×10^{10}	2266		
1.30×10^{10}	2347		
8.55×10^{9}	2355		
1.10×10^{10}	2357		
2.38×10^{10}	2468		
4.02×10^{7} (b) M=Ar, Br_2	1422		
6.71×10^{7}	1485		
5.73×10^{8}	1521		
2.68×10^{8}	1544		
4.05×10^{8}	1592		
3.06×10^{8}	1605		
4.49×10^{8}	1607		
7.89×10^{8}	1607		
9.89×10^{8}	1613		
1.25×10^{9}	1780		
7.41×10^{8}	1789		
1.50×10^{9}	1807		
7.62×10^{8}	1815		
2.05×10^{9}	1884		
2.62×10^{9}	1911		
2.54×10^{9}	1913		
1.63×10^{9}	2013		
4.97×10^{9}	2031		
5.60×10^{9}	2041		
4.49×10^{9}	2053		
4.65×10^{9}	2071		
4.65×10^{9}	2083		
6.19×10^{9}	2159		
7.69×10^{9}	2230		
2.07×10^{10}	2477		

$Br_2 + M \rightarrow Br + Br + M$

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$5.39\times10^{19}T^{-1.47}\exp(-22\ 900/T)$ M=Ar	298-2225	Least squares fit to shock tube data of (3) and k_{-1} data of STRONG *et al.* (1) at 298 and 430 K, including contribution from D(Br-Br). PALMER and HORNIG 1957 (3)	Dissociation energy D(Br-Br) taken as spectroscopic value, 190.4 kJ mol^{-1} (45.5 kcal mol^{-1}).
$2.06\times10^{16}T^{-0.4}\exp(-22\ 160/T)$ $M=Br_2$ $1.03\times10^{16}T^{-0.4}\exp(-22\ 160/T)$ M=Ar	298-2225 298-2225	Review. k_1 values of (3) converted to values of k_{-1} using equilibrium constant and empirical function for k_{-1} fitted to these and k_{-1} data of (1). K_1 used to re-convert to expressions for k_1. CAMPBELL and FRISTROM 1958 (4)	Temperature limits are those from (1 and 3). Expression $k_1(M=O_2)=1.5\times10^{16}T^{-0.5}\exp(-22\ 550/T)$ $cm^3\ mol^{-1}\ s^{-1}$ given without reference. KONDRATIEV (26) presents these expressions without halving A_1.
$1.1\times10^{13}T^{\frac{1}{2}}\exp(-21\ 740/T)$ M=Ar $1.5\times10^{13}T^{\frac{1}{2}}\exp(-20\ 330/T)$ $M=Br_2$	300-2225 300-1610	Low temperature data for k_{-1} from (5) converted to values of k_1 and combined with data of (3). GIVENS and WILLARD 1959 (5)	Alternative, classical form of rate constant expressions given as $k_1(M=Ar)=2.2\times10^{18}T^{-1.06}\exp(-22\ 900/T)$ and $k_1(M=Br_2)=2.8\times10^{26}T^{-3.46}\exp\ (22\ 900/T)$ $cm^3\ mol^{-1}\ s^{-1}$.
		Review. Data of WARSHAY (23) used as representative of Br_2 dissociation studies. TROE and WAGNER 1973 (31)	Simple Arrhenius expression compared with empirical expression of form $k_1=A(T/\bar{T})^n\ \exp(-D^o/RT)$, where D^o is bond energy (190.4 kJ mol^{-1}, 45.5 kcal mol^{-1} at 0 K) and $1/\bar{T}$ is the mean inverse experimental temperature for any particular study: $\bar{T}=2T_1T_2/(T_1+T_2)$, T_1 and T_2 being the experimental temperature limits. See entry under (11).

$Br_2 + M \rightarrow Br + Br + M$

THIRD BODY COLLISION EFFICIENCIES

EXPERIMENTAL DATA

M=Ar	Br_2	Br	He	N_2	CO	O_2	CO_2	Xe	Temperature	Reference
1	⩾8								1400-2700	Britton and Davidson 1956 (2).
1	1.9								1300	Palmer and Hornig 1957 (3).
1	1.7								1600	
1	9.4		1	0.7	0.7	1.7	1.3		1600	Britton 1960 (6).
1	6.5								1470	Hiraoka and Hardwick 1962 (7).
1		10±6							1600	Boyd et al. 1968 (15).
1		2±1.2							2200	
	3.8^a		1.3^a					1	1250	Warshay 1970 (22) and 1972 (24).
	1.5^a		0.8^a					1	1900	
1							1.07		1200	Warshay 1972 (27).
1							1.36		1800	

a: Efficiency relative to Xe.

Discussion

All the data available on the dissociation rate of molecular bromine have been obtained in shock tube studies, principally with argon as the collision partner.

$$Br_2 + M \rightarrow Br + Br + M \qquad (1)$$

Judging by the variation between k_1 (M=Ar) and k_1 (M=Br_2) as determined by Palmer and Hornig [3] the contribution to Br_2 dissociation from M=Br_2 only becomes appreciable (i.e., ⩾10%) with respect to the contribution from M=Ar in Br_2/Ar mixtures with Br_2 fractions greater than ~7%. Therefore in this evaluation we have only considered those studies in which the authors either specifically separate the effects of Br_2 and of Ar [3], or in which the Br_2 fraction in Ar was less than ~5% [6,8,11,20,24,29].

Burns et al. [12,19,34] have argued that most of the values of k_1 determined by absorption spectroscopy [2,3,6,7,8,10,24] are a factor of ~3 too high, as a result of coupling between dissociation and vibrational relaxation. However, those studies in which two-body Br emission has been used [15] and [20], and in which this coupling does not affect the measurements, provide values of k_1 which are little different from those of the absorption studies, using similar Br_2/Ar mixtures.

In their latest studies of bromine dissociation/recombination [32,34], Burns et al. appear to have reconciled the differences between the absorption spectroscopy data and the two-body Br emission results. They found that the latter decreased rapidly with temperature above 2000 K, due to initial reaction rates being too fast relative to the resolution time. They also found that the earlier results obtained by the former method were spuriously high, due to boundary layer effects, their own data being in agreement with the most recent absorption spectroscopy results [29] and the Br emission data [15,34] and high temperature flash photolysis data [12,18].

It is somewhat surprising that the activation energy of the data of Warshay [24] should be so much lower than that of the other studies, particularly as consideration of boundary layer effects allowed the author to increase the activation energy over that of the raw data. Moreover these data would produce a value of k_{-1}

$$Br + Br + M \rightarrow Br_2 + M \qquad (-1)$$

at low temperatures very much in excess of those determined experimentally (see section C2).

The data of Palmer and Hornig [3] and of Britton and Davidson [2] show considerable scatter and therefore we have attached little weight to them. Consequently the remaining data [8,20,29] lead us to recommend the expression

$$k_1\ (M{=}Ar) = 2.35\times10^{14} \exp(-21\,630/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the temperature range 1300–2500 K. Uncertainty limits of a factor of 3 must be allowed.

The data for k_1 (M=Br_2) [3,14] are widely scattered and there is no a priori reason for assuming the activation energy to be the same as for k_1 (M=Ar). Therefore no recommendation is made for M=Br_2.

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C2 $Br + Br + M \rightarrow Br_2 + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-192.811	-104.429	28.325	32.713
300	-192.824	-104.466	28.116	32.507
500	-193.803	-106.997	14.658	19.271
1000	-196.079	-110.135	4.490	9.404
1500	-198.991	-112.470	1.054	6.144
2000	-202.447	-114.458	-0.692	4.523
2500	-206.037	-116.056	-1.758	3.554
3000	-209.476	-117.315	-2.480	2.911
3500	-212.656	-118.294	-3.006	2.452
4000	-215.535	-119.068	-3.404	2.112
4500	-218.120	-119.675	-3.720	1.847
5000	-220.430	-120.160	-3.974	1.639

SI Units: $\log(Kp/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.0056$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 1.48 \times 10^{14} \exp(856/T)\ cm^6\ mol^{-2}\ s^{-1}$ (M=Ar)

$= 4.08 \times 10^{-34} \exp(856/T)\ cm^6\ molecule^{-2}\ s^{-1}$ (M=Ar)

(k is defined by $-d[Br]/dt = 2k[Br]^2[M]$)

Temperature Range: 290-2000 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.

Note: Values for third bodies other than Ar are given in the Discussion.

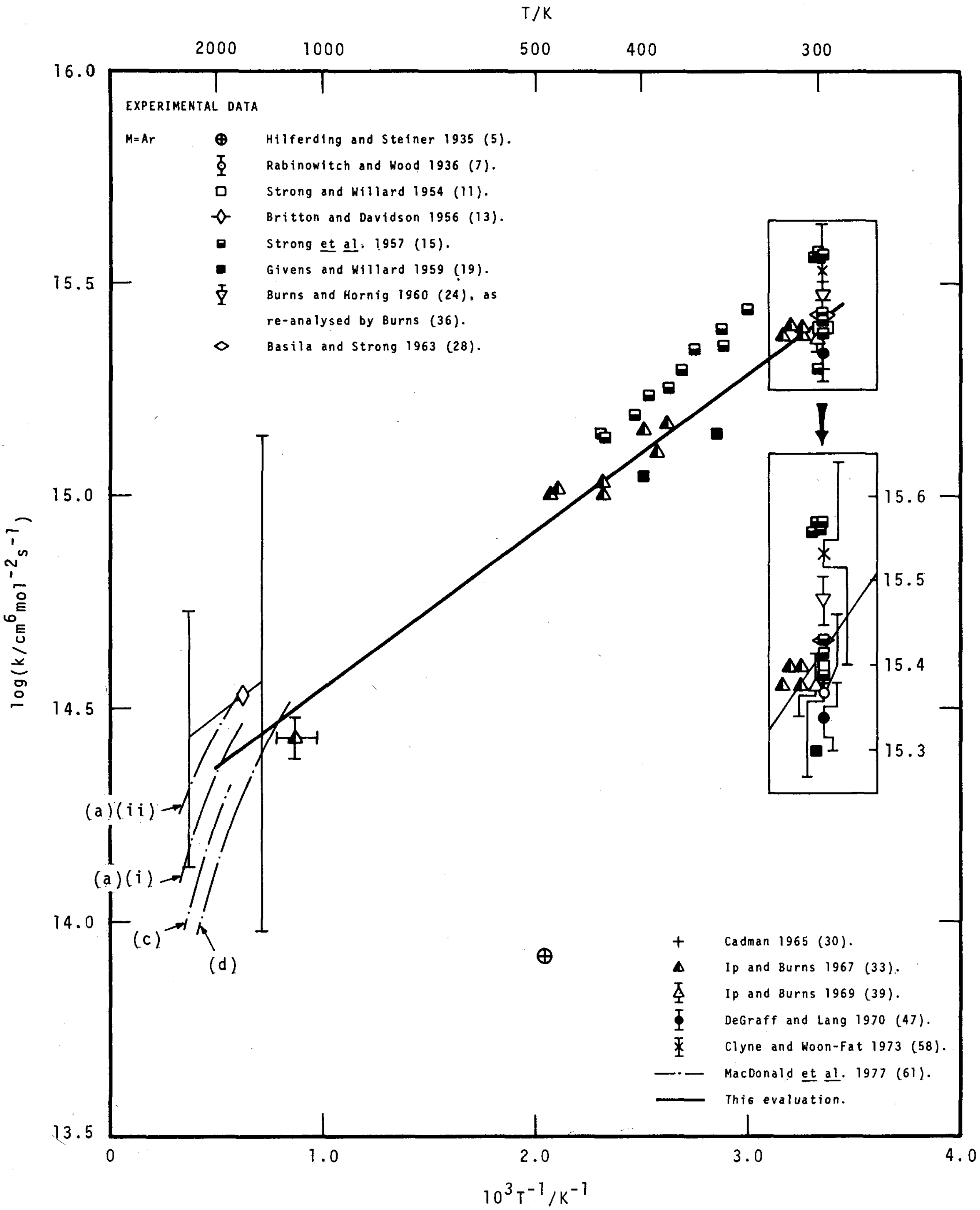
Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 14.17 \pm 0.18$

$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -33.39 \pm 0.18$

$E/J\ mol^{-1} = -7110 \pm 2340$

$E/cal\ mol^{-1} = -1700 \pm 560$

$Br + Br + M \rightarrow Br_2 + M$

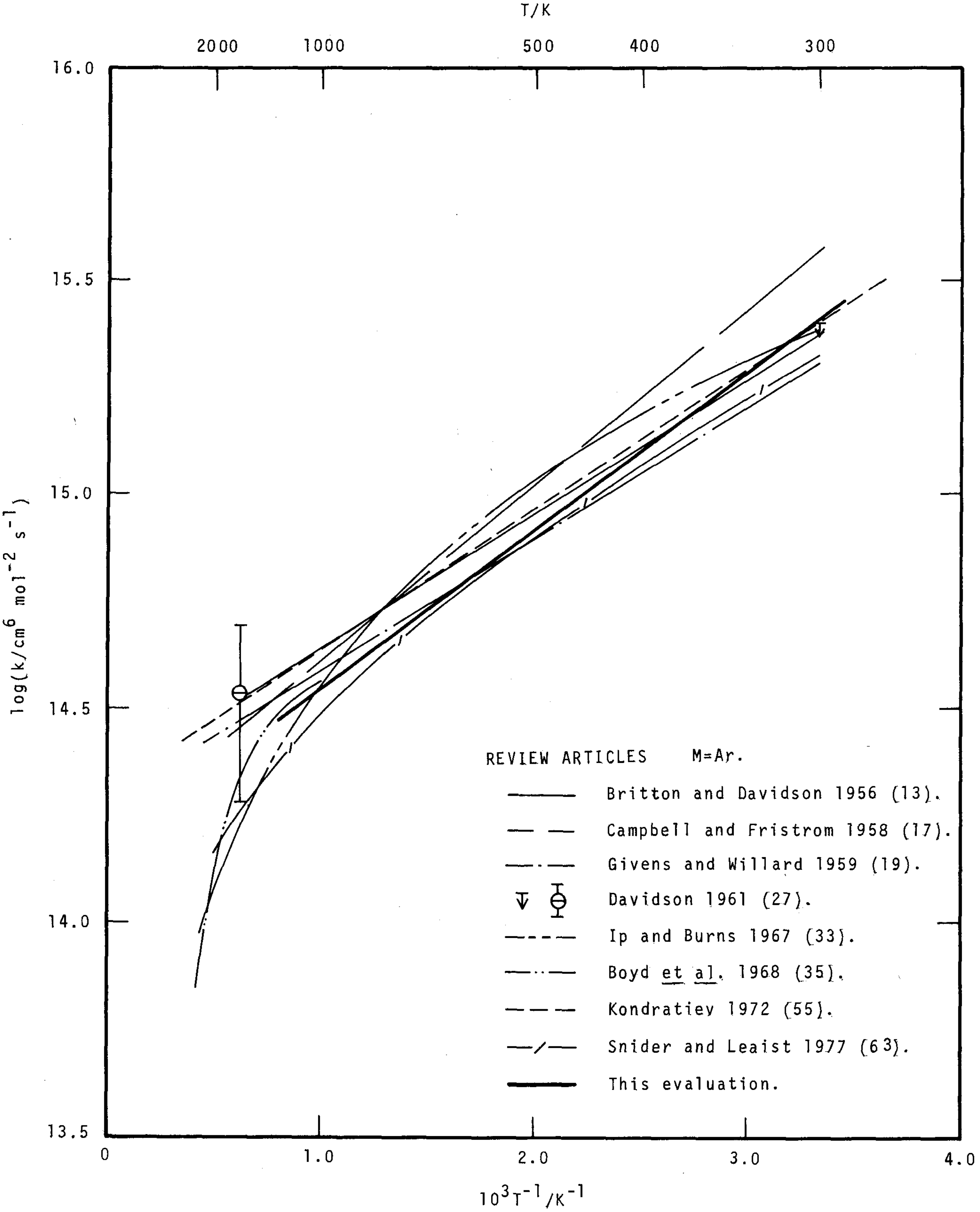


$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	303	Static photolysis system. H_2(647-648.2 mm Hg; 86.3-86.4 kPa)/Br_2(107.8-109.1 mm Hg; 14.4-14.5 kPa), and H_2(646.8-648.1 mm Hg; 86.2-86.4 kPa)/Br_2(107.9-109.2 mm Hg; 14.4-14.6 kPa)/HBr (625-650 mm Hg; 83.3-86.7 kPa) mixtures photolysed by sunlight. [HBr] in products determined by iodometry. BODENSTEIN and JUNG 1926 (2)	Original analysis assumed HBr yield determined by sequence $H + Br_2 \rightarrow HBr + Br$ $H + HBr \rightarrow H_2 + Br$ -2 SULLIVAN (38) re-interpreted these data in terms of reactions $Br + Br + H_2 \rightarrow 2HBr$ $Br + Br + M \rightarrow Br_2 + M$ 1 where M=HBr. Using $k_1(M=Br_2)$ (28) and $k_1(M=H_2)$ (7) with $E_1 = -5.1\ kJ\ mol^{-1}$ ($-1.22\ kcal\ mol^{-1}$), as for I atom recombination (25), SULLIVAN (38) re-calculated these to give $k_1(M=HBr) = 7.2 \times 10^{15}\ cm^6\ mol^{-2}\ s^{-1}$.
	499	Static system. Br_2($\sim$2.0-76 mm Hg; 0.27-10.13 kPa)/H_2 mixtures at total pressures 20.8-688.2 mm Hg (2.77-91.74 kPa) photolysed in regions of Br_2 continuum and bandspectrum. Br_2 absorption and pressure followed. JOST 1929 (3)	Reaction 1 acts as termination reaction in HBr synthesis mechanism $Br + Br + M \rightarrow Br_2 + M$ 1 From d[HBr]/dt and absorbed light intensity k_2 determined $Br + H_2 \rightarrow HBr + H$ From k_2(=$8.53 \times 10^5\ cm^3\ mol^{-1}\ s^{-1}$ at 499 K) author derives k_1 ($\propto k_2^2$) as $5.71 \times 10^{15}\ cm^6\ mol^{-2}\ s^{-1}$ ($M=H_2$, 499 K).
	473	Static system. Br_2 ($\sim$40 mm Hg; 5.3 kPa)/H_2 ($\sim$100 mm Hg; 13.3 kPa)/N_2($\sim$100 mm Hg; 13.3 kPa)/HBr($\sim$12-18 mm Hg; 1.6-2.4 kPa) mixtures with added gases: He(100-380 mm Hg; 13.3-50.7 kPa), Ar (122-435 mm Hg- 16.3-58.0 kPa), CO_2 (65-479 mm Hg; 8.7-63.9 kPa), O_2(0-459 mm Hg; 61.2 kPa), H_2(207-453 mm Hg; 27.6-60.4 kPa), and N_2 (101 547 mm Hg; 13.5-73.0 kPa). Photolysis performed at $\sim$420 nm through $CuSO_4$ filter, and transmitted light intensity used to monitor [Br_2]. Pressure also monitored. RITCHIE 1934 (4)	Variation of relative quantum efficiency of HBr formation, with added gas pressure, gives, for constant initial [H_2], [Br_2] and [HBr], dependence upon k_1. Relative rates only determined, i.e. $k_1(M=CO_2:N_2:H_2:He:Ar) = 2.2:1.6:0.8:0.6:1$. Value of $k_1(M=Br_2)/k_1(M=Ar)$ given to 'rough order of magnitude' as 1.1. Quoted by (8).

$Br + Br + M \rightarrow Br_2 + M$

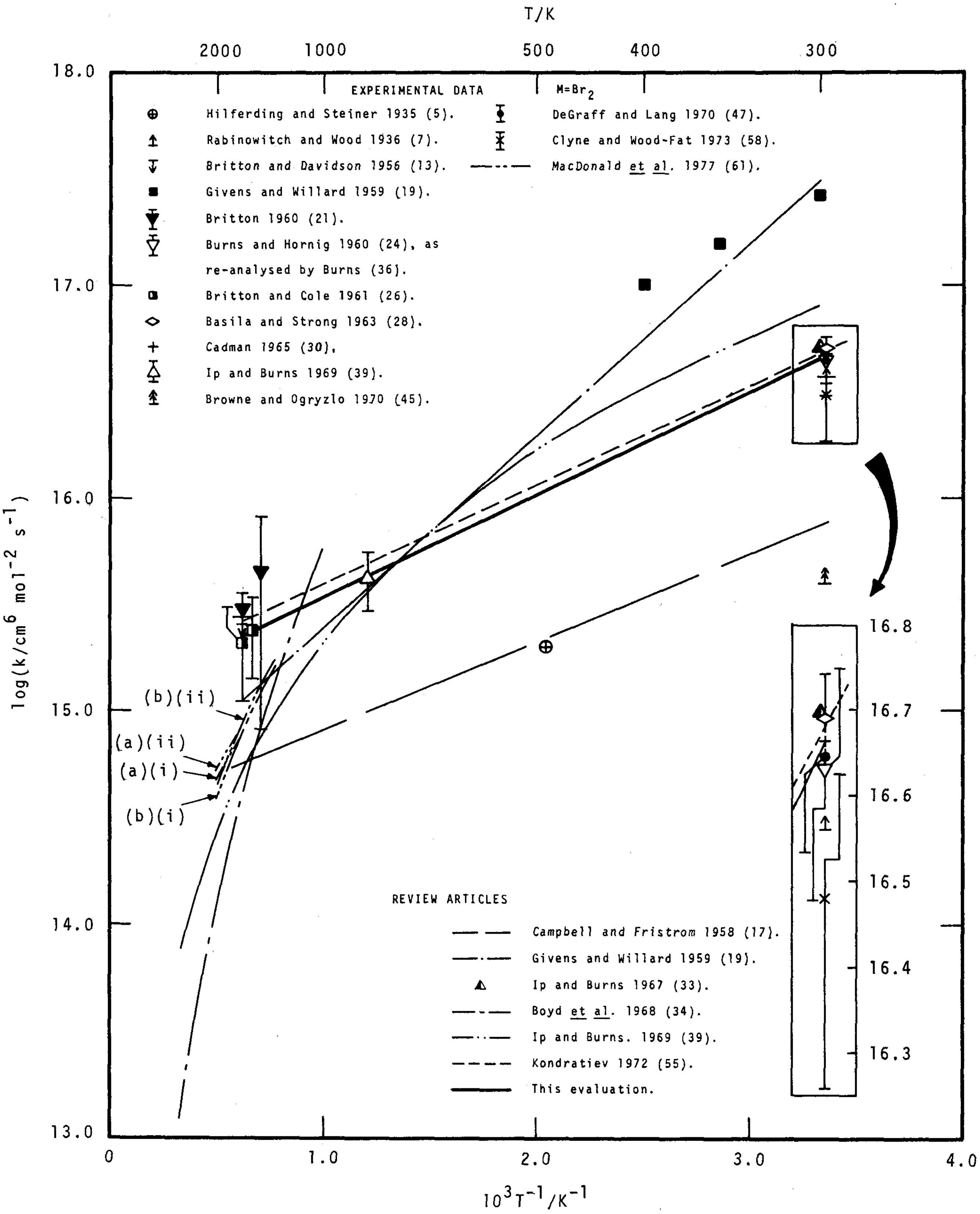


$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
		490	Static system. Br_2(5.1-229 mm Hg; 0.68-30.5 kPa)/H_2 (5.1-1197 mm Hg; 0.68-159.6 kPa), Br_2(20.5-35.3 mm Hg; 2.7-4.7 kPa)/H_2 (20.7-1188 mm Hg; 2.8-158.4 kPa)/Ar (0-739 mm Hg; 98.5 kPa), or He(0-991 mm Hg; 132.1 kPa), or N_2(0-581 mm Hg; 77.5 kPa), or HBr(0-632 mm Hg; 84.3 kPa), or HCl (0-631 mm Hg; 84.1 kPa), or CO (0-650 mm Hg; 86.7 kPa) mixtures. Two different sets of apparatus used, in which reaction followed by pressure change, or by absorption of Br_2 at 450 nm. HILFERDING and STEINER 1935 (5)	From reaction mechanism describing formation of HBr, k_1 given as proportional to k_2^2 $Br + H_2 \rightarrow HBr + H$ 2 From (1 and 3) authors derive k_2= $(5.6\pm0.6)\times10^5$ cm^3 mol^{-1} s^{-1} at 490 K, and give k_1 (490 K) as follows: M=Ar, 1.1×10^{14}; M=He, 4.7×10^{14}; M=H_2, 1.25×10^{15}; M=N_2, 8.2×10^{14}; M=Br_2, 2.6×10^{15}; M=HBr, 2.1×10^{15}; M=HCl, 4.7×10^{15}; and M=CO, 6.3×10^{15} cm^6 mol^{-2} s^{-1}. Extrapolating our recommended expression for k_2 (this Volume, section C4) slightly below our recommended temperature interval, we obtain for this work k_1(M=Ar)= 8.3×10^{13} and k_1(M=Br_2)=1.96×10^{15} cm^6 mol^{-2} s^{-1}.
1.36×10^{15}	M=He	298	Static system. Photolysis of Br_2(5 mm Hg; 666.5 Pa)/ He(0-760 mm Hg; 101.3 kPa) mixtures at ∿430 nm. [Br_2] monitored by absorption 400-500 nm. RABINOWITCH and LEHMANN 1935 (6)	Authors considered thermal effect upon [Br_2] to be 2-3 times smaller than that of homogeneous recombination, and upon absorption coefficient to be negligible. From extent of dissociation with pressure, authors determined Br-He diffusion coefficient and k_1 $Br + Br + M \rightarrow Br_2 + M$ 1 Authors give error limits on k_1 as ±30%
$(1.36\pm0.2)\times10^{15}$	M=He	298	Static system. Photolysis of Br_2(0.195-0.93 mm Hg; 26-124 Pa)/He (361-759 mm Hg; 49.2-101.2 kPa), Br_2 (0.281-0.339 mm Hg; 37.5-45.2 Pa)/Ar (90-490 mm Hg; 12-65.3 kPa), Br_2(0.312 and 0.525 mm Hg; 41.6, 70 Pa)/ H_2(251-672 mm Hg; 33.5-89.6 kPa), Br_2(0.28 mm Hg; 37.3 Pa)/N_2(109-500 mm Hg; 14.5 66.7 kPa), Br_2(0.29 mm Hg; 38.7 Pa)/O_2 (94-465 mm Hg; 12.5-62 kPa), Br_2 (0.403 mm Hg; 53.7 Pa)/CH_4(90-400 mm Hg; 12-53.3 kPa), and Br_2(0.28 mm Hg; 37.3 Pa)/	Extent of Br_2 dissociation varied with pressure such that formation of Br_3 or other complexes was not observed. Authors have obtained the most consistently high values of k_1. (38) uses k_1(M=Br_2).
$(2.36\pm0.5)\times10^{15}$	M=Ar	298		
$(3.99\pm0.9)\times10^{15}$	M=H_2	298		
$(4.53\pm0.7)\times10^{15}$	M=N_2	298		
$(5.80\pm1.1)\times10^{15}$	M=O_2	298		
$(6.53\pm1.1)\times10^{15}$	M=CH_4	298		
$(9.79\pm0.9)\times10^{15}$	M=CO_2	298		
$> 3.63\times10^{16}$	M=Br_2	298		

$Br + Br + M \rightarrow Br_2 + M$



$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
			CO_2(81-285 mm Hg; 10.8-38 kPa) and pure Br_2 mixtures. [Br_2] measured by absorption at 400-480 nm. RABINOWITCH and WOOD 1936 (7)	
		298	Static system. Br_2(50 mm Hg; 6.7 kPa)/N_2 (0-567.4 mm Hg; 75.6 kPa), Br_2(40 mm Hg; 5.3 kPa)/N_2(0-424.7 mm Hg; 56.6 kPa), Ar(0-538.5 mm Hg; 71.8 kPa), O_2(0-400 mm Hg; 53.3 kPa) or H_2(0-570 mm Hg; 76.0 kPa), and Br_2(40.4 mm Hg; 5.39 kPa)/CO_2 (0-513.4 mm Hg; 68.4 kPa) mixtures, illuminated at ∿420 nm through $CuSO_4$ filter. Transmitted light intensity and pressure monitored. SMITH, RITCHIE and LUDLAM 1937 (9)	Variation of pressure rise resulting from photolysis, with added gas pressure, gives values of k_1, presented only in relative form by authors: $k_1(M{=}Br_2:CO_2:O_2:N_2:H_2:Ar) = 2.0:1.8:1.8:1.6:1.2:1.$
1.95×10^{15} 5.00×10^{15}	M=N_2 M=O_2	298 298	Static system. Br_2 (20 mm Hg, 2.7 kPa)/N_2 (420 mm, 56 kPa) or O_2(180, 280 and 380 mm Hg; 24, 37.3 and 50.7 kPa) mixtures illuminated via $CuSO_4$-NH_4OH filter. Pressure changes monitored. SHIDA 1946 (10)	Pressure variation expressed in terms of wall reaction and reaction 1. $Br + Br + M \rightarrow Br_2 + M$ 1 k_1 obtained from behaviour after illumination shut off.
2.5×10^{15}	M=Ar	298	Flash photolysis study. No details given. STRONG and WILLARD 1954 (11)	Abstract only.
		1500	Shock tube study. 1%Br_2/1% H_2/Ar mixtures and 80%Br_2/20%H_2 mixtures behind incident shocks. Br_2 absorption monitored at 487 nm. BRITTON and DAVIDSON 1955 (12)	Mixtures highly dilute in Ar used to determine k_2 $Br + H_2 \rightarrow HBr + H$ 2 as 10^{11} $cm^3\ mol^{-1}\ s^{-1}$ (1500 K). Using this result Br_2/H_2 mixtures gave $k_1(M{=}Br_2)=3.4\times10^{14}$ and 7.0×10^{14} $cm^6\ mol^{-2}\ s^{-1}$ (1500 K).

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
		1400-2700	Shock tube study. Br_2(1%, 2%,4%,6% and 10%)/Ar mixtures behind incident shocks. Br_2 decay followed by absorption at 436 or 487 nm. BRITTON and DAVIDSON 1956 (13)	Dissociation profiles of Br_2 analysed in terms of k_1, using $k_{-1} = k_1/K_1$. Corrections made for effects of temperature change (particularly for higher percentages of Br_2) on extinction coefficient. Data are widely scattered. Fits to 1%Br_2/Ar mixture given as $k_1(M=Ar)=4.3\times10^{14}(T/1000)^{-0.52(\pm1.2)}$ and $2.0\times10^{14}\exp(820\pm1870/T)\ cm^6\ mol^{-2}\ s^{-1}$ (1400-2700 K). Authors believe value at 1600 K, $k_1(M=Ar)=3.4\times10^{14}\ cm^6\ mol^{-2}\ s^{-1}$, to be "fairly" accurate. Variation of k_1 between mixtures suggests $k_1(M=Br_2)/k_1(M=Ar)$ <8 at 1600 K.
$(2.46\pm0.09)\times10^{15}$	M=Ar	298	Flash photolysis study. Br_2(1.89×10^{-7}-2.46×10^{-7} mol cm^{-3})/Ar (2.70×10^{-5}-3.84×10^{-5} mol cm^{-3}), Br_2(2.28×10^{-7} and 2.45×10^{-7} mol cm^{-3})/O_2(2.69×10^{-5} and 2.70×10^{-5} mol cm^{-3}), and Br_2 (2.06×10^{-7}mol cm^{-3})/N_2 (2.67×10^{-5} mol cm^{-3}) mixtures. Br_2 followed by absorption at ∿400 nm. STRONG, CHIEN, GRAF and WILLARD 1957 (15)	No apparent thermal effect detected. Two distinctly different series of results reported by authors who quote average room temperature values of k_1 as $(3.6\pm0.2)\times10^{15}\ cm^6\ mol^{-2}\ s^{-1}$ and $2.9\times10^{15}\ cm^6\ mol^{-2}\ s^{-1}$ for each of the two series. Values of k_1 for T>300 K appear to be appropriate to the 'high' series. Nevertheless, temperature dependence of k_1(M=Ar) considered reliable by IP and BURNS (33). Authors quote activation energies for k_1(M=Ar), $k_1(M=O_2)$, as -8.37 kJ mol^{-1} (-2 kcal mol^{-1}) and -5.02 kJ mol^{-1} (-1.2 kcal mol^{-1}), respectively. CAMPBELL and FRISTROM (17) fitted the following expressions to the more consistent data: $k_1(M=Ar)=2.36\times10^{22}T^{-2.75(\pm0.05)}$ or $4.13\times10^{24}\ T^{-3.5(\pm0.05)}\exp(-268/T)\ cm^6\ mol^{-2}\ s^{-1}$. Data for k_1(M=Ar) used by (26). Expression $k_1=1.7\times10^{14}\exp(890/T)cm^6\ mol^{-2}\ s^{-1}$ attributed to this work used by (54) for use in H_2/O_2/HBr flames.
$(2.60\pm0.11)\times10^{15}$		298		
$(2.70\pm0.23)\times10^{15}$		298		
$(3.69\pm0.20)\times10^{15}$		298		
$(3.73\pm0.20)\times10^{15}$		298		
$(3.65\pm0.22)\times10^{15}$		298		
$(3.72\pm0.22)\times10^{15}$		300		
$(3.62\pm0.21)\times10^{15}$		302		
$(2.72\pm0.15)\times10^{15}$		333		
$(2.25\pm0.15)\times10^{15}$		347		
$(2.47\pm0.13)\times10^{15}$		348		
$(2.22\pm0.11)\times10^{15}$		364		
$(1.98\pm0.09)\times10^{15}$		372		
$(1.79\pm0.06)\times10^{15}$		380		
$(1.72\pm0.01)\times10^{15}$		394		
$(1.55\pm0.04)\times10^{15}$		405		
$(1.37\pm0.09)\times10^{15}$		429		
$(1.40\pm0.06)\times10^{15}$		433		
$(7.9\pm0.8)\times10^{15}$	$M=O_2$	300		
$(7.4\pm0.4)\times10^{15}$		308		
$(7.5\pm0.6)\times10^{15}$		331		
$(6.8\pm0.7)\times10^{15}$		339		
$(5.8\pm0.3)\times10^{15}$		363		
$(5.6\pm0.3)\times10^{15}$		370		
$(5.6\pm0.5)\times10^{15}$		393		
$(5.0\pm0.5)\times10^{15}$		397		
$(4.3\pm0.3)\times10^{15}$		424		
$(4.2\pm0.2)\times10^{15}$		431		
$(3.42\pm0.33)\times10^{15}$	$M=N_2$	298		
		293-323	Static system. Br_2(2-10×10^{-7} mol cm^{-3})/Cl_2 (∿5×10^{-7} mol cm^{-3})/CO_2(0-1.5×10^{-5} mol cm^{-3}) mixtures photolysed at 430 nm. Br_2 followed by absorption at	Chain reaction scheme proposed, from which dependence of quantum yield/absorbed light versus initial values of $[CO_2]$,$[Br_2]$ and $[Cl_2]$ gave values of k_1/k_3^2 for $k_1(M=CO_2,Cl_2$ and $Br_2)$.

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
		longer wavelength, and absorbed light by actinometry. CHRISTIE, ROY and THRUSH 1959 (18)	$Br + Br + M \rightarrow Br_2 + M$ 1 $Br + Cl_2 \rightarrow BrCl + Cl$ 3 Authors obtained k_3 using k_1(M=CO_2) from RABINOWITCH and WOOD (7). We present only the ratios k_1(M=CO_2):k_1(M=Cl_2):k_1(M=Br_2) obtained in this work: at 293 K, 313 K and 323 K values are 1:1.51 ±0.3:4.90±0.4, 1:1.86±0.3:4.64± 0.1 and 1:3.78:6.53. In this way the authors' neglect of temperature dependence of k_1(M=CO_2) is eliminated.
2.0×10^{15} M=Ar	300	Flash photolysis study. Br_2 (2.9-6.2 mm Hg, 287-827 Pa)/Ar (103-700 mm Hg; 13.7-93.3 kPa) and Br_2 (4.2 mm Hg; 560 Pa)/CO_2 (500 mm Hg; 66.7 kPa) mixtures. $[Br_2]/[Ar]$ ratios varied 4×10^{-3}-6×10^{-2}. $[Br_2]$ followed by absorption at 500 nm. GIVENS and WILLARD 1959 (19)	$[Br_2]$ profiles corrected for thermal effect by assuming step temperature change in temperature distribution. Apparent rate (=k_1(M)+k_1(M=Br_2)$[Br_2]/[M]$) determined for 283-439 K and values at these temperatures plotted vs. $[Br_2]/[M]$. k_1(M=Br_2) determined from Br_2/Ar mixtures used to correct for Br_2 effect in Br_2/CO_2 mixtures. Activation energies given as E_1(M=Ar)=-5.9 kJ mol^{-1} (-1.4 kcal mol^{-1}) and E_1(M=Br_2)= -12.1 kJ mol^{-1} (-2.9 kcal mol^{-1}).
1.4×10^{15} M=Ar	350		
1.1×10^{15} M=Ar	400		
2.6×10^{17} M=Br_2	300		
1.54×10^{17} M=Br_2	350		
1.0×10^{17} M=Br_2	400		
$\sim 7.8 \times 10^{15}$ M=CO_2	300		
(a) $4.06 \times 10^{13} \exp(3150 \pm 450/T)$ M=Ar+Br_2	1370-1880	Shock tube study. Br_2((a) 2% and (b) 5%)/Ar, 5%Br_2/He, 2%Br_2/N_2 and CO, 2%Br_2/10% CO/Ar, Br_2(2% and 5%)/O_2, and 2%Br_2/CO_2 mixtures. Incident shock conditions. Br_2 absorption and two-body Br recombination emission monitored at 500 nm. BRITTON 1960 (21)	Emission at temperatures <1900 K sufficiently low to be ignored. Initial slope of absorption profile used to determine k_{-1} $Br_2 + M \rightarrow Br + Br + M$ -1 and values converted to k_1 via equilibrium constant. No allowances made for variation in collision efficiency between Br_2 and various diluents, but comparison between 2% and 5% mixtures in Ar (1600 K) and O_2(1400 K) used to obtain k_1 (M=Br_2) at these temperatures. Analysis of slope of absorption profiles at 50% dissociation (in Ar diluent ?) gave k_1 (M=Br). Expression for k_1(M=O_2) and expression (c) for k_1(M=Ar) are derived from combining both 2% and 5% mixture data. Values of k_1(M=N_2 and CO) obtained assuming vibrational relaxation occurring at rate
(b) $4.16 \times 10^{13} \exp(3520 \pm 410/T)$ M=Ar+Br_2	1381-1848		
(c) $4.36 \times 10^{13} \exp(3200 \pm 400/T)$ M=Ar+Br_2	1370-1880		
$6.98 \times 10^{13} \exp(3250 \pm 1160/T)$ M=O_2+Br_2	1120-1800		
$7.67 \times 10^{13} \exp(2940 \pm 1510/T)$ M=CO_2+Br_2	1380-1622		
2.0×10^{14} M=CO+Br_2	1640		
1.4×10^{14} M=CO+Br_2	1748		
1.3×10^{14} M=CO+Br_2	1770		
1.2×10^{14} M=CO+Br_2	1785		
1.2×10^{14} M=CO+Br_2	1810		
1.2×10^{14} M=CO+Br_2	1892		
9.0×10^{13} M=CO+Br_2	1910		
$(4.4 \pm 3.6) \times 10^{15}$ M=Br_2	1400		
$(3.0 \pm 0.5) \times 10^{15}$ M=Br_2	1600		
$(4.0 \pm 1.0) \times 10^{15}$ M=Br	Unspecified		
$2.56 \times 10^{13} \exp(4010 \pm 550/T)$ M=He+Br_2	1469-1915		
$2.00 \times 10^{13} \exp(3930 \pm 650/T)$ M=N_2+Br_2	1400-1932		

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
		BRITTON 1960 (21) continued.	comparable to that of dissociation, in the latter case using relaxation rate 1/4 that in pure CO (20). Only values of k_1(M=CO) at highest temperatures obtained with any certainty, but high temperature dependence leads authors to consider that even these not too reliable. Fit to these values given as k_1(M=CO)= $1.67x10^{12}exp(7770 \pm 930/T)$ cm^6 mol^{-2} s^{-1}. Data for k_1(M=Ar) used by (26), who also give values k_1(M=Ar)=$(2.6 \pm 0.4)x10^{14}$ (1500 K) and $(2.3 \pm 0.4)x10^{14}$ cm^6 mol^{-2} s^{-1} (1600 K), and k_1(M=Br_2)=(3.7 ± 1.0) $x10^{15}$ cm^6 mol^{-2} s^{-1} (1500 K) from these data. Contribution of Br_2 to k_1 ignored by (40).
$<5.0x10^{16}$ M=Br_2 $(8.2 \pm 1.1)x10^{14}$ M=Ar^2 +Br+Br_2 $(1.3 \pm 0.1)x10^{15}$ M=He^2 +Br_2	298 950 298	Combined shock tube and flash photolysis study. (a) Static flash photolysis of Br_2($7.8x10^{-8}$-$2.05x10^{-7}$ mol cm^{-3})/Ar ($6.39x10^{-6}$-$3.88x10^{-5}$ mol cm^{-3}) mixtures, $[Br_2]/[Ar]$ ratios $2.0x10^{-3}$-$3.0x10^{-2}$, and Br_2 ($1.1x10^{-7}$ mol cm^{-3})/He ($3.92x10^{-5}$ mol cm^{-3}) mixtures. (b) 0.6% Br_2/Ar mixtures flash photolysed and then shock-heated (incident shock). $[Br_2]$ monitored by absorption at 442 nm in all cases. BURNS and HORNIG 1960 (23 and 24)	Low $[Br_2]/[M]$ ratios enabled thermal effects to be ignored. Br concentration prior to shock in series (b) determined by separate photolysis study of pure Br_2. Room temperature values (a) obtained by plotting overall rate constant vs. $[Br_2]/[M]$. At high values of this ratio heating by flash set up wave systems in reaction vessel. Overall rates given in this work quoted as values of k_1(M=Ar)(=$3.0x10^{15}$) and k_1(M=He)(=$1.3x10^{15}$ cm^6 mol^{-2} s^{-1}) at 298 K by IP and BURNS (39). Data re-analysed by BURNS (36) to give k_1(M=Br_2)=$(6 \pm 7)x10^{15}$ cm^6 mol^{-2} s^{-1} if thermal effects are ignored (298 K), or (4.3 ± 1.3) $x10^{16}$ cm^6 mol^{-2} s^{-1} if thermal effects are considered, and k_1(M=Ar)=$(3.0 \pm 0.2)x10^{15}$ cm^6 mol^{-2} s^{-1} (298 K).
$(3.6 \pm 0.4)x10^{14}$ } M=HBr $(2.8 \pm 0.4)x10^{14}$ } $(2.4 \pm 1.0)x10^{15}$ } M=Br_2 $(2.1 \pm 1.0)x10^{15}$ }	1500 1600 1500 1600	Shock tube study. Br_2(0.48, 1.0, 2.0 and 4.41%)/HBr, and 2%Br_2/20%HBr/Ar mixtures. Incident shocks. Shocked gas concentrations 10^{-6}-10^{-5} mol cm^{-3}. Br_2 absorption followed at 500 nm.	Emission negligible under conditions of this study. Initial slope of absorption profile used to obtain k_{-1}. Conversion to k_1 made using K_1. Experiments in very dilute Br_2/HBr mixtures showed vibrational relaxation of

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
			BRITTON and COLE 1961 (26)	HBr sufficiently rapid not to affect Br_2 profiles. Fits to Br_2/HBr/Ar mixture given as $k_1(M=Ar+HBr+Br_2)=1.84x10^{13}exp(4720±450/T)$ $cm^6\ mol^{-2}\ s^{-1}$ (1250-1850 K), and to Br_2/HBr mixtures as $k_1(M=HBr+Br_2)=4.94x10^{12}exp(5340/T)$, $1.33x10^{12}exp(8530/T)$, $5.75x10^{12}exp(6500/T)$, and $1.06x10^{13}exp(5530/T)$ $cm^6\ mol^{-2}\ s^{-1}$ (∿1400-∿1700 K) respectively. Separation of effects of HBr and Br_2, for all mixtures, gave values presented here. Authors consider as conservative error limits on $k_1(M=HBr, Br_2)$. Corrections for $k_1(M=Ar)$ made using expression $k_1(M=Ar)=1.4x10^{14}exp(930/T)$ $cm^6\ mol^{-2}\ s^{-1}$, derived from data of (15 and 21). Increased efficiency of HBr over Ar at 1400 K (30%) and 1600 K (20%) used with this expression to give $k_1(M=HBr)=1.14x10^{14}exp(1830/T)$ $cm^6\ mol^{-2}\ s^{-1}$ (1250-1850 K). SULLIVAN (38) used these increased efficiencies with $k_1(M=Ar)$ of IP and BURNS (33) to give $k_1(M=HBr)=2.19x10^{21}T^{-2.2}$ $cm^6\ mol^{-2}\ s^{-1}$.
$2.7x10^{15}$ $4.9x10^{16}$	M=Ar $M=Br_2$	298 298	Flash photolysis study. Br_2 in Ar (154-642 mm Hg; 20.5-85.6 kPa) mixtures, $[Br_2]/[Ar]$ ratio varied $6.15x10^{-3}-2.32x10^{-2}$. Absorption at 489 nm used to follow $[Br_2]$. BASILA and STRONG 1963 (28)	Initial slope of profiles of I/[Br] used to determine k_1 $Br + Br + M \rightarrow Br_2 + M$ 1 and contributions from $k_1(M=Ar)$ and $k_1(M=Br_2)$ separated. These values also given in (16), as reported by (19 and 23). $k_1(M=Br_2)$ used by (38).
$2.4x10^{15}$ $4.6x10^{16}$	M=Ar $M=Br_2$	298 298	Flash photolysis study. Br_2 (1-3.5 mm Hg; 133.3-467 Pa)/Ar mixtures, $[Br_2]/[Ar]$ ratios $2x10^{-3}-1.3x10^{-2}$. $[Br_2]$ monitored by absorption over range 375-500 nm. CADMAN 1965 (30)	Thermal effects avoided by using initial slope of inverse optical density profile. Variation of k_1 with monitoring wavelength observed. Values given are those determined at 418 nm, considered to be lower than true values of k_1.

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
(a) $(8\pm3)\times10^{14}$ (b) $(5\pm1)\times10^{14}$ (c) $(1.3\pm0.1)\times10^{15}$ M=He $+Br_2$	363 363 298	Flash photolysis study. Br_2/He mixtures (conditions not specified. Example given with $[Br_2]=1.15\times10^{-7}$, $[He]=3.2\times10^{-5}$ mol cm^{-3}). Br_2 absorption monitored at (a) 498 nm, and (b) 403.5 nm. BURNS 1967 (32)	Thermal effects avoided by filling reaction cell with analysing beam. Temperature at which k_1 measured taken to be average between that at 50% recombination and that at start of measurement (40 μs after flash initiation). Temperature subject to error of ±20 K. Result (a) considered more reliable due to near temperature independence of Br_2 absorption coefficients. Author quotes value (c) from his Ph.D dissertation (22), presumably obtained by similar methods. Room temperature value $k_1(M=He)=1.0\times10^{15}$ $cm^6\ mol^{-2}\ s^{-1}$ calculated from (a) by IP and BURNS (39).
2.49×10^{15} 2.40×10^{15} 2.49×10^{15} 2.40×10^{15} 1.48×10^{15} 1.26×10^{15} 1.42×10^{15} 1.07×10^{15} 1.00×10^{15} 1.03×10^{15} 1.00×10^{15} $(2.7\pm0.3)\times10^{14}$ M=Ar	307 307 312 316 381 390 397 431 431 475 482 1150	Flash photolysis study. Br_2/Ar mixtures, $[Br_2]/[Ar]<6\times10^{-3}$ for temperatures <480 K. $[Br_2]$ followed by absorption at 443 nm. IP and BURNS 1967 (33)	For 300<T<480 K, values of k_1 determined from linear plots of $[Br]^{-1}$ vs. time. For T>1000 K, redissociation of Br_2 was necessarily included, using $k_{-1}=k_1/K_1$. Value of $k_1(M=Ar)=(2.60\pm0.1)\times10^{15}$ $cm^6\ mol^{-2}\ s^{-1}$ (300 K) obtained from overall $k_1(=k_1(M=Ar)+k_1(M=Br_2)[Br_2]/[Ar])$ and $k_1(M=Br_2)=5\times10^{16}$ $cm^6\ mol^{-2}\ s^{-1}$ derived from data of (18,28 and 30). Above 1000 K values of k_1 corrected for thermal effects, corrections being ≤10%. High temperature value is average of values 1023-1273 K, other values taken from plot. k_1 at 300 K used by (43) assuming $k_1(M=HBr)/k_1(M=Ar)=2$. $Br + Br + M \rightarrow Br_2 + M$ 1
		Shock tube study. Pure Br_2 behind incident shocks. Growth of Br atoms monitored by two-body emission at 598 nm. BOYD, BROWN, BURNS and LIPPIATT 1968 (34)	Data analysed as for (35), giving $k_{-1}(M=Br_2)$ (presented as $k_{-1}K_1$) from initial slopes of emission profiles, and $k_1(M=Br)$ from computer matching of whole emission profiles. Data for k_1 (M=Br) only presented in combination with those of previous work (35). Boundary layer effects found to be small.

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$8.8\times10^{38}T^{-7.3}$	M=Br	1600-2240	Shock tube study. 1:10 Br_2/Ar mixtures. Incident shocks. Br growth followed by two-body emission at 598 nm. BOYD, BURNS, LAWRENCE and LIPPIATT 1968 (35)	Values of k_{-1} determined from initial slope of emission profile (see this Volume, section C1) presented as $k_{-1}K_1$ and fitted by expression $\log(k_1(M=Ar)/cm^6\ mol^{-2}\ s^{-1})=-98.03+71.51\ \log T-11.38(\log T)^2$ (1350-2400 K). k_1(M=Br) obtained from computer matching of complete emission profiles, assuming relation $k_1/k_{-1}=K_1$ to hold, and that $k_1(M=Br_2)/k_1(M=Ar)=2.0$ (14). (Variation of this ratio from 1 to 3 found ineffective). Lowest values for k_1(M=Br) obtained from series of experiments involving precautions against contamination. $Br_2 + M \rightarrow Br + Br + M$ -1
5.20×10^{14}	M=total flame gases	1417	Flame study. Laminar Br_2 (45.6%)/H_2 flame, at 0.118 atm (12 kPa). Br atoms monitored by microprobe sampling and hot wire technique. HORIE 1968 (37)	Few details. Abstract only.
$(2.4\pm0.2)\times10^{15}$ $(1.1\pm0.2)\times10^{15}$ $(3.3\pm0.2)\times10^{15}$ $(5.8\pm1.0)\times10^{15}$ $(1.5\pm0.1)\times10^{15}$ $(3.2\pm0.4)\times10^{15}$ $\leqslant 2.0\times10^{17}$ $(8\pm3)\times10^{15}$ $(4.2\pm1.3)\times10^{15}$	M=Ar M=He M=N_2 M=O_2 M=Ne M=Kr } M=Br M=Br_2	300 300 300 300 300 300 300 1200 825	Flash photolysis study. Br_2/Ar,He,N_2,O_2,Ne, or Kr mixtures, Br_2 percentage generally <1%, and only in a few experiments 3%. Br_2 absorption followed at 443 nm. IP and BURNS 1969 (39)	Values of k_1 determined from slope of $[Br]^{-1}$ profiles. Thermal effects neglected at room temperature, but for T> 1000 K effect of heat release on $[Br]_{eq}$ allowed for, giving <30% correction at 1200 K. Only room temperature values quoted, with least squares fits to rest of data given as $\log(k_1(M=Ar))=(15.38\pm0.02)-(2.29\pm0.13)\log(T/300)+(1.15\pm0.19)\log^2(T/300)$ (300-1275 K); $\log(k_1(M=He))=(15.07\pm0.02)-(1.26\pm0.04)\log(T/300)$ (300-1225 K); $\log(k_1(M=N_2))=(15.50\pm0.03)-(2.21\pm0.25)\log(T/300)+(0.89\pm0.41)\log^2(T/300$ (300-1225 K); $\log(k_1(M=O_2))=(15.77\pm0.02)-(1.58\pm0.06)\log(T/300)$ (300-1225 K); $\log(k_1(M=Ne)=(15.17\pm0.02)-(1.42\pm0.06)\log(T/300)$ (300-1225 K); and $\log(k_1(M=Kr)/cm^6\ mol^{-2}\ s^{-1})=(15.49\pm$

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
		IP and BURNS 1969 (39) continued.	0.02) - (2.77±0.18) log(T/300) + (1.47±0.30) $\log^2$(T/300) (300-1225 K). Upper limit to k_1(M=Br) obtained from behaviour of $[Br]^{-1}$ profiles at long times (≤5 ms) and using k_1(M=He) (this work) and $k_1(M=Br_2)=5.0\times10^{16}$ cm^6 mol^{-2} s^{-1} (300 K) derived from k_{-1} data of PALMER and HORNIG (14). $k_1(M=Br_2)$ at 825 K determined by ignoring k_1(M=Br) and plotting k_1(overall) vs. $[Br_2]/[M]$. k_1(M=Br) at 1200 K obtained using shock tube data for $k_1(M=Br_2)$ of BOYD *et al.* (34) and plotting overall k_1 vs. $[Br_2]/[M]$. Upper limit to k_1(M=Br) of (1.1±0.3)x10^{16} cm^6 mol^{-2} s^{-1} (1200 K) also obtained if assumption is that $k_1(M=Br_2)= k_1(M=Ar)$ as determined in this work. $k_1(M=O_2,Br_2)$ used by (56). Expression $k_1(M=Br_2)= 2.22\times10^{24}T^{-3.01}$ cm^6 mol^{-2} s^{-1} attributed to this work by (46). Data for M=Ar fitted to expression $\log(k_1(M=Ar)/cm^6\ mol^{-2}\ s^{-1}) = 13.99+537/T - 3.24\times10^4/T^2$ (298-1300 K) by (48). WAGNER (52) presents empirical expression $k_1(M=Ar)=1.23\times10^{19}T^{-1.5}$ cm^6 mol^{-2} s^{-1} for these data, over range 300-1275 K.
	Unspecified	Flame study. LOBACHEV and KAGANOVA 1969 (42)	Value 3.63×10^{15} cm^6 mol^{-2} s^{-1} used for k_1(M unspecified),"taken from experimental data", but no source given. Used by (51).
	288-318	Static system. HBr (<300 mm Hg; 40 kPa)/C_2H_4 (~60 mm Hg; 8 kPa)/C_3H_8 (259-390 mm Hg; 34.6-52 kPa) mixtures, reaction acetone-photosensitised 305-325 nm. Absorbed light intensity and pressure monitored. WONG and ARMSTRONG 1969 (44)	Reaction mechanism $Br + C_2H_4 \rightleftharpoons C_2H_4Br$ 4,-4 $HBr + C_2H_4Br \rightarrow Br + C_2H_5Br$ 5 $Br + Br + M \rightarrow Br_2 + M$ 1 initiated by photodissociation of HBr. Rate of C_2H_5Br production gives ratios $(2k_1[M])^{\frac{1}{2}}/k_5$ (4.27±0.2)x10^{20} $cm^{3/2}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ over range 288.3-318 K, for $[C_2H_5+C_3H_8]$ =440-445 mm Hg (58.6-59.4 kPa). Variation over these temperature and pressure ranges suggest $k_1(M=C_2H_4)\approx k_1(M=C_3H_8)$. Results from

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
			WONG and ARMSTRONG 1969 (44) continued.	mixtures in absence of C_3H_8 indicate $k_1(M=HBr) \leqslant k_1(M=C_3H_8)/10$.
$\geqslant 5x10^{15}$	$M=Br_2$	298	Discharge flow system. Br atoms ($5x10^{-11}<[Br]<6x10^{-10}$ mol cm^{-3}) generated in microwave discharge. Recombination followed by monitoring [Br], using Ni-plated isothermal calorimetric detector, and emission 400-3000 nm. BROWNE and OGRYZLO 1970 (45)	Principal source of error deterioration of catalytic surface of Br detector, particularly at high values of [Br]. Apparent third order rate constant k_1', defined by $I=k_1'[Br]^2[Br_2]$, expressed in terms of mechanism involving excited $^3\Pi$ states of Br_2. Steady-state assumptions for these states gives k_1 as function of k_1' and [Br].
$(2.2\pm0.2)x10^{15}$	M=Ar	298	Flash photolysis study. Br_2 mixtures in He, Ne, Ar, N_2, CO, CF_3Br, SF_6, CCl_4 and C_6H_6. Bromine pressures 2.2-3.2 mm Hg (293.3-426.6 Pa), and $[Br_2]/[M]$ ratios $2.5x10^{-3}$-$3x10^{-2}$ (for He, Ne and Ar). Br_2 absorption at 440 nm monitored. DeGRAFF and LANG 1970 (47)	Thermal effects eliminated by using data in early stages of recombination only (<1 ms). At longer times, particularly at high $[Br_2]/[M]$ ratios, curvature of second order [Br] plots observed. Contributions from M and Br_2 separated by plotting $k_1(M+Br_2)$ vs. $[Br_2]/[M]$. Contribution from $k_1(M=Br)$ neglected. Values of k_1(M=Ne, SF_6 and CCl_4) for T>298 K taken from plot. Expressions given to fit these data given as $k_1(M=Ne)=2.8x10^{14}$ exp(490/T), or $1.24x10^{19}T^{-1.58}$ cm^6 mol^{-2} s^{-1}; $k_1(M=SF_6)=3.7x10^{14}$exp(920/T) cm^6 mol^{-2} s^{-1}; and $k_1(M=CCl_4)=3.4x10^{14}$exp(1230/T) cm^6 mol^{-2} s^{-1}. Values of k_1 (M=CO, Br_2) used by (56), together with data of (39) to give $k_1(M=Br_2):k_1(M=CO):k_1(M=O_2)=$ 7.6:0.72:1.0. Value $k_1(M=H_2O)=4.0x10^{14}$ cm^6 mol^{-2} s^{-1} (433 K), assuming $k_1(M=H_2O)=k_1(M=CF_3Br)$ attributed to this work by (57).
$(1.2\pm0.1)x10^{15}$	M=He	298		
$(3.3\pm0.3)x10^{15}$	$M=N_2$	298		
$(4.2\pm0.4)x10^{15}$	M=CO	298		
$(8.4\pm0.8)x10^{15}$	$M=CF_3Br$	298		
$(2.58\pm0.3)x10^{16}$	$M=C_6F_6$	298		
$(4.42\pm1.0)x10^{16}$	$M=Br_2$	298		
$(1.5\pm0.1)x10^{15}$	M=Ne	298		
$1.37x10^{15}$		319		
$1.14x10^{15}$		349		
$1.08x10^{15}$		368		
$(8.1\pm0.8)x10^{15}$	$M=SF_6$	298		
$7.13x10^{15}$		312		
$6.31x10^{15}$		336		
$4.52x10^{15}$		370		
$(2.09\pm0.2)x10^{16}$	$M=CCl_4$	298		
$1.49x10^{16}$		327		
$1.20x10^{16}$		348		
$9.94x10^{15}$		369		
		300-1273	Flash photolysis study. Br_2/Xe, CF_4 and SF_6 mixtures, concentrations not given. Method as for (39). CHANG, CLARKE and BURNS 1971 (49)	Smooth curves fitted to experimental data : $\log(k_1(M=Xe)/cm^6\ mol^{-2}\ s^{-1}) = (15.61\pm0.02) - (3.48\pm0.20)\log(T/300) + (2.18\pm0.31)\log^2(T/300)$, 300<T<1273 K; $\log(k_1(M=CF_4)/cm^6\ mol^{-2}\ s^{-1}) = (16.05\pm0.04) - (3.79\pm0.74)\log(T/300) + (3.18\pm1.95)\log^2(T/300)$,

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
			CHANG, CLARKE and BURNS 1971 (49) continued.	$300<T<800$ K; $\log(k_1(M=SF_6)/cm^6\ mol^{-2}\ s^{-1}) = (16.06\pm0.04) - (3.28\pm0.44)\log(T/300) + (1.75\pm1.06)\log^2(T/300)$, $300<T<800$ K.
$(8.3\pm2.5)\times10^{14}$	M=HBr	1417	Flame study. Spherical Br_2 (45.3-45.8%)/H_2 flames at 89.0-89.6 mm Hg (∿11.9 kPa) pressure. [Br] measured by microprobe sampling, using Ni wire catalyst, and temperature monitored by thermocouple. HORIE and FRAZIER 1971 (50)	Thermocouple readings corrected for radiation. H atom assumed in steady-state, and principal Br removal process to be reaction 1, with M=HBr $Br + Br + M \rightarrow Br_2 + M$ 1 k_1 obtained in region where second order term and diffusion term in conservation equation considered small. From shock tube data (21, 26) and data of Ip and Burns (39) authors tentatively conclude $k_1(M=HBr)/k_1(M=Ar) = 2$ to 4.
$(3.41\pm0.9)\times10^{15}$	M=Ar	298	Discharge flow system. Br atoms produced either by discharge in Br_2, Br_2/Ar or He mixtures or by reaction of $O(^3P)$ atoms with Br_2. $1.7\times10^{-10}<[Br]<5\times10^{-9}$ mol cm^{-3}, total pressures 61-560 Pa. $[Br_2]$ followed by absorption at 415 nm. Flow tube coated with H_3PO_4. CLYNE and WOON-FAT 1973 (58)	Quenching of metastable Br atoms sufficiently fast for these to be eliminated. Recombination via reaction 1 predominated over wall recombination.
$(1.02\pm0.2)\times10^{15}$	M=He	298		
$(3.01\pm1.1)\times10^{15}$	$M=N_2$	298		
$(4.36\pm1.1)\times10^{15}$	$M=O_2$	298		
$(3.01\pm1.2)\times10^{16}$	$M=Br_2$	298		
(a) $2.19\times10^{16}T^{-(0.7\pm0.15)}$ (b) $3.09\times10^{17}T^{-(0.98\pm0.25)}$	M=Kr	1300-2800 1600-2500	Shock tube study. (a) Br_2 (0.8-2.8%)/Kr mixtures behind incident shocks. $[Br_2]$ followed by absorption, and [Br] by two-body emission at 598 nm. (b) Br_2(23%)/Kr mixtures, followed by laser schlieren technique. BOYD, BURNS and MACDONALD 1975 (60)	(a) Br_2 absorption profiles analysed by initial slope and also by plotting log(optical density) profiles, giving linear plots. [Br] profiles analysed by initial slope (35). Corrections for $k_1(M=Br_2)$ made using authors' unpublished data. All data combined represented by expression $k_1(M=Kr)=1.26\times10^{16}T^{-(0.61\pm0.17)}$.

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.28\times10^{17}T^{-1}$ M=Ar	2000-4500	Shock tube study. Br_2(5%)/Ar mixtures dissociated by reflected shocks, at pressures 5-30 atm (506.5 kPa -3.04 MPa). Expansion through nozzle caused Br atom recombination. Uv absorption at 414 and 490 nm used to monitor $[Br_2]$. GENICH, MANELIS and MYAGKOV 1977 (61)	Authors showed that Br_2 had vibrationally relaxed. Experimentally observed absorbance along nozzle matched by calculated values, with dissociation rate constant k_{-1} being converted to k_1 via equilibrium constant. $Br + Br + M \rightleftarrows Br_2 + M \quad 1,-1$ Allowance for Br and Br_2 as third bodies made using data of (40). Best fit given by k_1 as presented here.
(a) (i) $6.65\times10^{18}T^{-1.36\pm0.29}$ M=Ar $2.65\times10^{22}T^{-2.35\pm0.41}$ M=Br_2 (ii) $8.09\times10^{17}T^{-1.05\pm0.3}$ M=Ar $8.22\times10^{21}T^{-2.18\pm0.42}$ M=Br_2 (b) (i) $2.75\times10^{25}T^{-3.29\pm0.68}$ } M= Br_2 (ii) $1.16\times10^{25}T^{-3.16\pm0.68}$ } (c) $3.01\times10^{19}T^{-1.59\pm0.29}$ M=Ar (d) $7.25\times10^{19}T^{-1.74\pm0.3}$ M=Ar	1600-3000 1600-2000 1600-3000 1600-2000 1290-1980 1290-1980 1760-2850 1180-2420	Shock tube study. (a) Br_2 (4,9,23 and 52%)/Ar mixtures, and (b) 100% Br_2 behind incident shocks. Reaction followed by laser-schlieren technique. (c) Br_2 (0.92-7.07%)/Ar mixtures behind incident shocks. $[Br_2]$ followed by uv absorption at 441 nm. (d) Br_2 (0.92-10.8%)/Ar mixtures behind incident shocks. Two body emission at 598 nm used to monitor reaction. MACDONALD, BURNS and BOYD 1977 (62)	Effective recombination rate constant k_1 derived from $Br + Br + M \rightleftarrows Br_2 + M \quad 1,-1$ effective dissociation rate constant k_{-1} and equilibrium constant. Expressions for k_1(M=Br_2) obtained from pure Br_2 mixtures (b) studied by laser-schlieren used to give k_1(M=Ar) for methods (c) and (d). Data for laser-schlieren studies analysed assuming specific refractivity (R_λ) of Br atoms to be same as for (i) Br_2 and (ii) Kr. Little difference found between values of k_1(M=Ar or Br_2) determined by each method. Expressions for k_1(M=Ar) and k_1(M=Br_2) derived from results of studies (a) by separating data into values of effective k_1 at 200 K intervals and plotting vs. $[Br_2]/[Ar]$. Expressions for k_1(M=Ar) and k_1(M=Br_2) presented here are those preferred by authors, obtained by weighting values according to inverse of standard deviation, rather than by equal weighting. Authors quoted combined expression for data of (c) and (d) as k_1(M=Ar) = $7.21\times10^{18}T^{-1.42\pm0.18}$ $cm^6\ mol^{-2}\ s^{-1}$; combinations of data for k_1(M=Br_2) of methods (a) and (b) as (i) $1.68\times10^{22}T^{-2.29\pm0.4}$ and (ii) $6.05\times10^{21}T^{-2.14\pm0.42}$ $cm^6\ mol^{-2}\ s^{-1}$; and combinations of

$Br + Br + M \rightarrow Br_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
		MACDONALD, BURNS and BOYD 1977 (62) continued.	data for $k_1(M=Br_2)$ of (a) and (b), together with flash photolysis value at 825 K of IP and BURNS (39) as (i) $3.65x10^{23}$ $T^{-2.7\pm0.32}$ and (ii) $1.54x10^{23}$ $T^{-2.57\pm0.32}$ cm^6 mol^{-2} s^{-1}. Latter expressions believed to be "best high temperature values for $k_1(M=Br_2)$ presently available".
$(1.54\pm0.15)x10^{15}$ M=He	300	Flash photolysis study. Br_2(<0.3 mm Hg; 40 Pa)/He (1-100 atm; 101.3 kPa-10.1 MPa) mixtures. $[Br_2]$ followed by uv absorption at 436 nm. HIPPLER, LUU, TEITELBAUM and TROE 1978 (64)	Pseudo second order rate constants plotted vs. [He] to give k_1. Effects of Br_2 as third body considered negligible, based on data of (58).

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Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
$2.1x10^{14}$ exp(730/T) M=Ar	298-1600	Derived from room temperature value of STRONG and WILLARD (11) and value at 1600 K from authors' own results (13). BRITTON and DAVIDSON 1956 (13)	Alternative expression given as $k_1(M=Ar)=2.22x10^{18}T^{-1.19}$ cm^6 mol^{-2} s^{-1}.
$7.15x10^{13}T^{0.1}$ exp(1013/T) M=Ar $1.43x10^{14}T^{0.1}$ exp(1013/T) M=Br_2	298-1750 298-1750	Review. Data of PALMER and HORNIG (14) for k_{-1} converted to k_1. Their value at 1750 K combined with low temperature data of (15) to give expressions presented here. CAMPBELL and FRISTROM 1958 (17)	Expressions derived from (14) given as $k_1(M=Ar)=5.95x10^{25}$ $T^{-3.5(\pm0.5)}$ cm^6 mol^{-2} s^{-1} (1310-2225 K) and $k_1(M=Br_2)=4.89x10^{27}$ $T^{-4.0}$ cm^6 mol^{-2} s^{-1} (1220-1610 K). $k_1(M=Br_2)/k_1(M=Ar)$ taken as 2 in absence of accurate data. Expression $k_1(M=O_2)=1.04x10^{14}$ exp(624/T) cm^6 mol^{-2} s^{-1} given without reference, probably derived from data of (15).
$1.9x10^{14}$ exp(710/T) M=Ar $3.0x10^{14}$ exp(2080/T) M=Br_2	300-2225 300-1610	Derived from low temperature data of (19) and high temperature data for k_{-1}, converted using k_1, of PALMER and HORNIG (14). GIVENS and WILLARD 1959 (19)	Alternative fits to these data given as $k_1(M=Ar)=7.6x10^{17}$ $T^{-1.06}$ and $k_1(M=Br_2)=9.6x10^{25}$ $T^{-3.46}$ cm^6 mol^{-2} s^{-1}.

$Br + Br + M \rightarrow Br_2 + M$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$\leq 2.5\times10^{15}$ $(3.4\pm1.5)\times10^{14}$	M=Ar	300 1600	Review. Room temperature value of STRONG *et al.* (15) and average shock tube value (13) at 1600 K presented as best values. DAVIDSON 1961 (27)	These values fit temperature variation of $T^{-1.2}$, similar to that of recombination of I atoms (see this Volume, section D2).
$2.24\times10^{19}T^{-1.6}$ 5.0×10^{16}	M=Ar $M=Br_2$	300-2300 300	Expression derived from k_{-1} data of LAWRENCE and BURNS (41) and k_1 data of authors' own work (33). Value for $M=Br_2$ derived from (18,28 and 30). IP and BURNS 1967 (33)	Authors do not specify nature of M, but as k_{-1} data (41) is for M=Ar, we assume the expression to relate to Ar. k_1(M=Ar) used by SULLIVAN (38).
$3.6\times10^{32}T^{-5.6}$ $1.7\times10^{42}T^{-8.4}$	$M=Br_2$ M=Br	1000-2985 1000-2985	Expression for $k_1(M=Br_2)$ derived from shock tube emission (34) and absorption (14) measurements of $k_{-1}(M=Br_2)$, converted using K_1. Expression for M=Br derived from shock tube emission data for k_{-1}(M=Br) (34,35), presented as $k_{-1}K_1$. BOYD, BROWN, BURNS and LIPPIATT 1968 (34)	Only reliable results of authors' own work (34) used.
			Least squares fits made to (a) shock tube absorption data for k_{-1} of (14, 21,29 and 31), using K_1, and to (b) combination of these data with k_1(M=Ar) of IP and BURNS (33), for T>1000 K. BOYD, BURNS, LAWRENCE and LIPPIATT 1968 (35)	Expressions given as (a) $\log(k_1(M=Ar)/cm^6\ mol^{-2}\ s^{-1})=153.75-83.81\log T+12.59(\log T)^2$, for 1200-2225 K, and (b) $\log(k_1(M=Ar)/cm^6\ mol^{-2}\ s^{-1})=-25.22+26.70\log T-4.48(\log T)^2$, for 1000-2400 K. Expression (b) appears on the Arrhenius plot.
		300-2985	Expression for $k_1(M=Br_2)$ derived from authors' own data (39) at 825 K, k_1 data of (18,28,30 and 36), and k_{-1} data of (34 and 35). k_1(M=Br) derived from authors' own data, at 300 and 1200 K, and best k_{-1} data of (34 and 35). IP and BURNS 1969 (39)	Rate constant expressions given in form $\log(k_1(M=Br_2))=(16.89\pm0.85)-(3.01\pm0.28)\log(T/300)$, and $\log(k_1(M=Br)/cm^6\ mol^{-2}\ s^{-1})=(81.22\pm2.00)-(4.31\pm0.62)\log(T/300)$, latter being considered most reliable of three alternative expressions.

Br + Br + M → Br_2 + M

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Review. Br_2 dissociation rate constant (k_{-1}) data of (14,29,31 and 35) converted using K_1. IP and BURNS 1969 (40)	Comparisons made between resulting k_1 data obtained by $Br + Br + M \rightleftharpoons Br_2 + M$ 1,-1 flash photolysis (15 and 39), shock tube absorption (13,14,21, 29 and 31), and shock tube emission methods (35). Expressions given for converted data are: $k_1(M{=}Ar)=3.09\times10^{26}T^{-3.71}$ $cm^6\ mol^{-2}\ s^{-1}$, $1310<T<2250$ K (14); $k_1(M{=}Ar)=8.13\times10^{26}T^{-3.91}$ $cm^6\ mol^{-2}\ s^{-1}$, $1210<T<1840$ K, $k_1(M{=}Ne)=1.26\times10^{27}T^{-3.94}$ $cm^6\ mol^{-2}\ s^{-1}$, $1220<T<1740$ K, and $k_1(M{=}Kr)=1.35\times10^{24}T^{-3.03}$ $cm^6\ mol^{-2}\ s^{-1}$, $1170<T<2000$ K (31).
		Review. No recommendation. WAGNER 1971 (52), and TROE and WAGNER 1973 (59)	Comparison made between dissociation data (k_{-1}) converted according to $k_1/k_{-1}=K_1$, and recombination data k_1. Empirical expressions presented for data of (39 and 53).
$(2.0\pm0.3)\times10^{14}\exp(760\pm60/T)$ M=Ar	273-2700	Evaluation. $k_1(M{=}Ar)$ derived from data of (7, 12,13,15,19,24,26 and 28), $k_1(M{=}N_2)$ from (7,15 and 21), $k_1(M{=}Br_2)$ from (13, 17,18,21,26 and 28), and $k_1(M{=}CO_2)$ from (7,19 and 21). KONDRATIEV 1972 (55)	Alternative expressions given for $k_1(M{=}Ar)=(2.4\pm1.7)\times10^{18}$ $T^{-(1.21\pm0.08)}$ $cm^6\ mol^{-2}\ s^{-1}$, and $k_1(M{=}Br_2)=(1.26\pm1.5)\times10^{21}$ $T^{-(1.79\pm0.12)}$ $cm^6\ mol^{-2}\ s^{-1}$.
$5.62\times10^{19}T^{-1.68}$ M=N_2	290-1600		
$(1.32\pm0.2)\times10^{15}\exp(1070\pm860/T)$ M=Br_2	290-1610		
$2.46\times10^{20}T^{-1.8}$ M=CO_2	300-1600		
(a) $1.3\times10^{14}\exp(910/T)$ M=Ar	300-2000	Expressions derived to fit data of (39,49 and 53). SNIDER and LEAIST 1977 (63)	Expressions (c) found to give best fits to experimental data. Authors present theoretical justification for these functions.
(b) $5.71\times10^{18}T^{-1.4}$	300-2000		
(c) $4.0\times10^{14}\sinh(710/T)$	300-2000		
(a) $1.2\times10^{14}\exp(710/T)$ M=He	300-2000		
(b) $1.16\times10^{18}T^{-1.2}$	300-2000		
(c) $6.0\times10^{14}\sinh(420/T)$	300-2000		
(a) $1.2\times10^{14}\exp(810/T)$ M=Ne	300-2000		
(b) $2.30\times10^{18}T^{-1.3}$	300-2000		
(c) $5.0\times10^{14}\sinh(530/T)$	300-2000		
(a) $1.1\times10^{14}\exp(1010/T)$ M=Kr	300-2000		
(b) $2.27\times10^{19}T^{-1.6}$	300-2000		
(c) $3.0\times10^{14}\sinh(880/T)$	300-2000		
(a) $9.0\times10^{13}\exp(1160/T)$ M=Xe	300-2000		
(b) $8.54\times10^{19}T^{-1.8}$	300-2000		
(c) $2.0\times10^{14}\sinh(1040/T)$	300-2000		

$Br + Br + M \rightarrow Br_2 + M$

RELATIVE THIRD BODY COLLISION EFFICIENCIES

EXPERIMENTAL DATA

M=Ar	He	H_2	N_2	Br_2	Br	O_2	CO_2	CO	Cl_2	HBr	HCl	Ne	Kr	Xe	CH_4	CF_4	CCl_4	CF_3Br	SF_6	C_6H_6	Temperature (K)	Reference
1	0.6	0.8	1.6				2.2														473	Ritchie 1934 [4].
1	4.3	11.4	7.5	23.6				57.3		19.1	42.8										490	Hilferding and Steiner 1935 [5].
1	0.6	1.7	1.9	>15.4		2.5	4.1								2.8						298	Rabinowitch and Wood 1936 (7).
1		1.2	1.6	2.0		1.8	1.8														298	Smith et al. 1937 [9].
			1			2.6[a]															298	Shida 1946 [10].
1				<8																	1600	Britton and Davidson 1957 (13).
				4.9[b]			1		1.5[b]												293	Christie et al. 1959 [18].
1				130			~3.9														300	Givens and Willard 1959 [19].
1				13±3																	1600	Britton 1960 [21].
1				18																	298	Basila and Strong 1963 (28).
1				19.2																	298	Cadman 1965 (30).
1					10±6																1600	Boyd et al. 1968 [35].
1					2±1.2																2000	
1				14.3																	298	Burns 1968 [36], after Burns and Hornig 1960 [24].
1	0.5		1.4		≤83	2.4						0.6	1.3								300	Ip and Burns 1969 [39].
1	0.6		1.5	20.1				1.9				0.7					9.5	3.8	3.7	11.7	298	DeGraff and Lang 1970 [47].
														1		2.7[c]			2.5[c]		300	Chang et al. 1971 [49].
1	0.3		0.9	8.8		1.3															298	Clyne and Woon-Fat 1973 [58].

a=Efficiency relative to N_2
b=Efficiency relative to CO_2
c=Efficiency relative to Xe

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M=Ar	He	H_2	N_2	Br_2	Br	O_2	CO_2	Temperature (K)	Reference
1				2				1220-1610	Campbell and Fristrom 1958 [17].
1				152				300	Givens and Willard 1959 [19].
1				3.7				1600	
1			1.5	18.6			3.4	300	Kondratiev 1972 [55].
1			0.7	8.0			1.3	1600	
1	0.5		1.3	18.1				298	This evaluation

Discussion

The three body recombination of bromine atoms has been

$$\mathrm{Br} + \mathrm{Br} + \mathrm{M} \rightarrow \mathrm{Br_2} + \mathrm{M} \qquad (1)$$

extensively studied, principally by shock tube and photolysis methods. In order that the rate constants so determined agree with our definition

$$d[\mathrm{Br_2}]/dt = -(1/2)d[\mathrm{Br}]/dt = k_1[\mathrm{Br}]^2[\mathrm{M}]$$

the values for k_1 given by [6,7,10,17,18 and 30] have been halved before being presented in the table.

The determination of k_1 by photolysis, whether continuous [3,4,5,7,9,10,18] or flash [11,15,19,13,28,30,32,33,39,47,-49,64] is subject to errors associated with the "thermal effect," due to the heat released by the exothermic reaction 1 (ΔH°_{298}=–192.85 kJ mol^{-1}; –46.09 kcal mol^{-1}). As described in the Discussion of the recombination of iodine atoms (section D2), the use of absorption spectroscopy to monitor the recombination, as in all the photolysis studies of reaction 1, may result in underestimation of k_1. Only Burns [32], by filling the reaction vessel with the analysing beam, was able to average out the thermal gradients in the reaction mixture. Alternatively, the thermal effect may be eliminated by operating at low initial [$\mathrm{Br_2}$]/[M] ratios [7,15,23,28,30,33,-39,64], or may be neglected by only using measurements made early in the recombination [47]. Those photolysis studies in which compensation has not been made for the thermal effect [6,10,19] have not been considered in this evaluation.

Of the shock tube studies, Britton et al. [13,21,26] used the results from $\mathrm{Br_2}$ dissociation profiles (giving essentially k_{-1})

$$\mathrm{Br_2} + \mathrm{M} \rightarrow \mathrm{Br} + \mathrm{Br} + \mathrm{M} \qquad (-1)$$

to obtain k_1, via the equilibrium constant. But Burns et al. [33,40] have pointed out that values of k_1 obtained in this way are almost three times greater than those obtained by flash photolysis, possibly because of non-equilibration of internal degrees of freedom. Consequently we have not attached great weight to the results of Britton et al. [13,21,26].

Of the remaining results there is good agreement for k_1 (M=Ar) at room temperature between the data of [7,11,28,30,33 and 39], and the three lowest values of Strong et al. [15], which are the only values from the "low" series of data of the latter workers that we have considered. Their data at higher temperatures belong to their "high" series, and consequently our recommendation at high temperatures follows the data of Ip and Burns [33], and MacDonald et al. [62]. Thus our recommended expression, over the range 290–2000 K, is

$$k_1\ (\mathrm{M=Ar}) = 1.48\times10^{14}\ \exp(856/T)\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$$

with error limits of ±50%.

From our recommended expression for k_{-1} (M=Ar) (see section C1) and the equilibrium constant K_1 we derive the expression $k_1 = 1.08\times10^{14}\ \exp(760/T)$ cm^6 mol^{-2} s^{-1} for the temperature range 1300–2500 K. This expression yields values for k_1 within a factor of 1.5 of those from our recommended expression for k_1, well within the uncertainty limits for the expression for k_{-1} (a factor of 3).

The data of [24,28,30 and 47] for k_1 ($\mathrm{M=Br_2}$) at room temperature are in good agreement, and together with the reliable high temperature data of Ip and Burns [39] and MacDonald et al. [62], and the less reliable data of Britton et al. [13,21,26], lead us to recommend the expression (which is close to that of Kondratiev [55])

$$k_1\ (\mathrm{M=Br_2}) = 1.10\times10^{15}\ \exp(1110/T)\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$$

for temperatures 298–1600 K, with error limits of ±25% at 298 K, rising to a factor of 2 at 1600 K.

There are no high temperature data for k_1 (M=He) or k_1 ($\mathrm{M=N_2}$) but we are able to make recommendations at 298 K, giving k_1 (M=He)=$(1.15\pm0.15)\times10^{15}$ cm^6 mol^{-2} s^{-1}, based on the data of [22,39,47 and 58], and k_1 ($\mathrm{M=N_2}$)= $(3.26\pm0.25)\times10^{15}$ cm^6 mol^{-2} s^{-1}, derived from the data of [15,39,47 and 58].

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C3 $HBr + M \rightarrow H + Br + M$

THERMODYNAMIC DATA

T (K)	ΔH^o ($kJ\ mol^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	$\log K_p$ (K_p in atm)	$\log K_c$ (K_c in mol cm^{-3})
298	366.301	90.914	-59.425	-63.813
300	366.326	90.994	-59.029	-63.420
500	368.790	97.295	-33.445	-38.445
1000	374.292	105.018	-14.065	-18.979
1500	378.794	108.692	- 7.513	-12.603
2000	382.710	110.951	- 4.199	- 9.414
2500	386.204	172.508	- 2.192	- 7.504
3000	389.317	113.650	- 0.842	- 6.233
3500	392.095	114.508	0.130	- 5.328
4000	394.580	115.169	0.863	- 4.649
4500	396.794	115.696	1.437	- 4.128
5000	398.781	116.114	1.899	- 3.714

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.0056$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k = 8.5 \times 10^{21}\ T^{-2} \exp(-44\ 280/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)

$= 1.4 \times 10^{-2}\ T^{-2} \exp(-44\ 280/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)

Temperature Range: 1450-4000 K

Suggested Error Limits for Calculated Rate Constant: factor 3 over the given temperature range.

(Note: relative efficiency of HBr as third body given in Discussion)

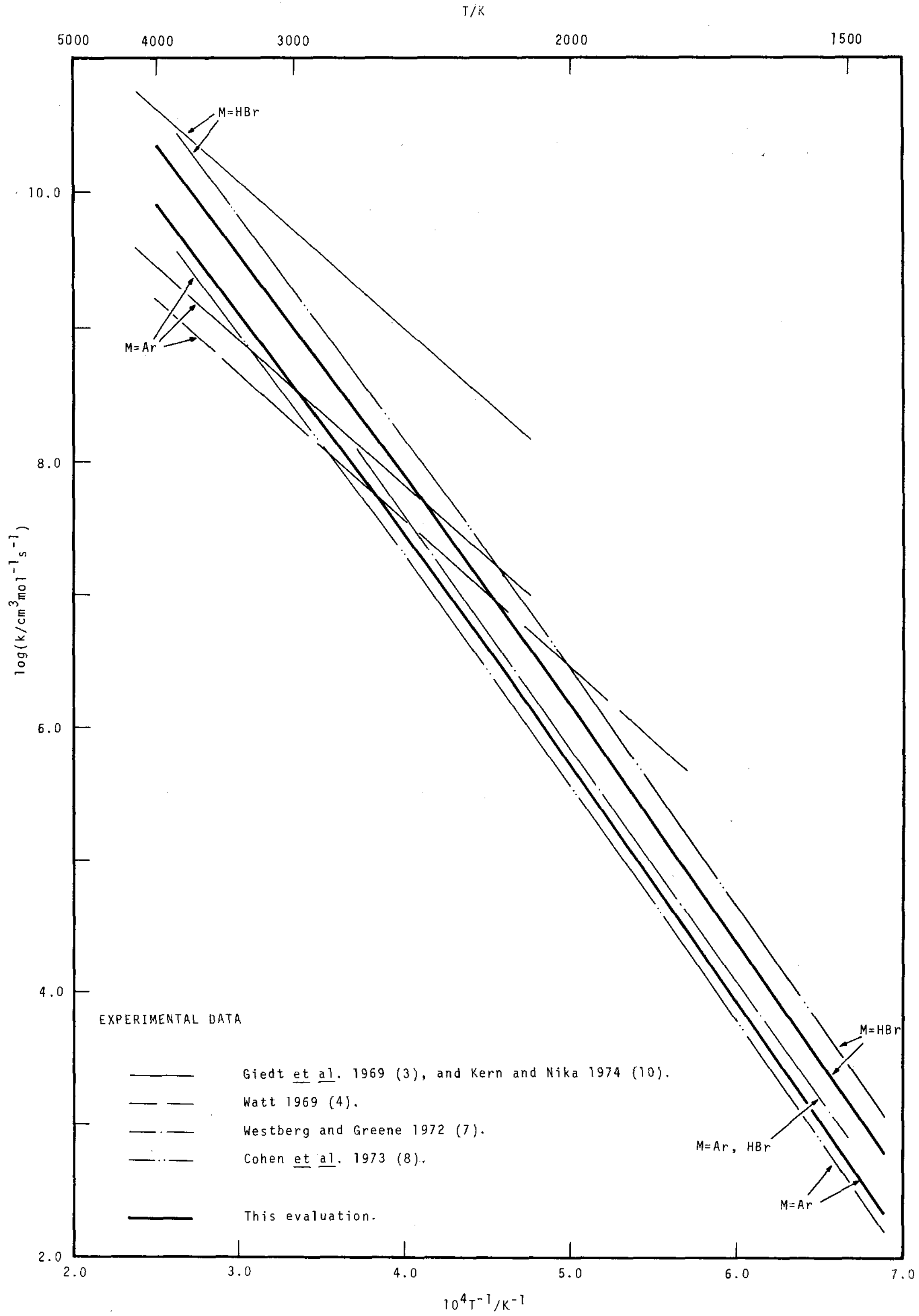
Rate Parameters: $\log(A'T^{-2}/cm^3\ mol^{-1}\ s^{-1}) = 21.93 \pm 0.5 - 2 \log T$

$\log(A'T^{-2}/cm^3\ molecule^{-1}\ s^{-1}) = -1.85 \pm 0.5 - 2 \log T$

$E'/J\ mol^{-1} = 368\ 000\ ^{+5\ 220}_{-81\ 880}$

$E'/cal\ mol^{-1} = 88\ 000\ ^{+1\ 250}_{-19\ 570}$

$HBr + M \rightarrow H + Br + M$



$HBr + M \rightarrow H + Br + M$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.55\times10^{12}\exp(-25\ 160/T)$ M=Ar,H,Br,H_2,Br_2 $2.34\times10^{13}\exp(-25\ 160/T)$ M=HBr	2100-4200 2100-4200	Shock tube study. HBr(2% and 10%)/Ar mixtures behind incident socks. Total pressures in region 1 to 4 atm (101 to 405 kPa). HBr followed by ir emission and by uv absorption at 235 nm. GIEDT, COHEN and JACOBS 1969 (3)	Rates of HBr disappearance at 20% and 40% reaction used to characterise dissociation. Expressions for k_1 adjusted to give good computed fit to data. Authors consider expressions reliable to within 20%-30%. $HBr + M \rightarrow H + Br + M$ 1 Data also reported by GIEDT *et al.* in (2). Good match obtained using this expression for k_1 to Br profiles communicated by WESTBERG and GREENE prior to publication. TROE and WAGNER (9) express these data as k_1(M=Ar)= $1.17\times10^{22}T^{-2}\exp(-44\ 280/T)$ cm^3 mol^{-1} s^{-1}.
$9.5\times10^{11}\exp(-25\ 410/T)$ M=Ar	1750-4000	Shock tube study. HBr(0.15% and 1%)/Ar mixtures behind incident shocks. Shocked gas pressures 0.3-1.0 atm (30.4-101 kPa). Br and H atoms monitored by vacuum uv absorption at 158 nm and 121.6 nm respectively. WATT 1969 (4)	Small formation rate of H atoms relative to Br formation rate led author to neglect contribution to d[Br]/dt of reaction 2 $H + HBr \rightarrow H_2 + Br$ 2
$1.2\times10^{22}T^{-2}\exp(-44\ 280/T)$ M=Ar,HBr	1500-2700	Shock tube study. HBr(2% and 100%)/Ar mixtures. Incident shocks. Two body emission from Br recombination measured at 438, 480, 595 and 620 nm. WESTBERG and GREENE 1972 (7)	Little difference between emission profiles observed at various wavelengths. Authors attempted computer match of their profiles using firstly k_1 of GIEDT *et al.*(3), $HBr + M \rightarrow H + Br + M$ 1 and obtained good fits for conditions similar to those of latter study. But for T<2100 K and [HBr]>2%, computed profiles also dependent upon k_3 and k_4 $Br + HBr \rightarrow H + Br_2$ 3 $Br_2 + M \rightarrow Br + Br + M$ 4 Authors also showed k_3 and k_4 affected computed profiles of GIEDT *et al.* (3). Accuracy of factor 3 claimed for k_1. In supplement to this study, authors find k_1(M=HBr)=(3 to 4)k_1(M=Ar) on basis of new data for k_3.

$HBr + M \rightarrow H + Br + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$6.03\times10^{21}T^{-2}\exp(-44\ 280/T)$ M=Ar $4.57\times10^{22}T^{-2}\exp(-44\ 280/T)$ M=HBr	1450-2300 1450-2300	Shock tube study. Pure HBr behind incident shocks. Pressures 1-6.3 atm (101-638 kPa). Br recombination emission monitored at 567, 600 and 633 nm. COHEN, GIEDT and JACOBS 1973 (8)	Inability to describe [Br] profiles by adjusting solely parameters of k_1 caused authors to review data used to specify k_1, k_3 and k_{-4} $Br + Br + M \rightarrow Br_2 + M$ -4 Good computer fits made to low temperature [Br] profiles, and fits to [HBr] profiles of (3) then possible with factor 4 limit on sensitivity to k_1. Mean value for A_1(M=Ar) taken. These expressions valid up to 3800 K.
$1.55\times10^{12}\exp(-25\ 160/T)$ M=Ar	(a) 2030-2515 (b) 2053-2438	Shock tube study. (a) HBr (1.5%)/D_2(1.5%)/Ar, HBr(3%)/D_2(3%)/Ar and (b) HBr (2%)/D_2(2%)/Ar(1%)/Ne mixtures behind reflected shocks. Total gas densities $1.68-1.92\times10^{-6}$ mol cm^{-3}. Reaction monitored by (a) ir emission from DBr at 5.37 μ and from HBr at 3.6 μ, and (b) tof mass spectrometry. KERN and NIKA 1974 (10)	Mechanism for DBr formation given as: $HBr + M \rightarrow H + Br + M$ 1 $Br + D_2 \rightarrow DBr + D$ 5 After showing [DBr] profiles calculated from [HBr] (observed at 3.6 μ) to be coincident with those observed at 5.37 μ, all following [DBr] data constructed from [HBr] profiles. Net rate constant for DBr production given by $0.75\ k_1k_5[M]$. Over range 2100-2400 K, limiting expressions for k_1 are $1.2\times10^{22}T^{-2}\exp(-42\ 770/T)$ $cm^3\ mol^{-1}\ s^{-1}$ and that of GIEDT et al. (3), giving the better fit.

Discussion

All the studies on the rate of dissociation of HBr have been made using shock tube methods

$$HBr + M \rightarrow H + Br + M \qquad (1)$$

In the earliest determination, by Giedt et al. [3], the authors found that for the conditions of their investigation the [HBr] profiles generated by computer modelling were much less sensitive to rate constants k_3 and k_4 than to k_1.

$$Br + HBr \rightarrow H + Br_2 \qquad (3)$$

$$Br_2 + M \rightarrow Br + Br + M \qquad (4)$$

Thus it was assumed that the expressions used for k_3 and k_4 in the modelling were satisfactory, and for the temperature range of their study (2100–4200 K) they found that a simple Arrhenius expression for k_1 gave a better match than did an expression in which the activation energy was set equal to the bond dissociation energy for HBr (368 kJ mol^{-1}; 88 kcal mol^{-1}), with a compensating temperature dependent factor in the pre-exponential term. Watt [4] analysed his data in much the same way, and also described k_1 by a simple Arrhenius form, with $E_1 <$ D(HBr).

However further investigation by Westberg and Greene [7] and Cohen et al.[8] showed that at lower temperatures (<2000 K) the rate constants k_3 and k_4 become more important. By using higher values of k_3 than those used initially [3] both sets of authors were able to reconcile the low temperature and high temperature data, i.e., profiles of both [Br] [7,8] and [HBr] [3], using expressions for k_1 (M=Ar) of the classical form.

Cohen et al. [8] found that having set k_3 and k_4 they were able to vary k_1 (M=Ar) by a factor of 4, so that their ratio k_1 (M=HBr)/k_1 (M=Ar) varied between 15 (as in the original study by these authors [3]) and 3.75, whereas Westberg and Greene [7] found little difference between the efficiencies of HBr and Ar.

Because the expressions for k_1 (M=Ar) of [7] and [8] differ by only a factor of 2, which is within the accuracy limits claimed in each study, we feel justified in recommending the expression

k_1 (M=Ar) = $8.5\times10^{21}T^{-2}\exp(-44\,280/T)$ cm^3 mol^{-1} s^{-1}

for the temperature range 1450–4000 K. Error limits of a factor 3 should be recognised.

There is a greater discrepancy, a factor 4, between the k_1 (M=HBr) expressions of [7] and [8] and so we only tentatively suggest use of the expression

k_1 (M=HBr) = $2.3\times10^{22}T^{-2}\exp(-44\,280/T)$ cm^3 mol^{-1} s^{-1}

over the same temperature range, but with larger error limits of a factor 5.

Third body collision efficiencies

M=Ar	HBr	H	Br	H_2	Br_2	Temp. (K)	Ref.
1	15	1	1	1	1	2100–4200	Giedt et al. 1969 [3].
1	1	1	1	1	1	1500–2700	Westberg and Greene 1972 [7].
1	7.5					1450–2300	Cohen et al. 1973 [8].
1	2.7					1450–4000	This evaluation

Rate of the Reverse Reaction

No experimental data have been reported for the three-body recombination of bromine atoms and hydrogen atoms

$$H + Br + M \rightarrow HBr + M. \qquad (-1)$$

The data for k_1 of Giedt et al. [3] were used by Wagner [6] to give k_{-1} (M=Ar)=$5.18\times10^{21}T^{-2}$ cm^6 mol^{-2} s^{-1}, and Willis et al. [5] estimated k_1 (M=HBr) as 10^{15} cm^6 mol^{-2} s^{-1} at 298 K, by analogy with rate constants given by Porter [1].

Using our expression for k_1 (M=Ar), we cannot fit the derived values for k_{-1} (M=Ar) to a simple Arrhenius plot over the temperature range 1500–4000 K, but we find that these data are well represented by the expression

$$k_{-1}\ (M=Ar) = 1.92\times10^{21}T^{-1.865}\ cm^6\ mol^{-2}\ s^{-1}.$$

The error limits are a factor 3, as for k_1 (M=Ar).

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C4 $Br + H_2 \rightarrow HBr + H$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	69.697	7.720	-11.807
300	69.697	7.720	-11.733
500	69.718	7.782	- 6.877
1000	70.199	8.385	- 3.229
1500	70.902	8.962	- 2.001
2000	71.103	9.088	- 1.383
2500	70.839	8.975	- 1.012
3000	70.262	8.761	- 0.766
3500	69.467	8.519	- 0.592
4000	68.463	8.251	- 0.463
4500	67.262	7.975	- 0.365
5000	65.869	7.678	- 0.287

RECOMMENDED RATE CONSTANT

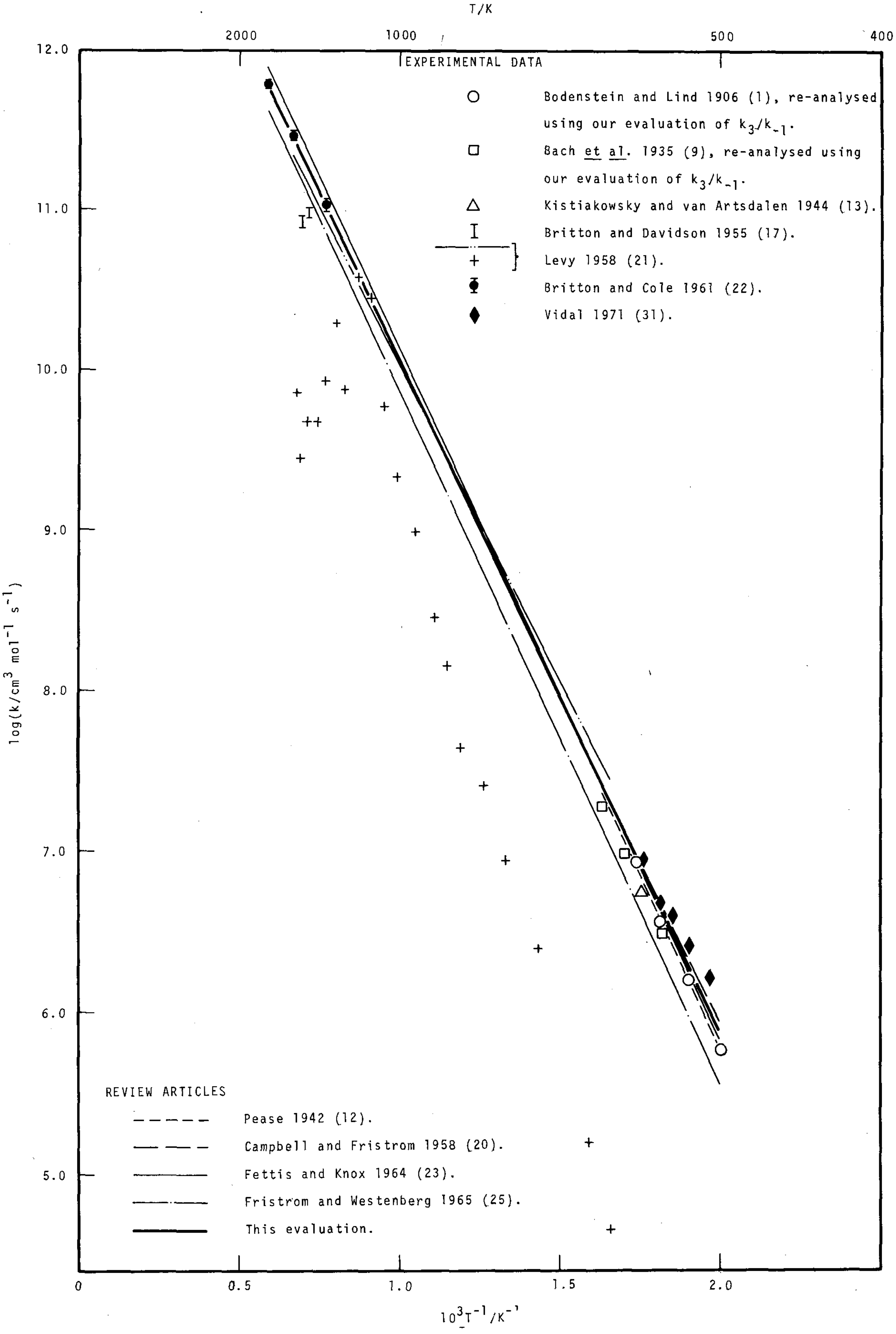
$$k = 1.70 \times 10^{14} \exp(-9640/T)\ cm^3\ mol^{-1}\ s^{-1}$$
$$= 2.82 \times 10^{-10} \exp(-9640/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

Temperature Range: 500-1700 K

Suggested Error Limits for Calculated Rate Constant: ±50% over the whole temperature range.

Rate Parameters:
$\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.23 \pm 0.18$
$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.55 \pm 0.18$
$E/J\ mol^{-1} = 80\ 150 \pm 4900$
$E/cal\ mol^{-1} = 19\ 160 \pm 1170$

$Br + H_2 \rightarrow HBr + H$

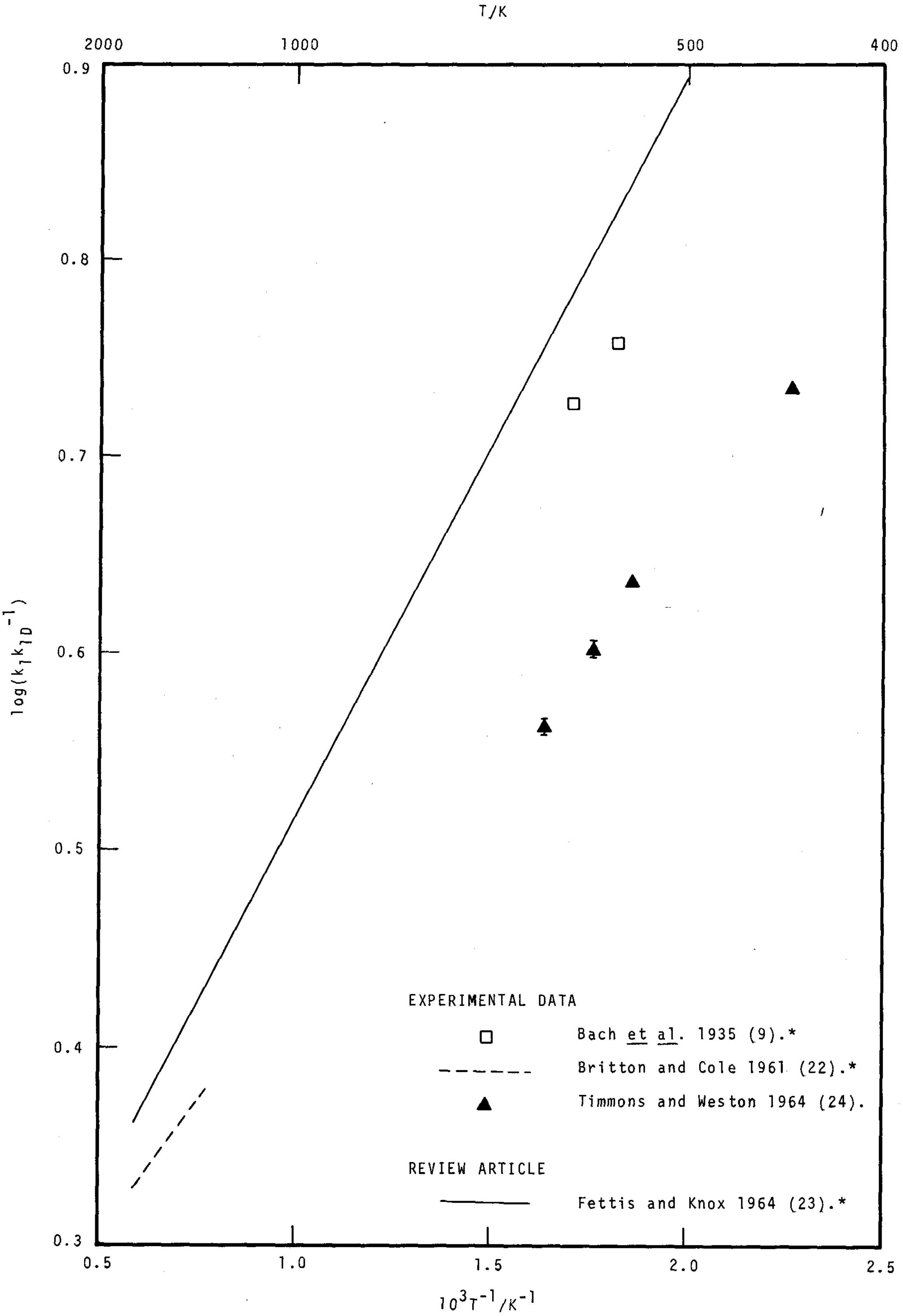


$Br + H_2 \rightarrow HBr + H$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	498-574	Static system. H_2(6.93x10^{-6}-4.0x10^{-5} mol cm^{-3})/ Br_2(6.77x10^{-6}-4.0x10^{-5} mol cm^{-3}) mixtures. Addition of KI solution, followed by $Na_2S_2O_3$ titration, used to determine product yield of HBr. BODENSTEIN and LIND 1906 (1)	Original analysis gave data in form of overall HBr production rate constant k. BODENSTEIN and LUTKEMEYER (6), following interpretation of HBr mechanism by CHRISTIANSEN (3), HERZFELD (4), and POLANYI (5), used data for K_2 of (2) to fit expression k_1= 7.28x10^{13} exp(-8880/T) $cm^3\ mol^{-1}\ s^{-1}$ to these data. $Br + H_2 \rightarrow HBr + H$ 1 $Br_2 + M \rightarrow Br + Br + M$ 2 KUCHER *et al.* (26) attribute k_1= 6.3x10^{13} exp(-8860/T) $cm^3\ mol^{-1}\ s^{-1}$ to this study. Re-analysis by BACH *et al.* (9), using same method as for their own results (q.v.), gave k_1=1.16x10^6 (498.9 K), 3.11x10^6 (524.6 K), 6.61x10^6 (550.7 K), and 1.47x10^7 $cm^3\ mol^{-1}\ s^{-1}$ (574.5 K). Error in this re-analysis exposed by PEASE (12), who made correct conversion, and used later evaluation of K_2 (8) to give these data as k_1=6.62x10^5 (497.8 K), 1.73x10^6 (524.5 K), 3.78x10^6 (550.6 K), and 1.00x10^7 $cm^3\ mol^{-1}\ s^{-1}$ (574.4 K). WHITE (32) fits expression k_1=3.1x10^{14}exp(-9980/T) $cm^3\ mol^{-1}\ s^{-1}$ to PEASE's data. Re-analysis by CAMPBELL and FRISTROM (20) gave k_1=8.68x10^5 (498.8 K), 2.27x10^6 (524.5 K), 4.97x10^6 (550.6 K), and 1.13x10^7 $cm^3\ mol^{-1}\ s^{-1}$ (574.4 K). VIDAL (31) converted these data using K_2 of (28) and gave k_1=1.08x10^6 (498.9 K), 2.70x10^6 (524.6 K), 5.64x10^6 (550.7 K), and 1.28x10^7 $cm^3\ mol^{-1}\ s^{-1}$ (574.5 K). COHEN *et al.* (33) used their own ratio k_3/k_{-1} with current data for K_3 $H + Br_2 \rightarrow HBr + Br$ 3 $H + HBr \rightarrow H_2 + Br$ -1 to give k_1=5.37x10^{13} exp(-9010/T) $cm^3\ mol^{-1}\ s^{-1}$ for this work, or, if some apparently spurious high-temperature data rejected, k_1= 9.33x10^{13} exp(-9310/T) $cm^3\ mol^{-1}\ s^{-1}$. Using current JANAF data

$Br + H_2$ / $Br + D_2$



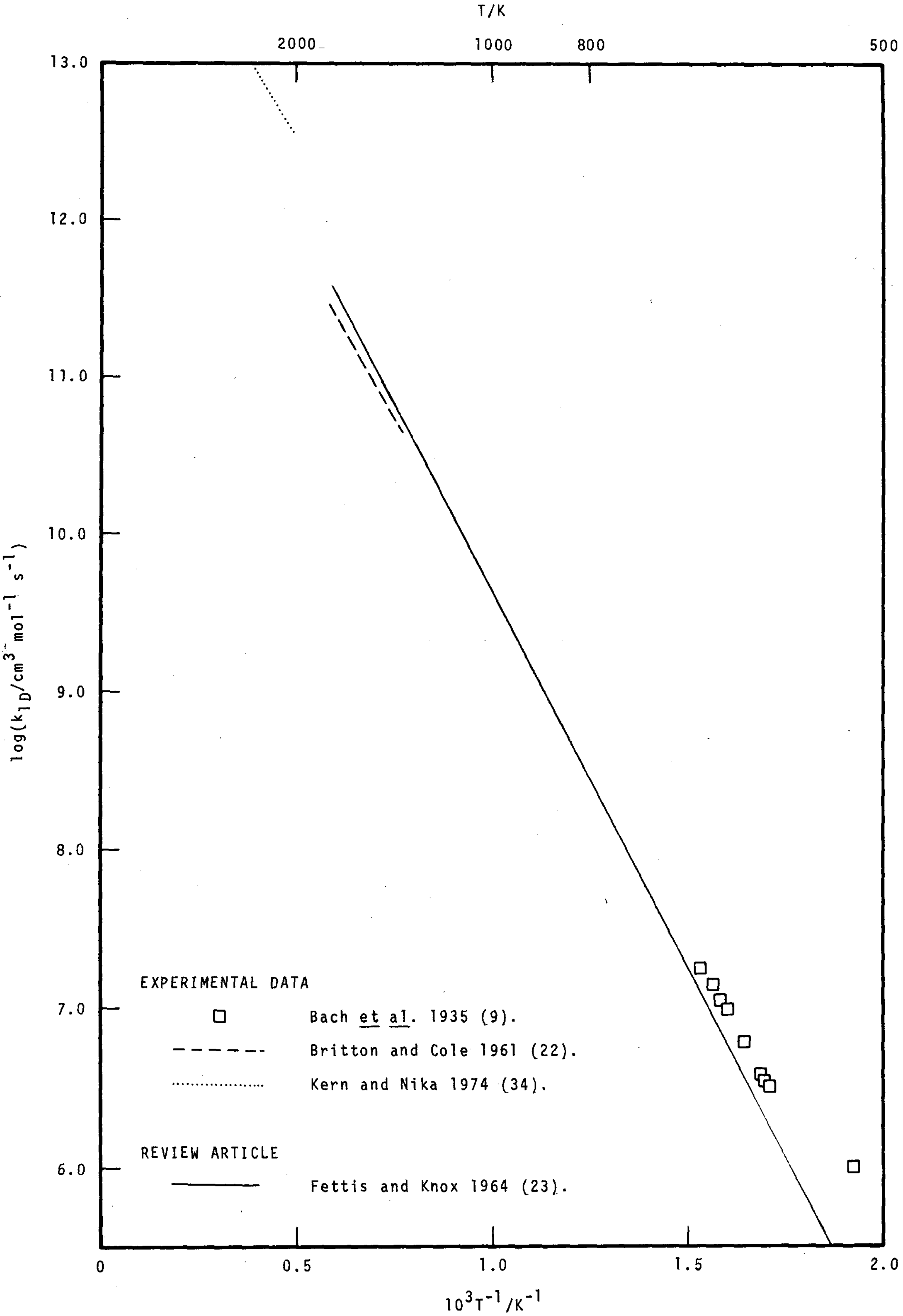
* Refer to values of k_1/k_{1D} obtained from absolute values of both k_1 and k_{1D}.

$Br + H_2 \rightarrow HBr + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		BODENSTEIN and LIND 1906 (1) continued.	for K_2, and our evaluation of k_3/k_{-1} we have re-calculated these data as k_1=5.72x10^5 (498.8 K) 1.57x10^6 (524.5 K), 3.59x10^6 (550.6 K) and 8.45x10^6 cm^3 mol^{-1} s^{-1} (574.4 K), as shown on Arrhenius plot.
5.62x10^6 1.50x10^7 1.69x10^7 3.01x10^7	549.0 585.4 585.6 612.1	Static system. H_2(2.35x10^{-6}-3.0x10^{-6} mol cm^{-3})/ Br_2(2.99x10^{-6}-3.27x10^{-6} mol cm^{-3}) mixtures. [Br_2] followed by light absorption. BACH, BONHOEFFER and MOELWYN-HUGHES 1935 (9)	Mechanism for HBr synthesis taken as reactions 1,-1,-2 and 3, together with initiation reaction 2 $Br_2 + M \rightarrow Br + Br + M$ 2 Rate equation for [HBr] thermal equivalent of photolytic expression used by BODENSTEIN and LUTKEMEYER (6). Authors used K_2 of (2) and k_3/k_{-1}=10 (1) to obtain values of k_1 given here, and gave k_1=6.92x10^{13}exp(-8930/T) cm^3 mol^{-1} s^{-1} as fit to these and data derived from their re-analysis of work of BODENSTEIN and LIND (1). MORRIS and PEASE (10), using later determination of K_2 (8), fit value E_1=74.1 kJ mol^{-1} (17.7 kcal mol^{-1}) to both these sets of data (1,9). PEASE (12), also using K_2 of (8), re-calculated data of BACH et al. (9) as k_1=3.19x10^6 (549.0 K), 9.7x10^6 (585.5 K), and 1.86x10^7 cm^3 mol^{-1} s^{-1} (612.1 K). Re-analysis by CAMPBELL and FRISTROM (20) gave k_1=4.17x10^6 (549 K), 1.23x10^7 (585.5 K), and 2.38x10^7 cm^3 mol^{-1} s^{-1} (612.1 K). FETTIS and KNOX (23) recalculate these data to give k_1=4.68x10^{13}exp -(8960±710)/T cm^3 mol^{-1} s^{-1}. VIDAL (31) converted these data using later K_2 (28) to give k_1= 4.99x10^6 (549 K), 1.33x10^7 (585.4 K) 1.51x10^7 (585.6 K), and 2.69 x10^7 cm^3 mol^{-1} s^{-1} (612.1 K). Using current JANAF data for K_2 and our evaluation of ratio k_3/k_{-1} we have recalculated these data as k_1=3.01x10^6 (549 K), 9.31x10^6 (585.5 K), and 1.86x10^7 cm^3 mol^{-1} s^{-1} (612.1 K), as presented on Arrhenius diagram.

$Br + D_2 \rightarrow DBr + D$



$Br + H_2 \rightarrow HBr + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	(a) 423,483 (b) 570	(a) static photolysis system. H_2/Br_2 mixtures. (b) static system. H_2 (405 and 431 mm Hg; 54 and 57.5 kPa)/Br_2(51.2 and 52.0 mm Hg; 6.8 and 6.9 kPa) mixtures. $[Br_2]$ followed by absorption at λ<436 nm. KISTIAKOWSKY and VAN ARTSDALEN 1944 (13)	(a) Photobromination of H_2 used as check on CH_4-Br_2 reaction study. Initial overall rate constant k, given by $(-d[Br_2]/dt)_o = k[H_2][Br_2]^{\frac{1}{2}}[M]^{-\frac{1}{2}}$, displayed activation energy 73.2 kJ mol^{-1} (17.5 kcal mol^{-1}). From steady state analysis of reaction mechanism $Br_2 + h\nu \rightarrow Br + Br$ $Br + H_2 \rightleftarrows HBr + H$ 1,-1 $H + Br_2 \rightarrow HBr + Br$ 3 $Br + Br + M \rightarrow Br_2 + M$ -2 rate equation for $[Br_2]$ led authors to attribute this value to rate-determining step, reaction 1. (b) Initial thermal bromination rate described by $(-d[Br_2]/dt)_o = k'[H_2][Br_2]^{\frac{1}{2}}$, where $k' = k_1 K_2^{\frac{1}{2}}$. Authors quote $k' = 1.96 \times 10^{-2}$ $cm^{3/2}$ $mol^{-\frac{1}{2}}$ s^{-1} at 570 K, from which we obtain $k_1 = 5.31 \times 10^6$ cm^3 mol^{-1} s^{-1}. Authors use E_1 and above value to give $A_1' T^{-\frac{1}{2}} = 1.14 \times 10^{12}$ cm^3 mol^{-1} s^{-1}.
8.9×10^{10}	1396	Shock tube study. H_2(1%)/Br_2(1%)/Ar mixtures behind incident shocks. Br_2 absorption followed at 487 nm. BRITTON and DAVIDSON 1955 (17)	From observed Br_2 decay rate, computed contribution due to reaction 2 (using authors' own value for k_2 (19)) subtracted. Resulting Br_2 rate assumed due to reactions 1 and 3. $Br_2 + M \rightarrow Br + Br + M$ 2 $Br + H_2 \rightarrow HBr + H$ 1 $H + Br_2 \rightarrow HBr + Br$ 3 k_2 (19) also used to calculate instantaneous values of [Br]. Values of k_1 obtained after 40 and 100 μs reaction time at each temperature. WHITE (32) attributes $k_1 = 2.58 \times 10^{14} \exp(-10\ 100/T)$ cm^3 mol^{-1} s^{-1} to this study.
1.03×10^{11}	1396		
7.9×10^{10}	1441		
9.1×10^{10}	1441		
4.54×10^4	603	Flow system. H_2(3.15×10^{-10} -4.5×10^{-6} mol cm^{-3})/Br_2 (3.65×10^{-10}-1.48×10^{-7} mol cm^{-3})/N_2 mixtures at total pressures 775-780 mm Hg (103.3-104 kPa). Reaction products analysed by	Values of k_1 derived from intergrated form of HBr rate equation, according to steady state treatment of mechanism $Br_2 + M \rightleftarrows Br + Br + M$ 2,-2 $Br + H_2 \rightleftarrows HBr + H$ 1,-1 $H + Br_2 \rightarrow HBr + Br$ 3
1.56×10^5	649		
2.46×10^6	700		
8.57×10^6	749		
2.52×10^7	790		
4.35×10^7	838		
1.42×10^8	869		
2.82×10^8	901		
9.79×10^8	950		
2.13×10^9	1003		
5.92×10^9	1049		

$Br + H_2 \rightarrow HBr + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2.80×10^{10}	1100	fractional separation and manometric methods. LEVY 1958 (21)	allowing for large degree of Br_2 dissociation at these temperatures. Author used expression for K_2 from fit to data of (14) and ratio $k_3/k_{-1}=8.4$ from (7), to convert least squares fit to overall HBr rate constant k to expression $k_1=2.04\times10^{12}T^{\frac{1}{2}}\exp(-8700/T)$ cm^3 mol^{-1} s^{-1}. There is discrepancy between this expression and the tabulated k_1 data. WHITE (32) attributes expression $k_1=10^{14}\exp(-9120/T)$ cm^3 mol^{-1} s^{-1} to this work.
3.79×10^{10}	1150		
7.56×10^{9}	1201		
1.97×10^{10}	1250		
8.49×10^{9}	1299		
4.75×10^{9}	1352		
4.72×10^{9}	1404		
2.78×10^{9}	1453		
7.15×10^{9}	1477		
(a) 1.16×10^{11}	1300	Shock tube study. (a) H_2(1%)/Br_2(1%)/Ar and H_2(1%)/Br_2(1%)/HBr(10%)/Ar, and (b) H_2(2%)/Br_2(2%)/Ar and H_2(2%)/Br_2(2%)/HBr(10%)/Ar mixtures. [Br_2] followed by absorption at 500 nm. BRITTON and COLE 1961 (22)	Emission negligible at 500 nm. From [Br_2] profiles, using mass balance to determine [HBr], net rate constant k obtained, where d[HBr]/dt=2k[Br][H_2]. Using steady state analysis $k=k_1/(1+k_{-1}[HBr]/k_3[Br_2])$. Values of k at 25% Br_2 disappearance used, as giving minimum errors. k_1 obtained from smoothed Arrhenius plots of k by comparing H_2/Br_2 mixtures with H_2/Br_2/HBr mixtures, for both sets (a) and (b). Average values of k_1 given as 1.07×10^{11} (1300 K), 2.92×10^{11} (1500 K), and 6.11×10^{11} cm^3 mol^{-1} s^{-1} (1700 K). Uncertainty conservatively estimated as ±25%. Expressions fitting these data given as $k_1=1.8\times10^{14}\exp\{-(9660\pm920)/T\}$, and $k_1=3.54\times10^{12}T^{\frac{1}{2}}\exp\{-(9220\pm910)/T\}$ cm^3 mol^{-1} s^{-1}. Authors give expressions to their data and those of (1 and 9) as $k_1=1.73\times10^{14}\exp\{-(9650\pm50)/T\}$ or $3.35\times10^{12}T^{\frac{1}{2}}\exp\{-(9220\pm50)/T\}$ cm^3 mol^{-1} s^{-1} (500-1700 K). WHITE (32) quotes $A_1=2.3\times10^{14}$ cm^3 mol^{-1} s^{-1} (rather than 1.8×10^{14} cm^3 mol^{-1} s^{-1}) for data of these authors.
3.07×10^{11}	1500		
6.34×10^{11}	1700		
(b) 9.8×10^{10}	1300		
2.76×10^{11}	1500		
5.88×10^{11}	1700		
2.29×10^{6}	508	Static system. H_2(2.54×10^{-6}-3.43×10^{-5} mol cm^{-3})/Br_2(1.91×10^{-6}-1.22×10^{-5} mol cm^{-3}) mixtures with [H_2]/[Br_2] in range 0.51-14.03.	From steady state treatment of mechanism $Br_2 + M \rightleftarrows Br + Br + M$ 2,-2 $Br + H_2 \rightleftarrows HBr + H$ 1,-1 $H + Br_2 \rightarrow HBr + Br$ 3
3.53×10^{6}	524		
5.40×10^{6}	539		
6.37×10^{6}	550		
1.18×10^{7}	566		

$Br + H_2 \rightarrow HBr + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$[Br_2]$ followed by absorption at 591 nm, and products dissolved in KI solution, followed by iodometry to determine residual $[Br_2]$, and acidometry to determine [HBr]. VIDAL 1971 (31)	author obtained rate equation in terms of degree of reaction. Further manipulation of this equation enable straight line plots to be drawn, the intercept giving $k_1K_2^{\frac{1}{2}}$, and the gradient $k_1 K_2^{\frac{1}{2}}k_3/k_{-1}$. Alternatively $k_1K_2^{\frac{1}{2}}$ obtained from initial HBr production rate, according to $(d[HBr]/dt)_0=2k_1K_2^{\frac{1}{2}}[H_2][Br_2]^{\frac{1}{2}}$. Author used K_2 from (28) to derive these values of k_1. Expression k_1=1.35x10^{14}exp(-9260/T) cm^3 mol^{-1} s^{-1} given for these data and those of (1,9,17,21 and 22). Using current JANAF data for K_2, we re-calculate the intercept data to give k_1=1.62x10^6 (508 K), 2.52x10^6 (524 K), 3.89x10^6 (539 K), 4.69x10^6 (550 K), and 8.83x10^6 cm^3 mol^{-1} s^{-1} (566 K), as shown on Arrhenius plot.
		REVIEW ARTICLES	
4.56x$10^{12}T^{\frac{1}{2}}$exp(-9450/T)	498-612	Review and re-analysis of data of BODENSTEIN and LIND (1), and BACH et al. (9). PEASE 1942 (12)	Later values of K_2 (8) used in this re-analysis than in that of BACH et al. (9). Expression obtained by fitting experimental data to form derived from collision theory. COOLEY and ANDERSON (15) altered this expression to give k_1=8.05x10^{10}T exp(-8920/T) cm^3 mol^{-1} s^{-1}.
3.46x10^{10}T exp(-8380/T)	498-612	Review and re-analysis of data of (1 and 9). CAMPBELL and FRISTROM 1958 (20)	K_2 of (14) and k_3/k_{-1}=8.4 (7) used in this re-analysis. Best fit to all data except value at 574.4 K (1) (which persistently showed greatest deviation) obtained by trial and error adjustment of E_1, after temperature exponent arbitrarily fixed at 1.0 due to relative insensitivity to this parameter
2.69x10^{14}exp{-(9920±190)/T}	500-1700	Review. FETTIS and KNOX 1964 (23)	Based on data of (9 and 11), with restriction that ratio A_1/A_{1D} agrees with theoretical predictions. This expression observed to give excellent agreement with data of (22).

$Br + H_2 \rightarrow HBr + H$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		FETTIS and KNOX 1964 (23) continued.	$Br + H_2 \rightarrow HBr + H$ 1 $Br + D_2 \rightarrow DBr + D$ 1D Used by (27,29,30 and 33).
$1.4 \times 10^{14} \exp(-9910/T)$	500-1700	Review. FRISTROM and WESTENBERG 1965 (25)	Expression fit to data of (17,21, 22) and data attributed to (20 and 18).
3.92×10^{-9} 1.02×10^{-3}	220 300	Review. WATSON 1974 (35)	Values quoted without source. Also reported by HAMPSON and GARVIN (36) in addenda.

ISOTOPIC REACTIONS $Br + HD \rightarrow HBr + D$, $Br + DH \rightarrow DBr + H$, $Br + HT \rightarrow HBr + T$ AND $Br + TH \rightarrow TBr + H$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	440-620	Static thermal and photolysis systems. $H_2/HD/Br_2$ and $H_2/HT/Br_2$ mixtures. Br_2 in tenfold excess. $[H_2+HD]$ or $[H_2+HT]$ measured manometrically, $[HD]/[H_2]$ ratio by mass spectrometry, and $[HT]/[H_2]$ ratio by scintillation counting. TIMMONS and WESTON 1964 (24)	From relative consumption of H_2 and HD (or HT), ratio $k_1/(k_{1HD}+k_{1DH})$ (or $k_1/(k_{1HT}+k_{1TH})$) obtained. $Br + HD \rightarrow HBr + D$ 1HD $Br + DH \rightarrow DBr + H$ 1DH $Br + HT \rightarrow HBr + T$ 1HT $Br + TH \rightarrow TBr + H$ 1TH Reactions -1 and isotopic equivalents considered unimportant under conditions of Br_2 excess. $H + HBr \rightarrow H_2 + Br$ -1 Authors obtained following results: T/K — $k_1/(k_{1HD} + k_{1DH})$ 440.9 — 2.22 ± 0.03 498.3 — 2.07 ± 0.02 528.9 — 2.00 ± 0.02 550.1 — 1.95 ± 0.02 571.5 — 1.92 ± 0.02 586.3 — 1.89 ± 0.01 622.1 — 1.83 ± 0.01 $k_1/(k_{1HT} + k_{1TH})$ 440.9 — 2.59 ± 0.02 538.9 — 2.26 565.7 — 2.19 ± 0.01 574.8 — 2.15 ± 0.01 609.2 — 2.11 ± 0.01

ISOTOPIC REACTION $Br + D_2 \rightarrow DBr + D$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
9.81×10^5	549.0	Static system. D_2 (2.59×10^{-6}-5.57×10^{-6} mol cm^{-3})/Br_2(3.0×10^{-6}-3.14×10^{-6} mol cm^{-3}) mixtures. BACH, BONHOEFFER and MOELWYN-HUGHES 1935 (9)	Mechanism for HBr synthesis taken as $Br_2 + M \rightarrow Br + Br + M$ 2 $Br + D_2 \rightleftharpoons DBr + D$ 1D,-1D $D + Br_2 \rightarrow DBr + Br$ 3D $Br + Br + M \rightarrow Br_2 + M$ -2 and steady state analysis as for reaction 1 (see comments column
3.17×10^6	585.6		
3.41×10^6	587.7		
3.82×10^6	590.3		
5.96×10^6	608.9		
9.46×10^6	623.8		
1.08×10^7	631.2		
1.39×10^7	639.5		
1.72×10^7	652.7		

$Br + H_2 \rightarrow HBr + H$

ISOTOPIC REACTION $Br + D_2 \rightarrow DBr + D$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BACH, BONHOEFFER and MOELWYN-HUGHES 1935 (9) continued.	under (9)). Authors assumed k_{3D}/k_{-1D}=10 as for k_3/k_{-1} $H + HBr \rightarrow H_2 + Br$ -1 $H + Br_2 \rightarrow HBr + Br$ 3 to obtain these values of k_{1D}. Arrhenius expression given for these data as $k_{1D}=8.34\times10^{13}\exp(-10\,000/T)$ $cm^3\ mol^{-1}\ s^{-1}$. FETTIS and KNOX (23) recalculate these data to give $k_{1D}=7.59\times10^{13}\exp\{-(10\,210\pm400)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$.
$1.21\times10^{14}\exp\{-(10\,270\pm480)/T\}$	1300-1700	Shock tube study. D_2(1% and 2%)/Br_2(1% and 2%)/Ar mixtures. $[Br_2]$ followed using absorption at 500 nm. BRITTON and COLE 1961 (22)	Data analysed as for reaction 1 (see Comments column under (22)), giving k_{1D} in terms of ratio k_{3D}/k_{-1D}. Latter ratio taken as 8.6, as found for k_3/k_1. Alternative expression given as $k_{1D}=1.91\times10^{12}T^{\frac{1}{2}}\exp\{-(9980\pm450)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$, both being derived from average results of 1% and 2% mixtures. Expressions to fit both these data and those of (9) given as $k_{1D}=9.66\times10^{13}\exp\{-(9400\pm20)/T\}$ and $1.84\times10^{12}T^{\frac{1}{2}}\exp\{-(9930\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$ (550-1700 K).
	440-610	Static thermal and photolysis systems. H_2/D_2 (∿1%) mixtures added to Br_2 in tenfold excess. $[H_2+D_2]$ measured manometrically, and $[D_2]/[H_2]$ ratio by mass spectrometry. TIMMONS and WESTON 1964 (24)	Ratio k_1/k_{1D} obtained from relative consumption of H_2 and D_2. Reactions -1 and -1D considered unimportant under Br_2 excess. $H + HBr \rightarrow H_2 + Br$ -1 $D + DBr \rightarrow D_2 + Br$ -1D Authors obtained $k_1/k_{1D}=(5.44\pm0.08)$ at 440.9 K, (4.33 ± 0.03) at 536.8 K, (4.00 ± 0.04) at 566.7 K, and (3.66 ± 0.04) at 610.3 K, to which they fit expression $k_1/k_{1D} = (1.32\pm0.04)\exp(631\pm19/T)$.
$4.79\times10^{14}\exp(-9920/T)$	2030-2515	Shock tube study. (a) HBr (1.5% and 3%)/D_2(1.5% and 3%)/Ar mixtures, total concentrations 1.68-1.92x10^{-6} mol cm^{-3}; (b) HBr(2%)/D_2(2%)/Ne(0.96%)/Ar mixtures, total concentrations 1.83-1.92x10^{-6} mol cm^{-3}. Reflected shock	Considering growth of DBr governed by sequence $HBr + M \rightarrow H + Br + M$ 4 $Br + D_2 \rightarrow DBr + D$ 1D authors compared DBr rate equation derived from above mechanism with empirical growth equation during initial period, obtaining overall rate constant

$Br + H_2 \rightarrow HBr + H$

ISOTOPIC REACTION $Br + D_2 \rightarrow DBr + D$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		region. Reaction followed by (a) ir emission at 3.6 μm (HBr) and 5.37 μm (DBr), and (b) tof mass spectrometry. KERN and NIKA 1974 (34)	$k=\frac{3}{4}k_{1D}k_4[M]$. Best fit with experimental data computed with quoted expression.
		REVIEW ARTICLE	
$1.95\times10^{14}\exp\{-(10\ 790\pm190)/T\}$	500-1700	Review. FETTIS and KNOX 1964 (23)	Based on data of (9) such that ratio $A_1/A_{1D}=1.4$, in agreement with theoretical predictions. Excellent agreement noted between this expression and data of (22).

Discussion

The reaction between hydrogen and atomic bromine

$$Br + H_2 \rightarrow HBr + H \qquad (1)$$

is the first step—after the dissociation (thermal or photolytic) of Br_2—in the synthesis of HBr. The chain mechanism has long been recognised [3,4,5] as

$$Br_2 + h\nu \rightarrow Br + Br$$

or

$$Br_2 + M \rightarrow Br + Br + M \qquad (2)$$

$$Br + H_2 \rightarrow HBr + H \qquad (1)$$

$$H + Br_2 \rightarrow HBr + Br \qquad (3)$$

$$H + HBr \rightarrow H_2 + Br \qquad (-1)$$

$$Br + Br + M \rightarrow Br_2 + M \qquad (-2)$$

Applying the steady state approximation to [H] and [Br], the rate equation for [HBr] is derived as

$$d[HBr]/dt = \frac{2k_1K_2^{1/2}[H_2][Br_2]^{1/2}}{1+k_{-1}[HBr]/k_3[Br_2]}$$

which is to be compared with the expression in terms of the overall rate constant k [1,32] for HBr synthesis:

$$d[HBr]/dt = \frac{k[H_2][Br_2]^{1/2}}{m+[HBr]/[Br_2]}$$

giving $k=2k_1k_3K_2^{1/2}/k_{-1}$ and $m=k_3/k_{-1}$. Therefore in H–Br systems, values of k_1 cannot be obtained independently of K_2 [13,31] or of a combination of K_2 and the ratio m [1,9,21,22]. Consequently the earliest determinations of k_1 [1,9] have been subject to repeated re-analysis [12,20,23,31] with successive improvements in K_2 [2,8,14,16,28] and re-determination of k_3/k_{-1} [1,7,31]. It has therefore been necessary for us also to evaluate the latter ratio before re-calculating values of k_1 from available data on overall rate constants k. (See the Discussion of reaction 3, section C6, for our consideration of k_3/k_{-1}.) Current JANAF data over the required temperature range were used to derive a simple Arrhenius expression for K_2, which was used to re-calculate k_1 from the original data for k of [31] and, using our evaluation of k_3/k_{-1}, the data of [1] and [9]. (Using the simple Arrhenius form of k_3/k_{-1} gives slightly lower values of k_1, but the variation is within the error limits of the data of [1] and [9].) Investigation of the data of Levy [21] showed that his derived values of k and his experimental values of k_1 did not agree, according to his Arrhenius equation for k_2 and the value 8.4 [7] for k_3/k_{-1}. Nor did his tabulated values of k_1 agree with his final expression for k_1 as derived from a least squares fit to the values of k. We have chosen to assume that his expression for k_1 is the better reflection of the results of this work, because it gives closer agreement with other data.

All the available data for k_1 were obtained using H_2/Br_2 or $H_2/Br_2/HBr$ mixtures, and there is good agreement between the data from static pyrolysis [1,9,13,31] and flow systems [21], and the higher temperature shock tube studies [17,22]. (We have considered the earlier study [17] to be merely a preliminary assessment of k_1, superseded by the more refined results of [22], and therefore we have ignored the results of the former in favour of those of the latter.)

Therefore on the basis of the results of [1,9,13,21,22 and 31] we recommend the expression

$$k_1 = 1.70\times10^{14} \exp(-9640/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the temperature range 500–1700 K, within uncertainty limits of ±50% over the whole range.

$Br + D_2 \rightarrow DBr + D$

There are considerably fewer data for the reaction of bromine atoms with deuterium than with hydrogen

$$Br + D_2 \rightarrow DBr + D \qquad (1D)$$

and both the data for the absolute rate constant k_{1D} and for the ratio k_1/k_{1D} are widely scattered. The more recent shock tube data [34] for k_{1D} and static thermal and photolytic data [24] for k_1/k_{1D} give values of k_{1D} higher than a combination of the data of [9] and [22].

As we have used the data of these latter studies to derive our recommendation for k_1, we must reserve judgement on the later work [24,34] until further data are available. No recommendation is made for k_{1D}.

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C5 $H + HBr \rightarrow H_2 + Br$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-69.697	-7.720	11.807
300	-69.697	-7.720	11.733
500	-69.718	-7.782	6.877
1000	-70.199	-8.385	3.229
1500	-70.902	-8.962	2.001
2000	-71.103	-9.088	1.383
2500	-70.839	-8.975	1.012
3000	-70.262	-8.761	0.766
3500	-69.467	-8.519	0.592
4000	-68.463	-8.251	0.463
4500	-67.262	-7.975	0.365
5000	-65.869	-7.678	0.287

RECOMMENDED RATE CONSTANT

$$k = 6.25 \times 10^{13} \exp(-1210/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$= 1.04 \times 10^{-10} \exp(-1210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

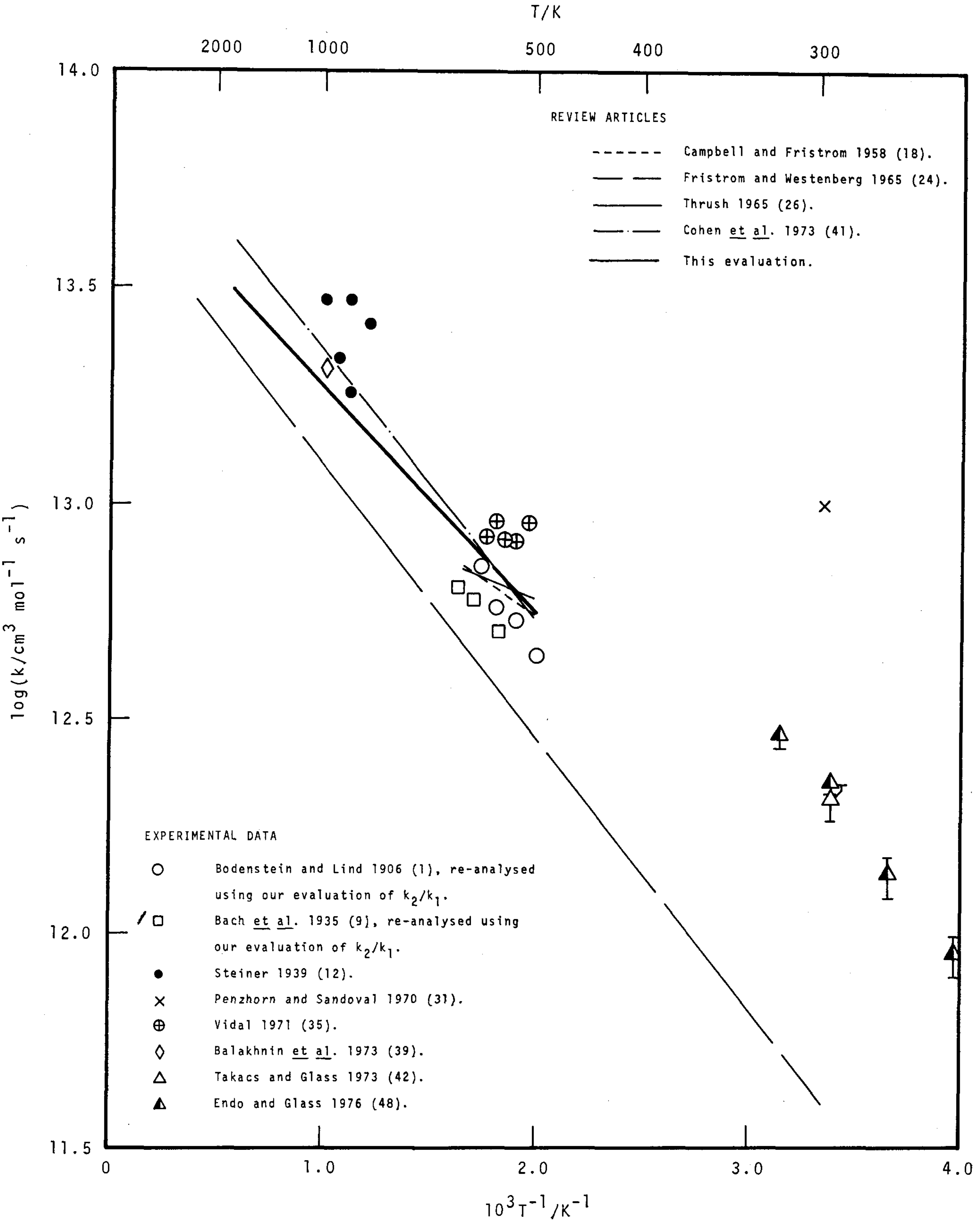
Temperature Range: 500-1700 K

Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.

Note: this expression is derived from the reverse rate constant and equilibrium data.

Rate Parameters:
$\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.80 \pm 0.18$
$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -9.98 \pm 0.18$
$E/\text{J mol}^{-1} = 10\,080 \pm 4900$
$E/\text{cal mol}^{-1} = 2\,410 \pm 1170$

$H + HBr \rightarrow H_2 + Br$



$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	498-574	Static system. H_2(6.93x10^{-6}-4.0x10^{-5} mol cm^{-3})/ Br_2(6.77x10^{-6}-4.0x10^{-5} mol cm^{-3}) mixtures. [HBr] in products determined by iodometry. BODENSTEIN and LIND 1906 (1)	Original analysis by these authors gave data in form of overall HBr production rate constant. Theoretical interpretation of HBr synthesis mechanism by CHRISTIANSEN (2), HERZFELD (3), and POLANYI (4) (CHP), enabled parameter m (found to be 5.0 in this study) to be identified (2,5,13) with the ratio $k_2/2k_1$, $H + HBr \rightarrow H_2 + Br$ 1 $H + Br_2 \rightarrow HBr + Br$ 2 i.e. k_2/k_1=10.0. BODENSTEIN and LÜTKEMEYER (5) considered experimental errors in this work allowed k_2/k_1 limiting values of 6 and 20. Value of 10 used by (9,13). COHEN *et al*. (41) compute k_1=4.0x10^{14}exp(-10 120/T) cm^3 mol^{-1} s^{-1} for this study, using PEASE's (13) re-calculations. From our re-calculated data for k_2 and k_2/k_1 (this Volume, section C6) we obtain values of k_1 as 4.46x10^{12} (498.8 K), 5.37x10^{12} (524.5 K), 5.74x10^{12} (550.6 K), and 7.18x10^{12} cm^3 mol^{-1} s^{-1} (574.4 K) for this work.
	(a) 303 (b) 575	Static system. (a) H_2(∿648 mm Hg; 86.4 kPa)/Br_2 (∿108 mm Hg; 14.4 kPa)/HBr (0 and 625-650 mm Hg; 83.3-86.7 kPa) mixtures photolysed by sunlight. (b) H_2(∿647 mm Hg; 86.3 kPa)/Br_2 (∿109 mm Hg; 14.5 kPa)/HBr (0 and 598-640 mm Hg; 79.7-85.3 kPa) mixtures. Iodometry used to determine yield of [HBr]. BODENSTEIN and JUNG 1926 (6)	Using CHP (2,3,4) analysis of HBr mechanism, comparison of HBr yields with and without added HBr gave ratio k_2/k_1 directly. Photolytic reaction (a) gave average value k_2/k_1=8.61 (303 K), and thermal reaction (b) gave k_2/k_1=8.22 (575 K). Authors concluded ratio k_2/k_1 invariant with temperature within limits of experimental error. Value 8.4 used by (10,18,19). Results of this study re-interpreted by SULLIVAN (28) as effects of HBr production and removal by reactions 3 and -4 (M=HBr), and not by reactions 2 and 1 $Br + Br + H_2 \rightarrow 2HBr$ 3 $Br + Br + HBr \rightarrow Br_2 + HBr$ -4

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	549-612	Static system. H_2(2.35x10^{-6} mol cm^{-3})/Br_2 (2.99x10^{-6}-3.27x10^{-6} mol cm^{-3}) mixtures. [Br_2] followed by light absorption. BACH, BONHOEFFER and MOELWYN-HUGHES 1935 (9)	Following initiation reaction 4 $Br_2 + M \rightarrow Br + Br + M$ 4 mechanism for HBr synthesis taken as that proposed by CHP (2,3,4). From our calculated values of k_2 (see this Volume, section C6) derived from the overall HBr production rate constants of this study, we obtain, using our evaluation of k_2/k_1 (this Volume, section C6) the following values of k_1: 5.03x10^{12} (549 K), 6.00x10^{12} (585.5 K), and 6.41x10^{12} cm^3 mol^{-1} s^{-1} (612.1 K).
(a) 2.2x10^{13}	821	Static system. (a) H_2(2.03x10^{-8}-1.8x10^{-6} mol cm^{-3})/HBr (2.03x10^{-8}-1.68x10^{-6} mol cm^{-3}) mixtures, with [H_2]:[HBr] ratios 0.56-3.0. (b) D_2(1.28x10^{-7} -4.3x10^{-7} mol cm^{-3})/HBr (1.39x10^{-7}-4.2x10^{-7} mol cm^{-3}) mixtures at ∿1:1 ratio. Thermal conductivity used to determine [H_2^p] and [D_2]. STEINER 1939 (12)	(a) HBr-catalysed conversion of ortho-para hydrogen analysed by steady state treatment of mechanism $H_2 + M \rightleftharpoons H + H + M$ 5,-5 $H + HBr \rightleftharpoons H_2^p + Br$ 1',-1' $H + HBr \rightleftharpoons H_2^o + Br$ 1",-1" Integrated rate equation for [H_2^o] used to obtain $(k_{1'}+k_{1''})K_5^{\frac{1}{2}}$. Absence of systematic variation of data with pressure indicated direct conversion $H_2^p + HBr \rightarrow H_2^o + HBr$ insignificant, and experiment performed in packed vessel showed lack of surface effects. Author used K_5 from (7) to obtain these values of $k_1(=(k_{1'}+k_{1''}))$. Using current JANAF data for K_5 we calculate k_1=2.59x10^{13} (821 K), 2.96x10^{13} (881 K), 2.18x10^{13} (931 K), and 2.95x10^{13} cm^3 mol^{-1} s^{-1} (984 K). (b) Mechanism for D_2-HBr exchange taken as $D_2 + M \rightleftharpoons D + D + M$ 5D,-5D $D + HBr \rightarrow DBr + H$ 6 $D + HBr \rightarrow HD + Br$ 7 $H + HBr \rightarrow H_2 + Br$ 1 $Br + D_2 \rightarrow DBr + D$ -1D Reverse reactions neglected as results taken from initial reaction only. Rate equation for [D] obtained in terms of k_1 or k_7 according to whether $k_6 >> k_1$ or $k_6 << k_1$, respectively. Predominant H_2 production showed
2.5x10^{13}	881		
2.0x10^{13}	931		
2.5x10^{13}	984		
(b) -	884		

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		STEINER 1939 (12) continued.	$k_6 >> k_1$, therefore authors could give $k_1 = 3.36\ K_{5D}^{-\frac{1}{2}}\ cm^{3/2}\ mol^{-\frac{1}{2}}\ s^{-1}$ at 884 K. Using K_{5D} of (8) they converted these data to 881 K and misquoted $1.7 \times 10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ (instead of $k_1 = 1.7 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$). Using current data (32) to obtain K_{5D}, we calculate $k_1 = 1.83 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$. TAKACS and GLASS (42) report $k_1 = 1.3 \times 10^{13} \exp(-450/T)\ cm^3\ mol^{-1}\ s^{-1}$ for these data (821-984 K), as used by (40 and 44).
	375-462	Static photolysis system. HBr(75.6-240.5 mm Hg; 10.1-32.1 kPa)/HI(140.5-182.7 mm Hg; 18.7-24.4 kPa)/I_2 (10.5-13.72 mm Hg; 1.4-1.8 kPa) mixtures photolysed at 253.7 nm. Absorbed light intensity measured by actinometry, $[H_2]$ measured manometrically during course of reaction, and final $[I_2]$ determined by iodometry. WILLIAMS and OGG 1947 (14)	Steady state treatment of mechanism $HI + h\nu \rightarrow H + I$ $H + HI \rightarrow H_2 + I$ 8 $H + HBr \rightarrow H_2 + Br$ 1 $Br + HI \rightarrow HBr + I$ $I + I + M \rightarrow I_2 + M$ $H + I_2 \rightarrow HI + I$ 9 gave rate equation for $[H_2]$ in terms of ratio $k_9[I_2]/(k_1[HBr] + k_8[HI])$. Integrated rate equation used with trial and error to obtain 'effective [HI]' = $[HI] + k_1[HBr]/k_8$. Authors give following values for ratio k_8/k_1 T/K — k_8/k_1 375 — 2.4 375 — 3.0 427.5 — 1.8 (2 points) 427.5 — 2.0 462 — 1.4 462 — 1.7 462 — 2.4 and give $k_8/k_1 = 0.54 \exp(500/T)$ as fit to these data. Authors remark upon neglect of hot H atom effects.
	303	Static photolysis system. HBr and HBr/H_2 mixtures (ratios $[HBr]:[H_2]$ 0.13-0.36) photolysed at 253.7 nm. Absorbed light intensity measured by actinometry, and final $[Br_2]$ in products by iodometry. SCHWARZ, WILLIAMS and HAMILL 1952 (16)	Steady state treatment of HBr photolysis mechanism $HBr + h\nu \rightarrow H^* + Br$ $Br + Br + M \rightarrow Br_2 + M$ -4 $H^* + HBr \rightarrow H_2 + Br$ 1* $H^* + Br_2 \rightarrow HBr + Br$ 2* $H^* + M \rightarrow H + M$ $H + HBr \rightarrow H_2 + Br$ 1 $H + Br_2 \rightarrow HBr + Br$ 2 (where H* represents 'hot' H-atoms) gave rate equation for

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		SCHWARTZ, WILLIAMS and HAMILL 1952 (16) continued.	$[Br_2]$. Ratio R (=(Br_2 removal rate constant)/(HBr removal rate constant)) obtained from integrated form of rate expression. Results of low precision due to low light absorption and long illumination times. In pure HBr, ratio $R=R_o=k_{2*}/k_{1*}$=0.55, 0.69 and 0.75 (average 0.66). Extrapolation of R vs. $[HBr]/[H_2]$ to $[H_2] = \infty$ gave $R_\infty = k_2/k_1$=(9.5±1).
	∿1400	Shock tube study. HBr(2%) /H_2(1%)/Br_2(1%)/Ar mixture. Absorption at 487 nm used to follow $[Br_2]$. BRITTON and DAVIDSON 1955 (17)	Few details given. Ratio k_2/k_1 quoted as in range 5-15.
	1300-1700	Shock tube study. (a) H_2 (1%)/Br_2(1%)/Ar and H_2(1%) /Br_2(1%)/HBr(10%)/Ar mixtures, and (b) H_2(2%)/ Br_2(2%)/Ar and H_2(2%)/Br_2 (2%)/HBr(10%)/Ar mixtures. $[Br_2]$ followed by absorption at 500 nm. BRITTON and COLE 1961 (20)	[Br] derived from $[Br_2]$ profiles, and [HBr] and $[H_2]$ obtained by successive mass balancing. Net rate constant k (where d[HBr]/dt = $k[H_2][Br]$) determined at 25% Br_2 disappearance, where errors considered minimum. From steady state analysis of HBr mechanism, $k=2k_{-1}/(1+k_1[HBr]/k_2[Br_2])$. From smoothed Arrhenius plots of k, comparison between results of H_2/Br_2 and $H_2/Br_2/HBr$ mixtures, for both sets (a) and (b), gave k_2/k_1. $H + HBr \rightleftharpoons H_2 + Br$ 1,-1 $H + Br_2 \rightarrow HBr + Br$ 2 T/K k_2/k_1: (a) (b) average 1300 9.5 12.7 11.1 1500 8.8 12.8 10.8 1700 8.5 8.2 8.4 Overall average quoted at (10.1± 1.7) over whole temperature range.

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	295	Static photolysis system. D_2/HBr mixtures, ratios $[D_2]:[HBr]$ 1.1 and 2.5. Mass spectrometry used to analyse products for H_2, HD and D_2. DE VRIES and KLEIN 1964 (21)	Formation of HD and H_2 only by reactions 10 and 1, respectively $H + D_2 \rightarrow HD + D$ 10 $H + HBr \rightarrow H_2 + Br$ 1 due to negligibly slow rate of reaction -1D $Br + D_2 \rightarrow DBr + D$ -1D Using steady state analysis, HD and H_2 yields give $k_{10}/k_1 \approx 0.55$. Using either the recommended expression of SCHOFIELD (27) or the (extrapolated) recommendation of KONDRATIEV (38) - giving $k_{10} = 7.75 \times 10^6$ and 1.47×10^7 cm^3 mol s^{-1} respectively - we obtain $k_1 \approx 1.41 \times 10^7$ and 2.67×10^7 cm^3 mol^{-1} s^{-1} respectively. These values not shown on Arrhenius plot.
	300-523	Static photolysis system. Pure HBr(15 mm Hg; 2.0 kPa) photolysed at 185 and 248 nm, and HBr(7-15 mm Hg; 0.933-2 kPa)/He ($\leqslant$1400 mm Hg; 186.6 kPa), or CO_2 ($\leqslant$ 600 mm Hg; 80 kPa), or H_2 ($\sim$500 mm Hg; 66.7 kPa) mixtures photolysed at 185 nm. Rapid photolysis at 185 nm used to convert HBr to Br_2, giving $[Br_2]:[HBr]$ ratios 0.1-0.6, H_2 formed being pumped off. $[Br_2]$ determined by absorption at 416 nm, and $[HBr]$ by uv absorption at 210 nm. Actinometry used to measure absorbed light intensity. FASS 1970 (30)	Steady state treatment of HBr photolysis mechanism used to give rate equation for $[Br_2]$. Rearrangement gave inverse Br_2 yield as linear function of $[Br_2]/[HBr]$, with gradient k'_2/k'_1 (=R (16)). For pure HBr mixtures $k'_2/k'_1 = k_{2*}/k_{1*} = 5.3$ at 300 K, and for HBr/He (600 mm Hg; 80 kPa) mixtures k'_2/k'_1 assumed = $k_2/k_1 = 22.7$ (300 K). $H^* + HBr \rightarrow H_2 + Br$ 1* $H^* + Br_2 \rightarrow HBr + Br$ 2* $H + HBr \rightarrow H_2 + Br$ 1 $H + Br_2 \rightarrow HBr + Br$ 2 Alternative analysis of HBr/He mixtures, whereby integrated form of $[Br_2]$ rate equation used, gave $k_2/k_1 = 25$ (300 K). But data for HBr/H_2, and HBr/He (1400 mm Hg; 186.6 kPa) mixtures, gave $k_2/k_1 \approx 26.8$, indicating incomplete thermalisation at lower He pressures. Further data, taken from graph, presented as T/K k_2/k_1 333 25.7 350 18.9 386 20.1 423 22.3 456 13.8 519 16.2 Author expressed these data by $k_2/k_1 = (6.8 \pm 2) \exp(400 \pm 150/T)$.

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		FASS 1970 (30) continued.	Ratio used by (40 and 46), and room temperature value of k_2/k_1 recommended by (43).
	298	Static photolysis system. HBr(1.51-2.1 mm Hg; 201.3-280 Pa)/C_2H_4 (2.75-24.16 mm Hg; 0.37-3.2 kPa), 0.06⩽ [HBr]:[C_2H_4]⩽0.76; HBr(1.5-8.5 mm Hg; 0.2-1.1 kPa)/ C_2FH_3(2.13-22.58 mm Hg: 0.28-3.0 kPa), 0.07⩽[HBr]: [C_2FH_3]⩽ 0.94; HBr (1.03 mm Hg; 137 Pa)/cis-$C_2F_2H_2$ (1.08-12.54 mm Hg; 0.14-1.7 kPa), 0.08⩽[HBr]:[cis-$C_2F_2H_2$]⩽0.95; HBr(1.6 and 1.9 mm Hg; 213 and 253 Pa)/ trans-$C_2F_2H_2$(3-22.7 mm Hg; 0.4-3.0 kPa), 0.08⩽[HBr]: [trans-$C_2F_2H_2$]⩽0.63; HBr (1.43-4.3 mm Hg; 191-573 Pa)/1,1-$C_2F_2H_2$ (1.2-43.09 mm Hg; 0.16-5.74 kPa), 0.03 ⩽[HBr]:[1,1-$C_2F_2H_2$]⩽0.93; HBr(2.1 and 7 mm Hg; 280 and 933 Pa)/C_2F_3H(2.1-15.7 mm Hg; 0.28-2.09 kPa), 0.13⩽[HBr]:[C_2F_3H]⩽1.0; and HBr(1.5-7.5 mm Hg;200-1000 Pa)/C_2F_4(2.1-23.25 mm Hg; 0.28-3.1 kPa), 0.07⩽[HBr]: [C_2F_4]⩽1.0 mixtures, with CO_2 moderator at ∿300 mm Hg (40 kPa). Product yield of H_2 measured manometrically. PENZHORN and SANDOVAL 1970 (31)	CO_2 pressure sufficiently high to thermalise hot H-atoms produced by photolysis of HBr. H_2 yield (ΦH_2) defined as ratio of H_2 production rate with and without olefin $C_2F_xH_y$. Steady state treatment of reactions subsequent to photolysis gave $\Phi H_2/(1-\Phi H_2)$ as linear function of [HBr]:[$C_2F_xH_y$] ratio, with slope $k_1/(k_{11}+k_{13})$ and intercept $k_{12}/(k_{11}+k_{13})$. Contribution of reaction 13 to H-removal $H + HBr \rightarrow H_2 + Br$ 1 $H + C_2F_xH_y \rightarrow C_2F_xH_{y+1}$ 11 $H + C_2F_xH_y \rightarrow C_2F_xH_{y-1} + H_2$ 12 $H + C_2F_xH_y \rightarrow C_2F_{x-1}H_y + HF$ 13 considered negligible, allowing authors to tabulate data as k_{11}/k_1 C_2H_4 $(8.43\pm0.08)\times10^{-2}$ C_2FH_3 $(6.62\pm0.26)\times10^{-2}$ cis-$C_2F_2H_2$ $(5.89\pm0.14)\times10^{-2}$ trans-$C_2F_2H_2$ $(9.83\pm0.27)\times10^{-2}$ 1,1-$C_2F_2H_2$ $(1.223\pm0.091)\times10^{-1}$ C_2F_3H $(1.39\pm0.039)\times10^{-1}$ C_2F_4 $(1.425\pm0.037)\times10^{-1}$ k_{12}/k_1 C_2H_4 - C_2FH_3 $(2.97\pm1.78)\times10^{-2}$ cis-$C_2F_2H_2$ $(5.77\pm1.32)\times10^{-2}$ trans-$C_2F_2H_2$ $(1.07\pm0.077)\times10^{-1}$ 1,1-$C_2F_2H_2$ $(1.96\pm0.54)\times10^{-1}$ C_2F_3H $(5.28\pm1.28)\times10^{-2}$ C_2F_4 Using the recommended expression of KERR and PARSONAGE (37), $k_{11}(C_2H_4)=8.32\times10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K, we obtain $k_1=(9.87\pm0.09)\times10^{12}$ cm^3 mol^{-1} s^{-1} (298 K).

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Static photolysis study. HBr/C_2H_4, C_2FH_3 or C_2F_4 mixtures, and HBr/I_2 mixtures, with CO_2 moderator at ∿250 mm Hg (33.3 kPa). $[H_2]$ in products determined manometrically. LETELIER, SANDOVAL and PENZHORN 1971 (34)	Data analysed as in (31). Results for olefins $C_2F_xH_y$ as given in (31), and ratio k_9/k_1 given as (19.05±0.63) $H + HBr \rightarrow H_2 + Br$ 1 $H + I_2 \rightarrow HI + I$ 9
	508-566	Static system. $H_2(2.54\times10^{-6}-3.43\times10^{-5}\ mol\ cm^{-3})/Br_2(1.91\times10^{-6}-1.22\times10^{-5}\ mol\ cm^{-3})$ mixtures with $[H_2]:[Br_2]$ in range 0.51 to 14.03. $[Br_2]$ determined by absorption at 591 nm, and products analysed by iodometry for residual $[Br_2]$, and by acidimetry for $[HBr]$. VIDAL 1971 (35)	Steady state treatment of CHP mechanism used to express rate equation in terms of degree of reaction. Further manipulation gave linear expression of gradient $2k_1/k_{-1}k_2K_4^{\frac{1}{2}}$ and intercept $k_{-1}K_4^{\frac{1}{2}}$. $H + HBr \rightleftharpoons H_2 + Br$ 1,-1 $H + Br_2 \rightarrow HBr + Br$ 2 $Br_2 + M \rightarrow Br + Br + M$ 4 Values of k_2/k_1 given as 12.7 (508 K), 11.8 (524 K), 11.7 (539 K), 14.4 (550 K), and 10.7 (566 K). Using the values of k_2 calculated for this work from the author's original data, we re-calculate (using our evaluation of k_2/k_1, this Volume, section C6) k_1 as 9.08×10^{12} (508 K), 8.17×10^{12} (524 K), 8.20×10^{12} (539 K), 9.07×10^{12} (550 K), and $8.42\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ (566 K).
	984	Flow system. $HBr/O_2/Ar$ mixture added through moveable inlet to H_2 stream, giving $[H_2]:[O_2]=1:1.25$, at total pressure 1.8 mm Hg (240 Pa). $[H]$, $[O]$, $[OH]$ and $[O_2]$ measured by esr spectrometry, $[H_2]$ by O_2 consumption. BALAKHNIN, GRYZUNOVA and EGOROV 1973 (39)	$[HBr]$ measurement from $[Br]$ confounded by low $[Br]$. From rate equations for $[H]$, $[O]$, and $[OH]$, authors obtain ratios k_{14}/k_1 and k_{15}/k_1, removing need for knowing $[HBr]$. $O + HBr \rightarrow OH + Br$ 14 $OH + HBr \rightarrow H_2O + Br$ 15 $H + HBr \rightarrow H_2 + Br$ 1 Authors quote $k_{14}/k_1=0.12$ and $k_{15}/k_1=1.44$. However, using their quoted values for various concentrations and rate constants we obtain $k_{14}/k_1=2.93\times10^{-2}$ and $k_{15}/k_1=0.763$. Authors use $k_1=2.5\times10^{13}\exp(-780/T)\ cm^3\ mol^{-1}\ s^{-1}$ (33) to derive k_{14} and k_{15}.

$H + HBr \rightarrow H_2 + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		BALAKHNIN, GRYZUNOVA and EGOROV 1973 (39) continued.	Extrapolating our expression for k_{14} (this Volume, section C9) we obtain (using our re-calculated value for k_{14}/k_1) k_1=2.06x10^{13} cm^3 mol^{-1} s^{-1} at 984 K.
(2.05±0.2)x10^{12}	295	H_2-discharge flow system. HBr(2.1x10^{-10}-1.3x10^{-9} mol cm^{-3}) added by moveable inlet to H(1.1x10^{-10}-1.7x10^{-9} mol cm^{-3})/Ar mixtures at total pressures 0.5-1.5 mm Hg (66.7-200 Pa). Flow tube coated with fluorinated halocarbon wax. [H] and [Br] monitored by epr spectrometry. TAKACS and GLASS 1973 (42)	Wax coating of tube eliminated measurable surface recombination of Br atoms. Values of k_1 calculated from (a) pseudo first order decay of [H], when HBr in excess; (b) second order integrated rate equation, using [H] decay or [Br] growth; and (c) integrated rate equation, for $[H]_o$ = $[HBr]_o$. Used by (47).
(6.87±0.4)x10^{11}	230	H_2-discharge flow system. HBr(1.28x10^{-10}-2.47x10^{-10} mol cm^{-3}) added to H(1.13x10^{-11}-4.75x10^{-11} mol cm^{-3})/Ar mixtures at total pressures 1.22-1.45 mm Hg (162.6-193.3 Pa). Method as for (42), but with improved epr spectrometer. ENDO and GLASS 1976 (48)	k_1 calculated as previously (42). Corrections made for axial diffusion of H atoms. Authors expressed these data by k_1= (1.67 ±0.2)x10^{14} exp{-(1290±55)/T} cm^3 mol^{-1} s^{-1}.
(8.91±1.02)x10^{11}	252		
(1.37±0.15)x10^{12}	273		
(2.23±0.08)x10^{12}	295		
(2.90±0.18)x10^{12}	318		

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	500-600	Review. MORRIS and PEASE 1935 (11)	From activation energy E_{-1}=74.1 kJ mol^{-1} (17.7 kcal mol^{-1}), authors derive E_1=4.2 kJ mol^{-1} (1.0 kcal mol^{-1}) from thermodynamic data for H_2, Br_2 and HBr. $H + HBr \rightleftharpoons H_2 + Br$ 1,-1
7.65x$10^{11}T^{0.5}$exp(-560/T)	500-600	Evaluation. CAMPBELL and FRISTROM 1958 (18)	Expression obtained from authors' recommended k_{-1} and expression fitted to K_1 data (15). Recommended by KONDRATIEV (38). Expression k_1=6.14x10^{13}exp(-1100/T) cm^3 mol^{-1} s^{-1} attributed to this evaluation by (25).
5.3x10^{13}exp(-1460/T)	300-2500	Review. FRISTROM and WESTENBERG 1965 (24)	Expression derived from K_1k_{-1}, using authors' own expression for k_{-1}.

$H + HBr \rightarrow H_2 + Br$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.5\times10^{13}\exp(-450/T)$	500-600	Review. THRUSH 1965 (26)	Expression derived from K_1k_{-1}, using k_{-1} of BODENSTEIN et al. (1,5). Used by (29).
$1.45\times10^{14}T^{-0.055}\exp(-1470/T)$	500-1700	Review. COHEN, GIEDT and JACOBS 1973 (41)	Derived from k_{-1} (from data of FETTIS and KNOX (22)) and K_1, so that ratio k_2/k_1 agreed with their own recommended expression k_2/k_1=5.2 exp(550/T). $H + Br_2 \rightarrow HBr + Br$ 2

ISOTOPIC REACTION $D + DBr \rightarrow Br + D_2$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298-473	Static photolysis system. DBr(8-16 mm Hg; 1.07-2.13 kPa)/D_2 (0 and 700 mm Hg; 93.3 kPa) mixtures photolysed at 213.9 nm. Rapid photolysis used to generate Br_2, giving [Br_2]:[DBr] ratios in range 0.01-0.5. Absorbed light intensity by actinometry, [Br_2] by absorption at 416 nm. FASS, HOOVER and SIMPSON 1972 (36)	Analysis as by FASS (30) for reaction 1 (see Comments column). In pure DBr mixtures, hot D atom (D*) rates obtained as k_{2D^*}/k_{1D^*} = (6.7±0.13), 298-393 K. $D^* + DBr \rightarrow D_2 + Br$ 1D* $D^* + Br_2 \rightarrow DBr + Br$ 2D* DBr mixtures with D_2 moderator gave k_{2D}/k_{1D}= (58±1.7) at 298 K, (44±2.2) at 333 K, (35±1.5) at 393 K, (36±1.5) at 428 K, and (32±0.6) at 473 K. Authors gave Arrhenius fit to these data as k_{2D}/k_{1D}=(12±2.8)exp(450±80/T). $D + DBr \rightarrow D_2 + Br$ 1D $D + Br_2 \rightarrow DBr + Br$ 2D
	300	Static photolysis system. HBr(6%-36%)/DBr/He mixtures ([DBr]:[HBr] ratios = 0.24) at total pressures 50-250 mm Hg (6.7-33.3 kPa), photolysed at 213.8 and 253.7 nm. H_2 and isotopes measured by mass spectrometry. PERSKY and KUPPERMANN 1974 (45)	Steady state analysis of thermalised reaction mechanism gave relative yields of HD and D_2, at 2 different photolysis wavelengths, as functions of rate constants k_1, k_{1D}, k_{1HD}, k_7, k_6 and k_{-6} $H + HBr \rightarrow H_2 + Br$ 1 $D + DBr \rightarrow D_2 + Br$ 1D $H + DBr \rightarrow HD + Br$ 1HD $D + HBr \rightarrow DH + Br$ 7 $H + DBr \rightleftarrows HBr + D$ -6,6 Authors used thermodynamic data to derive k_6/k_{-6}, and with k_{-1}/k_{-1D} data of (23) derived k_1/k_{1D}, and obtained ratios k_{1HD}/k_1 = k_{1D}/k_7 = 0.44.

ISOTOPIC REACTION $D + DBr \rightarrow Br + D_2$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.70 \pm 0.55) \times 10^{11}$	252	H_2-discharge flow system. DBr(1.47×10^{-10}-2.56×10^{-10} mol cm^{-3}) added via moveable inlet to D(1.68×10^{-11}-3.22×10^{-11} mol cm^{-3})/Ar mixtures, at total pressures 1.15-1.31 mm Hg (153.3-174.6 Pa). [D] and [Br] monitored by epr spectrometry. ENDO and GLASS 1976 (48)	Values of k_{1D} determined from pseudo first order decay of [D], and occasionally by variation in $\ln\{[DBr]_0-[Br]\}$ with time. Corrections made for axial diffusion of D atoms. Authors express these data by $k_{1D}=(1.37 \pm 0.1) \times 10^{13} \exp\{-(850 \pm 65)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$.
$(6.08 \pm 0.54) \times 10^{11}$	273		
$(7.47 \pm 0.9\ ) \times 10^{11}$	295		
$(9.52 \pm 0.3\ ) \times 10^{11}$	318		

Discussion

There have been only three determinations [12,42,48] of the rate constant of the chain propagating step

$$H + HBr \rightarrow H_2 + Br \qquad (1)$$

in the synthesis of HBr that have not relied on other experimental data. Competition with the alternative reaction

$$H + Br_2 \rightarrow HBr + Br \qquad (2)$$

dictates that most of the data be presented in the form of the rate constant ratio k_2/k_1 [1,6,9,16,17,20,30,35]. For our evaluation of the data for this ratio see the Discussion of reaction 2 in section C6.

From the original data of several of the static H_2–Br_2 system studies we have been able to calculate k_2 [1,9,35] and therefore using our evaluation of k_2/k_1 we have also calculated the appropriate values of k_1, which appear on the Arrhenius plot.

The results of Glass et al. [42,48] are the only truly independent measurements of k_1, but those of Steiner [12] depend only upon values of the equilibrium constant K_5.

$$H_2 + M \rightarrow H + H + M \qquad (5)$$

Other values for k_1 have been obtained relative to k_8 [14], to k_9 [34], to k_{10} [21],

$$H + HI \rightarrow H_2 + I \qquad (8)$$

$$H + I_2 \rightarrow HI + I \qquad (9)$$

$$H + D_2 \rightarrow HD + D \qquad (10)$$

and relative to k_{11} and k_{12} for a variety of fluorinated olefins [31]:

$$H + C_2F_xH_y \rightarrow C_2F_xH_{y+1} \qquad (11)$$

$$\rightarrow C_2F_xH_{y-1} + H_2 \qquad (12)$$

where $(x+y)=4$, and $x=0$ to 4.

Our recommendation for k_8 (section D4) is unreliable outside the range 600–1000 K, and therefore we cannot extract any values of k_1 from the data of [14], which were obtained at temperatures below 470 K.

The ratio k_9/k_1 [34] has been used in this evaluation to derive k_9 (see section D5) in view of the greater volume of data available for k_1.

De Vries and Klein [21] omitted to allow for the reactions of "hot" hydrogen atoms in their HBr photolysis study, and consequently their ratio k_{10}/k_1 is too high by three orders of magnitude, giving an absurdly low value for k_1.

Using the recommended value of Kerr and Parsonage [37] for k_{11} (C_2H_4) at 298 K to convert the data of [31] we have obtained $k_1=(9.87 \pm 0.09) \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$. Kerr and Parsonage's [37] values for k_{11} (C_2FH_3 to C_2F_4) were all derived from Penzhorn and Sandoval's [31] data relative to k_{11} (C_2H_4), and so no further information can be extracted from [31].

Because of the difference between the data of [1] and [9] and [35] of over 50%, and the fact that the independent low temperature values of [42] and [48] are nearly a factor of 3 higher than the extrapolation of the latest review evaluation of Cohen et al. [41], we prefer to use our recommended expression for k_{-1} (section C4), and the equilibrium constant K_1, to determine k_1. To within ±50% (as determined by the limits on k_{-1}) the expression

$$k_1 = 6.25 \times 10^{13} \exp(-1210/T)\ cm^3\ mol^{-1}\ s^{-1}$$

is an adequate representation of the data [1,9,12,35,39] over the temperature range 500–1700 K.

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C6 $H + Br_2 \rightarrow HBr + Br$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-173.490	13.514	31.100
300	-173.502	13.473	30.913
500	-174.987	9.703	18.787
1000	-178.213	5.117	9.575
1500	-179.803	3.778	6.459
2000	-180.264	3.506	4.891
2500	-180.167	3.548	3.950
3000	-179.841	3.665	3.322
3500	-179.439	3.787	2.876
4000	-179.046	3.900	2.541
4500	-178.674	3.979	2.283
5000	-178.351	4.046	2.075

RECOMMENDED RATE CONSTANT

$k = 2.28 \times 10^{11} T \exp(-220/T)$ cm^3 mol^{-1} s^{-1}

$= 3.79 \times 10^{-13} T \exp(-220/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 500-1700 K.

Suggested Error Limits for Calculated Rate Constant: less than a factor of 2 over the quoted temperature range.

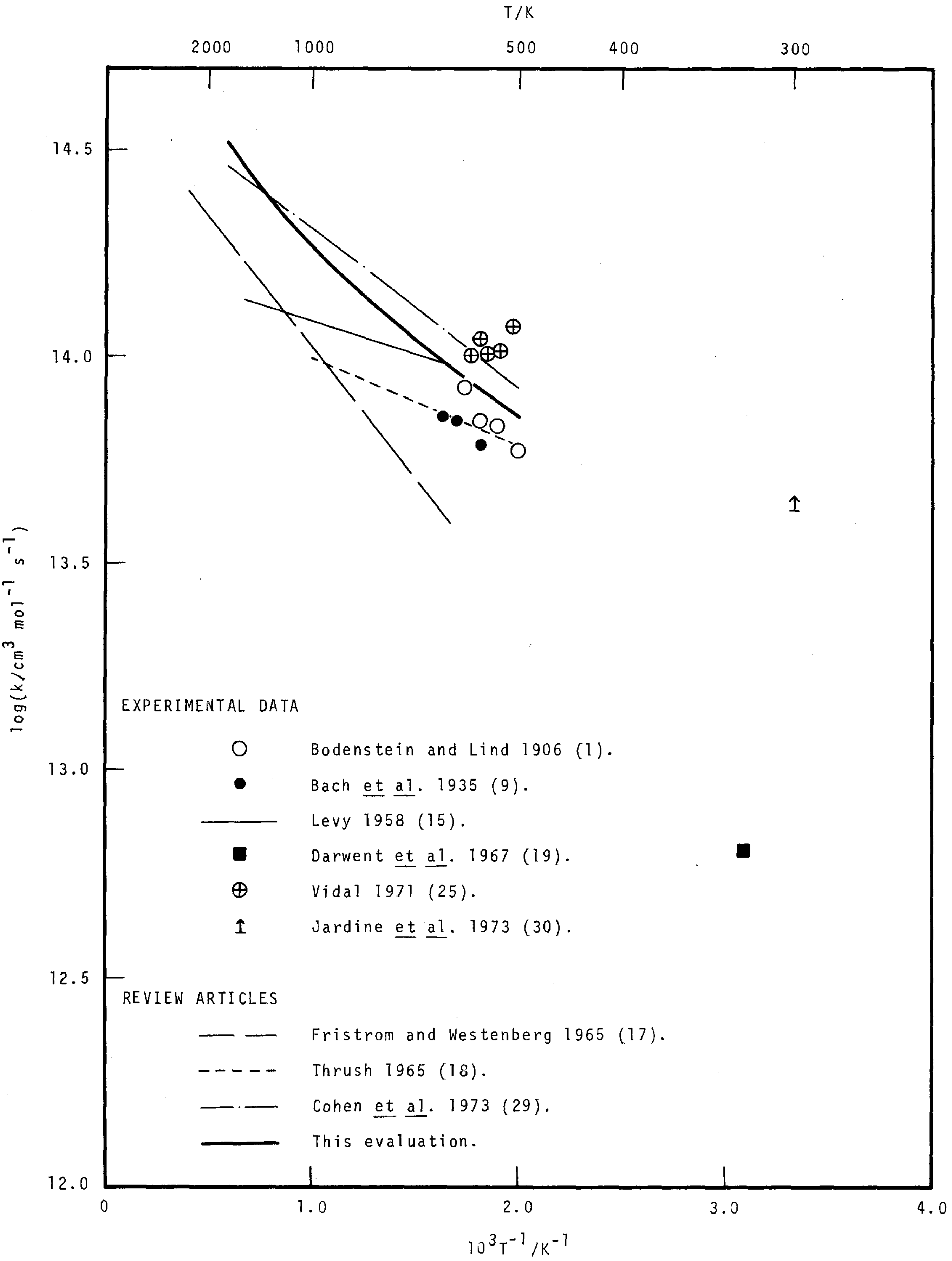
Rate Parameters: $\log(A'T/cm^3\ mol^{-1}\ s^{-1}) = 11.36 \pm 0.3 + \log T$

$\log(A'T/cm^3\ molecule^{-1}\ s^{-1}) = -12.42 \pm 0.3 + \log T$

$E'/J\ mol^{-1} = 1\ 830 \pm 8\ 130$

$E'/cal\ mol^{-1} = 440 \pm 1\ 950$

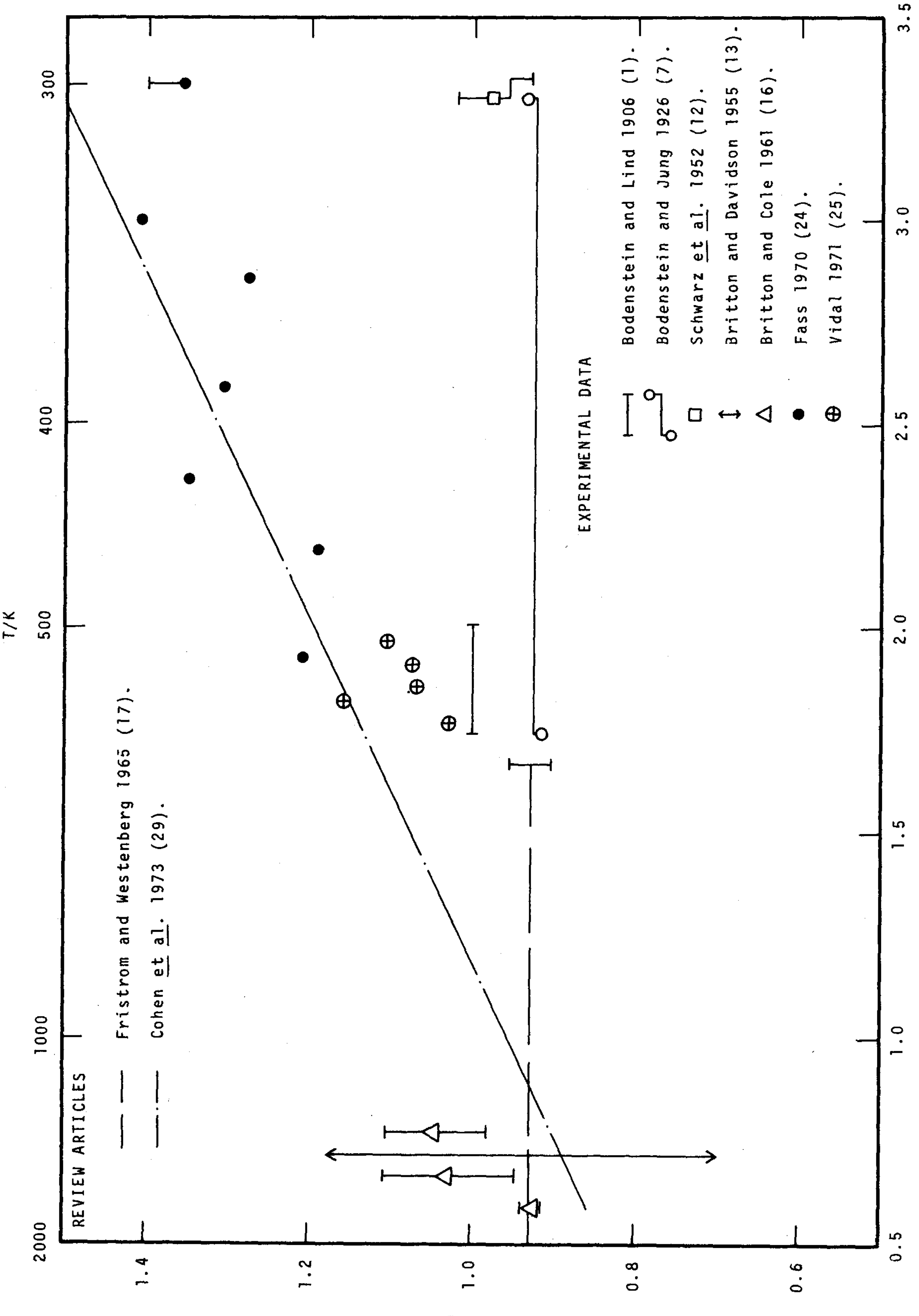
$H + Br_2 \rightarrow HBr + Br$



$H + Br_2 \rightarrow HBr + Br$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	498-574	Static system. H_2(6.93x10^{-6}-4.0x10^{-5} mol cm^{-3})/Br_2(6.77x10^{-6}-4.0x10^{-5} mol cm^{-3}) mixtures. [HBr] in products determined by iodometry. BODENSTEIN and LIND 1906 (1)	Original analysis by these authors gave data in form of overall HBr production rate constant k, as $dx/dt=k(a-x)(b-x)^{\frac{1}{2}}/(m+x)/(b-x))$, where a=[$H_2$], b=[$Br_2$], and x=[HBr]/2. As a result of the interpretation of HBr mechanism by CHRISTIANSEN (2), HERZFELD (3), and POLANYI (4) (CHP), the parameter m (found to be 5.0 in this study) was identified (2,6,11) with the ratio $k_1/2k_2$ $H + Br_2 \rightarrow HBr + Br$ 1 $H + HBr \rightarrow H_2 + Br$ 2 i.e. k_1/k_2=10.0. BODENSTEIN and LÜTKEMEYER (6) believed uncertainties in this work allowed this ratio to lie between 6 and 20. Value of 10 used by (9,11). From values of overall rate constant $k(=k_1k_{-2}K_3^{\frac{1}{2}}/2k_2)$, as given by (11 and 27), we obtain following values of k_1 $(=2kK_2/K_3^{\frac{1}{2}})$: 5.90x$10^{13}$ (498.8 K), 6.77x10^{13} (524.5 K), 6.95x10^{13} (550.6 K), and 8.41x10^{13} cm^3 mol^{-1} s^{-1} (574.4 K). $Br + H_2 \rightarrow HBr + H$ -2 $Br_2 + M \rightarrow Br + Br + M$ 3
	(a) 303 (b) 575	Static system. (a) H_2(647-648.2 mm Hg; 86.3-86.4 kPa)/Br_2(107.8-109.1 mm Hg; 14.4-14.5 kPa) and H_2(646.8-648.1 mm Hg; 86.2-86.4 kPa)/Br_2(107.9-109.2 mm Hg; 14.4-14.6 kPa)/HBr (625-650 mm Hg; 83.3-86.7 kPa) mixtures photolysed by sunlight. (b) H_2(646.7-647.1 mm Hg; 86.2-86.3 kPa)/Br_2 (108.9-109.3 mm Hg; 14.5-14.6 kPa) and H_2(646.7-647 mm Hg; 86.2-86.3 kPa)/Br_2 (109-109.3 mm Hg; 14.5-14.6 kPa)/HBr(598-640 mm Hg; 79.7-85.3 kPa) mixtures. [HBr] in products determined by iodometry. BODENSTEIN and JUNG 1926 (7)	Comparison of HBr yields with and without added HBr gave ratio k_1/k_2 directly. For photolytic reaction (a) average value k_1/k_2 =8.61 (303 K), and for thermal reaction (b) k_1/k_2=8.22 (575 K). Authors considered these values essentially equal within experimental accuracy. Value 8.4 used by (10,14,15). This study reinterpreted by SULLIVAN (21) as giving HBr formation and self-inhibition not by reactions 1 and 2 but by reactions 4 and -3 (M=HBr). $Br + Br + H_2 \rightarrow 2HBr$ 4 $Br + Br + HBr \rightarrow Br_2 + HBr$ -3



H + Br$_2$ / H + HBr

T/K
300
400
500
1000
2000
$10^3T^{-1}/K^{-1}$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$\log(k_1k_2^{-1})$
1.4
1.2
1.0
0.8
0.6
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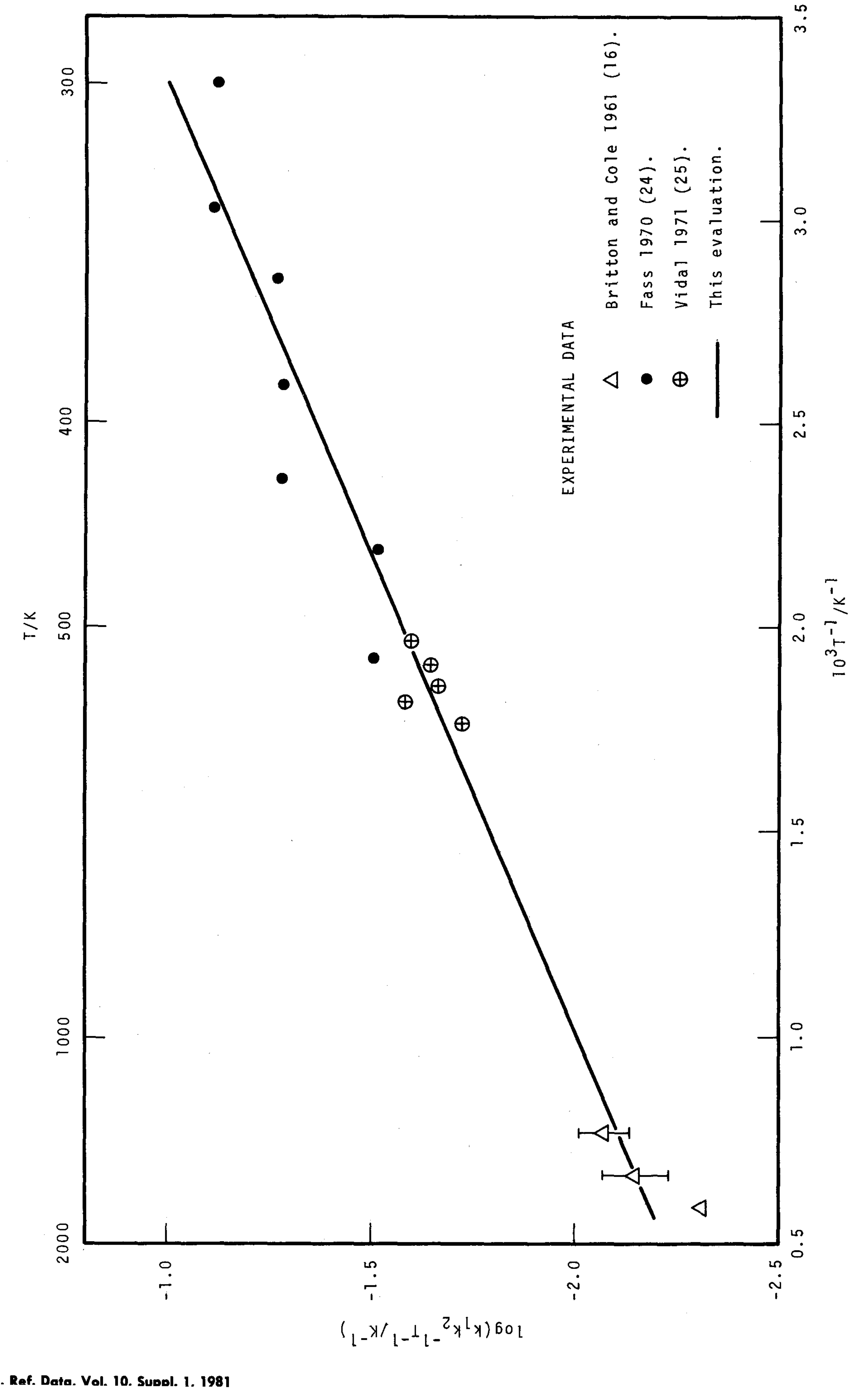
Fass 1970 (24).
Vidal 1971 (25).

$H + Br_2 \rightarrow HBr + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	549-612	Static system. H_2(2.35x10^{-6}-3.0x10^{-6} mol cm^{-3})/ Br_2(2.99x10^{-6}-3.27x10^{-6} mol cm^{-3}) mixtures. [Br] followed by light absorption. BACH, BONHOEFFER and MOELWYN-HUGHES 1935 (9)	Using thermal form of CHP (2,3,4) mechanism, authors' original analysis gave overall HBr synthesis rate constant k as in (1), from which they obtained k_{-2}, using ratio k_1/k_2=10.0 (1). From values of k given by (11 and 27) we calculate following values of k_1(=$2kK_2/K_3^{\frac{1}{2}}$):6.10x10^{13} (549 K), 6.93x10^{13} (585.5 K), and 7.20 x10^{13} cm^3 mol^{-1} s^{-1} (612.1 K).
	303	Static photolysis system. HBr and HBr/H_2 mixtures (ratio [HBr]:[H_2] 0.13-0.36) photolysed at 253.7 nm. Absorbed light intensity measured by actinometry, and final [Br_2] in products by iodometry. SCHWARZ, WILLIAMS and HAMILL 1952 (12)	Steady state analysis of HBr photolysis mechanism $HBr + h\nu \rightarrow H^* + Br$ $Br + Br + M \rightarrow Br_2 + M$ -3 $H^* + HBr \rightarrow H_2 + Br$ 2* $H^* + Br_2 \rightarrow HBr + Br$ 1* $H^* + M \rightarrow H + M$ $H + HBr \rightarrow H_2 + Br$ 2 $H + Br_2 \rightarrow HBr + Br$ 1 (where H* represents 'hot' H-atoms) gave rate equation for [Br_2]. Integrated form of this equation yielded ratio R(=(Br_2 removal rate constant)/(HBr removal rate constant)). Results have low precision due to low light absorption and long illumination times. In pure HBr mixtures, ratio $R=R_0=k_{1*}/k_{2*}$= 0.55, 0.69 and 0.75 (average 0.66). Extrapolation of R against [HBr]/[H_2] to [H_2]= ∞ gave R_∞= k_1/k_2=(9.5±1).
	∿1400	Shock tube study. HBr(2%)/ H_2(1%)/Br_2(1%)/Ar mixture. [Br_2] monitored by absorption at 487 nm. BRITTON and DAVIDSON 1955 (13)	Few details given. Authors quote k_1/k_2=5 to 15.
	603-1477	Flow system. H_2(3.15x10^{-10} -4.5x10^{-6} mol cm^{-3})/Br_2 (3.65x10^{-10}-1.48x10^{-7} mol cm^{-3})/N_2 mixtures at total pressures 775-780 mm Hg (103.3-104 kPa). Reaction products analysed by fractional separation and	Steady state analysis of CHP mechanism, allowing for large degree of Br_2 dissociation at high temperatures, enabled author to obtain overall HBr synthesis rate constant k from k_{-2}, using ratio k_1/k_2=8.4 (7). From expression for k given by

$H + Br_2 / H + HBr$


T/K
300
400
500
1000
2000
-1.0
-1.5
-2.0
-2.5
$\log(k_1k_2^{-1}T^{-1}/K^{-1})$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$10^3T^{-1}/K^{-1}$
EXPERIMENTAL DATA
△ Britton and Cole 1961 (16).
● Fass 1970 (24).
⊕ Vidal 1971 (25).
This evaluation.

$H + Br_2 \rightarrow HBr + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		manometric methods. LEVY 1958 (15)	author, we calculate the expression $k_1 (=2kK_2/K_3^{\frac{1}{2}}) = 3.0 \times 10^{14} \exp(-690/T)\ cm^3\ mol^{-1}\ s^{-1}$, using least squares fits to current JANAF data for K_2 and K_3 over the appropriate temperature range.
	1300-1700	Shock tube study. (a) H_2(1%)/Br_2(1%)/Ar and H_2(1%)/Br_2(1%)/HBr(10%)/Ar mixtures, and (b) H_2(2%)/Br_2(2%)/Ar and H_2(2%)/Br_2(2%)/HBr(10%)/Ar mixtures. Br_2 absorption followed at 500 nm. BRITTON and COLE 1961 (16)	Values of [Br] obtained from [Br_2] profiles, and [HBr] and [H_2] derived by successive mass balances. Net rate constant k, defined by $d[HBr]/dt = k[Br][H_2]$, determined at 25% Br_2 disappearance, where errors considered minimised. Using steady state analysis, $k = 2k_{-2}/(1+k_2[HBr]/k_1[Br_2])$. From smoothed Arrhenius plots of k, comparison between results of H_2/Br_2 and H_2/Br_2/HBr mixtures, for both conditions (a) and (b), gave k_1/k_2: $H + Br_2 \rightarrow HBr + Br$ 1 $H + HBr \rightleftharpoons H_2 + Br$ 2,-2 T/K k_1/k_2 (a) (b) average 1300 9.5 12.7 11.1 1500 8.8 12.8 10.8 1700 8.5 8.2 8.4 Overall average ratio quoted as (10.1±1.7) over whole temperature range.
	323	Static photolysis system. H_2S(9.0 mm Hg; 1.2 kPa)/Br_2(1.0 mm Hg; 133.3 Pa)/CO_2(0 and 600 mm Hg; 80 kPa) mixtures photolysed at 253.7 nm. Products analysed by unspecified method for H_2. DARWENT, WADLINGER and ALLARD 1967 (19)	Decrease of H_2 yield in CO_2-moderated mixtures suggested deactivated H* atoms react more rapidly with Br_2 than with H_2S. If all H atoms thermalised by CO_2, then perturbation of H_2 yield gave ratio $k_1/k_5 = 11.7$ $H + Br_2 \rightarrow HBr + Br$ 1 $H + H_2S \rightarrow H_2 + HS$ 5 Using our expression for k_5 (Volume 3, p.445) we obtain $k_1 = 6.37 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ (323 K).
	300-523	Static photolysis system. Pure HBr(15 mm Hg; 2.0 kPa) photolysed at 185 and 248 nm, and HBr(7-15 mm Hg; 0.933-2.0 kPa)/He (≤1400 mm Hg; 186.6 kPa), or CO_2 (≤600 mm Hg; 80 kPa), or H_2(∿500 mm Hg; 66.7 kPa)	Steady state treatment of CHP (2,3,4) mechanism, including hot H atoms, H*, $HBr + h\nu \rightarrow H^* + Br$ $H^* + HBr \rightarrow H_2 + Br$ 2* $H^* + Br_2 \rightarrow HBr + Br$ 1* $H^* + M \rightarrow H + M$ $H + HBr \rightarrow H_2 + Br$ 2

$H + Br_2 \rightarrow HBr + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		mixtures photolysed at 185 nm. Rapid photolysis at 185 nm used to generate Br_2, giving $[Br_2]:[HBr]$ ratios 0.1-0.6, H_2 formed being pumped off. $[Br_2]$ determined by absorption at 416 nm, and [HBr] by uv absorption at 210 nm. Actinometry used to measure absorbed light intensity. FASS 1970 (24)	$H + Br_2 \rightarrow HBr + Br$ 1 $Br + Br + M \rightarrow Br_2 + M$ -3 gave rate equation for $[Br_2]$. Author re-arranged this so that inverse Br_2 yield linear function of $[Br_2]/[HBr]$, with gradient k_1'/k_2', where k_1' and k_2' are the net rate constants for Br_2 and HBr removal, respectively, by some combination of thermal and hot H atoms. For pure HBr mixtures $k_1'/k_2' = k_{1*}/k_{2*} = 5.3$ at 300 K, and for HBr/He (600 mm Hg; 80 kPa) mixtures, k_1'/k_2' assumed $= k_1/k_2 = 22.7$ (300 K). Alternative analysis used in HBr/He photolysis, whereby integrated form of $[Br_2]$ rate equation used, gave $k_1/k_2 = 25$ (300 K). However data for HBr/H_2 mixture, and HBr/He (1400 mm Hg; 186.6 kPa) mixture, gave $k_1/k_2 \approx 26.8$, indicating thermalisation incomplete for $p_{He} \leqslant 600$ mm Hg (80 kPa). Further data, taken from graph, presented as T/K k_1/k_2 333 25.7 350 18.9 386 20.1 423 22.3 456 13.8 519 16.2 Authors give fit to these data as $k_1/k_2 = (6.8 \pm 2)\exp(400 \pm 150/T)$. Ratio used by (28).
	508-566	Static system. H_2 (2.54×10^{-6} - 3.43×10^{-5} mol cm^{-3})/Br_2 (1.91×10^{-6}-1.22×10^{-5} mol cm^{-3}) mixtures with $[H_2]/[Br_2]$ in range 0.51-14.03. $[Br_2]$ measured by absorption at 591 nm, and products analysed by iodometry to determine residual $[Br_2]$, and by acidimetry to determine [HBr]. VIDAL 1971 (25)	Steady state treatment of thermal HBr synthesis mechanism $Br_2 + M \rightleftharpoons Br + Br + M$ 3,-3 $Br + H_2 \rightleftharpoons HBr + H$ -2,2 $H + Br_2 \rightarrow HBr + Br$ 1 used to express rate equation in terms of degree of reaction. Further manipulation gave linear expression of gradient $2k_2/k_1k_{-2}K_3^{\frac{1}{2}}$ and intercept $k_{-2}K_3^{\frac{1}{2}}$. From the gradient we have calculated k_1 as tabulated here with author's values of k_1/k_2 T/K k_1/k_2 $k_1/cm^3mol^{-1}s^{-1}$ 508 12.7 1.18×10^{14} 524 11.8 1.03×10^{14}

$H + Br_2 \rightarrow HBr + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		VIDAL 1971 (25) continued.	539 11.7 $1.01x10^{14}$ 550 14.4 $1.10x10^{14}$ 566 10.7 $9.97x10^{13}$
	300±5	Static photolysis system. Br_2/HCl mixtures ($[Br_2]$:$[HCl] \leq 0.17$) and $Br_2/HCl/CO_2$ mixtures ($[Br_2]:[HCl]:[CO_2] = (10^{-3}-9x10^{-3}):1:(8.2±0.1)$) photolysed at 184.9 nm. Br_2 pressures possibly in region 10-70 mm Hg (1.3-9.3 kPa). H_2 yield measured manometrically. JARDINE, BALLASH and ARMSTRONG 1973 (30)	In CO_2-moderated Br_2/HCl mixtures, H_2 yield reduced to 20% at $[Br_2]:[HCl] = 2.5x10^{-3}$. Consequently upper limit to fraction of thermal H atoms reacting with HCl set at 0.2. From steady state approximation this fraction given by $1/(1+k_1[Br_2]/k_6[HCl])$. $H + Br_2 \rightarrow HBr + Br$ 1 $H + HCl \rightarrow H_2 + Cl$ 6 Hence $k_1/k_6 \geq 1600$. Authors use $k_6=6.7x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ at 300 K (22) to give $k_1 \geq 1.1x10^{14}\ cm^3\ mol^{-1}\ s^{-1}$. Using our recommendation for k_6 (this Volume, section B5) we obtain $k_1 \geq 4.27x10^{13}\ cm^3\ mol^{-1}\ s^{-1}$.

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.5x10^{14}\ exp(-1460/T)$	600-2500	Review. Expression derived from 'best weighted' value for k_1/k_2 of (8.5±0.5) (11, 16) and k_2. FRISTROM and WESTENBERG 1965 (17)	Expression for k_2 obtained as K_2k_{-2}, using k_{-2} also derived in $H + Br_2 \rightarrow HBr + Br$ 1 $H + HBr \rightleftharpoons H_2 + Br$ 2,-2 this work.
$1.5x10^{14}\ exp(-450/T)$	Unspecified	Review. THRUSH 1965 (18)	Expression attributed to (5 and 8). Used by (20 and 23).
$7.5x10^{14}T^{-0.055}\ exp(-920/T)$	500-1700	Review. COHEN, GIEDT and JACOBS 1973 (29)	Ratio $k_1/k_2 = 5.2\ exp(550/T)$ derived from data of (15,16,24 and 25), and expression for k_1 derived from this and k_2 as also calculated in this review.

ISOTOPIC REACTION $D + Br_2 \rightarrow DBr + Br$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298-473	Static photolysis system. DBr (8-16 mm Hg; 1.07-2.13 kPa)/D_2(0 and 700 mm Hg; 93.3 kPa) mixtures photolysed at 213.9 nm. Rapid photolysis used to generate Br_2, giving $[Br_2]:[DBr]$ ratios 0.01-0.5. Absorbed light intensity by actino-	Analysis as by FASS (24) as for reaction 1 (see Comments column for latter). In pure DBr mixtures, hot D atom rates obtained as $k_{1D*}/k_{2D*} = (6.7±0.13)$, 298-393 K. $D* + Br_2 \rightarrow DBr + Br$ 1D* $D* + DBr \rightarrow D_2 + Br$ 2D* Moderated DBr/D_2 mixtures gave

$H + Br_2 \rightarrow HBr + Br$

ISOTOPIC REACTION $D + Br_2 \rightarrow DBr + Br$ - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		metry, Br_2 by absorption at 416 nm. FASS, HOOVER and SIMPSON 1972 (26)	k_{1D}/k_{2D} = (58±1.7) at 298 K, (44±2.2) at 333 K, (35±1.5) at 393 K, (36±1.5) at 428 K, and (32±0.6) at 473 K. Authors gave Arrhenius fit to these data as k_{1D}/k_{2D} = (12±2.8) exp(450±80 /T). $D + Br_2 \rightarrow DBr + Br$ 1D $D + DBr \rightarrow D_2 + Br$ 2D

Discussion

There are no absolute determinations of the rate of the chain propagating step

$$H + Br_2 \rightarrow HBr + Br \qquad (1)$$

in the synthesis of HBr. The bulk of the data comes from studies of H_2/Br_2 and $H_2/Br_2/HBr$ mixtures in static systems, reaction being initiated either thermally [1,9,25] or photolytically [7,12,24]. According to steady state treatment of the mechanism

$$Br + H_2 \rightarrow HBr + H \qquad (-2)$$

$$H + Br_2 \rightarrow HBr + Br \qquad (1)$$

$$H + HBr \rightarrow H_2 + Br \qquad (2)$$

$$Br + Br + M \rightarrow Br_2 + M \qquad (-3)$$

the rate equation for the production of HBr is obtained as a function of the quantities k_1/k_2 and $k_{-2}K_3^{1/2}$ (see Discussion of reaction -2, section C4). These quantities are easily separated, and most of the data for k_1 are presented in terms of the ratio k_1/k_2.

Photolysis of mixtures including HBr [12,24], HCl [30], or H_2S [19] requires that "hot" H atoms (H*), those with excess translational energy, be considered. These hot H atoms undergo reactions parallel to those of thermal H atoms

$$H^* + Br_2 \rightarrow HBr + Br \qquad (1^*)$$

$$H^* + HBr \rightarrow H_2 + Br \qquad (2^*)$$

and the yield of Br_2 or of H_2 must be expressed in terms of net rate constants for Br_2 and HBr removal by combinations of thermal and hot H-atoms. In the presence of large concentrations of a moderating gas hot H atoms are rapidly thermalised: complete thermalisation is indicated when the overall Br_2/HBr removal rate constant ratio R [12] becomes independent of moderator pressure [24]. Schwarz et al. [12] did not cover a sufficiently large excess of moderator to demonstrate this effect, and consequently their low temperature value for k_1/k_2 is too low. Bodenstein and Jung [7] also obtained low values for this ratio—their results have been reinterpreted by Sullivan [21] in terms of the formation of HBr and the subsequent inhibition of further reaction by the sequence

$$Br + Br + H_2 \rightarrow 2HBr \qquad (4)$$

$$Br + Br + HBr \rightarrow Br_2 + HBr \qquad (-3)$$

and not by reactions 1 and 2.

We have considered the shock tube data of Britton and Davidson [13] to be merely a preliminary assessment of k_1/k_2, superseded by the more accurate data of Britton and Cole [16].

When plotted as a simple Arrhenius function (fig. 2), the reliable data for k_1/k_2 [16,24,25] display considerable scatter. A better straight line fit to these data is obtained by plotting log (k_1/k_2T) vs. T^{-1} (fig. 3), which gives slightly higher values of k_1/k_2 than the simple Arrhenius plot at the higher temperatures. The least squares fit shown in figure 3 is given by the expression

$$k_1/k_2 = 3.64\times10^{-3}\ T\ \exp(990/T)$$

with error limits of ±40% over the temperature range 300–1700 K.

For those studies [1,9,15] in which the overall HBr production rate constant $k(=k_1k_{-2}K_3^{1/2}/2k_2)$ is presented, we have been able to calculate $k_1(=2kK_2/K_3^{1/2})$, using least squares fits to current JANAF data for K_2 and K_3 over the appropriate temperature range. The product of the parameters l and k as presented by Vidal [25] has enabled us to calculate $k_1(=10^{3/2}lkK_2/K_3^{1/2})$ from this work also.

The substantial agreement between the values of k_1 obtained by the above calculations indicates that the low temperatures value of Darwent et al. [19] is far too low: a low activation energy such as displayed by the expression given by Cohen et al. [29] is more appropriate.

We have given little weight to the data of Levy [15] who used $k_1/k_2=8.4$ over the whole temperature range of his determination of k_{-2}: this value is too low at the lower end of his temperature range (cf. fig. 2) and results in overestimated values of k_1.

Because of the scatter of the remaining reliable data for k_1 [1,9,25] we have chosen to use our expression for k_2 (see section C5) and our evaluation of the ratio k_1/k_2 (see above) to obtain k_1. Combining our two expressions for these parameters we obtain

$$k_1 = 2.28\times10^{11}\ T\ \exp(-220/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \quad \text{(A)}$$

for temperatures in the range 500–1700 K. If we take individual values from these two expressions and fit a simple Arrhenius expression to their products we obtain

$$k_1 = 5.85\times10^{14}\ \exp(-1100/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}} \quad \text{(B)}$$

over the same temperature interval. Expression (B) is not more than 10% different from expression (A) at either limit. Both expressions cannot be considered accurate to within less than a factor 2, due to the uncertainty limits imposed upon k_2 and upon k_1/k_2.

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C7 $Br + HBr \rightarrow H + Br_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	173.490	-13.514	-31.100
300	173.502	-13.473	-30.913
500	174.987	- 9.703	-18.787
1000	178.213	- 5.117	- 9.575
1500	179.803	- 3.778	- 6.459
2000	180.264	- 3.506	- 4.891
2500	180.167	- 3.548	- 3.950
3000	179.841	- 3.665	- 3.322
3500	179.439	- 3.787	- 2.876
4000	179.046	- 3.900	- 2.541
4500	178.674	- 3.979	- 2.283
5000	178.351	- 4.046	- 2.075

RECOMMENDED RATE CONSTANT

$k_1 = 2.72 \times 10^{14} \exp(-22\,340/T)$ cm^3 mol^{-1} s^{-1}

$= 4.52 \times 10^{-10} \exp(-22\,340/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 500-1700 K

Suggested Error Limits for Calculated Rate Constant: A factor of 2 over the quoted temperature range.

Note: this expression has been derived from equilibrium data and $k(H+Br_2)$.

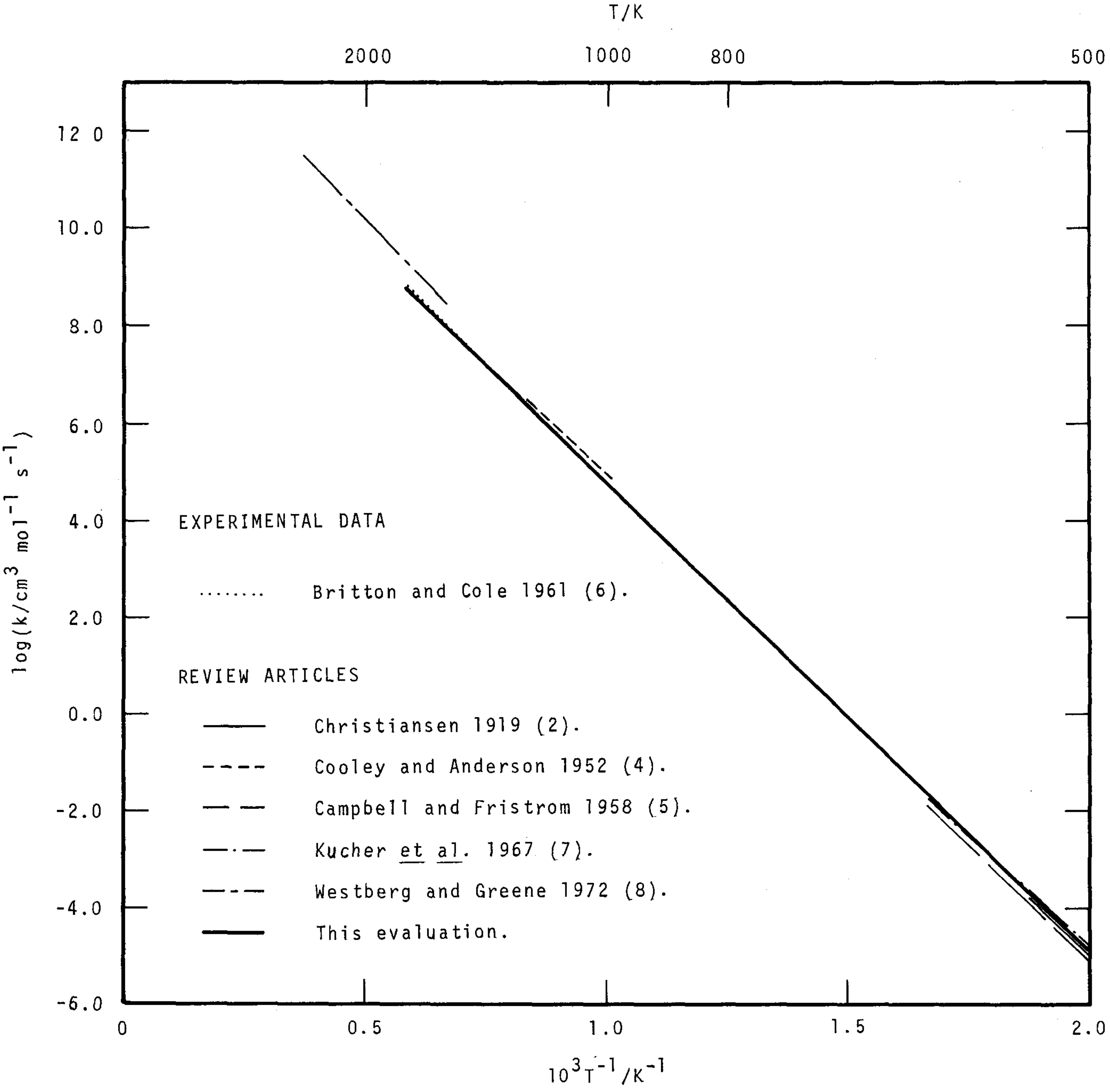
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.44 \pm 0.3$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.35 \pm 0.3$

$E/J\ mol^{-1} = 185\,770 \pm 8140$

$E/cal\ mol^{-1} = 44\,400 \pm 1950$

$Br + HBr \rightarrow H + Br_2$



Discussion

Only one experimental determination has been made of the rate constant for the reaction

$$Br + HBr \rightarrow H + Br_2, \qquad (1)$$

i.e., that of Britton and Cole [6] in which 0.5% Br_2/HBr mixtures were studied behind incident shocks at temperatures around 1600 K. $[Br_2]$ profiles were obtained by absorption at 500 nm, and by successive mass balancing (assuming [H] to be negligibly small) these profiles were converted to $[H_2]$ profiles. From a steady state analysis of the HBr mechanism values of k_1 were obtained at 25% Br_2 disappearance, in order to minimise errors in temperature estimation and in [Br]. Using the ratio k_{-1}/k_2 determined in the same work, these authors

$$H + Br_2 \rightarrow HBr + Br \qquad (-1)$$

$$H + HBr \rightarrow H_2 + Br \qquad (2)$$

obtained $k_1 = 8.1 \times 10^{12}\ T^{1/2} \exp(-22\,390/T)$ $cm^3\ mol^{-1}\ s^{-1}$, with about 10% scatter in the results. White [9] attributes the expression $k_1 = 5.1 \times 10^{14} \exp(-23\,150/T)$ $cm^3\ mol^{-1}\ s^{-1}$ to this work.

A similar expression, $k_1 = 2.6 \times 10^{13}\ T^{1/2} \exp(-22\,650/T)$ $cm^3\ mol^{-1}\ s^{-1}$, was used by Westberg and Greene [8] in their computer fitting of HBr emission profiles behind incident shocks over the temperature range 1500–2700 K.

All other quoted expressions have been derived from k_{-1} and the equilibrium constant, viz., Christiansen [2] $k_1 = 1.66 \times 10^{14} \exp(-22\,000/T)$ $cm^3\ mol^{-1}\ s^{-1}$, from the data of

Bodenstein and Lind [1]; Campbell and Fristrom [5], $k_1 = 6.45 \times 10^{10}\ T \exp(-21\,400/T)$ cm^3 mol^{-1} s^{-1}, from their own derived expression for k_2 (q.v.); Cooley and Anderson [4], $k_1 = 9.31 \times 10^{10}\ T \exp(-20\,980/T)$ cm^3 mol^{-1} s^{-1}, using "kinetic data"; and Kucher et al. [7], $k_1 = 2.95 \times 10^{13} \exp(-21\,040/T)$ cm^3 mol^{-1} s^{-1} from data of Bodenstein [1,3]. Using our recommended expression for k_{-1} we obtain

$$k_1 = 2.72 \times 10^{14} \exp(-22\,340/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the temperature range 500–1700 K. Uncertainty limits of a factor of 2 must be considered.

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C8 $Br + CH_4 \rightarrow HBr + CH_3$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	72.258	31.602	-11.008
300	72.279	31.669	-10.941
500	74.241	36.773	- 5.835
1000	75.362	38.702	- 1.915
1500	73.258	37.054	- 0.616
2000	69.806	35.079	0.008
2500	65.852	33.321	0.364
3000	61.768	31.828	0.587
3500	57.710	30.577	0.735
4000	53.752	29.522	0.840
4500	49.930	28.623	0.935
5000	46.246	27.845	0.971

RECOMMENDED RATE CONSTANT

$$k_1 = 4.7 \times 10^{13} \exp(-9180/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$= 7.8 \times 10^{-11} \exp(-9180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Temperature Range: 200-600 K

Suggested Error Limits for Calculated Rate Constant: less than a factor of 2 over the whole temperature range.

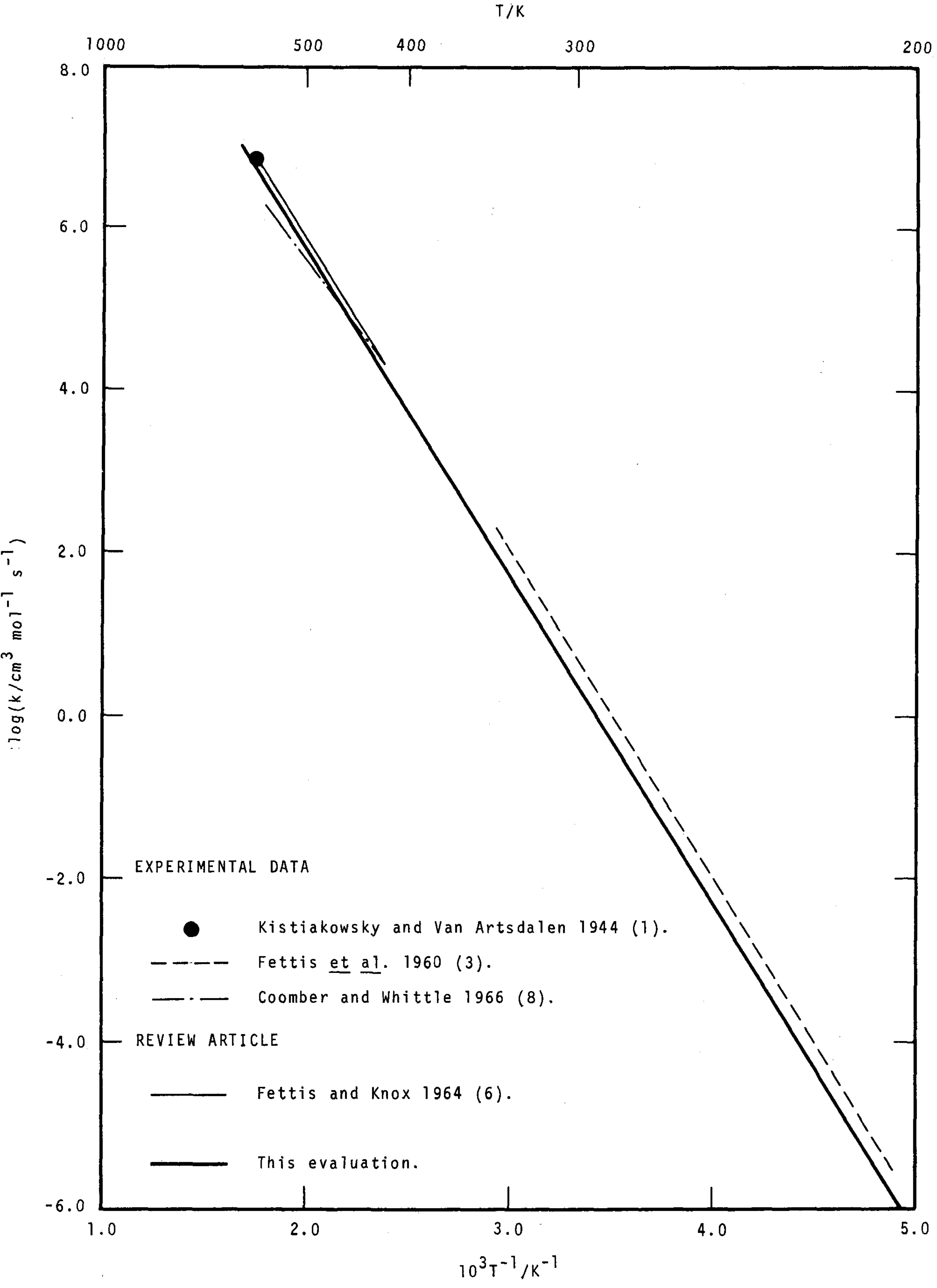
Rate Parameters: $\log(A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 13.67 \pm 0.3$

$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -10.11 \pm 0.3$

$E/\text{J mol}^{-1} = 76\ 270 \pm 3430$

$E/\text{cal mol}^{-1} = 18\ 230 \pm 820$

$Br + CH_4 \rightarrow HBr + CH_3$



$Br + CH_4 \rightarrow HBr + CH_3$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	(a) 423,453, 483,503 (b) 570	Static system. (a) Photolysis of CH_4(210-641 mm Hg; 28-85.5 kPa)/Br_2(16.3-45.8 mm Hg; 2.2-6.1 kPa) mixtures. (b) Thermal reaction of CH_4(227-517 mm Hg; 30.3-69 kPa)/Br_2 (22-55.5 mm Hg; 2.9-7.4 kPa) mixtures. [Br_2] followed by absorption at λ<436 nm. KISTIAKOWSKY and VAN ARTSDALEN 1944 (1)	(a) Rate of CH_4 photobromination given by $-d[Br_2]/dt = k[CH_4][Br_2]^{\frac{1}{2}}[M]^{-\frac{1}{2}}$, and Arrhenius plot for k gave activation energy of 76.5 kJ mol^{-1} (18.25 kcal mol^{-1}). Authors preferred expression of form $k = A'T^{\frac{1}{2}}\exp(-E'/RT)$, and quoted E' as 74.5 kJ mol^{-1} (17.8 kcal mol^{-1}). From form of kinetic equation authors ascribe this activation energy to rate-determining step, reaction 1 $Br + CH_4 \rightarrow HBr + CH_3$ 1 (b) Thermal bromination rate given by $-d[Br_2]/dt = k'[CH_4][Br_2]^{\frac{1}{2}}$, where $k' = k_1(K_2)^{\frac{1}{2}}$, assuming mechanism $Br_2 + M \rightarrow Br + Br + M$ 2 $Br + CH_4 \rightarrow HBr + CH_3$ 1 $CH_3 + Br_2 \rightarrow CH_3Br + Br$ $CH_3 + HBr \rightarrow CH_4 + Br$ -1 $Br + Br + M \rightarrow Br_2 + M$ -2 Authors quote $k' = 2.48 \times 10^{-2}\ cm^{3/2}\ mol^{-\frac{1}{2}}\ s^{-1}$ at 570 K, from which we obtain $k_1 = 6.58 \times 10^6\ cm^3\ mol^{-1}\ s^{-1}$. AMPHLETT and WHITTLE (10) recalculated k_1 as $6.53 \times 10^6\ cm^3\ mol^{-1}\ s^{-1}$. Authors give $A_1'T^{-\frac{1}{2}} = 1.48 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$. Arrhenius expression for these data given as $k_1 = 5.0 \times 10^{13}\exp(-9210/T)\ cm^3\ mol^{-1}\ s^{-1}$ by (2).
	204-341	Static photolysis of $CH_4/CH_3Cl/C_2H_6/Br_2$ mixtures at total pressures 150-200 mm Hg (20-26.7 kPa). C_2H_6 pressures 3-20 mm Hg (0.4-2.7 kPa), Br_2 pressure ∿100 mm Hg (13.33 kPa), and $[CH_3Cl]/[CH_4]$ ratio 2-5. Product analysis by gas chromatography. FETTIS, KNOX and TROTMAN-DICKENSON 1960 (3)	For low consumption of CH_4 and CH_3Cl, ratio k_1/k_3 given by $k_1/k_3 = [CH_3Cl][CH_3Br]/[CH_4][CH_2BrCl]$. $Br + CH_4 \rightarrow HBr + CH_3$ 1 $Br + CH_3Cl \rightarrow HBr + CH_2Cl$ 3 Authors give expression $k_1/k_3 = 2.78\exp(-1910/T)$. From other experiments in CH_3Cl/C_2H_6 and CH_3Br/C_2H_6 mixtures, and using $k_4 = 5.37 \times 10^{13}\exp(-8080/T)\ cm^3\ mol^{-1}\ s^{-1}$ $Br + CH_3Br \rightarrow HBr + CH_2Br$ 4 as standard, authors give $k_1 = 10^{14}\exp(-9210/T)\ cm^3\ mol^{-1}\ s^{-1}$.

$Br + CH_4 \rightarrow HBr + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	554	Static photolysis system. CH_4(25 mm Hg; 3.3 kPa)/CF_3H (534 mm Hg; 71.2 kPa)/Br_2(37 mm Hg; 4.9 kPa) mixtures. Br_2 pressures measured before and after photolysis, products analysed by gas chromatography. CORBETT, TARR and WHITTLE 1963 (5)	Approximate values given for [CF_3Br] and [CH_3Br] in products, from which authors obtained $k_1/k_5 \simeq 10^3$ $Br + CH_4 \rightarrow HBr + CH_3$ 1 $Br + CF_3H \rightarrow HBr + CF_3$ 5 Only approximate value possible due to difference between k_1 and k_5.
	(a) 396-581 (b) 398-573 (c) 419-590	Static photolysis system. (a) $CH_4/CH_3F/Br_2$ (5mm Hg; 666.5 Pa) mixtures at 110 mm Hg (14.7 kPa) total pressure. [CH_4]/[CH_3F] ratio 4.01. Products analysed for CH_3Br and CH_2BrF by gas chromatography. (b) $CH_4/CH_2F_2/Br_2$ (5mm Hg; 666.5 Pa) mixtures at 100 mm Hg (13.3 kPa) total pressure, ratio [CH_4]/[CH_2F_2] = 2.99. Product analysis as for (a). (c) $CH_4/C_2F_5H/Br_2$ (9 mm Hg; 1.2 kPa) mixtures at 125 mm Hg (16.7 kPa) total pressure, with [C_2F_5H]/[CH_4] = 2.49. Gas chromatography used to determine [CH_3Br] and [C_2F_5Br] in products. TARR, COOMBER and WHITTLE 1965 (7)	Low consumption (∿1%) of reactants enabled authors to use expressions such as $k_1/k_6 = [CH_3F](d[CH_3Br]/dt)/[CH_4](d[CH_2BrF]/dt)$ $Br + CH_3F \rightarrow HBr + CH_2F$ 6 Effects of variation of percentage Br_2 consumption and of [CH_4]/[competitor] ratio studied, and ratios k_1/k_6, k_1/k_7 and k_1/k_8 determined in most reliable ranges. $Br + CH_2F_2 \rightarrow HBr + CHF_2$ 7 $Br + C_2F_5H \rightarrow HBr + C_2F_5$ 8 From three sets of data authors determined $k_6/k_1 = (0.56\pm0.03)\exp(1250\pm20/T)$, $k_7/k_1 = (0.24\pm0.01)\exp(1010\pm20/T)$, and $k_1/k_8 = (8.88\pm0.85)\exp(362\pm45/T)$. Similar experiments in C_2F_5H/CF_3H mixtures gave k_8/k_5 $Br + CF_3H \rightarrow HBr + CF_3$ 5 and hence $k_1/k_5 = (7.2\pm0.9)\exp(1890\pm70/T)$. Authors used $k_1 = 1.4\times10^{13}\exp\{-(8710\pm500)/T\}$ cm^3 mol^{-1} s^{-1}, source unquoted. Used by (8). Ratio k_1/k_5 used by AMPHLETT and WHITTLE (10).
	(a) 419-559 (b) 369-503	Static photolysis system. (a) $CH_4/C_3F_7H/Br_2$(5 mm Hg; 666.5 Pa) mixtures, [C_3F_7H]/[CH_4] = 2.64, and (b) $CH_4/C_2H_4F_2/Br_2$ (10 mm Hg; 1.3 kPa) mixtures, [CH_4]/[$C_2H_4F_2$] = 10.1. Total pressures of all mixtures 100-130 mm Hg (13.3-17.3 kPa). Gas chromatography	Method of analysis as for (7). Authors quote ratios $k_9/k_1 = (8.5\pm0.8)\times10^{-2}\exp\{-(240\pm40)/T\}$ and $k_1/k_{10} = (4.27\pm0.2)\exp\{-(2030\pm15)/T\}$ $Br + CH_4 \rightarrow HBr + CH_3$ 1 $Br + C_3F_7H \rightarrow HBr + C_3F_7$ 9 $Br + C_2H_4F_2 \rightarrow HBr + C_2H_3F_2$ 10 Similar experiments in CF_3H/C_3F_7H mixtures gave k_9/k_5

$Br + CH_4 \rightarrow HBr + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		used for product analysis. COOMBER and WHITTLE 1966 (8)	$Br + CF_3H \rightarrow HBr + CF_3$ 5 and hence k_1/k_5 = (8.2±1.3) exp(1870±60/T). Using this ratio, together with k_1/k_5 from (7), AMPHLETT and WHITTLE (10) use average k_1/k_5 expression with absolute expression for k_5 (10) to give k_1 = (9.80±1.2)x10^{13} exp{-(9350±70)/T} cm^3 mol^{-1} s^{-1}. E_1 quoted by (11 and 12).

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Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
6.03x10^{13} exp{-(9150±280)/T}	423-570	Derived from data of KISTIAKOWSKY and VAN ARTSDALEN (1). FETTIS and KNOX 1964 (6)	Expression for k_1 from least squares treatment of data of (1) assuming E_{-2} = 0 $Br + CH_4 \rightarrow HBr + CH_3$ 1 $Br + Br + M \rightarrow Br_2 + M$ -2 Error limits on k_1 given as ±82%. COOMBER and WHITTLE (9) use k_1= 8.0x10^{13} exp(-9160/T) cm^3 mol^{-1} s^{-1}, attributed to this work.

EXPERIMENTAL DATA

ISOTOPIC REACTION $Br + CD_4 \rightarrow DBr + CD_3$

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	562-637	Static system. Br_2(∿1.9x10^{-6}-1.02x10^{-5} mol cm^{-3})/ CH_4 (∿1.80x10^{-8}-3.22x10^{-8} mol cm^{-3})/CD_4(∿8.92x10^{-9}-1.63x10^{-8} mol cm^{-3}) mixtures. Reaction products analysed for unreacted CH_4 and CD_4 by mass spectrometry. YOKOTA and TIMMONS 1970 (12)	Corrections allowed for small CD_3H impurities. Ratio k_1/k_{1D} $Br + CH_4 \rightarrow HBr + CH_3$ 1 $Br + CD_4 \rightarrow DBr + CD_3$ 1D obtained directly from ($[CH_4]_r/[CH_4]_o$)/($[CD_4]_r/[CD_4]_o$), where subscripts o and r refer to initial and remaining concentrations, respectively. Authors give results as T/K — k_1/k_{1D} 562 — 3.02 562 — 3.03 562 — 3.12 579 — 2.86 596 — 2.69 605 — 2.60 618 — 2.50 619 — 2.62 636 — 2.47 637 — 2.43 637 — 2.51 No variation of k_1/k_{1D} found with reacted fraction of (CH_4+CD_4).

Discussion

The only absolute data for the rate of the bromine atom reaction with methane

$$Br + CH_4 \rightarrow HBr + CH_3 \qquad (1)$$

are those of Kistiakowsky and Van Artsdalen [1], who only obtained one value for k_1, at 570 K, from the thermal CH_4 bromination rate. These authors also attributed the activation energy of the CH_4 photobromination rate (76.5 kJ mol^{-1}; 18.25 kcal mol^{-1}) to reaction 1 (although they preferred the form $k_1=A'T^{1/2}\exp(-E'/RT)$). The latter identification is correct as long as reaction –2 has zero activation energy which is approximately true.

$$\mathrm{Br + Br + M \rightarrow Br_2 + M} \qquad (-2)$$

Fettis et al. [3], and Coomber and Whittle [8], obtained expressions for k_1 from rates relative to k_4 and k_5, respectively.

$$\mathrm{Br + CH_3Br \rightarrow HBr + CH_2Br} \qquad (4)$$

$$\mathrm{Br + CF_3H \rightarrow HBr + CF_3} \qquad (5)$$

Consequently, although no data may be directly compared, we present as a *tentative recommendation* the expression

$$k_1 = 4.70\times10^{13} \exp(-9180/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 200–600 K, derived from all the available results. This expression should be considered within error limits of a factor 2.

Rate of the Reverse Reaction

Kerr and Parsonage [13] have summarised the available data on the reverse reaction and their evaluation led to a

$$\mathrm{CH_3 + HBr \rightarrow Br + CH_4} \qquad (-1)$$

recommendation of the expression of Fettis and Trotman-Dickenson [4], $k_{-1}=5.37\times10^{12} \exp(-810/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 300–500 K. Error limits were estimated as $\pm100\%$.

Taking this recommendation and our own recommended expression for k_1, we derive an equilibrium constant K_1 at 298 K that is lower by 50% than the value presented in the Thermodynamic Data for this section. The value of $\Delta H^\circ_{f,298}(\mathrm{CH_3})$ derived from this K_1 is 147.1 kJ mol^{-1} (35.2 kcal mol^{-1}). This is higher by 6.3 kJ mol^{-1} (1.5 kcal mol^{-1}) than the value derived in section B7.

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C9 $O + HBr \rightarrow Br + OH$

THERMODYNAMIC DATA

T (K)	ΔH^o ($kJ\ mol^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	log K
200	-61.12	-0.92	15.92
298	-61.16	-1.03	10.66
300	-61.16	-1.04	10.59
500	-61.22	-1.19	6.33
1000	-61.68	-1.80	3.13
1500	-62.10	-2.15	2.05
2000	-62.07	-2.14	1.51
2500	-61.74	-1.98	1.19
3000	-61.29	-1.82	0.97
3500	-60.88	-1.70	0.82
4000	-60.56	-1.62	0.71
4500	-60.40	-1.57	0.62
5000	-60.39	-1.57	0.55

RECOMMENDED RATE CONSTANT

$$k = 2.4 \times 10^{12} \exp(-1360/T)\ cm^3\ mol^{-1}\ s^{-1}$$
$$= 4.0 \times 10^{-12} \exp(-1360/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

Temperature Range: 265-430 K.

Suggested Error Limits for Calculated Rate Constant: ±50% at 298 K rising to a factor of 2 at 265 and 430 K.

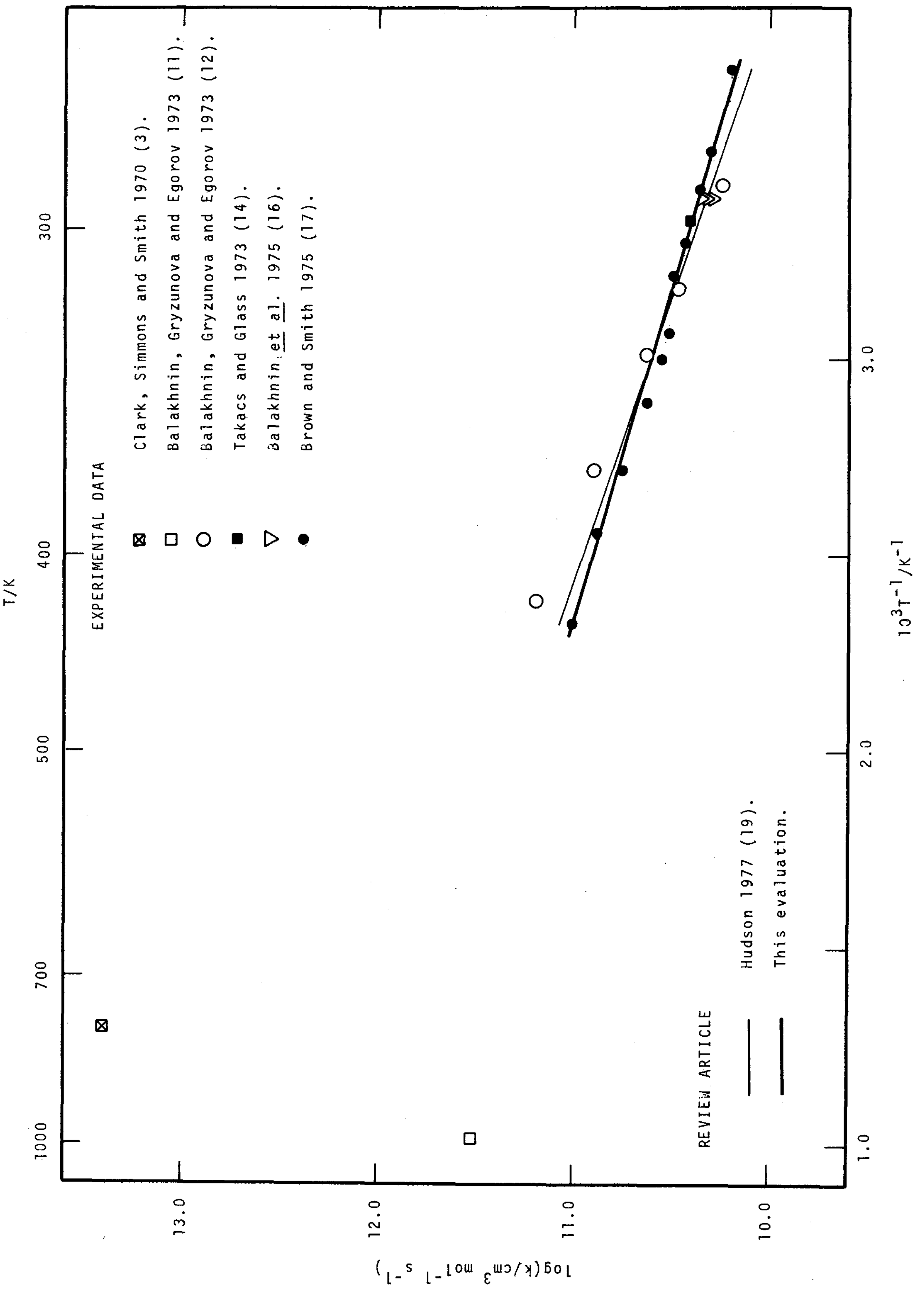
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 12.4 \pm 0.3$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -11.4 \pm 0.3$

$E/J\ mol^{-1} = 11\ 310 \pm 8100$

$E/cal\ mol^{-1} = 2\ 700 \pm 1935$

O + HBr → Br + OH

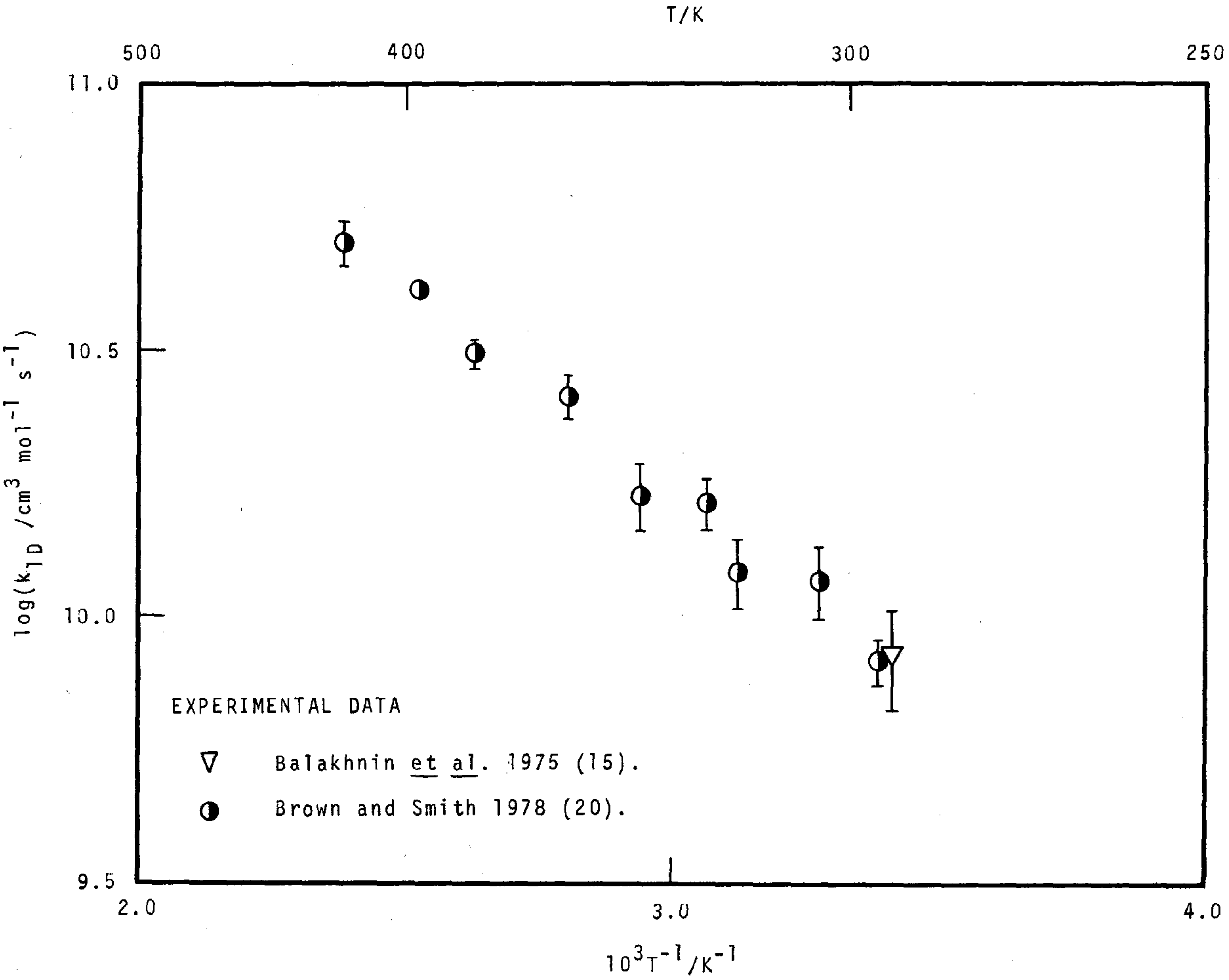

T/K
300
400
500
700
1000
EXPERIMENTAL DATA
☒ Clark, Simmons and Smith 1970 (3).
□ Balakhnin, Gryzunova and Egorov 1973 (11).
○ Balakhnin, Gryzunova and Egorov 1973 (12).
■ Takacs and Glass 1973 (14).
▽ Balakhnin et al. 1975 (16).
● Brown and Smith 1975 (17).
REVIEW ARTICLE
Hudson 1977 (19).
This evaluation.
13.0
12.0
11.0
10.0
log(k/cm^3 mol^{-1} s^{-1})
1.0
2.0
3.0
10^3T^{-1}/K^{-1}

$O + HBr \rightarrow Br + OH$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.5×10^{13}	773	Static system. Mixtures of H_2 (mol fraction 0.07-0.86), O_2 (mol fraction 0.07-0.72) and HBr (mol fraction 1×10^{-4}-5×10^{-4}) and N_2. Pressure at second explosion limit monitored. CLARK, SIMMONS and SMITH 1970 (3)	Variation of second explosion limit as function of [HBr] measured using pressure reduction by gas withdrawal technique. Multi-step reaction mechanism proposed from which complex expression for overall rate derived. Numerical integration of this expression by computer using literature values for rate $O + HBr \rightarrow Br + OH$ 1 constants where known (3 values other than k_1 unknown) enabled value for k_1 commensurate with experimental data to be estimated. Authors note error limits are large. Three of the 'known' rate constants appear to be either quoted or calculated incorrectly. Quoted by (14).
	984	Flame study. HBr(0.1%) inhibited H_2/O_2 mixtures (1:1.25) plus Ar at total pressure of 1.8 mm Hg (240 Pa). [H], [O] and [OH] monitored by esr. BALAKHNIN, GRYZUNOVA and EGOROV 1973 (11)	[Br] below detection threshold. Authors gave two values for k_1, 2×10^{12} $cm^3\ mol^{-1}\ s^{-1}$ and 1.2×10^{12} $cm^3\ mol^{-1}\ s^{-1}$, both calculated incorrectly using $k_2=1.55\times10^{12}$ $OH + H_2 \rightarrow H_2O + H$ 2 $O + OH \rightleftharpoons H + O_2$ 3,-3 $O + H_2 \rightarrow H + OH$ 4 $H + HBr \rightarrow Br + H_2$ 5 $cm^3\ mol^{-1}\ s^{-1}$, $k_{-3}=3.1\times10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$, $k_4=1.6\times10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$ (6), $k_5=1.11\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ (7) and $k_3/k_{-3}=270$ (2). We calculate $k_1=3.3\times10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$ from these data.
1.8×10^{10} 3.0×10^{10} 4.3×10^{10} 7.9×10^{10} 1.54×10^{11}	290 314 332 368 420	Discharge flow system. Excess HBr added to O atoms in Ar at total pressure of 0.72 mm Hg (96 Pa). [O] monitored by esr. BALAKHNIN, GRYZUNOVA and EGOROV 1973 (12)	Authors considered that as [HBr] >>[O], role played by reaction 3 $OH + HBr \rightarrow Br + H_2O$ 6 was negligible, OH from reaction 1 being removed essentially completely by reaction 6. Deduced that observed rate constant was k_1. Calculated $k_1=1.4\times10^{13}\exp(-1910/T)$ $cm^3\ mol^{-1}\ s^{-1}$.

$O + DBr \rightarrow Br + OD$



$O + HBr \rightarrow Br + OH$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(2.6\pm0.6)\times10^{10}$	298	Discharge flow system. Excess HBr (6.4×10^{-10}-5.9×10^{-9} mol cm^{-3}) added to O atoms (1.5×10^{-10}-6.4×10^{-10} mol cm^{-3}) in Ar(2.1×10^{-8}-5.3×10^{-8} mol cm^{-3}) produced either by titration of N atoms with NO or by discharge through O_2. [O], [OH], [Br] and [H] monitored by esr. TAKACS and GLASS 1973 (14)	Both growth of [Br] and decay of [O] monitored. Data interpreted in terms of mechanism comprising reactions 1,3,5 and 6. k_1 values calculated from computer simulation of data using $k_5=2.0\times10^{12}$ cm^3 mol^{-1} s^{-1}, $k_6=3.1\times10^{12}$ cm^3 mol^{-1} s^{-1} (13) and $k_3=2.6\times10^{13}$ cm^3 mol^{-1} s^{-1} (4). Quoted value is an average of 11 determinations.
2.05×10^{10} (2 points)	293	Discharge flow system. O_2/He mixture passed through discharge, and HBr/He mixtures added downstream, such that [HBr] in excess over [O] by more than 2 orders of magnitude: $1.8\times10^{-9}\leqslant[HBr]\leqslant6.6\times10^{-9}$ mol cm^{-3}, $1.7\times10^{-11}\leqslant[O]\leqslant9.1\times10^{-11}$ mol cm^{-3}. Total pressures 1.5-2.5 mm Hg (200-333.3 Pa). Variety of surface coatings used. Esr spectrometry used to determine [O]. BALAKHNIN, DEMENT'EV, EGOROV and KONDRATIEV 1975 (16)	Reaction mechanism describing [O] in presence and absence of HBr taken as $O + HBr \rightarrow Br + OH$ 1 $OH + HBr \rightarrow Br + H_2O$ 6 $O + OH \rightarrow H + O_2$ 3 $H + HBr \rightarrow Br + H_2$ 5 giving overall rate constant nk_1. Assuming [OH] in steady state n given by expression involving k_3 and k_6. Taking $k_3=3.10\times10^{12}$ and $k_6=2.60\times10^{13}$ cm^3 mol^{-1} s^{-1} (4) at 298 K, authors found $n\simeq1.0$. Lowest values of k_1 obtained on fluorinated hydrocarbon surface coating. Analysis of possible mechanisms involving heterogeneous reactions showed higher values of k_1 obtained on H_3PO_4 and H_3BO_3 to be consistent with such mechanisms. Values at 293 K converted to values (2.29-2.59)$\times10^{10}$ cm^3 mol^{-1} s^{-1} at 298 K, assuming $E_1=15.9$ kJ mol^{-1} (3.8 kcal mol^{-1}). Expression $k_1=1.57\times10^{13}\exp(-1510/T)$ cm^3 mol^{-1} s^{-1} (310-403 K) attributed in this work to (8), but there is no mention of reaction 1 in latter.
2.17×10^{10}	293		
2.35×10^{10}	293		

$O + HBr \rightarrow Br + OH$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.6\pm0.2)\times10^{10}$	267	Discharge flow study. Excess HBr added to O atoms, produced by titrating N atoms with NO, in N_2 at 1.5-2.0 mm Hg (200-267 Pa). [O] monitored spectroscopically by NO+O afterglow. BROWN and SMITH 1975 (17)	Authors suggested mechanism consisting of reactions 1,3,5,6, 7,8 and 9. $O + Br_2 \rightarrow Br + BrO$ 7 $O + BrO \rightarrow Br + O_2$ 8 $Br + wall \rightarrow \frac{1}{2} Br_2$ 9 O atom wall decay shown to be negligible. Measured k_9=3.2 s^{-1} and used this together with k_3= 2.5×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ (10), k_5= $6.6\times10^{13}\exp(-1005/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (13), k_6=3.1×10^{12} $cm^3\ mol^{-1}\ s^{-1}$ (13), k_7=5.2×10^{12} $cm^3\ mol^{-1}\ s^{-1}$ (9) and k_8=4.0×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ (5), to run computer simulation of data from which listed k_1 values were derived. Calculated $k_1=(2.4\pm0.4)\times10^{12}\exp\{-(1360\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. Used by (18).
$(2.0\pm0.1)\times10^{10}$	283		
$(2.3\pm0.1)\times10^{10}$	291		
$(2.7\pm0.1)\times10^{10}$	303		
$(3.1\pm0.3)\times10^{10}$	311		
$(3.2\pm0.3)\times10^{10}$	326		
$(3.6\pm0.2)\times10^{10}$	333		
$(4.2\pm0.2)\times10^{10}$	346		
$(5.5\pm0.2)\times10^{10}$	368		
$(7.6\pm0.3)\times10^{10}$	391		
$(9.9\pm1.0)\times10^{10}$	419		
$(10.7\pm0.7)\times10^{10}$	430		

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Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.58\times10^{12}\exp(-1571/T)$	267-430	Preferred expression. Based on data of (14 and 17). HUDSON 1977	Expression for use in modelling of effects of halogenated methanes on stratospheric ozone.

ISOTOPIC REACTION $O + DBr \rightarrow Br + OD$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(8.43\pm1.8)\times10^{9}$	293	Discharge flow system. O_2/He mixture passed through discharge, and DBr/He mixtures added downstream. $1.83\times10^{-9} \leqslant [DBr] \leqslant 3.49\times10^{-9}$ mol cm^{-3}, and $[O] \approx 1.7\times10^{-11}$ mol cm^{-3}. Total pressures 2.4 mm Hg (320 Pa). [O] measured by esr spectrometry. BALAKHNIN, DEMENT'EV and EGOROV 1975 (15)	Method as for reaction 1 in (16, above). Value for k_{1D} at 293 K obtained in freshly treated (fluorinated hydrocarbon coating) reactor $O + DBr \rightarrow Br + OD$ 1D Further experiments at higher temperatures (303-355 K) gave values of k_{1D} expressed as k_{1D}= $8.43\times10^{12}\exp(-1810/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Extrapolation to 293 gave k_{1D} higher by factor 2 than original value. Authors confirmed by observing establishment of steady state [O] that this was due to decreased effectiveness, at high temperatures, of surface coating in reducing heterogeneous effects.

O + HBr → Br + OH

ISOTOPIC REACTION O + DBR → BR + OD - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(8.19\pm0.8)\times10^{9}$	295	Discharge flow system. O atoms produced by titrating N atoms with NO, in N_2 at pressures probably as for (17). Excess DBr added, giving 8<[DBr]/[O]<129. NO_2 afterglow monitored spectroscopically. BROWN and SMITH 1978 (20)	First order plot of variation of afterglow intensity with distance from DBr input gave values of k_{1D}, as in (17). Stoichiometry calculated as always <1.3. These data expressed as $k_{1D}=(3.49\pm0.3)\times10^{12}\exp\{-(1760\pm100)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$.
$(1.16\pm0.2)\times10^{10}$	305		
$(1.20\pm0.2)\times10^{10}$	320		
$(1.63\pm0.2)\times10^{10}$	326		
$(1.69\pm0.2)\times10^{10}$	340		
$(2.59\pm0.2)\times10^{10}$	356		
$(3.10\pm0.2)\times10^{10}$	380		
$(4.10\pm0.1)\times10^{10}$	396		
$(5.03\pm0.5)\times10^{10}$	419		

Discussion

In common with many bromine compounds, hydrogen bromide is a known combustion inhibitor. Among other reactions of HBr, that with oxygen atoms is almost certainly of importance in these

$$O + HBr \rightarrow Br + OH \qquad (1)$$

systems.

The first estimate of k_1, obtained by Clark, Simmons and Smith [3] at 773 K using a computer simulation of the overall reaction data for the effect of HBr inhibition on the second explosion limit of H_2/O_2 mixtures, is in poor agreement with extrapolations from subsequent data. In addition two other observations suggest that this estimate is unreliable. First the authors note that the computed fits to the data were insensitive to the magnitude of k_1 within wide limits, and secondly, an examination of the rate constants employed in the calculation shows that at least three of them have been evaluated incorrectly.

The second determination of k_1 is equally unreliable despite its apparent fair agreement with the extrapolations from lower temperature data. In the report of this work Balakhnin, Gryzunova and Egorov [11] give two different values for k_1, neither of which has been calculated correctly! Values of the rate constants for reactions 2,3,–3,4 and 5 are required for this computation. Unfortunately the expression for k_1 derived from the proposed

$$OH + H_2 \rightarrow H + H_2O \qquad (2)$$

$$O + OH \rightleftharpoons H + O_2 \qquad (3,-3)$$

$$O + H_2 \rightarrow H + OH \qquad (4)$$

$$H + HBr \rightarrow Br + H_2 \qquad (5)$$

mechanism involves differences of large terms of similar magnitude in both the numerator and denominator and its value is therefore very sensitive to those of the input data and rate constants. Consequently these measurements cannot yield k_1 with any degree of accuracy, except fortuitously.

Four discharge flow system investigations of reaction 1 have been carried out. Both Takacs and Glass [14], who confined their studies to room temperature, Balakhnin et al. [16], and Brown and Smith [17] considered the effects of fast secondary reactions. Computer simulations of the data to correct for these were used in the derivation of k_1 by [14] and [17]. These three sets of results are in excellent agreement. In their earlier study, Balakhnin et al. [12] assumed that as HBr was in large excess in their experiments (reactant concentrations were unfortunately not reported in [12]), atoms would only be removed by reaction 1 and secondary reactions were neglected in consequence. The experimental rate constant for O atom removal was therefore equated directly with k_1. The values obtained are in good agreement with the other data at low temperatures but are somewhat larger at higher temperatures resulting in a predicted activation energy (and Arrhenius *A*-factor) that is larger than that found by Brown and Smith.

We consider that the Arrhenius expression derived by Brown and Smith [17] is the best expression currently available for calculating k_1 in the temperature range 265–430 K. We recommend

$$k_1 = 2.4\times10^{12}\exp(-1360/T)\ cm^3\ mol^{-1}\ s^{-1}$$

that it be used with error limits of ±50% at 298 K rising to a factor of two at 265 and 430 K.

Rate of the Reverse Reaction

There are no experimental data available for the rate of the

$$Br + OH \rightarrow O + HBr \qquad (-1)$$

reverse reaction between Br atoms and OH radicals. Mayer and Schieler have however estimated $k_{-1}=5.8\times10^{11}T^{0.5}$ $\exp(-7500/T)$ $cm^3\ mol^{-1}\ s^{-1}$ using the Johnston-Parr method [1]. Combining our recommended expression for k_1 with the equilibrium constant $K_{1,-1}$ calculated from known thermodynamic data enables us to derive

$$k_{-1} = 2.75\times10^{12}\exp(-8715/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the temperature range 265–430 K, with error limits of a factor of 2.

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Note Added in Proof

Singleton and Cvetanovic (Can. J. Chem. **56**, 2934 (1978)) have determined the rate constant for reaction 1

$$\mathrm{O} + \mathrm{HBr} \rightarrow \mathrm{OH} + \mathrm{Br} \qquad (1)$$

by the phase shift method. Oxygen atoms were generated by modulated mercury photosensitised decomposition of N_2O and were monitored by the chemiluminescence from their reaction with NO. Measurements of k_1 over the temperature range 298–554 K could be represented by $k_1 = (8.09 \pm 0.86) \times 10^{12} \exp\{-(1800 \pm 40)/T\}$ cm^3 mol^{-1} s^{-1}. This expression is in agreement with our recommended expression within the quoted error limits.

Our expression is based on experimental results from discharge flow studies in which secondary reactions and wall reactions complicate the determinations. The phase shift method is largely free of such complications and it therefore suggests that our recommended energy of activation and A factor may be slightly low.

C10 $OH + HBr \rightarrow Br + H_2O$

THERMODYNAMIC DATA

T (K)	ΔH^o (KJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-133.22	46.43	36.97
300	-133.23	46.49	36.73
500	-134.00	52.20	20.64
1000	-134.77	62.24	8.49
1500	-134.45	68.93	4.41
2000	-133.21	74.07	2.37
2500	-131.53	78.30	1.14
3000	-129.59	81.90	0.36
3500	-127.55	85.01	-0.27
4000	-125.54	87.76	-0.71
4500	-123.60	90.22	-1.05
5000	-121.74	92.43	-1.32

RECOMMENDED RATE CONSTANT

$k = 2.9 \times 10^{12}$ cm^3 mol^{-1} s^{-1}

$= 4.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}

Temperature: 295 K.

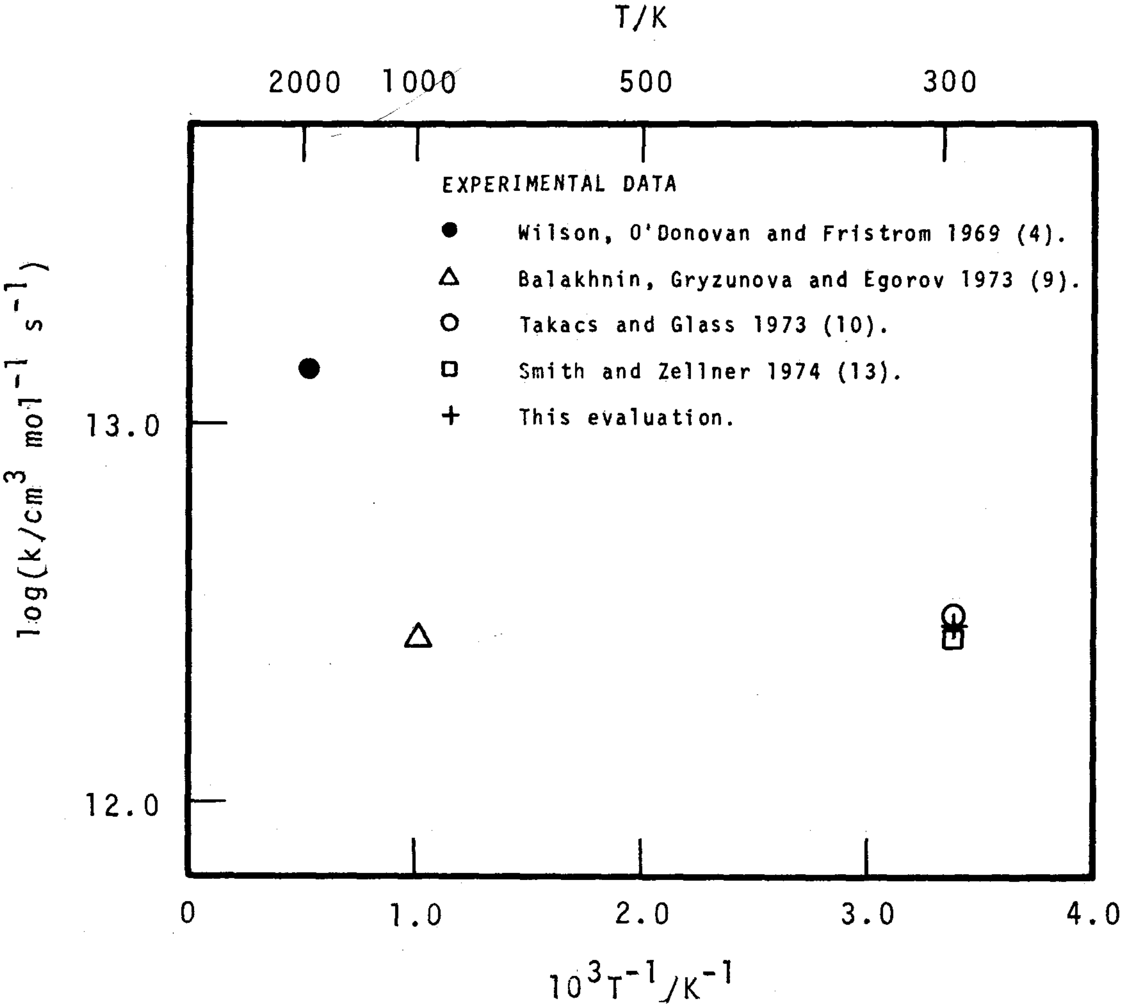
Suggested Error Limits for Rate Constant:

a factor of 3.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	1875-1975	Flame study. HBr inhibited CH_4/O_2 mixtures at 0.05 atm (5.07 kPa) total pressure. $[CH_4]$, $[HBr]$, $[CO]$, $[CO_2]$ and other species monitored by mass spectrometric probe. WILSON, O'DONOVAN and FRISTROM 1969 (4)	OH concentration profiles computed by authors using $k_2=5.8 \times 10^{11} \exp(-483/T)$ cm^3 mol^{-1} s^{-1} $OH + HBr \rightarrow H_2O + Br$ 1 $OH + CO \rightarrow CO_2 + H$ 2 (3), thereby deriving $k_1=1.6 \times 10^{13}$ cm^3 mol^{-1} s^{-1}. Using our value $k_2=6.76 \times 10^{10} \exp(9.07 \times 10^{-4}T)$ cm^3 mol^{-1} s^{-1} (Volume III, p.203), we calculate $k_1=1.4 \times 10^{13}$ cm^3 mol^{-1} s^{-1}. Reported by (7) with error limits for log k_1 of ±0.5. Quoted by (13,14). Used by (10).

$OH + HBr \rightarrow Br + H_2O$



$OH + HBr \rightarrow Br + H_2O$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	*Temperature* (K)	*Method and Reference*	*Comments*
	984	Flame study. HBr (0.1%) inhibited H_2/O_2 mixtures (1:1.25) plus Ar, at 1.8 mm Hg (240 Pa). [H], [O] and [OH] measured by esr. BALAKHNIN, GRYZUNOVA and EGOROV 1973 (9)	[Br] below detection threshold. Authors give two values for k_1, $OH + H_2 \rightarrow H_2O + H$ 3 $H + O_2 \rightarrow OH + O$ 4 $O + OH \rightarrow H + O_2$ 5 $O + H_2 \rightarrow OH + H$ 6 $H + HBr \rightarrow H_2 + Br$ 7 1.75×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ and 1.4×10^{13} $cm^3\ mol^{-1}\ s^{-1}$, both apparently incorrectly calculated using $k_3 = 1.55 \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$, $k_4 = 3.1 \times 10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$, $k_6 = 1.6 \times 10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$ (8), $k_7 = 1.11 \times 10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ (6), and $k_5/k_4 = 270$ (1). We calculate $k_1 = 2.7 \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ from these data (1,6,8).
$(3.1 \pm 0.6) \times 10^{12}$	295	Discharge flow system. HBr ($4.1\text{-}6.6 \times 10^{-10}$ mol cm^{-3}) added to OH (ca. $2.4\text{-}6.2 \times 10^{-11}$ mol cm^{-3}). [OH] and [Br] monitored by esr spectroscopy. TAKACS and GLASS 1973 (10)	Pseudo first-order conditions. Br combination eliminated by fluorohalocarbon flow-tube wall coating. [Br] produced equated with [HBr] consumed. Minor effects of reactions 5,7,8 and 9 $OH + OH \rightarrow H_2O + O$ 8 $OH \rightarrow wall$ allowed for in k_1 calculation by computer fit of data using measured k_8 and k_9 values of 9.64×10^{11} $cm^3\ mol^{-1}\ s^{-1}$ and 60 s^{-1} respectively. Derived $k_1 = (2.2 \pm 0.4) \times 10^{13} \exp(-(580 \pm 70)/T)$ $cm^3\ mol^{-1}\ s^{-1}$ using k_1 from (4). Used by (12). Quoted by (11,13,14,15,16,17).
$(2.7 \pm 0.6) \times 10^{12}$	295	Flash photolysis study. Either H_2O/HBr or $N_2O/H_2/HBr$ mixtures (unspecified); $\lambda > 165$ nm. [OH] monitored by time resolved resonance absorption. SMITH and ZELLNER 1974 (13)	Preliminary study. Rate constant obtained by matching observed [OH] decay to artificially generated exponential by procedure analogous to that used by these authors to investigate the reaction rate of OH with HCl (see this Volume, section B9)
		REVIEW ARTICLE	
3.5×10^{14}	1000	Selected value. CREITZ 1970 (5)	Based on assumption that $E_1 = 0$, estimate of $k_1/k_{10} = 160$, (2), $OH + CH_4 \rightarrow H_2O + CH_3$ 10 and $k_{10} = 2.65 \times 10^{13} \exp(-2515/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Not plotted.

Discussion

Both hydrogen and hydrocarbon fuel flames are known to be inhibited by hydrogen bromide, as a result of reactions that partially remove the flame propagating chain carriers. One such participating process is reaction 1.

$$OH + HBr \rightarrow Br + H_2O \qquad (1)$$

Very few measurements of its rate have been carried out. Wilson, O'Donovan and Fristrom [4] attempted to obtain k_1 by studying the structure of HBr inhibited CH_4/O_2 flames at 1875–1975 K. Mass spectrometry was used to monitor the concentrations of various molecular species present in the flame. Their derived value for k_1, 1.6×10^{13} cm^3 mol^{-1} s^{-1}, depends on the value chosen for k_2.

$$OH + CO \rightarrow H + CO_2 \qquad (2)$$

Unfortunately there are no other measurements of k_1 in this temperature regime and its accuracy is therefore difficult to assess. We consider however that in view of the fact that the method used for its determination is both chemically complex and involves unproven assumptions concerning the reaction mechanism, it is unreliable. Furthermore the k_{11} value derived by these

$$OH + HCl \rightarrow Cl + H_2O \qquad (11)$$

authors [4] using the same experimental methods appears to be in error (section B9).

Balakhnin, Gryzunova and Egorov [9] studied the HBr inhibition of a hydrogen/oxygen flame by measuring the concentrations of the H, O and OH present with an e.s.r. spectrometer. Their data were analysed by applying a kinetic analysis to a reaction scheme comprising the usual hydrogen/oxygen reaction mechanism plus the reactions of OH, H and O with HBr. In deriving k_1 it was necessary that rate constants for all of these processes except the latter be known, together with the active concentrations of H, O, OH, H_2 and O_2. Values of k_1 thus calculated are however sufficiently sensitive to the magnitude of these substituted parameters that their associated errors introduce an order of magnitude uncertainty in k_1. We therefore reject the value obtained and consider that under the experimental conditions employed, no useful information concerning the rate of reaction 1 can be obtained.

Only one discharge flow study has been carried out to investigate reaction 1. In this Takacs and Glass [10] added excess HBr to a stream of OH radicals, produced by the fast reaction of H atoms with NO_2, in argon. E.s.r. spectrometry was used to follow the decay of the OH radicals. In computing k_1, found to be $(3.1\pm0.6)\times10^{12}$ cm^3 mol^{-1} s^{-1} at 295 K, due account was taken of the minor effects of OH decay both at the wall and by self reaction. This value is in good agreement with that obtained by Smith and Zellner [13] in their preliminary flash photolysis study, ($k_1=(2.7\pm0.6)\times10^{12}$ cm^3 mol^{-1} s^{-1} at 295 K). Very few experimental details, other than the implication that resonance absorption was used to monitor OH concentrations, are given for this investigation. One difficulty noted by the authors however, was that repeated flashing of the same photolysis mixture led to an increased decay rate for OH. Results were therefore limited to those gas mixtures that had only been photolysed once.

We consider that the best available value for k_1 is

$$k_1 = 2.9\times10^{12}\ cm^3\ mol^{-1}\ s^{-1};\ T=295\ K$$

obtained by averaging the results of [10] and [13]. Error limits of a factor of three are appropriate for this value. A comparison of the rate constants for the reactions of OH with HX, where X=Cl,

$$OH + HCl \rightarrow Cl + H_2O \qquad (11)$$

$$OH + HI \rightarrow I + H_2O \qquad (12)$$

Br and I shows that, as expected, $k_{11}<k_1<k_{12}$, that is the reaction becomes faster as the exothermicity increases, and it would be somewhat surprising if E_1 were to exceed 3.45 kJ mol^{-1} (0.83 kcal mol^{-1}), the recommended value for E_{11}.

There are no experimental data for analogous reactions to 1 of OD and/or DBr.

Rate of the Reverse Reaction

There are no data for reaction −1. Combining our

$$Br + H_2O \rightarrow OH + HBr \qquad (-1)$$

recommended value for k_1 with the known thermodynamic data leads to

$$k_{-1} = 1.1\times10^{-25}\ cm^3\ mol^{-1}\ s^{-1}$$

with error limits of a factor of 3 at 295 K.

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C11 $HBr + O_2 \rightarrow Br + HO_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	169.222	-1.184	-29.709
300	169.218	-1.201	-29.525
500	168.946	-1.958	-17.752
1000	169.481	-1.280	- 8.919
1500	170.594	-0.389	- 5.961
2000	171.992	0.414	- 4.469
2500	173.247	0.975	- 3.568
3000	174.100	1.289	- 2.964
3500	174.456	1.402	- 2.530
4000	174.335	1.368	- 2.205
4500	173.778	1.238	- 1.952
5000	172.870	1.050	- 1.751

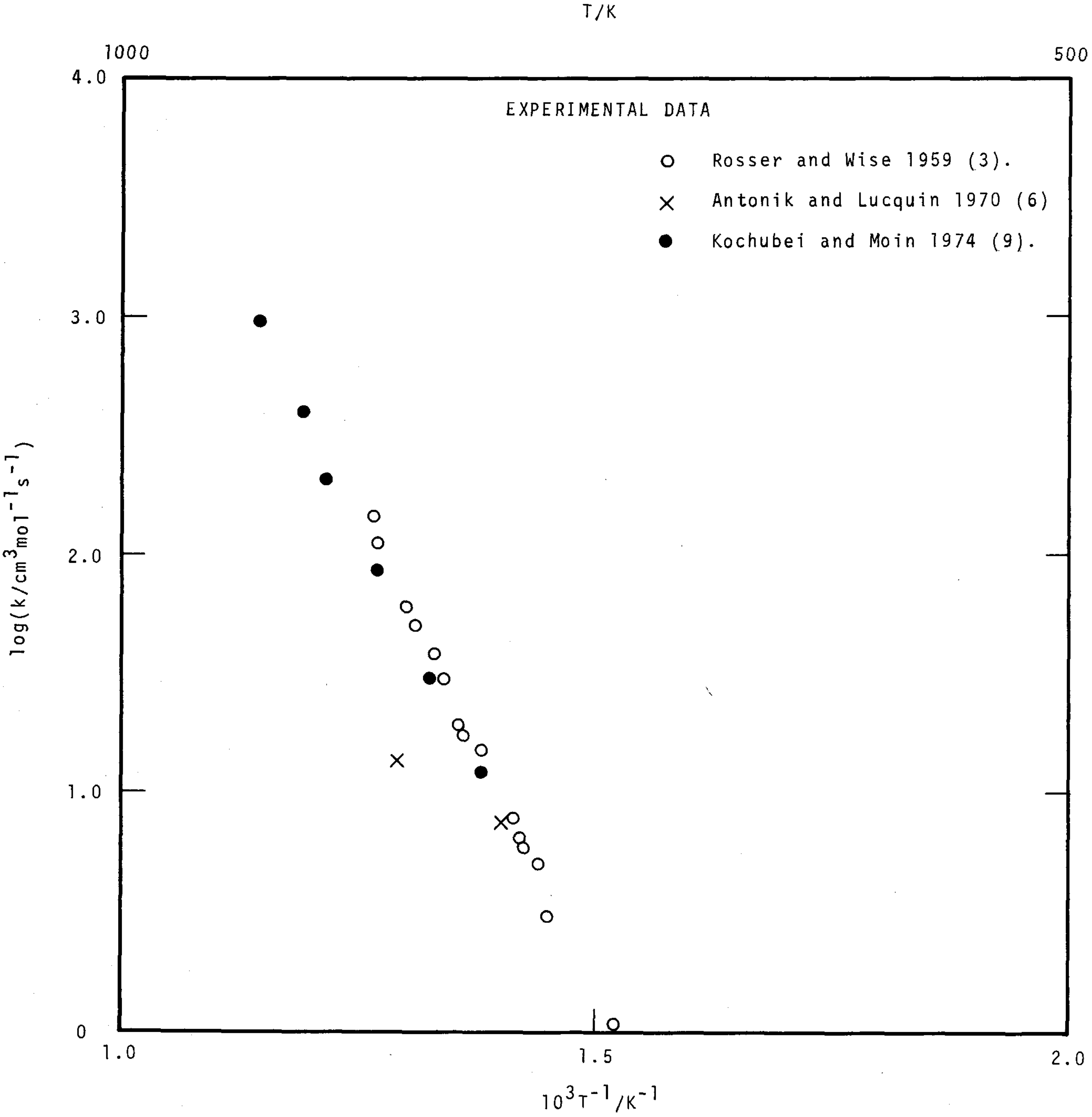
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1.1	658	Static system. HBr/O_2 mixtures, both reactants at 0.58-66.5 kPa pressure, total pressure $\not>$80 kPa. $[Br_2]$ followed by absorption of light at 420 nm. Overall reaction followed manometrically. ROSSER and WISE 1959 (3)	Reaction 1 assumed to be initiation step in 6-step mechanism, with Br atoms rapidly removed by reaction 2. $HBr + O_2 \rightarrow Br + HO_2$ 1 $Br + Br + M \rightarrow Br_2 + M$ 2 Reaction studied in several vessels and found to be totally homogeneous. Authors derive the expression $k_1 = 3.0 \times 10^{12} \exp(-19\ 000/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 700-800 K. Quoted by (7 and 9).
3.0	688		
5.0	694		
5.7	702		
6.3	704		
7.6	707		
15.0	726		
17.0	733		
19.0	738		
30.0	746		
38.0	754		
50.0	762		
63.0	768		
1.1×10^2	787		
1.4×10^2	791		

$HBr + O_2 \rightarrow HO_2 + Br$



$HBr + O_2 \rightarrow Br + HO_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
7.0	713	Static system. HBr (1.5-10%)/O_2 mixtures at a total pressure of 66.7 kPa. Reaction followed by periodic determination of pH and by polarographic methods. No further details given. ANTONIK and LUCQUIN 1970 (6)	Oxidation found to be slow, only 25% of HBr being removed at 713 K and 50% at 773 K, in an hour. It was found to be first order in HBr, and thus the authors concluded reaction 1 to be the rate-determining initial step, although their subsequent mechanism is different from that in (3). Rate constants have been calculated, but do not agree with the figure of 151 kJ mol^{-1} (36 kcal mol^{-1}) given by them for E_1. E_1 quoted by (9).
14.0	773		
12.0	723	Static system. HBr (4-80%)/O_2 (0.35-4%)/N_2 or He mixtures at a total pressure of 1 atm. (101 kPa). $[O_2]$ followed by gas chromatography. KOCHUBEI and MOIN 1974 (9).	Third bodies had no effect. An overall expression k_1=1.2x10^{12} exp(-18 300/T) cm^3 mol^{-1} s^{-1} was obtained from the experimental data, in good agreement with (3).
30.0	754		
89.0	787		
2.1x10^2	823		
4.0x10^2	840		
9.6x10^2	873		

Discussion

Hydrogen halides have frequently been added to hydrocarbon oxidation systems, HBr being the most common additive [1,2,4,5,6].

Rust and Vaughan [1] noted that HBr catalysed hydrocarbon oxidations, and a reaction between HBr and O_2 was suspected. No exhaustive study has been made of the mechanism of such a reaction, but it is generally agreed that reaction 1 is the initiation step.

$$HBr + O_2 \rightarrow Br + HO_2 \qquad (1)$$

The three investigations of hydrogen bromide oxidation have all been in static systems, at moderate temperatures where the reaction is conveniently measureable [3,6,9].

A variety of techniques was employed to follow the reaction, and a wide range of HBr and O_2 concentrations used. Both Antonik and Lucquin [6] and Kochubei and Moin [9] are sparing in their experimental details; but overall the agreement is good for E_1 and also for A_1. However, the activation energy is low compared with the endothermicity and it may be that the mechanism of this reaction is more complex than suspected. The rate constant derived from the experimental results, $k_1 = 8.3 \times 10^{11}$ exp$(-18\,000/T)$ cm^3 mol^{-1} s^{-1}, should therefore be used with caution.

Rate of the Reverse Reaction

The rate of the reverse reaction -1 has not been determined directly. Day et al. [8] estimate $k_{-1}/k_3 = 0.37 \pm 0.10$ at ~1000 K, from measurements on the inhibition of $H_2/O_2/N_2$ flames by HBr.

$$Br + HO_2 \rightarrow HBr + O_2 \qquad (-1)$$

$$H + HO_2 \rightarrow H_2 + O_2 \qquad (3)$$

The flames were investigated at 1 atm. pressure, adding trace amounts of HBr to H_2 (18.8%)/O_2 (4.6%)/N_2 mixtures. Burning velocities were measured, and concentration profiles computed to fit a 27-step reaction mechanism. Using our expression for k_3 (Volume 1, p. 161), we obtain $k_{-1} = 6.5 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 1000 K. This is about a factor of 2 lower than the value of k_{-1} obtained from Kk_1 at this temperature, but as our expressions for k_1 and k_3 are only valid to 800 K, we can draw no conclusions from this, and can make no recommendation for k_{-1}.

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C12 $O + Br_2 \rightarrow BrO + Br$

THERMODYNAMIC DATA

(There are no thermodynamic data available for BrO)

RECOMMENDED RATE CONSTANT

$k_1 = 8.38 \times 10^{12}$ cm^3 mol^{-1} s^{-1}

$= 1.39 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}

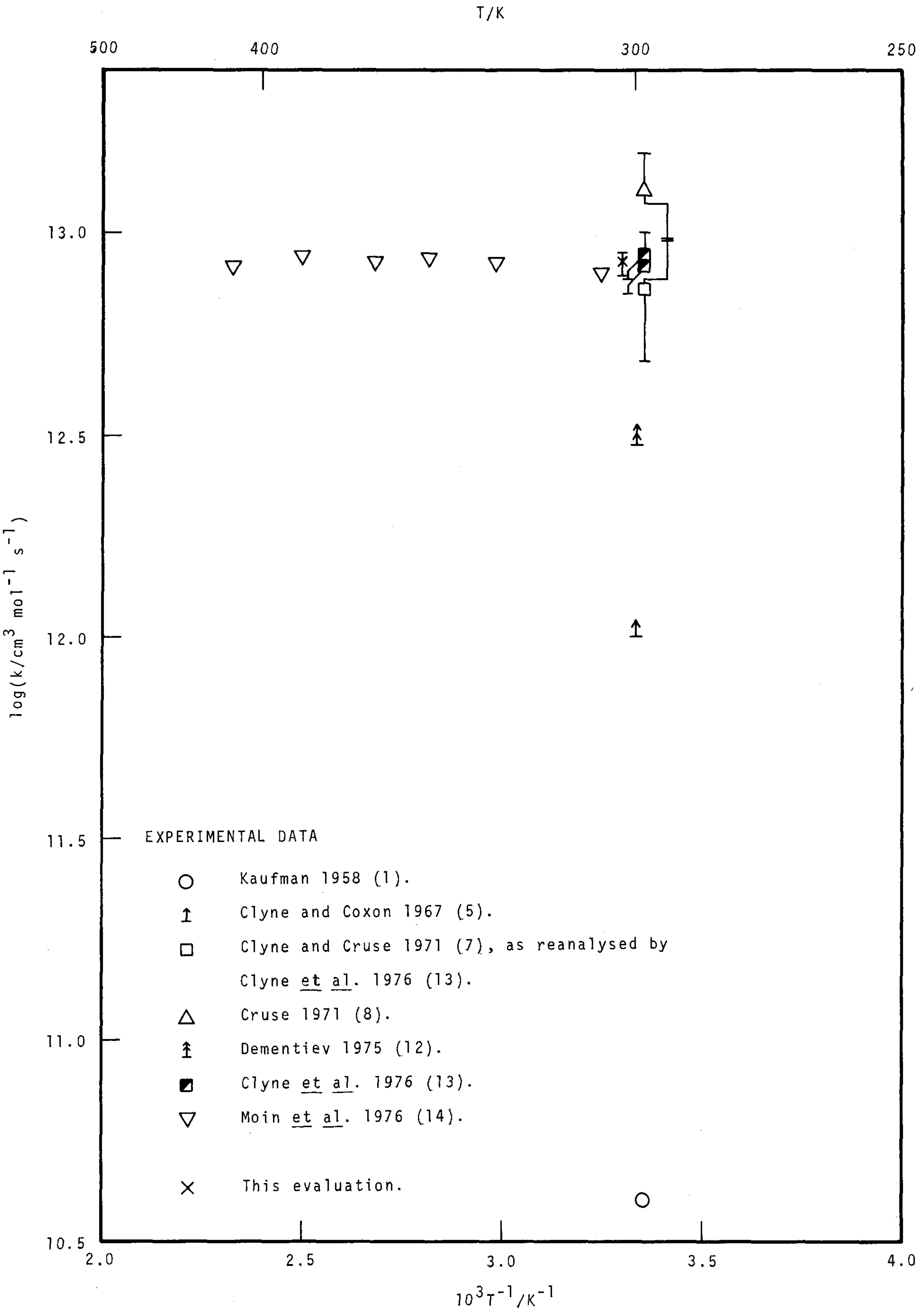
Temperature: 303 ± 3 K

Suggested Error Limits: ± 15% at 303 K

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
4×10^{10}	298	O_2-discharge flow system. Br_2 added to O/NO mixtures. Air afterglow intensity monitored. KAUFMAN 1958 (1)	Few details given. Early stages of reaction first order in O and Br_2. Value of k_1 only approximate. $O + Br_2 \rightarrow BrO + Br$ 1
$>10^{12}$	300	Discharge flow system. O atoms produced either by passing O_2/Ar mixtures through discharge, or by reaction N+NO. Br_2 added downstream. Chemiluminescence from 2-body Br recombination, and reaction 2, followed. CLYNE and COXON 1967 (5)	In presence of excess Br_2, chemiluminescence from reaction 2 $O + NO \rightarrow NO_2 + h\nu$ 2 replaced by that from Br recombination $Br + Br \rightarrow Br_2\ (^3\Pi)$ $Br_2(^3\Pi) \rightarrow Br_2(^1\Sigma_g^+) + h\nu$ No details given as to derivation of this lower limit, but presumably it was obtained from competition between NO and Br_2 for O atoms. BrO radical undetected, even with $[Br_2]/[O]=10$, indicating rapid removal of BrO by $O + BrO \rightarrow Br + O_2$ 3 Stoichiometry of O atom removal by Br_2, following reaction sequence 1 and 3, is therefore 2.
	293	O_2-discharge flow system. Large excess of Br_2 added to stream of O atoms ($[O]=2\times10^{-9}$ mol cm^{-3}). BrO monitored by uv absorption at 338 nm. CLYNE and CRUSE 1970 (6)	On basis of reaction sequence $O + Br_2 \rightarrow BrO + Br$ 1 $O + BrO \rightarrow Br + O_2$ 3 steady state value for [BrO] given by $k_1[Br_2]/k_3$. Measurement of 2 independent values of $[BrO]/[Br_2]$ gave $k_1/k_3=0.025$. We have used this data in the evaluation of k_3 only (this Volume, section C15).

$O + Br_2 \rightarrow BrO + Br$



$O + Br_2 \rightarrow BrO + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(5.24\pm1.81)\times10^{12}$	298	N_2-discharge flow system. Excess NO added to N/N_2 stream ($[N_2]\simeq7.2\times10^{-8}$ mol cm^{-3}) giving $1.8\times10^{-11}\leqslant[O]\leqslant1.0\times10^{-10}$ mol cm^{-3}. Br_2 (2.5×10^{-11}-8.6×10^{-11} mol cm^{-3}) added downstream, giving $0.48\leqslant[O]/[Br_2]\leqslant2.0$. [O] determined either by resonance absorption at 130 nm or by intensity of O+NO emission (both calibrated by NO titration), and $[Br_2]$ by Br atom fluorescence at 163.4 nm (caused by Lyman-α photolysis of Br_2). CLYNE and CRUSE 1971 (7)	Stoichiometry of O atom removal firstly determined, to allow for contribution of reaction 3. $O + BrO \rightarrow Br + O_2$ 3 k_1 found from measured stoichiometry of 2 and second order decay of [O]. Reaction 4 too slow (see this Volume, section C13) to compete with reaction 3 for removal of BrO $BrO + BrO \rightarrow Br + Br + O_2$ 4 k_1 given by second order analysis of O atom decay. CLYNE <u>et al</u>. (13) re-interpreted this result to allow for removal of O by NO_2, giving $k_1=(7.23\pm2.41)\times10^{12}$ cm^3 mol^{-1} s^{-1}. CLYNE and WATSON (11) report this re-interpretation as giving $(1.02\pm0.4)\times10^{13}$ cm^3 mol^{-1} s^{-1} at 300 K.
(a) $(1.27\pm0.1)\times10^{13}$ (b) $(1.27\pm0.3)\times10^{13}$	298 298	Discharge flow system. N_2-discharge followed by N+NO used to produce O atoms. (a) Br_2 (3.8×10^{-12}-1.5×10^{-11} mol cm^{-3}) added downstream in excess of O atoms. [O] followed by resonance fluorescence at 130 nm. (b) Br_2 added with O atoms in excess (2×10^{-12}-8.0×10^{-12} mol cm^{-3}), [Br] followed by resonance fluorescence at 157.7 nm. CRUSE 1971 (8)	(a) Secondary removal of O atoms by reaction 3 gives observed $O + BrO \rightarrow Br + O_2$ 3 rate as $k_1[Br_2]\leqslant-d(\ln[O])/dt\leqslant2k_1[Br_2]$. Removal of BrO by excess NO likely, rate thus tending to $k_1[Br_2]$. (b) Lack of curvature of plots of $\ln(\Delta[Br])$ vs time indicated negligible effect of reaction 3.
$>3\times10^{12}$	300	Method probably as for (14). No details available. DEMENTIEV 1975 (12)	Reported by MOIN <u>et al</u>. (14).
(a) $(8.85\pm1.21)\times10^{12}$ (b) $(8.31\pm1.21)\times10^{12}$	298 297-303	Discharge flow system. O atoms produced by reaction N+NO or from small O_2 impurities in He passed through discharge. (a) Br_2 (3.3×10^{-12}-2.8×10^{-11} mol cm^{-3}) added downstream to O stream ($[O]=1.16\times10^{-12}$-2.0×10^{-12} mol cm^{-3}), such that $[Br_2]/[O]$ varied in range 3-20. Total pressures	k_1 determined by (a) first order decay of O atoms and (b) by variation of $\Delta[Br_2]$ (change of $[Br_2]$ over a constant time interval). Overall mean value from (a) and (b) given as $(8.61\pm1.21)\times10^{12}$ cm^3 mol^{-1} s^{-1} (298-299 K). Absence of NO enables reactions 3 and 4 to contribute to (a) O, and (b) Br behaviour $O + BrO \rightarrow Br + O_2$ 3

$O + Br_2 \rightarrow BrO + Br$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		~200 Pa. NO added at large concentrations (~1.7×10^{-10} mol cm^{-3}) to suppress reaction 3. [O] monitored by resonance absorption at 130.5 nm. (b) Br_2 (1.0×10^{-12}-2.3×10^{-12} mol cm^{-3}) added to O (3.3×10^{-12}-1.0×10^{-11} mol cm^{-3})/NO (1.0×10^{-10}-2.5×10^{-10} mol cm^{-3}) mixtures, with $[O]/[Br_2] \approx 4$. [Br] monitored by resonance fluorescence at 157.7 nm. CLYNE, MONKHOUSE and TOWNSEND 1976 (13)	$BrO + BrO \rightarrow Br + Br + O_2$ 4 Mean value quoted by (9). Authors use their value with a weighting of 2, and the data of CRUSE (8), with unity weighting, to give "final" result $k_1 = (9.94 \pm 1.8) \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K. Value of 9.03×10^{12} cm^3 mol^{-1} s^{-1} quoted for this work by (10 and 11).
	306-425	O_2-discharge flow system. O_2/Ar mixture passed through discharge, giving $[O] = 3.3 \times 10^{-11}$ mol cm^{-3}. Br_2 (at about same as [O]) or Cl_2 added ($[Cl_2] = 1.7 \times 10^{-10}$-$1.7 \times 10^{-9}$ mol cm^{-3}). Total pressures ~2.4 mm Hg (320 Pa). [O] monitored by esr. MOIN, YURKEVICH and DROGO'ITSKII 1976 (14)	Authors adjusted Cl_2 and Br_2 flow rates in turn to achieve same reduction in [O]. Then because secondary reactions 3 and 5 are both fast ratio k_1/k_6 $O + BrO \rightarrow Br + O_2$ 3 $O + ClO \rightarrow Cl + O_2$ 5 was given by the ratio of flow rates of Cl_2 and Br_2 $O + Br_2 \rightarrow BrO + Br$ 1 $O + Cl_2 \rightarrow ClO + Cl$ 6 assuming first order decay of O in both cases. We have taken the following values of k_1/k_6 from authors' graph, and used our recommended expression for k_6 (this Volume, section B12) to obtain listed values of k_1: T/K $k_1 k_6^{-1}$ k_1/cm^3 mol^{-1} s^{-1} 308 2.70×10^2 7.97×10^{12} 335 1.98×10^2 8.38×10^{12} 355 1.62×10^2 8.65×10^{12} 373 1.32×10^2 8.43×10^{12} 400 1.07×10^2 8.79×10^{12} 426 81.5 8.24×10^{12} Authors fitted expression $k_1/k_6 = 10^{0.6 \pm 0.53} \exp\{-(1310 \pm 45)/T\}$ to these data, and incorrectly used the expression of CLYNE and COXON (3) for k_6 to derive $k_1 = (2.5 \pm 1.5) \times 10^{13} \exp\{-(500 \pm 180)/T\}$ cm^3 mol^{-1} s^{-1}.

Discussion

The reaction between atomic oxygen and molecular bromine has been of use as a source of BrO radicals [2,4,11]

$$O + Br_2 \rightarrow BrO + Br \qquad (1)$$

The principal difficulty in measuring the rate constant k_1 is that BrO is rapidly removed by excess O atoms in the subsequent reaction

$$O + BrO \rightarrow Br + O_2 \qquad (3)$$

Clyne and Cruse [6,7] measured the stoichiometry of the overall O/Br_2 reaction, and obtained a mean value of (2.0 ± 0.1). In the latter study $[Br_2]$ and [O] were comparable, so that pseudo-first order kinetics were inapplicable and k_1 was determined from a second order kinetics analysis of $-d[O]/dt$. However these authors failed to allow for the effects of the presence of excess NO which removes BrO via reaction 7

$$NO + BrO \rightarrow Br + NO_2 \qquad (7)$$

and also for the subsequent removal of O atoms via

$$O + NO_2 \rightarrow NO + O_2$$

As the re-analysis of these results by Clyne et al. [13] is only approximate, we give no further consideration to this value of k_1.

Clyne's latest study of this reaction [13] made full use of NO to eliminate reaction 3, and obtained similar values of k_1 by following both [O] and [Br].

Moin et al. [14] did not eliminate reaction 3, but compared the flow rates of Br_2 and of Cl_2 required to produce the same overall reduction in [O], giving k_1/k_6.

$$O + Cl_2 \rightarrow ClO + Cl \qquad (6)$$

Their resulting value for k_1 (using our recommended expression for k_6, from section B12) at 308 K agrees to within 10% with Clyne's value [13] at ~300 K. Consequently we recommend the value at 303 K of $k_1 = (8.38\pm1.3)\times10^{12}$ cm^3 mol^{-1} s^{-1}.

Moin et al. [14] have made the only study of the temperature dependence of k_1, obtaining a low activation energy of ~4.2 kJ mol^{-1} (1 kcal mol^{-1}), according to their own interpretation. Although this low value compares well with the low activation energy for reaction 6 (see section B12) in the absence of confirmatory data we make no recommendation for the temperature dependence of k_1.

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C13 BrO + BrO → products

THERMODYNAMIC DATA

(There are no thermodynamic data available for BrO)

RECOMMENDED RATE CONSTANT

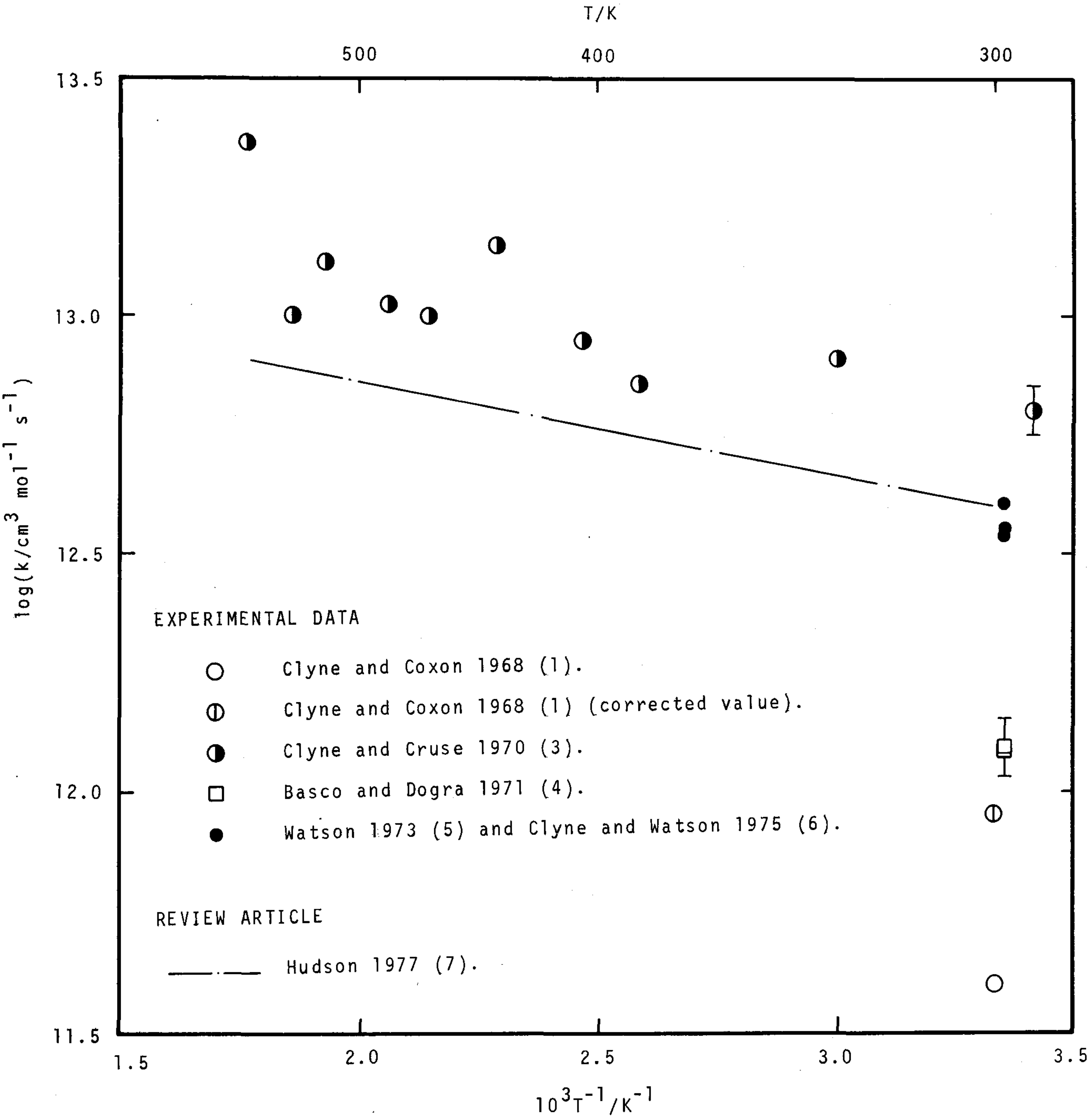
(No recommendation, see Discussion)

k is defined by $-d[BrO]/dt = k[BrO]^2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	300	Cl_2-discharge flow system. Br_2 added downstream, at total pressures ∿1.4 mm Hg (186.6 Pa), and then O_3 in ratio 1:1 with Br. Uv absorption of BrO monitored at 328.9 and 333.3 nm. CLYNE and COXON 1968 (1)	From second order decay of BrO, authors obtained $k_1/\varepsilon = (4.5\pm0.5) \times 10^5\ cm\ s^{-1}$ (where ε= extinction coefficient of BrO) $BrO + BrO \rightarrow Br + BrOO$ 1 From comparison of BrO absorption with that of ClO, authors took $\varepsilon \approx \varepsilon_{ClO} = 1.92 \times 10^6\ cm^2\ mol^{-1}$. This value gives $k_1 \approx 9 \times 10^{11}\ cm^3\ mol^{-1}\ s^{-1}$, and not $4 \times 10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ as quoted by these authors. WATSON (5) gives $k_1 \approx 8 \times 10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ for this work, and BASCO and DOGRA (4) give $\varepsilon = 8.9 \times 10^5\ cm^2\ mol^{-1}$.
	293-673	Flash photolysis study. Br_2 (5-20 mm Hg; 0.67-2.67 kPa)/O_2 (150-750 mm Hg; 20-100 kPa)/Ar mixtures at total pressures 169-785 mm Hg (22.5-105 kPa). [BrO] measured by uv absorption at unspecified wavelength. BROWN and BURNS 1970 (2)	BrO decay second order, with $E_1 = (2.72\pm0.21)\ kJ\ mol^{-1}$ (0.65±0.05 kcal mol^{-1}) for T< 450 K, and $E_1 = (18.83\pm1.26)\ kJ\ mol^{-1}$ (4.5±0.3 kcal mol^{-1}) for T> 450 K. Authors preferred BrO decomposition mechanism as $BrO + BrO \rightleftharpoons Br_2O_2$ 1a $Br_2O_2 \rightarrow 2Br + O_2$ Absolute values of k_{1a} not retrievable from Arrhenius plot.
$(6.3\pm0.9) \times 10^{12}$	293	Br_2-discharge flow system. Br_2/Ar mixtures in discharge, O_3 added downstream giving $4 \times 10^{-12} < [BrO] < 4 \times 10^{-11}\ mol\ cm^{-3}$. Total pressures 0.53 -1.63 mm Hg (70.7-217.3 Pa). [BrO] determined by uv absorption at 338.3 nm. CLYNE and CRUSE 1970 (3)	Preliminary experiments into BrO production and removal mechanism, in excess O_3 $Br + O_3 \rightarrow BrO + O_2$ 2 $BrO + BrO \rightarrow Br + BrOO$ 1 showed reaction 3 to have negligible effect $BrO + O_3 \rightarrow Br + 2O_2$ 3 and gave $\varepsilon = (4.8\pm0.5) \times 10^5\ cm^2\ mol^{-1}$ at 293 K. Authors obtained $k_1/\varepsilon = (1.32\pm0.15) \times 10^6\ cm\ s^{-1}$ (293 K) from second-order decay of BrO, in absence of O_3, and hence value
8.1×10^{12}	333		
7.2×10^{12}	386		
8.9×10^{12}	405		
1.4×10^{13}	436		
1.0×10^{13}	465		
1.1×10^{13}	485		
1.3×10^{13}	518		
1.0×10^{13}	537		
2.3×10^{13}	566		

BrO + BrO → products



BrO + BrO → products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		CLYNE and CRUSE 1970 (3) continued.	at 293 K tabulated here. Other values taken from Arrhenius plot of k_1. Authors gave alternative forms for k_1 as $3.2x10^{13}$ exp{-(450±300)/T} $cm^3\ mol^{-1}\ s^{-1}$ and $10^{12}T^{\frac{1}{2}}$exp{-(250±300)/T} $cm^3\ mol^{-1}\ s^{-1}$ (293-573 K) within error factor of 2.
(a) $(1.26±0.18)x10^{12}$ (b) $(1.24±0.12)x10^{12}$	298 298	Flash photolysis study. Br_2(2.8-5 mm Hg; 370-670 Pa)/O_2 (400-780 mm Hg; 53.3 -104 kPa) mixtures. Reaction followed by monitoring uv absorption by BrO at (a) 320.8 and (b) 338.3 nm. BASCO and DOGRA 1971 (4)	Second order decay of BrO at wavelengths (a) and (b) (corresponding to (8,0) and (4,0) BrO absorption bands respectively) gave $k_{1b}/\varepsilon(8,0) = (5.42±0.67)x10^5$ $cm^3 s^{-1}$ and $k_{1b}/\varepsilon(4,0) = (4.36±0.16)$ $x10^5$ cm s^{-1}. From flash photolysis of Br_2/ClO_2/Ar, or N_2, mixtures, ε(8,0) found as $(2.32±0.16)x10^6$ $cm^2\ mol^{-1}$, and ε(4,0)= $(2.83±0.25)x10^6$ $cm^2\ mol^{-1}$ at 298 K. $BrO + BrO \rightarrow Br_2 + O_2$ 1b
(a) $3.59x10^{12}$ $4.03x10^{12}$ (b) $3.48x10^{12}$	298 298 298	Discharge flow system. (a) O_2/He discharge, excess Br_2 added downstream, or (b) Br_2/He discharge with O_3 added downstream ([Br]>[O_3]). [BrO] measured by mass spectroscopy, calibrated by titration with excess NO. WATSON 1973 (5) and CLYNE and WATSON 1975 (6)	For method (a), performed in two flow tubes of different design, excess Br_2 partially suppressed secondary reaction 3 $O + BrO \rightarrow Br + O_2$ 3 Corrections for pressure gradient in earlier flow system thought to give k_1 (larger value) less accurate than in later system. Allowance made in method (b) for small [NO_2] produced with O_3 in ozoniser. Authors weight data to give mean $k_1 = (3.82±0.8)x10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$.

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$1.75x10^{13}$ exp(-450/T)	298-566	Recommended expression for use in stratospheric modelling. Derived from activation energy of (3) and pre-exponential factor adjusted to give k_1 at 298 K of (6). HUDSON 1977 (7)	

Discussion

Although the reaction between two BrO radicals has been studied in some detail in discharge flow [1,3,5,6] and flash photolysis [2,4] systems, all these investigations have been made by monitoring the second order decay of BrO. Consequently (a) the preferred route of the reaction has not been identified

$$\mathrm{BrO} + \mathrm{BrO} \rightarrow \mathrm{Br} + \mathrm{BrOO} \qquad (1)$$

$$\rightarrow \mathrm{Br_2O_2} \qquad (1a)$$

$$\rightarrow \mathrm{Br_2} + \mathrm{O_2} \qquad (1b)$$

and (b) all the rate constants but those of [5,6] have been determined in terms of the ratio k_1/ϵ, where ϵ is the absorption coefficient of the particular BrO transition used. Watson and Clyne [5,6] escaped this restriction by using mass spectrometry to monitor BrO, and their result is probably the most accurate.

However, there is no confirmatory evidence, and the large discrepancy between the discharge flow system data of Clyne and Coxon [1], the flash photolysis data of Basco and Dogra [4], and the discharge flow results of Clyne and Cruse [3] prevent us from making any recommendation for k_1.

Moreover there is also a large difference between the temperature dependence of the second order BrO disappearance as observed by Brown and Burns [2] and as observed by Clyne and Cruse [3], thereby increasing the uncertainty over the value of k_1.

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Note Added in Proof

In a recent room temperature study in which $O(^1D)$ was produced by flash photolysis of O_3, Gillespie et al. (J. Photochem. **7**, 29 (1977)) found that, in the presence of CF_3Br, BrO was produced by the rapid reaction

$$O(^1D) + CF_3Br \rightarrow CF_3 + BrO$$

The [BrO] was monitored by u.v. absorption and plate photometry and was found to undergo relatively slow second order decay. Analysis of the decay gave a value of k_1/ϵ which, when combined with the value of ϵ of Clyne and Cruse [3] yielded $k_1=(2.4\pm1.2)\times10^{12}$ cm^3 mol^{-1} s^{-1}.

This value lies in the middle of the range spanned by the other room temperature values.

C14 $Br + O_3 \rightarrow BrO + O_2$

THERMODYNAMIC DATA

(There are no thermodynamic data available for BrO).

RECOMMENDED RATE CONSTANT

$$k = 5.40 \times 10^{12} \exp(-640/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$
$$= 8.97 \times 10^{-12} \exp(-640/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Temperature Range: 200-360 K.

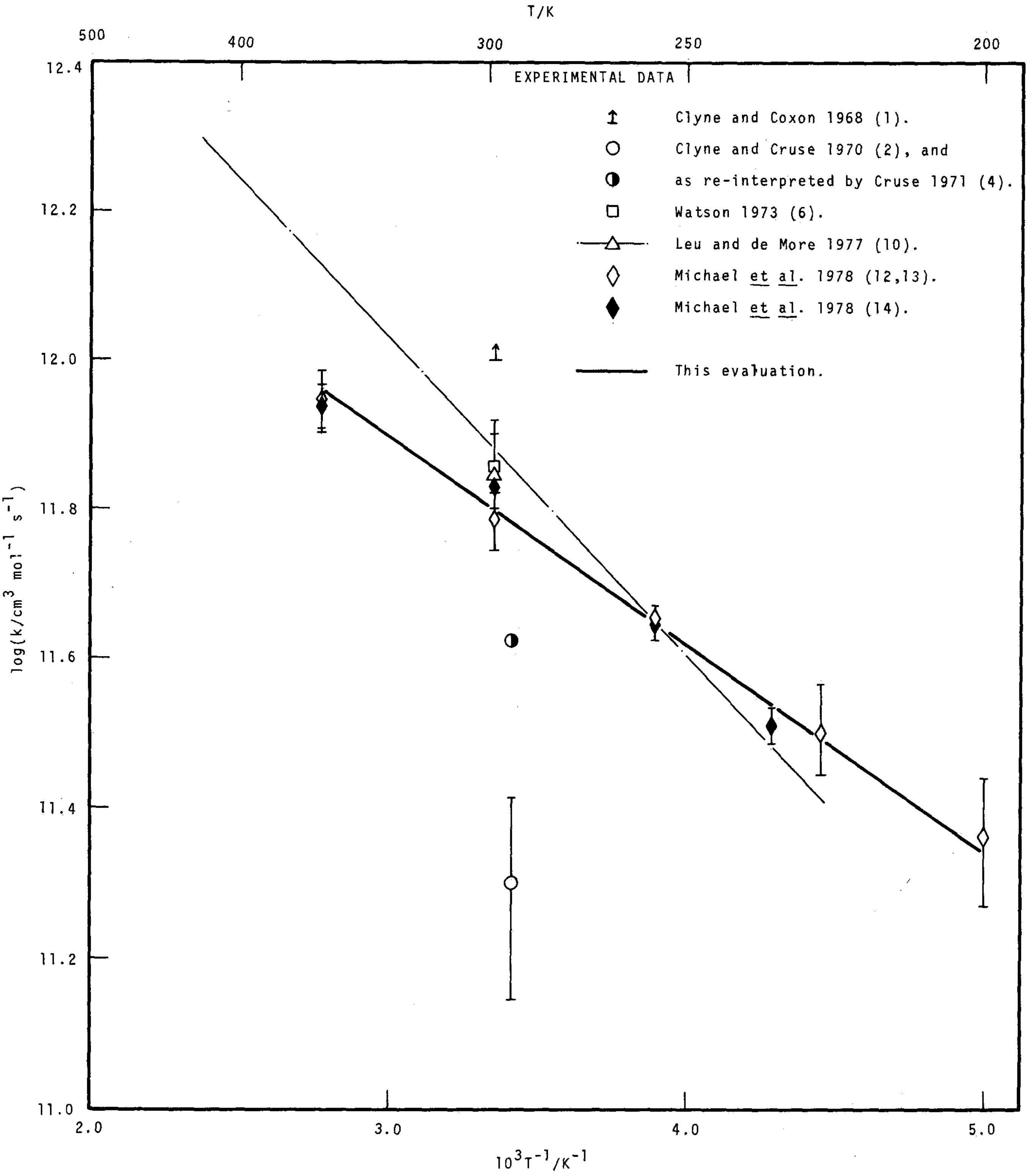
Suggested Error Limits for Calculated Rate Constant: ±50% over the whole temperature range.

Rate Parameters: $\log(A/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 12.732 \pm 0.18$
$\log(A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = -11.047 \pm 0.18$
$E/\mathrm{J\ mol^{-1}} = 5\ 320 \pm 3\ 100$
$E/\mathrm{cal\ mol^{-1}} = 1\ 270 \pm 740$

EXPERIMENTAL DATA

Rate Constant k ($\mathrm{cm^3\ mol^{-1}\ s^{-1}}$)	Temperature (K)	Method and Reference	Comments
$>1 \times 10^{12}$	298	Discharge flow system. Cl_2/Ar mixtures passed through discharge. Br_2 and O_3 added consecutively downstream. Total pressures ∿1.4 mm Hg (186.6 Pa). $[O_3]/[Br]$ ratios 1 and 3. $[O_3]$ followed by uv absorption. CLYNE and COXON 1968 (1).	Preliminary study. Br atoms formed by reaction $Cl + Br_2 \rightarrow BrCl + Br$ Reaction 1 found to be rapid $Br + O_3 \rightarrow BrO + O_2$ 1 and used as source of BrO radicals.
$(2.0 \pm 0.6) \times 10^{11}$	293	Discharge flow system. Br_2/Ar mixtures passed through discharge, and O_3 added downstream. Total pressures 1.5 mm Hg (200 Pa). Reaction followed by uv absorption of Br (416 nm), O_3 (250 nm) and BrO (338.3 nm). CLYNE and CRUSE 1970 (2)	First order decay of $[O_3]$ and mean values of $[Br]$ used to derive k_1, in order to allow for regeneration of Br by sequence $Br + O_3 \rightarrow BrO + O_2$ 1 $BrO + BrO \rightarrow Br + BrO_2$ 2 This work reinterpreted by CRUSE (4) to give $k_1 \approx 4.22 \times 10^{11}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$, reported by CLYNE (5) as $k_1 = (4.0 \pm 2.0) \times 10^{11}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ at 294 K.

$Br + O_3 \rightarrow BrO + O_2$



$Br + O_3 \rightarrow BrO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(7.17 \pm 1.14) \times 10^{11}$	298	Discharge flow system. Br_2/He mixtures at ∿120 Pa passed through discharge, giving $5.3 \times 10^{-11} \leqslant [Br] \leqslant 4.1 \times 10^{-10}$ mol cm^{-3}. O_3 added downstream, $4.0 \times 10^{-12} \leqslant [O_3] \leqslant 2.3 \times 10^{-11}$ mol cm^{-3}. Decay of $[O_3]$ followed by mass spectrometry, and [Br] determined (a) by titration with NOCl, (b) mass spectrometrically using difference between $[Br_2]$ with and without discharge in operation. WATSON 1973 (6) and CLYNE and WATSON 1975 (8)	k_1 determined from pseudo first order decay of O_3. WATSON (7) reports $E_1 \leqslant 10.98$ kJ mol^{-1} (2.62 kcal mol^{-1}).
$(6.99 \pm 1.0) \times 10^{11}$ $(2.01 \pm 0.2) \times 10^{13} \exp\{-(978 \pm 36)/T\}$	298 224-422	Discharge flow system. Br_2 (0.2-1%)/He mixtures passed through discharge, and O_3 added downstream through moveable inlet. Initial conditions $8.3 \times 10^{-14} \leqslant [O_3] \leqslant 5 \times 10^{-12}$ mol cm^{-3}, $8.8 \times 10^{-11} \leqslant [Br] \leqslant 5.7 \times 10^{-10}$ mol cm^{-3}, and $5 \times 10^{-8} \leqslant [He] \leqslant 1.0 \times 10^{-7}$ mol cm^{-3}. Mass spectrometry used to follow $[O_3]$ decay, and [Br] determined by monitoring either decrease in $[Br_2]$, or [BrCl] upon titration with NOCl. LEU and DE MORE 1977 (10)	Pseudo first order decay of $[O_3]$ used to determine k_1. $Br + O_3 \rightarrow BrO + O_2$ 1 Wall loss of Br atoms found to be <26% for 238-298 K, so average value of [Br] taken. Authors quoted average value of k_1 at 298 K, and weighted least squares Arrhenius fit to 35 values over range 224-422 K. HUDSON (9) gives slightly different expression, $k_1 = 1.81 \times 10^{13} \exp(-937/T)$ cm^3 mol^{-1} s^{-1}, for this work.
$(2.31 \pm 0.5) \times 10^{11}$ $(3.16 \pm 0.4) \times 10^{11}$ $(4.51 \pm 0.1) \times 10^{11}$ $(6.10 \pm 0.6) \times 10^{11}$ $(8.81 \pm 0.8) \times 10^{11}$	200 225 257 298 360	Flash photolysis flow system. CH_3Br (7.5-101 μm Hg; 1-13.5 Pa)/O_3(4.4-89.3 μm Hg; 0.6-11.9 Pa)/Ar(15-70 mm Hg; 2-9.3 kPa) mixtures photolysed at λ>165 nm. [Br] followed by resonance fluorescence at 145<λ<165 nm, and $[O_3]$ by uv absorption at 253.7 nm. MICHAEL, LEE, PAYNE and STIEF 1978 (12 and 13)	Pseudo first order conditions used, giving $[O_3] >> [Br]$. Values of k_1 derived only from initial pseudo first order [Br] decays, owing to non-linearity observed at long reaction times. This attributed to re-formation of Br atoms by reaction of O atoms (formed by photolysis of O_3) and product BrO $Br + O_3 \rightarrow BrO + O_2$ 1 $O + BrO \rightarrow Br + O_2$ 3 Least squares Arrhenius expression given as $(4.66 \pm 0.3) \times 10^{12} \exp\{-(603 \pm 16)/T\}$ cm^3 mol^{-1} s^{-1}.

$Br + O_3 \rightarrow BrO + O_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		MICHAEL, LEE, PAYNE and STIEF 1978 (12 and 13) continued.	This expression previously reported in (11).
$(3.25\pm0.2)x10^{11}$ $(4.46\pm0.2)x10^{11}$ $(6.74\pm0.4)x10^{11}$ $(8.67\pm0.6)x10^{11}$	233.5 257 298 360	Discharge flow system. Br_2/He mixtures passed through discharge, and O_3/He mixtures added downstream through sliding inlet. $5x10^{-11} \leq [O_3] \leq 1.3x10^{-9}$ mol cm^{-3}, with $[O_3] >> [Br]$, at total pressures 1.09-3.34 mm Hg (145.3-445.2 Pa). [Br] followed by resonance fluorescence at $145 < \lambda < 165$ nm, and $[O_3]$ determined by uv absorption at 253.7 nm.	Wall complications (recombination of Br atoms, reaction of O_3 with absorbed Br) required experiments to be performed using comparison of [Br] with and without O_3. Pseudo first order decay of [Br] used to determine k_1. Arrhenius form quoted as $k_1=(5.69\pm1.5)x10^{12}$ $exp\{-(659\pm64)/T\}$ cm^3 mol^{-1} s^{-1}. Authors consider agreement between this work and (12) shows allowance for reaction 3 in latter was adequate.
		MICHAEL and PAYNE 1978 (14)	

Discussion

The reaction between atomic bromine and ozone has been useful as a source of BrO radicals [2,3,4,6,8]

$$Br + O_3 \rightarrow BrO + O_2 \qquad (1)$$

Up to 1977 all the measurements of k_1 had been made at room temperature by Clyne's group, using discharge flow systems [1,2,6,8]. Following the concern over the effects of halogens upon the ozone layer, further studies have been made since 1977 in which the variation of k_1 with temperature was examined, using again discharge flow systems [10,14], and also flash photolysis [12,13].

The room temperature values from the latest studies are in good agreement with the earlier data of [6 and 8]. Within the various error limits for these results, there is no systematic variation with method or with reactant ratios, i.e., with excess Br [8,10] or excess O_3 [12,14]. The mean value of these data is 6.74×10^{11} cm^3 mol^{-1} s^{-1} (298 K), within error limits of $\pm20\%$.

Michael et al. obtained essentially the same temperature dependence for k_1 using both flash photolysis [12] and discharge flow systems [14]. However, the results of these measurements differ strongly from the temperature variation determined by Leu and de More [10]. The principal difference between the conditions under which these measurements were made is that Leu and de More [10] followed $[O_3]$ decay in excess Br atoms, whereas Michael et al. [12,14] followed the removal of Br in excess O_3. If reaction 2 were responsible for regenerating Br atoms

$$BrO + BrO \rightarrow Br + BrO_2 \qquad (2)$$

then the values of k_1 of [12 and 14] could be expected to be up to a factor of 2 below those of [10], over the whole temperature range. In fact the room temperature values are in good agreement, and Leu and de More's results, higher at $T > 300$ K, become lower for $T < 250$ K. Michael and Payne [14] were unable to attribute the discrepancy to any particular aspect of Leu and de More's method.

We recommend the expression $k_1 = 5.40\times10^{12}$ $exp(-640/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 200-360 K, which is based on the data of Michael et al. [12,14] plus the room temperature values of [8] and [10]. Suggested error limits are $\pm50\%$ which encompass all the results used.

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Miscellaneous Reaction Involving Br and O

C15 $O + BrO \rightarrow Br + O_2$

In the presence of excess O atoms, the production of BrO radicals in the fast reaction

$$O + Br_2 \rightarrow BrO + Br \qquad (2)$$

is followed rapidly by reaction 1

$$O + BrO \rightarrow Br + O_2 \qquad (1)$$

(there are no thermodynamic data available for BrO)

Reaction 1 has received little study. Clyne and Cruse [2] followed [BrO] by monitoring its u.v. absorption at 338.3 nm in a Br_2-discharge flow system. [BrO] was generated by reaction 2 ([O] initially 2×10^{-9} mol cm^{-3}), giving typical [BrO] values of 5×10^{-11} mol cm^{-3}. Assuming that the reaction mechanism consists of reactions 1 and 2, and using the steady-state approximation for [BrO], these authors found $k_2/k_1=0.025$ at 293 K. Using Clyne and Coxon's lower limit of 10^{12} cm^3 mol^{-1} s^{-1} [1] for k_2 they quote $k_1\geqslant4\times10^{13}$ cm^3 mol^{-1} s^{-1}. Using our value for k_2 at 300 K (section C12) we obtain $k_1=3.35\times10^{14}$ cm^3 mol^{-1} s^{-1}.

Further study by Clyne et al. [5] using a discharge flow system enabled an estimate of k_1 at 298 K to be obtained, by comparing the behaviour of Br formation and O decay in O/Br_2 systems, in the presence and absence of excess NO. O atoms were produced by the reaction N+NO, or from the O_2 impurities present in a He stream passed through a discharge. The O atom decay experiments were performed by adding $Br_2(3.3\times10^{-12}$–2.8×10^{-11} mol cm^{-3}) to the O atom stream ($1.16\times10^{-12}\leqslant[O]\leqslant2.0\times10^{-12}$ mol com^{-3}), such that the $[Br_2]/[O]$ ratio was varied from 3 to 20, and observing the first order decay of [O] (giving k_2) both with NO ($\sim1.7\times10^{-10}$ mol cm^{-3}) and without. Total pressures were $\sim$200 Pa, and [O] was monitored by resonance absorption at 130.5 nm. The formation of Br in Br_2 (1.0×10^{-12}–2.3×10^{-12} mol cm^{-3})/O (3.3×10^{-12}–1.0×10^{-11} mol cm^{-3}) mixtures ($[O]/[Br_2]\cong4$) was followed by resonance fluorescence at 157.7 nm, again with NO (1.0×10^{-10}–2.5×10^{-10} mol cm^{-3}) and without NO. From the variation of Δ[Br] (the change of [Br] over a constant time interval t_2–t_1) with t_2, values of k_2 were obtained.

The addition of excess NO served to suppress reaction 1 by removing BrO

$$NO + BrO \rightarrow NO_2 + Br$$

and therefore the rate constant k_2' observed in the absence of NO refers to the removal of O, or the formation of Br, by the reaction sequence (2+1), whereas k_2, the rate constant obtained in

$$O + Br_2 \rightarrow BrO + Br \qquad (2)$$

$$O + BrO \rightarrow Br + O_2 \qquad (1)$$

the presence of NO refers only to the effects of reaction 2. Computer simulations were made of both the O atom decay and Br atom production experiments, and the effect of varying k_1 was observed upon the computed values of k_2. Using the experimental values of k_2' enabled values of k_1 of $(4.2^{+2.4}_{-3.6})\times10^{13}$ cm^3 mol^{-1} s^{-1} and $(6.0^{+12.0}_{-4.0})\times10^{12}$ cm^3 mol^{-1} s^{-1} to be obtained from the O and Br atom experiments, respectively. The various error limits are a result of consideration of possible experimental errors. From the overlap of the limits of these values the authors estimated k_1 as $(1.51^{+1.51}_{-0.9})\times10^{13}$ cm^3 mol^{-1} s^{-1} at 298 K. Clyne and Watson [4] attribute a pre-publication value of $(3.01\pm1.21)\times10^{13}$ cm^3 mol^{-1} s^{-1} to [5], and Watson [3] quotes unpublished work of Clyne and Townsend as giving $k_1=4.8\times10^{13}$ cm^3 mol^{-1} s^{-1}.

Because the result of Clyne et al. [5] is only an estimate, within wide limits of error, and the ratio of the values k_1 and k_2 (see section C12) obtained in this work is an order of magnitude higher than than obtained earlier by Clyne and Cruse [2], we make no recommendation for this rate constant.

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Miscellaneous Reactions Involving Br, N and O Species

C16 $N + Br_2 \rightarrow NBr + Br$

Phillips [1,2] has studied the reaction between nitrogen atoms and bromine in an analogous manner to that between N atoms and Cl_2, again coming to the conclusion that reaction 1 was the initial step, followed by reaction 2.

$$N + Br_2 \rightarrow NBr + Br; \qquad (1)$$

$$\Delta H^\circ_{298}=-90.935 \text{ kJ mol}^{-1} \ (-21.734 \text{ kcal mol}^{-1})$$

$$N + NBr \rightarrow N_2 + Br \qquad (2)$$

In both cases, active nitrogen was produced by a discharge through 100% N_2, a pressure of 400 Pa being quoted in [2]. Br_2 was added downstream, and the nitrogen afterglow monitored at 625 nm. Emission from NBr was also observed [1], but no attempt was made to quantify this. Rate constants $k_1=1\times10^{10}$ (1) and $k_1=2.0\times10^9$ (2) cm^3 mol^{-1} s^{-1} were obtained at 293 K. In the later study, the temperature range was extended, and an expression $k_1=4.4\times10^{10}\exp(-900/T)$ cm^3 mol^{-1} s^{-1} was derived over the range 291–328 K. In this work, a correction was made for heterogeneous recombination of Br, which the authors claim accounts for the lower values of k_1 obtained.

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C17 $NO + BrO \rightarrow Br + NO_2$

The reaction between nitric oxide and BrO radicals is believed to have a rate constant of the same order of magnitude as the corresponding NO/ClO reaction [3]. However, its use as a titration reaction for BrO is limited because of the considerably faster disproportionation of BrO radicals compared with ClO [2].

$$NO + BrO \rightarrow NO_2 + Br \qquad (1)$$

Reaction 1 was first studied by Clyne and Cruse [2] in an attempt to examine its potential as a titration reaction for BrO. They used a discharge flow system, producing BrO radicals by adding O_3 in excess to the products of a discharge in Br_2/Ar mixtures at total pressures of 48.7–244 Pa. NO was added downstream at 73.1–439 mPa pressure. [BrO] was monitored by electronic absorption spectrometry. The increase in the rate of disappearance of BrO radicals when [NO]> >[BrO] was attributed to reaction 1, and using their own value for k_2 [1] obtained $k_1 = (1.5 \pm 0.5) \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 293 K.

$$BrO + BrO \rightarrow Br + BrOO \qquad (2)$$

This value is criticised by Clyne and Watson [3], on account of the short reaction time studied, and they consider it to be a lower limit. In their determination of k_1, they obtained low concentrations of BrO radicals as an impurity in a discharge through Br_2/He mixtures at a total pressure of 120 Pa. NO was added downstream in excess of 4.49–60.0 mPa pressure, and the reaction followed mass spectrometrically. Using the value of k_2 determined in the same study, they obtained $k_1 = 1.3 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 298 K. Clyne prefers this to the earlier determination, but in the absence of confirmatory work, no recommendation is made for k_1.

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C18 $NOBr + M \rightarrow NO + Br + M$

The only study of the unimolecular decomposition of nitrosyl bromide has been a shock-tube study by Maloney and Palmer [1],

$$NOBr + M \rightarrow NO + Br + M; \qquad (1)$$

$$\Delta H^\circ_{298} = 120.04 \text{ kJ mol}^{-1} \text{ (28.69 kcal mol}^{-1}\text{)}$$

They shocked mixtures of NOBr (0.43–2.45%) in Ar at total pressures of 60.1–106 kPa, over the temperature range 769–1117 K. They monitored the incident shocks, following [NOBr] by u.v. absorption at 270 nm. Assuming that NOBr decomposed in similar fashion to NOCl, and that there was no bimolecular contribution at the temperatures and pressures used, the authors obtained $k_1 = 1.2 \times 10^{15}$ exp(−12 600/T) cm^3 mol^{-1} s^{-1}, over the stated temperature range.

Reference

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C19 $N_2O + Br \rightarrow N_2 + BrO$

The reaction between nitrous oxide and bromine atoms was first studied by Musgrave and Hinshelwood [1].

$$Br + N_2O \rightarrow N_2 + BrO; \qquad (1)$$

thermodynamic data unavailable for BrO.

They allowed either Br_2 (0–3.60 kPa) or C_3H_7Br (0–6.67 kPa) to decompose in the presence of N_2O (40.0 kPa) over the temperature range 953–1018 K, following the reaction manometrically. When a second order rate constant is derived from their values using data from JANAF for the Br_2/Br equilibrium the derived second order rate constant is found to vary with [Br]. An apparent activation energy of 203 kJ mol^{-1} (48.5 kcal mol^{-1}) was obtained by Musgrave and Hinshelwood from their pseudo-first order rate constant.

Volmer and Bogdan [2] used a similar system with Br_2 (5.43–31.4 kPa)/N_2O (2.43–5.59 kPa) mixtures over the temperature range 793–867 K. They corrected their activation energy for the effects of reaction 2 to obtain $E_1 = 149$ kJ mol^{-1} (35.5 kcal mol^{-1}).

$$Br_2 + M \rightleftharpoons Br + Br + M \qquad (2)$$

Using their original data we obtain $k_1 K_2^{1/2} = 5 \times 10^{14}$ exp(−30 000/T) cm$^{3/2}$ mol$^{-1/2}$ s^{-1} over the given temperature range and, from this expression, we derive $k_1 = 2.9 \times 10^{14}$ exp(−18 700/T) cm^3 mol^{-1} s^{-1} using JANAF thermodynamic data to obtain K_2.

Kaufman et al. [3] in their system used Br_2 (0.13–2.13 kPa)/N_2O (2.67 kPa) mixtures, correcting for the effects of reactions 2 and 3.

$$N_2O + M \rightarrow N_2 + O + M \qquad (3)$$

$(-d[N_2O]/dt)/(-d[Br]/dt)$ they found to be 0.8, supporting their mechanism, and indicating that BrOO is unlikely to play a significant role here (c.f. section B56). Over the temperature range 876–973 K they obtain $k_1 = 2.0 \times 10^{14}$ exp(−18 600/T) cm^3 mol^{-1} s^{-1}.

This expression is in good agreement with that derived from the data of Volmer and Bogdan.

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C20 NO_2 + HBr → HNO_2 + Br

The reaction between nitrogen dioxide and hydrogen bromide is believed to proceed by a similar path to the NO_2/HCl reaction, the overall products being NO, H_2O and Br_2 (1).

$$NO_2 + HBr \rightarrow HNO_2 + Br; \qquad (1)$$

$$\Delta H^\circ_{298} = 37.530 \text{ kJ mol}^{-1} \text{ (8.970 kcal mol}^{-1})$$

Rosser and Wise [1] studied the reaction with the same technique as they used in the NO_2/HCl work, using approximately equal concentrations of NO_2 and HBr, at total pressures of 0.18–2.91 kPa, and over the temperature range 363–583 K. [NO_2] was followed by absorption of light at 340 nm, *while absorption by both* NO_2 *and* Br_2 *at* 420 *nm* showed the stoichiometry to be the same as for NO_2 + HCl. An expression $k_1 = 1.0 \times 10^{11} \exp(-6500/T)$ cm^3 mol^{-1} s^{-1} was obtained, implying a similar activation energy for the reverse reaction –1.

Reference

[1] Rosser, W. A., Jr., and Wise, H., J. Physic. Chem. **64**, 602 (1960).

C21 N + HBr → NH + Br

The reaction between active nitrogen and hydrogen bromide has been studied at length by Dunford et al. [1,2]. In the initial flame study [1], emission from NBr was observed, and the reaction seen as a means of catalysing N atom recombination.

$$N + HBr \rightarrow NH + Br; \qquad (1)$$

$$\Delta H^\circ_{298} = 14.560 \text{ kJ mol}^{-1} \text{ (3.480 kcal mol}^{-1})$$

In a more detailed study [2], Milton and Dunford first followed reaction 1 in a stirred flow reactor, producing active nitrogen by a discharge through pure N_2. However, they found it impossible to obtain turbulence under the conditions chosen, and could only give an estimate for the lower limit of $k_1 > 3 \times 10^9$ cm^3 mol^{-1} s^{-1} at 343 K. Following the reaction in a diffusion flame, adding the active nitrogen stream to one of HBr at ~115 Pa, they were able to observe a pale orange *flame, which was replaced by the bright orange* NBr *flame* when the flow rate of HBr was reduced. A value of k_1 was calculated from diffusion flame kinetics to give $k_1 = 2.3 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 313 K.

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C22 $NO + NO + Br_2 \rightarrow 2NOBr$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-47.225	-119.859	2.011	6.399
300	-47.229	-119.897	1.960	6.351
500	-47.555	-120.821	-1.344	3.269
1000	-46.476	-119.416	-3.810	1.104
1500	-45.037	-118.244	-4.608	0.482
2000	-43.723	-117.487	-4.994	0.221
2500	-42.585	-116.985	-5.220	0.092
3000	-41.656	-116.637	-5.368	0.023
3500	-40.936	-116.503	-5.470	-0.012
4000	-40.417	-116.273	-5.546	-0.030
4500	-40.099	-116.202	-5.604	-0.037
5000	-39.999	-116.185	-5.650	-0.037

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.006$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 4.75 \times 10^{10} \exp(-630/T)\ cm^6\ mol^{-2}\ s^{-1}$

$= 1.31 \times 10^{-37} \exp(-630/T)\ cm^6\ molecule^{-2}\ s^{-1}$

(k is defined by $-\frac{1}{2}d[NO]/dt = -d[Br_2]/dt = k[NO]^2[Br_2]$)

Temperature Range: 270-330 K

Suggested Error Limits for Calculated Rate Constant: ±30% over the quoted temperature range.

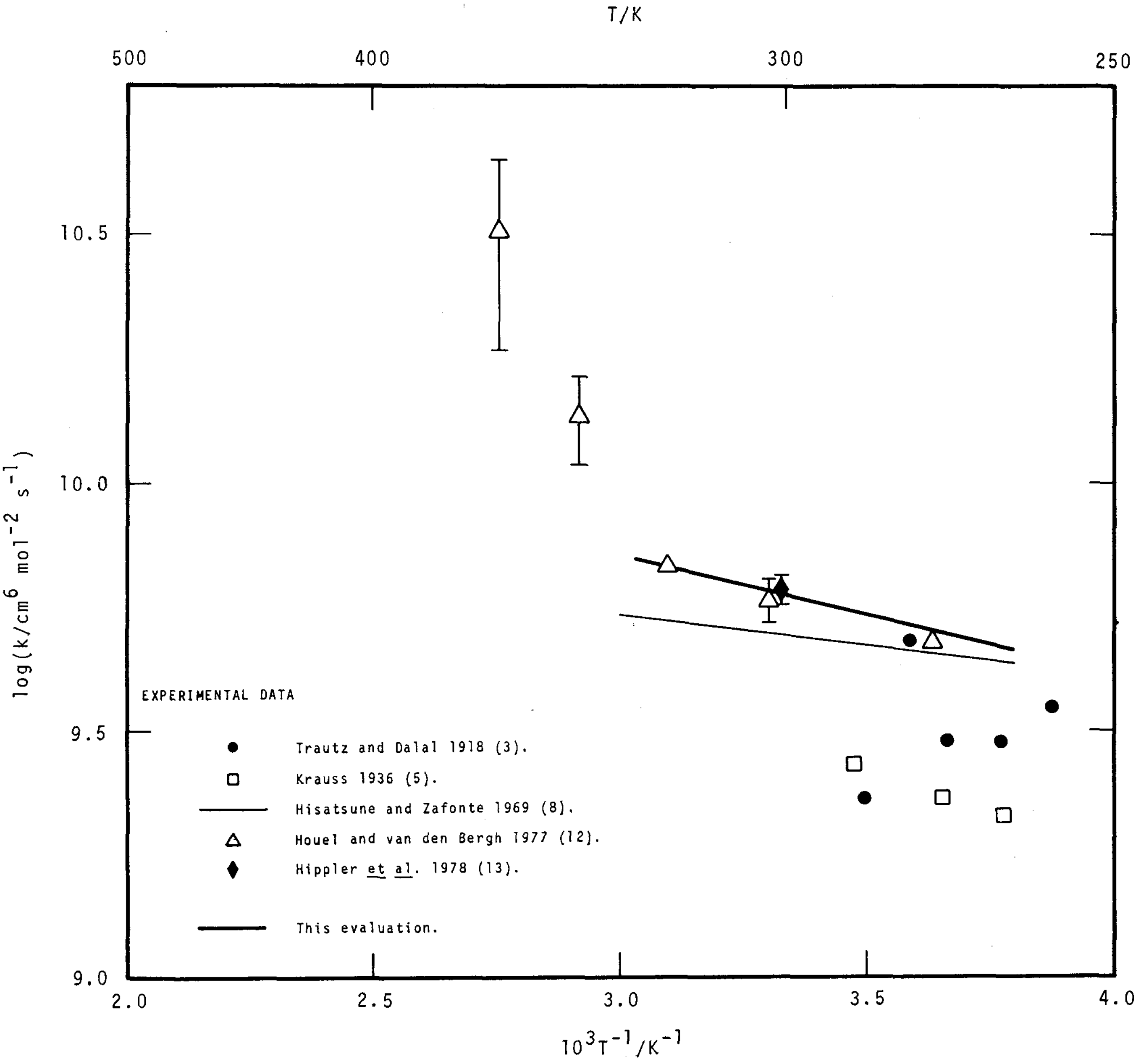
Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 10.677 \pm 0.12$

$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -36.883 \pm 0.12$

$E/J\ mol^{-1} = 5\ 240 \pm 6\ 820$

$E/cal\ mol^{-1} = 1\ 250 \pm 1\ 630$

$NO + NO + Br_2 \rightarrow 2NOBr$



$NO + NO + Br_2 \rightarrow 2NOBr$

EXPERIMENTAL DATA

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
3.5×10^9	258	Static system. Br_2(1.52-3.52 kPa)/NO (2.88-3.15 kPa) mixtures. Reaction followed manometrically. TRAUTZ and DALAL 1918 (3)	Authors base calculations on those made for the corresponding Cl_2 reaction (1,2), using TRAUTZ's revised reaction rate theory (2). A_1 and E_1 were calculated from collision theory, taking the diameter of the NOBr molecule as (a) equal to that of NOCl, and (b) greater than that of NOCl by the ratio of the cube roots of their molecular weights. $NO + NO + Br_2 \rightarrow 2NOBr$ 1 This gives two expressions:- (a) $k_1 = 1.7 \times 10^{14} T^{-1} \exp(-1460/T)$ cm^6 mol^{-2} s^{-1} and (b) $k_1 = 5.0 \times 10^{14} T^{-1} \exp(-1750/T)$ cm^6 mol^{-2} s^{-1}. They note that a large error is possible in both A_1 and E_1 without seriously altering the value of k_1 over the small temperature range, and recommend an average value of E_1=12.9 kJ mol^{-1} (3.08 kcal mol^{-1}). When excess NO was used, the overall rate decreased, and the authors postulated the following mechanism: $NO + Br_2 \rightarrow NOBr_2$ 2 $NOBr_2 + NO \rightarrow 2NOBr$ 3
3.0×10^9	265		
3.0×10^9	273		
4.8×10^9	279		
2.3×10^9	286		
2.1×10^9	265	Static system. Br_2(8.60-31.2 kPa)/NO(16.5-41.4 kPa) mixtures. Reaction followed manometrically. KRAUSS 1936 (5)	Reaction third order under all conditions of [NO]. No evidence found for TRAUTZ's mechanism. Using these data, TROTMAN-DICKENSON (6) obtains the expression $k_1 = 4.0 \times 10^{10} \exp(-800/T)$ cm^6 mol^{-2} s^{-1}. Quoted by (7, 9). Used by (11).
2.3×10^9	274		
2.7×10^9	288		
$(1.3 \pm 0.1) \times 10^{10} \exp(-290/T)$	263-333	Static system. NO(>1.63 kPa)/Br_2(>125 Pa) mixtures at total pressures ≯ 64.0 kPa. [NOBr] followed by i.r. spectroscopy at 18.9 μm. HISATSUNE and ZAFONTE 1969 (8)	Reaction studied over wide pressure range, and no deviation from third order kinetics found. Some experiments were carried out in which ∿2% Cl_2 was added to a 1:50 [Br_2]/[NO] mixture in an attempt to elucidate the reaction mechanism. At 303 K, reaction 1 was found to be the initiating reaction with $k_1 = 4.8 \times 10^9$ cm^6 mol^{-2} s^{-1}, in good agreement with the other experiments. Quoted by (10).

$NO + NO + Br_2 \rightarrow 2NOBr$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.70\pm0.07)\times10^9$ $(5.80\pm0.59)\times10^9$ $(6.82\pm0.24)\times10^9$ $(1.37\pm0.27)\times10^{10}$ $(3.16\pm1.30)\times10^{10}$	275 303 323 343 363	Static system. $NO(2.6\times10^{-7}-5.8\times10^{-7}\ mol\ cm^{-3})/Br_2(8.7\times10^{-9}-1.1\times10^{-8}\ mol\ cm^{-3})$ mixtures. [NOBr] monitored by uv absorption at 220 nm. HOUEL and VAN DEN BERGH 1977 (12)	Preliminary experiments performed to determine extinction coefficient for NOBr. Growth of NOBr described by $d[NOBr]/dt=2k_1[Br_2][NO]^2 - 2k_{-1}[NOBr]$ $NO + NO + Br_2 \rightleftharpoons 2NOBr$ 1,-1 k_{-1} replaced by k_1/K_1. Authors quote $E_1=(5.7\pm5.3)$ kJ mol^{-1} ((1.35±1.27) kcal mol^{-1}) over range 275-323 K.
$(6.1\pm0.4)\times10^9$	300	Flash photolysis study. Br_2(<0.3 mm Hg; 40 Pa)/He (1-100 atm; 101.3 kPa - 10.1 MPa)/NO (100-200 mm Hg; 13.3-26.7 kPa) mixtures. [NOBr] monitored by uv absorption at 248 nm, and $[Br_2]$ at 436 nm. HIPPLER, LUU, TEITELBAUM and TROE 1978 (13)	Corrections made for cross-interference between Br_2 and NOBr. Excess NO converts Br_2 to NOBr via reaction 1 $NO + NO + Br_2 \rightarrow 2NOBr$ Flash photolysis then followed by sequence $Br + NO + M \rightarrow NOBr + M$ 4 $Br + NOBr \rightarrow NO + Br_2$ 5 giving value of [NOBr] intermediate between post-flash value and intial, pre-flash value. This intermediate [NOBr] determined by relative importance of reactions 4 and 5. Slow pseudo first order return of [NOBr] to initial value gave k_1.

Discussion

The termolecular reaction between nitric oxide and bromine proceeds by a similar mechanism to the corresponding reaction between NO and Cl_2 (section B37) but is about two orders of magnitude faster at room temperature. There are, however, only three sets of data available on the reaction, and its rate is not known as accurately as the corresponding NO/Cl_2 reaction.

$$NO + NO + Br_2 \rightarrow 2NOBr \qquad (1)$$

We define the rate constant discussed in this evaluation by the expression:

$$-d[NO]/dt = -2d[Br_2]/dt = d[NOBr]/dt = 2k_1\ [NO]^2[Br_2].$$

Trautz and Dalal [3], and Krauss [5] followed Bodenstein's practice and defined k_1 according to the expression

$$-d[Br_2]/dt = k_1\ (\text{Bodenstein})\ (\tfrac{1}{2}[NO])^2[Br_2]$$

and their figures have thus been divided by four to comply with our definition. Hisatsune and Zafonte [8] have defined k_1 in terms of the rate of production of NOBr, and their expression has therefore been divided by two.

The two early studies of the reaction [3,5] were both made following the pressure changes in the reaction vessel. In experiments with excess NO, Trautz and Dalal [3] noted a fall-off in the reaction rate, attributing it to the formation of $NOBr_2$ as an intermediate, but this was not observed by subsequent workers [5,8]. The spread of Trautz's results is such that no activation energy can be calculated from them over the narrow temperature range. Trautz himself calculates a series of expressions from collision theory, all agreeing with his experiments at those temperatures. Krauss [5] obtained a true Arrhenius plot, but again over a narrow temperature range. He made no calculations from his data, but Trotman-Dickenson [6] derived an activation energy only half the value calculated by Trautz.

Hisatsune and Zafonte [8] monitored NOBr formation spectroscopically, and obtained an activation energy very much lower again. Both they and Kiss [4] studied the effects of adding small amounts of Cl_2 to the system to try to elucidate the mechanism. Both agreed that reaction 1 is still the initiating reaction, but, following only pressure changes, Kiss was unable to measure a rate, and concluded that reaction 1 was followed by the slow reaction

$$2NOBr + Cl_2 \rightarrow 2NOCl + Br_2$$

Hisatsune and Zafonte made the more plausible suggestion that BrCl acted as an intermediate in subsequent reactions before NOCl was formed.

The two most recent studies [12,13] give values of k_1 in good agreement at ~300 K, but about a factor of 2 higher than the data of [3 and 5]. In view of the higher reliability of the recent spectroscopically derived data [8,12,13], and the wide scatter of Trautz and Dalal's results, we recommend the expression

$$k_1 = 4.75\times10^{10}\ \exp(-630/T)\ \mathrm{cm^6\ mol^{-2}\ s^{-1}}$$

for the temperature range 270–330 K. This expression is subject to uncertainty limits of ~30% over this range.

Above 360 K, from the results of Houel and van den Bergh [12], it is evident that a more rapid NOBr-producing reaction is taking place. These authors could not positively identify this as a heterogeneous reaction, as experiments in vessels with different s/v ratios gave no significant difference.

Rate of the Reverse Reaction

There are no data available on the rate of reaction -1.

$$\mathrm{NOBr + NOBr \rightarrow 2NO + Br_2} \qquad (-1)$$

Trotman-Dickenson [6], using the expression for k_1 calculated from Krauss' data [5] and the expression for K_1 given therein, obtained $k_{-1}=6.3\times10^{13}\ \exp(-7100/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$. From our recommended expression for k_1 and the JANAF thermodynamic data we derive $k_{-1}=1.2\times10^{12}\ \exp(-5990/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ for temperatures 270–330 K.

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Miscellaneous Reaction Involving Br and S

C23 $\mathrm{S + Br_2 \rightarrow SBr + Br}$

The reaction between sulphur atoms and bromine is difficult to study due to the significant removal of Br_2 by impurity species.

$$\mathrm{S + Br_2 \rightarrow SBr + Br;} \qquad (1)$$

thermodynamic data unavailable for SBr.

Clyne and Townsend [1] followed reaction 1 in a flow system, producing S atoms by a discharge through SO_2 (~0.1%)/Ar mixtures, and adding Br_2 downstream so that $[Br_2]\sim10\text{–}30[S]$. Total pressure ~20 Pa. The [S] was monitored by resonance fluorescence at 180 nm or by titration with O_2, [O] being monitored at 130 nm.

$$\mathrm{S + O_2 \rightarrow SO + O}$$

The rates of reactions 2 and 3 are sufficiently great for impurity O atoms to cause problems. The authors subjected their results to a computer analysis, taking k_2 and k_3 from [2]. Preliminary work by them on reaction 4 has given $k_4<3.0\times10^{13}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$, not fast enough to interfere in the overall scheme.

$$\mathrm{O + Br_2 \rightarrow BrO + Br} \qquad (2)$$

$$\mathrm{O + BrO \rightarrow Br + O_2} \qquad (3)$$

$$\mathrm{S + BrO \rightarrow Br + SO} \qquad (4)$$

On this basis they found $k_1=(5.7\pm1.0)\times10^{13}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ at 298 K. In view of the complicated nature of the S-Br_2 reaction, and uncertainties in k_2, k_3 and k_4, we feel that larger error limits should be attached to this value than to the rate constant for the S/Cl_2 reaction.

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D1 $I_2 + M \rightarrow I + I + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	151.084	100.763	-21.206	-25.594
300	151.093	100.793	-21.043	-25.434
500	151.963	103.031	-10.494	-15.107
1000	153.896	105.726	- 2.516	- 7.430
1500	155.712	107.198	0.178	- 4.912
2000	157.628	108.299	1.540	- 3.675
2500	159.837	109.282	2.368	- 2.944
3000	162.348	110.198	2.930	- 2.461
3500	165.092	111.035	3.336	- 2.122
4000	167.929	111.797	3.646	- 1.870
4500	170.757	112.462	3.892	- 1.675
5000	173.502	113.043	4.092	- 1.521

S.I. Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.0056$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k = 8.25 \times 10^{13} \exp(-15\ 250/T)$ cm^3 mol^{-1} s^{-1} (M=Ar,N_2)

$= 1.37 \times 10^{-10} \exp(-15\ 250/T)$ cm^3 $molecule^{-1}$ s^{-1} (M=Ar,N_2)

(k is defined by $-d[I_2]/dt = k[I_2][M]$)

Temperature Range: 800-2000 K

Suggested Error Limits for Calculated Rate Constant: ±20% over the specified temperature range.

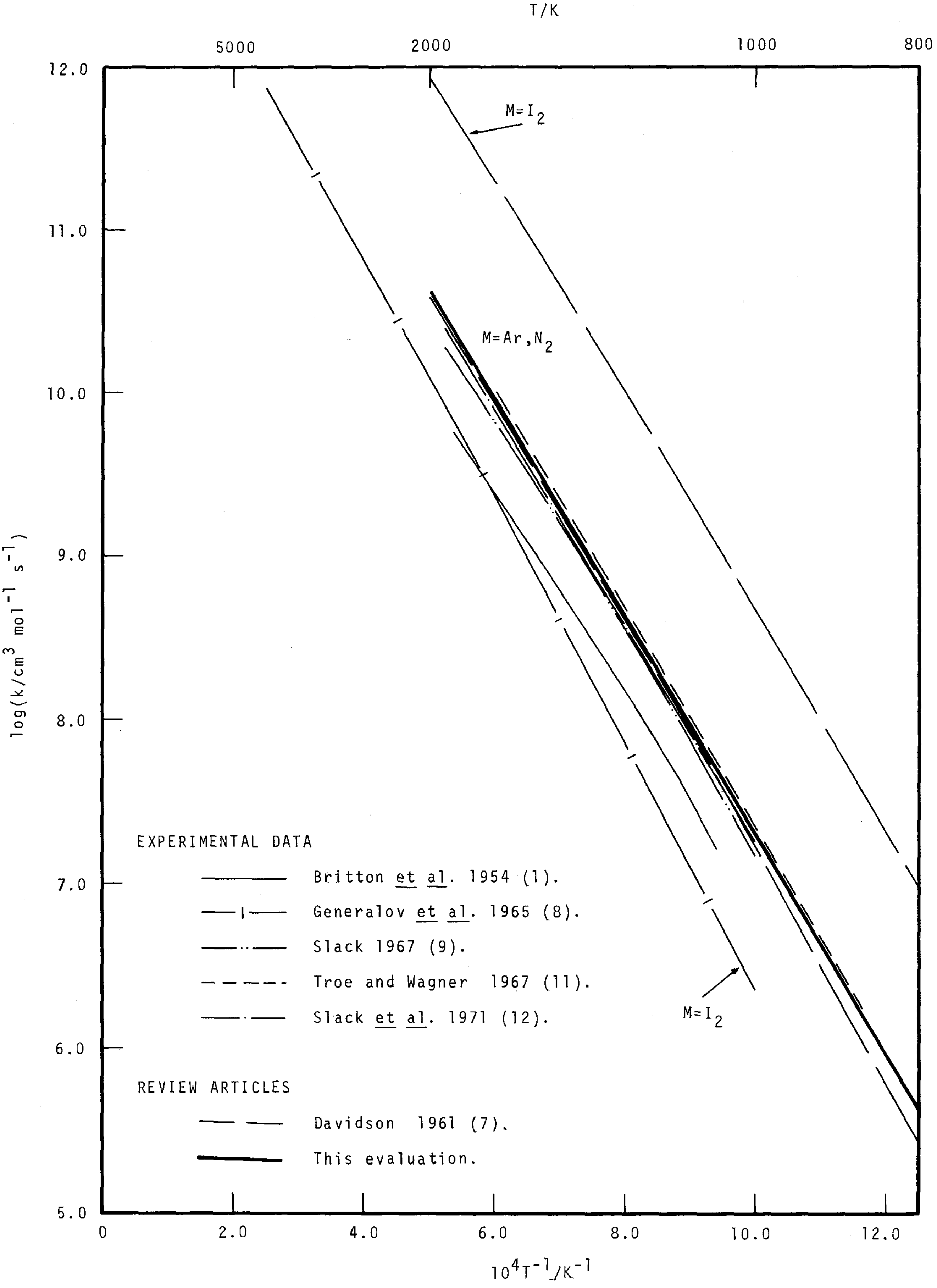
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.92 \pm 0.08$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.86 \pm 0.08$

$E/J\ mol^{-1} = 126\ 800 \pm 4\ 800$

$E/cal\ mol^{-1} = 30\ 310 \pm 1\ 150$

$I_2 + M \rightarrow I + I + M$



$I_2 + M \rightarrow I + I + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.62\times10^{22}T^{-2.53}\exp(-17\ 900/T)$ M=Ar $1.66\times10^{22}T^{-2.54}\exp(-17\ 900/T)$ M=N_2	1060-1860	Shock tube study. I_2(~1%) /Ar (or N_2) mixtures behind incident shocks. I_2 followed by uv absorption at 490 and 436 nm. BRITTON, DAVIDSON and SCHOTT 1954 (1)	Dissociation of I_2 analysed using net rate in terms of $k_{-1}(=k_1/K_1)$ $I_2 + M \rightleftharpoons I + I + M$ 1,-1 k_{-1} assumed to be independent of temperature, giving individual values of k_1 in error by 5%. Only expression for k_1 given for M=Ar. We have used their expression for k_{-1}(M=Ar) to derive their K_1 (which gives values consistently lower by a factor 4 than those tabulated by us) and hence k_1(M=N_2). Presented in Arrhenius form $k_1=8.8\times10^{13}\exp(-15\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$ (1000-1600 K) by (10). Quoted by (14).
$4.11\times10^{15}T^{-\frac{1}{2}}\exp(-17\ 860/T)$ M=I_2	1000-4000	Shock tube study. Pure I_2 behind incident shocks. Details only of pre-shock conditions given. Absorption 466-700 nm used to follow I_2. GENERALOV, LOSEV, KOSYNKIN and OVECHKIN 1965 (8)	Scale of graphical presentation of data too small to retrieve individual values of k_1. Values for k_1 of 1.0×10^{8} and 1.5×10^{11} $cm^3\ mol^{-1}\ s^{-1}$ at 1000 and 4000 K respectively quoted by authors: these are not fitted by the "approximate" expression presented here. Authors also quote E_1=105 kJ mol^{-1} (25 kcal mol^{-1}) for alternative Arrhenius form.
$1.78\times10^{21}T^{-2.1}\exp(-17\ 880/T)$ M=Ar,N_2	1000-1900	Shock tube study. I_2 (0.3-3%)/Ar, I_2 (0.4-1.4%)/CO_2/Ar (CO_2:Ar ratio 0.44) and I_2(0.6-1%)/N_2 mixtures. Incident shocks. Decay of I_2 monitored by uv absorption at 492.5 nm. SLACK 1967 (9)	Expression for k_1 in 69.4%Ar/30.6%CO_2 mixture given as $k_1=1.88\times10^{21}\ T^{-2.1}\exp(-17\ 880/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over range 1080-1700 K, from which we derive k_1(M=CO_2)= $2.11\times10^{21}T^{-2.1}\exp(-17\ 880/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Expression given in abstract k_1(M=Ar,N_2) lower than quoted expression by factor 100.
$9.8\times10^{13}\ \exp(-15\ 300/T)$ M=Ar	860-1660	Shock tube study. I_2(0.1-0.15%)/Ar mixtures. Incident shocks. Total concentrations 3×10^{-5}-2×10^{-4} mol cm^{-3}. No details given of measurements made. TROE and WAGNER 1967 (11).	Fall-off to high pressure region found for [Ar]>10^{-5} mol cm^{-3}. Temperature range given in (10) as 850-1650 K. Empirical expression $k_1=1.59\times10^{22}T^{-2.4}\exp(-17910/T)$ $cm^3\ mol^{-1}\ s^{-1}$ given by (13) for this work, over range 850-1600K. Quoted by (14). Listed by (15).

$I_2 + M \rightarrow I + I + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(6.9 \pm 2) \times 10^{13} \exp(-15\ 200/T)$ M=Ar,N_2	1000-1915	Shock tube study. I_2 (0.3 -3%)/Ar (or N_2) mixtures behind incident shocks. I_2 followed by uv absorption at 492.5 nm. SLACK, BRAY, EAST and PRATT 1971 (12)	No distinguishable dependence upon diluent was observed.
REVIEW ARTICLES			
$2.59 \times 10^{20} T^{-1.8} \exp(-17\ 900/T)$ M=Ar $1.09 \times 10^{17} T^{-\frac{1}{2}} \exp(-15\ 800/T)$ M=I_2	300-2000 300-2000	Evaluation. DAVIDSON 1961 (7)	k_1(M=Ar) derived from K_1 (as given by author) and combination of k_{-1}(M=Ar) at 300 K from (3,4 and 6) and at 1300 K from (1 and 2). We have calculated k_1(M=I_2) from K_1 and author's preferred expression for k_{-1}(M=I_2), close to that of (3 and 6). $I_2 + M \rightleftharpoons I + I + M$ 1,-1
(a) $1.59 \times 10^{22} T^{-2.4} \exp(-17\ 910/T)$ M=Ar (b) $7.92 \times 10^{20} T^{-2} \exp(-17\ 910/T)$ M=Ar	850-1600 302- 548	Review. WAGNER 1971 (13) and TROE and WAGNER 1973 (15)	Empirical expressions used to fit (a) k_1 from I_2 dissociation data (11) and (b) k_1 from $k_{-1}K_1$, using k_{-1} from I atom recombination data (5).

Discussion

Measurements of the dissociation rate of molecular iodine

$$I_2 + M \rightarrow I + I + M \tag{1}$$

have been restricted to shock tube methods, using Ar or N_2 as diluent gases (cf. the vast array of diluents used in the determinations of k_{-1} (section D2))

$$I + I + M \rightarrow I_2 + M \tag{-1}$$

Britton et al. [1] analysed this data solely in terms of k_{-1}, even in cases where the recombination reaction could be ignored. This approach conceals the true temperature variation of either rate constant and so these data have been given little weight, particularly as their data for K_1 are incorrect. Generalov et al. [8] have been the only authors to study the dissociation of pure iodine, but it is not clear why they have quoted an expression for k_1(M=I_2) that clearly disagrees with their graphical presentation. Consequently we have only considered the remaining data [9,11,12], for k_1(M=Ar or N_2) in this evaluation, and of these, that of [12] is merely a later appreciation of the original data of Slack [9].

On the basis of the two sets of data [12 and 11] we tentatively recommend the expression

$$k_1(M=Ar,N_2) = 8.25 \times 10^{13} \exp(-15\ 250/T)\ cm^3\ mol^{-1}\ s^{-1}$$

over the range 800–2000 K, with error limits of ±20% over the whole range. The above expression is compatible with our recommendation for k_{-1}, using the equilibrium constant K_1, for the region of temperature overlap between the two expressions.

Third body collision efficiencies

M = Ar	N_2	I_2	CO_2	Temperature	Reference
Experimental Data					
1	1.05			1060–1860	Britton et al. 1954 [1].
1	1		1.18	1080–1700	Slack 1967 [9].
1	1			1000–1915	Slack et al. 1971 [12].
Review Articles					
1		755		300	Davidson 1961 [7].
1		24		2000	
1	1			800–2000	This evaluation.

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D2 $I + I + M \rightarrow I_2 + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm^{-1})	log K_c (K_c in cm^3 mol^{-1})
298	-151.084	-100.763	21.206	25.594
300	-151.093	-100.793	21.043	25.434
500	-151.963	-103.031	10.494	15.107
1000	-153.896	-105.726	2.516	7.430
1500	-155.712	-107.198	-0.178	4.912
2000	-157.628	-108.299	-1.540	3.675
2500	-159.837	-109.282	-2.368	2.944
3000	-162.348	-110.198	-2.930	2.461
3500	-165.092	-111.035	-3.336	2.122
4000	-167.929	-111.797	-3.646	1.870
4500	-170.757	-112.462	-3.892	1.675
5000	-173.502	-113.043	-4.092	1.521

SI Units: $\log(K_p/Pa^{-1}) = \log(K_p/atm^{-1}) - 5.0056$

$\log(K_c/m^3\ mol^{-1}) = \log(K_c/cm^3\ mol^{-1}) - 6.000$

RECOMMENDED RATE CONSTANT

$k = 2.36 \times 10^{14} \exp(754/T)\ cm^6\ mol^{-2}\ s^{-1}$ (M=Ar)

$= 6.51 \times 10^{-34} \exp(754/T)\ cm^6\ molecule^{-2}\ s^{-1}$ (M=Ar)

(k is defined by $-d[I]/dt = 2k[I]^2[M] = 2d[I_2]/dt$)

Temperature Range: 290-1250 K.

Suggested Error Limits for Calculated Rate Constant: ±30% over the quoted temperature range.

Note: Expressions for other third bodies are presented in the Discussion.

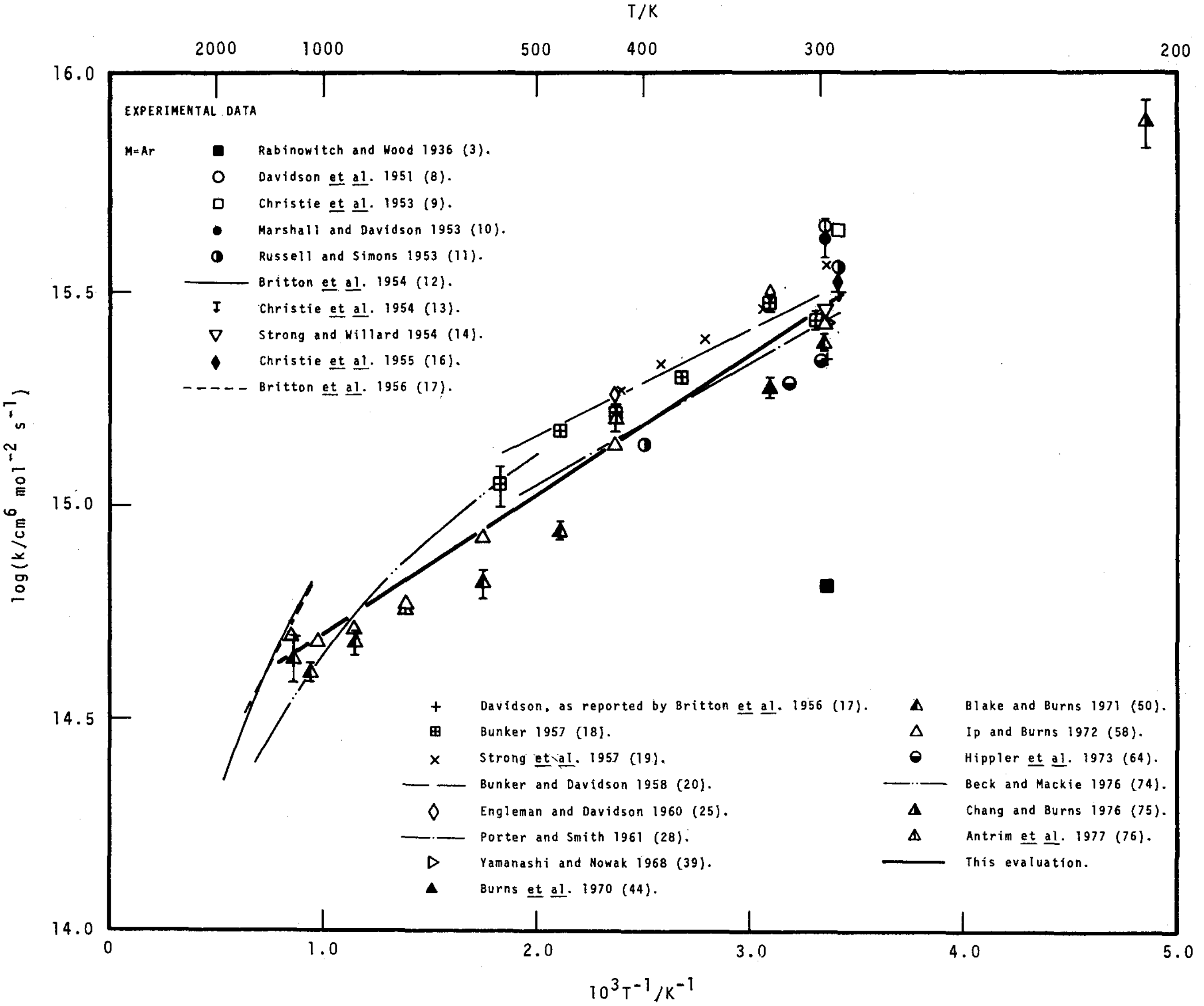
Rate Parameters: $\log(A/cm^6\ mol^{-2}\ s^{-1}) = 14.37 \pm 0.1$

$\log(A/cm^6\ molecule^{-2}\ s^{-1}) = -33.19 \pm 0.1$

$E/J\ mol^{-1} = -6276 \pm 1300$

$E/cal\ mol^{-1} = -1500 \pm 310$

$I + I + M \rightarrow I_2 + M$

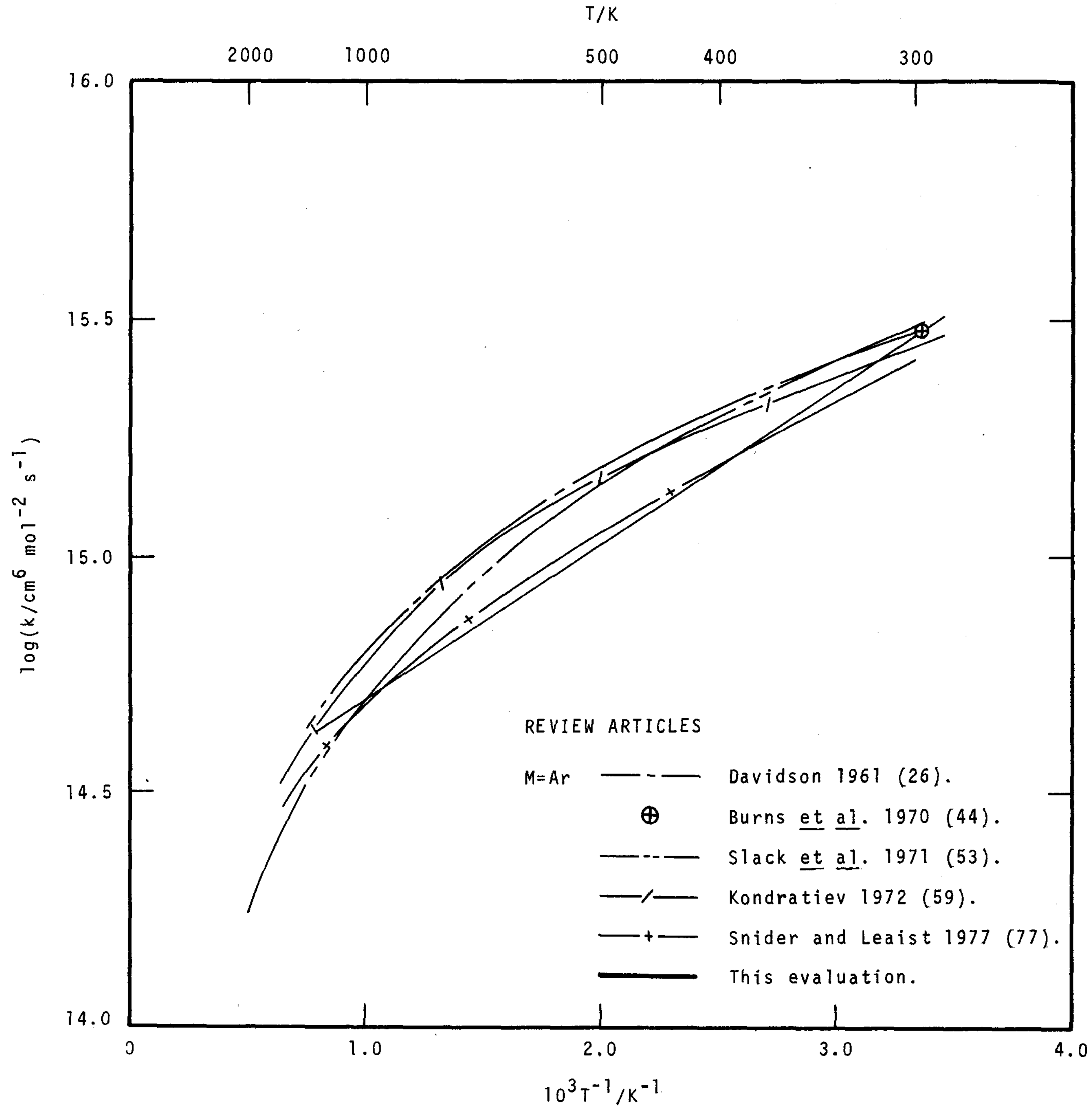


$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
3.35×10^{15} M=He 6.5×10^{14} M=Ar 1.2×10^{16} M=N_2 7.25×10^{15} M=H_2 1.9×10^{16} M=O_2 3.3×10^{16} M=CO_2 2.2×10^{16} M=CH_4 1.75×10^{17} M=C_6H_6	298 298 298 298 298 298 298 298	Static system. Photolysis of I_2(0.14-0.16 mm Hg; 18.7-21.3 Pa)/He, Ar,N_2, H_2,O_2,CO_2,CH_4 or C_6H_6 mixtures (total pressures 15.2-754 mm Hg; 2.03-100.5 kPa). I_2 followed by uv absorption 440-520 nm. RABINOWITCH and WOOD 1936 (3)	Corrections made for thermal effects of reaction. Value of k_1(M=Ar) quoted as 6.9×10^{15} $cm^6\ mol^{-2}\ s^{-1}$ in (2,4 and 5). $I + I + M \rightarrow I_2 + M$ 1 Authors made no allowance for efficiency of I_2 as collision partner. Value 9.8×10^{15} $cm^6\ mol^{-2}\ s^{-1}$ for k_1(M=He,Ar,H_2,N_2 and O_2) quoted by (7).
4.5×10^{15} M=Ar	298	Flash photolysis study. I_2($\sim1\times10^{-8}$ mol cm^{-3})/Ar mixtures at total pressures of $\sim$1 atm (101.3 kPa). I_2 followed by uv absorption - no wavelength given. DAVIDSON, MARSHALL, LARSH and CARRINGTON 1951 (8)	Authors believed k_1 showed signs of decreasing with increasing [M], but related this to an unexplained systematic error, rather than to transition to high-pressure region, or to effects of higher collision efficiency of I_2.
3.14×10^{15} M=He 4.39×10^{15} M=Ar 3.37×10^{15} M=Ne 6.18×10^{15} M=Kr 6.24×10^{15} M=Xe $\leqslant3.63\times10^{16}$ M=I_2	293 293 293 293 293 293	Flash photolysis study. I_2 /inert gas mixtures at total pressures 25-400 mm Hg (3.3-53.3 kPa). [I_2] monitored by uv absorption 490-560 nm. CHRISTIE, NORRISH and PORTER 1953 (9)	Authors estimated overall error as ±5%. Upper limit of k_1(M=I_2) estimated from deviation of low pressure (M=Ar) results from those at high pressure. No account taken of efficiency of I_2. k_1(M=I_2) misquoted as 1.7×10^{18} $cm^6\ mol^{-2}\ s^{-1}$ by (57). Used by (22).
$(4.2\pm0.4)\times10^{15}$ M=Ar $(6.5\pm0.6)\times10^{16}$ M=C_5H_{12} $(5.8\pm0.4)\times10^{16}$ M=neo-C_5H_{12} 5.9×10^{16}	298 298 298 473	Flash photolysis study. I_2/Ar, C_5H_{12} or neo-C_5H_{12} mixtures at total pressures 206-1580 mm Hg (27.5-210.6 kPa) (Ar), 48.6-71.8 mm Hg (6.5-9.6 kPa) (C_5H_{12}), and 38.5-77 mm Hg (5.1-10.3 kPa) (neo-C_5H_{12}). [I_2] (1-1.8$\times10^{-8}$ mol cm^{-3}) monitored by uv absorption at 546 or 487 nm. MARSHALL and DAVIDSON 1953 (10)	Evaluation of heterogeneous wall recombination showed this effect to be negligible. Greatest source of error believed to be in extinction coefficient measurement. Efficiency of I_2 as third body not recognised.

$I + I + M \rightarrow I_2 + M$

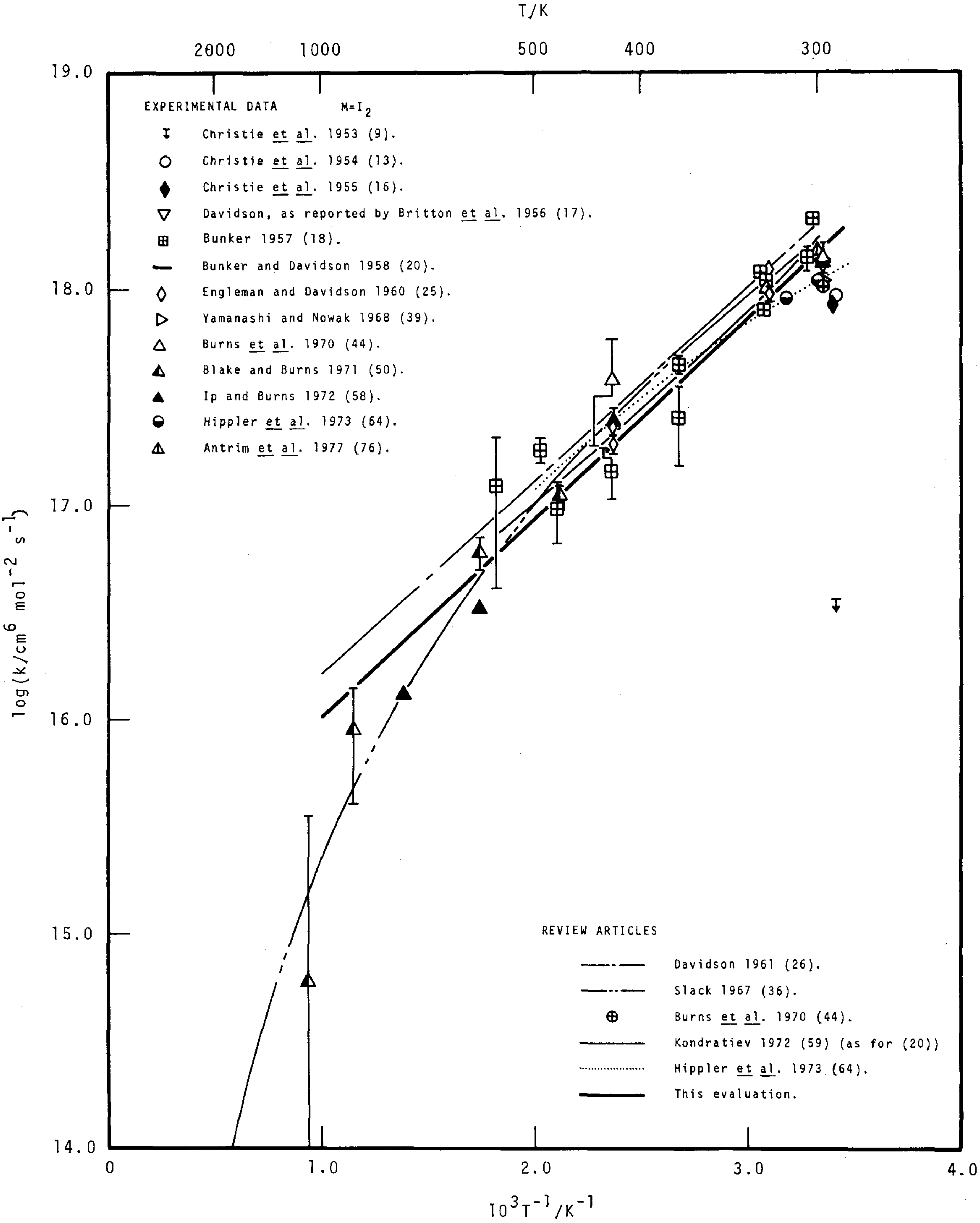


$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
1.7 x10^{15}	M=He	293	Flash photolysis study. I_2/He,Ar,Ne,H_2,N_2,O_2,CO_2,CH_4,C_2H_4 and I_2/Ar/C_3H_8,C_5H_{12},$C_3H_6(CH_3)_2$,C_2F_4,$C_6H_3F_3$,$C_6H_5CH_3$,$C_6H_4(CH_3)_2$, $C_6H_3(CH_3)_3$,H_2O,CH_3OH,C_2H_5Cl,C_2H_5Br,C_2H_5I mixtures. I_2 followed by absorption of blue-green light. RUSSELL and SIMONS 1953 (11)	Ar added to those mixtures for which k_1>1.8x10^{16} cm^6 mol^{-2} s^{-1} in order to suppress thermal effects. Temperature variation expressed as activation energy of -8.4 kJ mol^{-1}(-2.0 kcal mol^{-1}). No correction made for I_2 as third body. Rough corrections made by (25) to give k_1(M=He)= 1.38x10^{15} cm^6 mol^{-2} s^{-1} (293 K) and 8.2x10^{14} cm^6 mol^{-2} s^{-1} (400 K); k_1(M=C_6H_6)=1.04x10^{17} cm^6 mol^{-2} s^{-1} (293 K) and 4.75x10^{16} cm^6 mol^{-2} s^{-1} (400 K). Authors admit result for k_1(M=CH_3NO_2) may be inaccurate. k_1(M=N_2) used by (23 and 65). k_1(M=He,Ne,Ar) used by (22). Value of k_1(M=CO_2) used in (23) 10% lower than value given here, and k_1(M=Ne) 50% higher. Authors noted linear dependence of log k_1(M) upon boiling-point of M, being a measure of the van der Waals attraction.
8.5 x10^{14}		400		
3.6 x10^{15}	M=Ar	293		
1.4 x10^{15}		400		
4.5 x10^{15}	M=N_2	293		
1.8 x10^{15}		400		
1.4 x10^{16}	M=CO_2	293		
5.4 x10^{15}		400		
8.6 x10^{16}	M=C_6H_6	293		
2.8 x10^{16}		400		
1.8 x10^{15}	M=Ne	293		
4.8 x10^{15}	M=H_2	293		
6.7 x10^{15}	M=O_2	293		
8.9 x10^{15}	M=CH_4	293		
3.05x10^{16}	M=C_3H_8	293		
4.1 x10^{17}	M=$C_6H_3(CH_3)_3$	293		
2.5 x10^{17}	M=C_2H_5I	293		
3.95x10^{16}	M=c-C_3H_6	293		
4.70x10^{16}	M=n-C_5H_{12}	293		
4.35x10^{16}	M=neo-C_5H_{12}	293		
5.44x10^{16}	M=c-C_6H_{14}	293		
1.71x10^{16}	M=C_2H_4	293		
2.10x10^{16}	M=C_2F_4	293		
8.78x10^{16}	M=$C_6H_3F_3$	293		
2.10x10^{17}	M=$C_6H_5CH_3$	293		
3.32x10^{17}	M=p-$C_6H_4(CH_3)_2$	293		
4.97x10^{16}	M=H_2O	293		
6.49x10^{16}	M=CH_3OH	293		
6.18x10^{16}	M=$(CH_3)_2O$	293		
4.77x10^{16}	M=CH_2Cl_2	293		
5.08x10^{16}	M=CCl_4	293		
4.77x10^{16}	M=CH_3Cl	293		
8.02x10^{16}	M=CH_3Br	293		
1.87x10^{17}	M=CH_3NO_2	293		
3.72x10^{20}$T^{-1.9\pm0.14}$	M=Ar	1060-1860	Shock tube study. I_2(∿1%)/Ar mixtures behind incident shocks. Uv absorption 436 and 490 nm used to follow $[I_2]$. BRITTON, DAVIDSON and SCHOTT 1954 (12)	Net removal rate of I_2 expressed in terms of k_1 only, conversion of dissociation rate constant k_{-1} being made using K_1 $I + I + M \rightleftharpoons I_2 + M$ 1,-1 Possible errors in shock velocity measurement gave possible 26% error in values of k_1. Value k_1(M=N_2) is that for vibrationally unexcited N_2. Listed by (41). No allowance for I_2 as third body.
3.8 x10^{20}$T^{-1.91\pm.29}$	M=N_2	1060-1860		
∿9.07x10^{17}	M=I_2	293	Method presumably as for (9). CHRISTIE, NORRISH and PORTER 1954 (13)	Continuation of study described in (9), over wider range of conditions. Decrease in k_1 during recombination, and increase in k_1 with ratio $[I_2]$/$[Ar]$ observed. We have assumed k_1 defined as in (9) and have consequently halved the quoted values.
$\le$3.17x10^{15}	M=Ar	293		

$I + I + M \rightarrow I_2 + M$

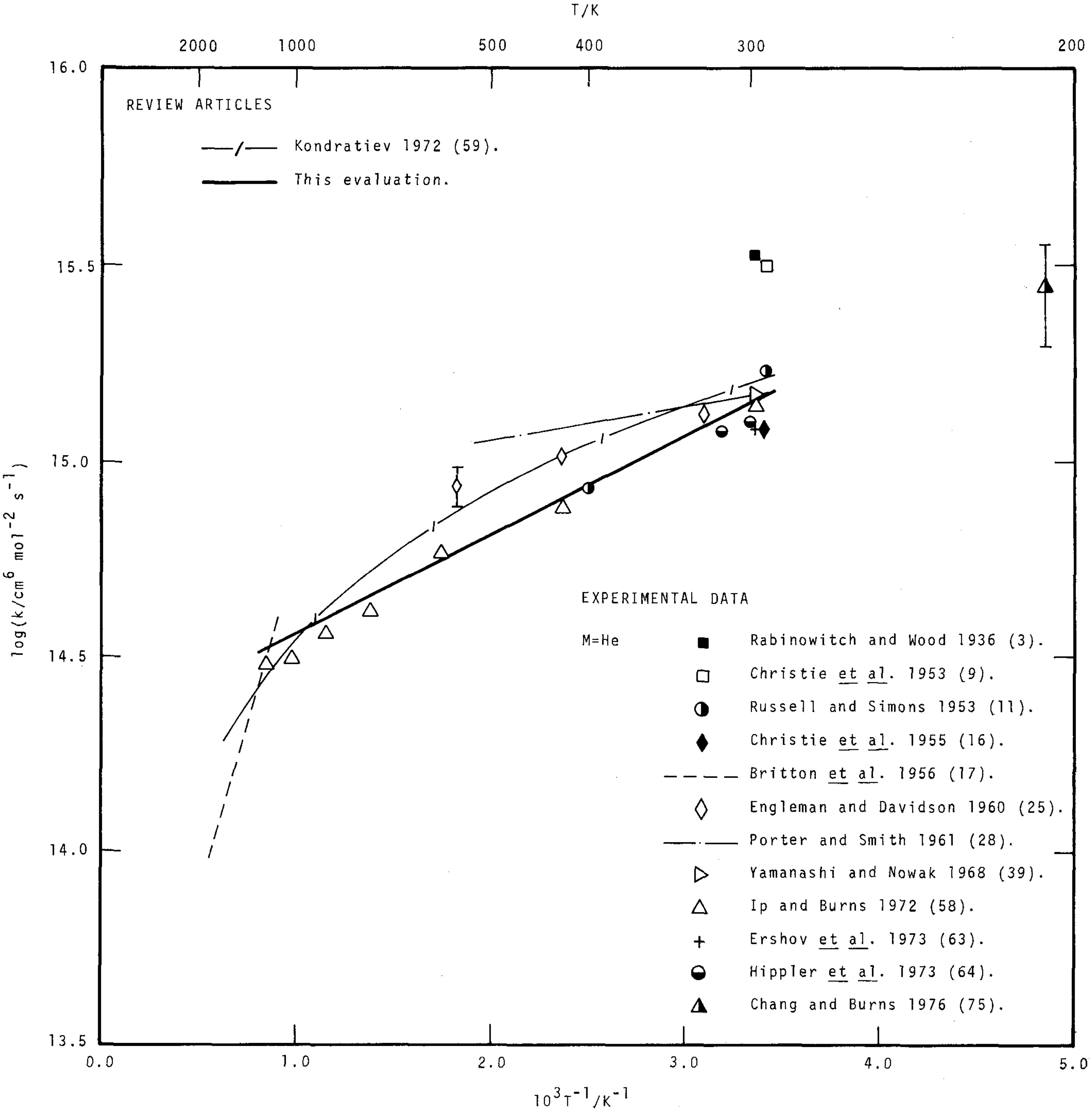


$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(2.9\pm0.2)\times10^{15}$ M=Ar 5.7×10^{15} M=CCl_4	298 298	Flash photolysis study. I_2 /Ar mixtures, $[I_2]$ 9.3-12.4x10^{-9} mol cm^{-3}, and $[I_2]/[Ar]$ = 3-3.8x10^{-4}. I_2 followed by uv absorption at unspecified wavelength. STRONG and WILLARD 1954 (14)	Quoted value for M=Ar is average of 4 values at 298 K. Reported by (16 and 19).
3.34×10^{15} M=Ar 1.22×10^{15} M=He 1.67×10^{15} M=Ne 4.08×10^{15} M=Kr 5.42×10^{15} M=Xe 8.53×10^{17} M=I_2	294 294 294 294 294 294	Flash photolysis study. I_2(0.03-0.18 mm Hg; 4-24 Pa)/inert gas mixtures. Ratio $[M]/[I_2]$ varied 2.8x10^2-3.3x10^4. I_2 followed by uv absorption 360-580 or 510-650 nm. CHRISTIE, HARRISON, NORRISH and PORTER 1955 (16)	Fuller description of phenomena reported in (13). Authors argued that thermal effects caused decrease in k_1 as recombination proceeded, and that high collision efficiency of I_2 relative to inert gas gave dependence upon $[I_2]/[M]$. Maximum values of k_1 at start of reaction taken as true values of k_1. For $[I_2]/[M] \leqslant 10^{-3}$, k_1 falls below extrapolation of linear relationship. Data quoted by (32), k_1(M=I_2) used by (42). Slightly different values quoted by CHRISTIE (29) after omission of less reliable data.
$7.6\times10^{13}\exp(2300\pm160/T)$ M=Ar $1.04\times10^{13}\exp(4000\pm500/T)$ M=He $1.3\times10^{14}\exp(4760/T)$ M=CO_2 $6.8\times10^{13}\exp(2430\pm330/T)$ M=N_2 5.3×10^{14} M=O_2	1080-1570 1100-1800 1000-1400 1100-1740 1275	Shock tube study. Mixture ratios I_2/M and initial shocked gas (incident shock) pressures: 0.025-0.075 atm (3.3-10 Pa), 0.002-0.018 (M=Ar); 0.015-0.03 atm (2-4 Pa), 0.007-0.011 (M=He); 0.01-0.05 atm (1.3-6.7 Pa), 0.005-0.02 (M=CO_2); 0.01-0.05 atm (1.3-6.7 Pa), 0.004-0.02 (M=N_2); and ∿0.03 atm (4 Pa), 0.007 (M=O_2). I_2 followed by uv absorption at 484 (M=He,O_2), 487 and 437 nm. BRITTON, DAVIDSON, GEHMAN and SCHOTT 1956 (17)	Values of k_1 obtained via k_{-1} and K_1, as for (12). No theoretical basis for simple Arrhenius plot, so authors give alternative expressions: k_1(M=Ar)=$1.49\times10^{20}T^{-1.77\pm0.12}$; k_1(M=He)=$1.88\times10^{23}T^{-2.85\pm0.8}$; k_1(M=CO_2)=$2.66\times10^{28}T^{-4.74}$; k_1(M=N_2)=$6.06\times10^{19}T^{-1.65\pm0.24}$ $cm^6\ mol^{-2}\ s^{-1}$. Vibrational relaxation data for N_2, O_2 (15) and CO_2 (6) used to show N_2 unexcited, and CO_2 and O_2 vibrationally excited. Authors also quote unpublished room temperature work: k_1(M=Ar)=2.2×10^{15}, k_1(M=I_2)=1.3×10^{18} $cm^6\ mol^{-2}\ s^{-1}$, reported by (19) and listed by (41).
$(2.72\pm0.13)\times10^{15}$ $(2.99\pm0.13)\times10^{15}$ $(2.01\pm0.08)\times10^{15}$ $(1.66\pm0.05)\times10^{15}$ $(1.50\pm0.06)\times10^{15}$ $(1.13\pm0.11)\times10^{15}$ M=Ar	302 323 373 423 473 548	Flash photolysis study. Details given in (20). BUNKER 1957 (18)	Data presented here used by (20) as basis for Arrhenius and other fitted expressions.

$I + I + M \rightarrow I_2 + M$

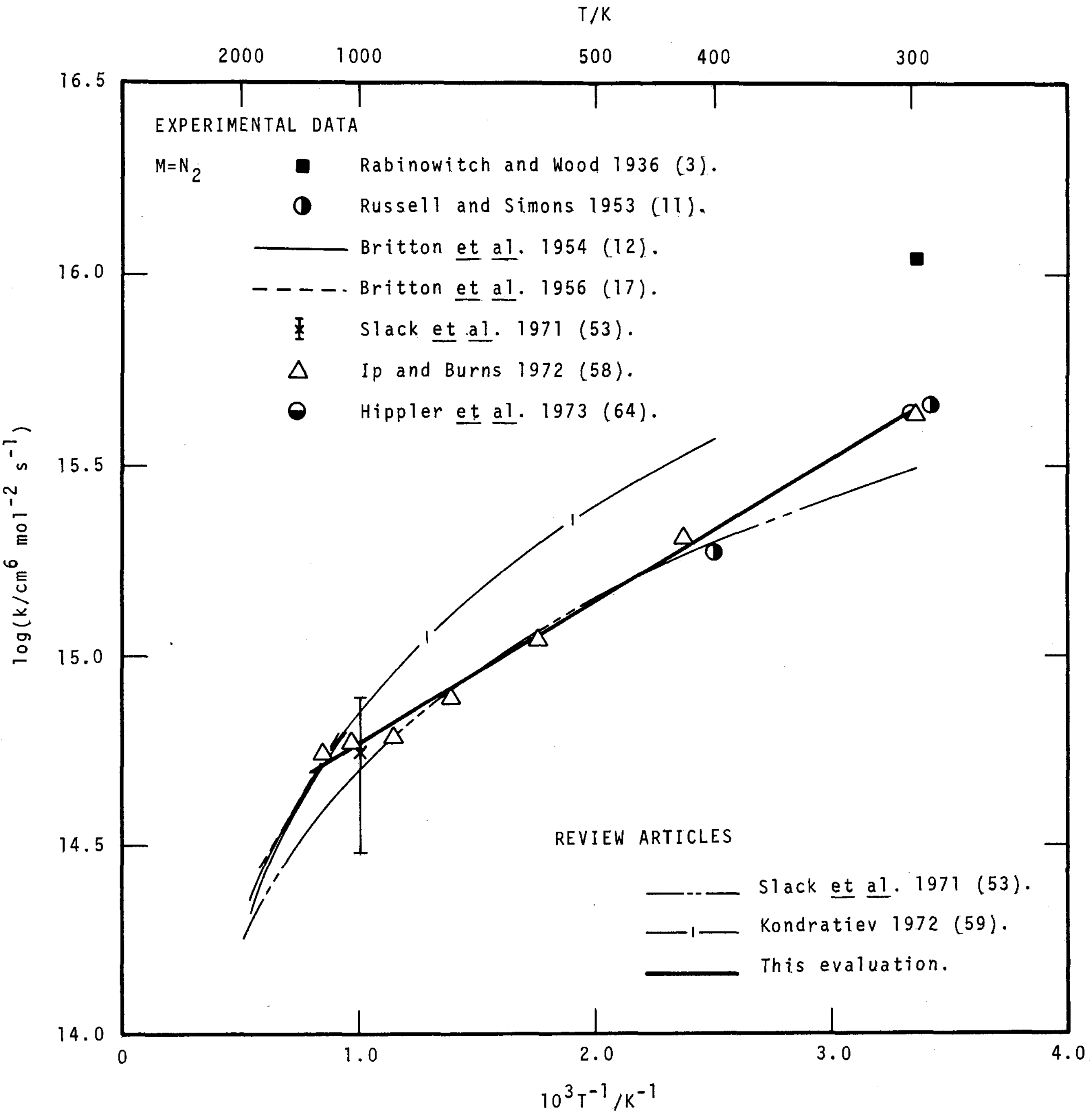


$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$(2.11\pm0.18)\times10^{18}$	M=I_2	302	BUNKER 1957 (18) continued.	
$(1.73\pm0.22)\times10^{18}$		305		
$(1.07\pm0.18)\times10^{18}$		323		
$(7.54\pm0.22)\times10^{17}$		325		
$(1.20\pm0.05)\times10^{18}$		326		
$(2.5\pm1)\times10^{17}$		373		
$(4.42\pm0.42)\times10^{17}$		373		
$(1.43\pm0.38)\times10^{17}$		423		
$(9.6\pm3.0)\times10^{16}$		473		
$(1.79\pm0.22)\times10^{17}$		493		
$(1.23\pm0.82)\times10^{17}$		548		
$(3.36\pm0.16)\times10^{16}$	M=n-C_4H_{10}	305		
$(2.17\pm0.2)\times10^{16}$		373		
$(1.20\pm0.1)\times10^{16}$		493		
$(4.43\pm0.08)\times10^{15}$	M=H_2	326		
$(3.97\pm0.04)\times10^{15}$	M=D_2	325		
$(3.65\pm0.15)\times10^{15}$	M=Ar	298	Flash photolysis study. I_2/Ar mixtures, $[I_2]$ 1.24-1.28x10^{-8} mol cm^{-3}, and $[I_2]/[Ar]$ = 3.8-4.4x10^{-4}. I_2 followed by uv absorption at unspecified wavelength. STRONG, CHIEN, GRAF and WILLARD 1957 (19)	Apparent activation energy E_1= -5.9 kJ mol^{-1} (-1.4 kcal mol^{-1}) fitted by authors to these data. $I + I + M \rightarrow I_2 + M$ 1 No variation in values of k_1 observed when only photolysis >500 nm permitted, indicating no effects from excited I ($^2P_{\frac{1}{2}}$) atoms.
$(2.92\pm0.07)\times10^{15}$		328		
$(2.45\pm0.05)\times10^{15}$		359		
$(2.15\pm0.08)\times10^{15}$		388		
$(1.87\pm0.07)\times10^{15}$		418		
$4.68\times10^{14}\exp(570/T)$	M=Ar	302-548	Flash photolysis study. I_2/Ar, n-C_4H_{10},H_2 or D_2 mixtures. Ratios $[I_2]/[Ar]<2.5\times10^{-3}$,$[I_2]/[n\text{-}C_4H_{10}]<1.75\times10^{-2}$, and $[I_2]/[H_2,D_2]<3.25\times10^{-3}$. $[I_2]$ monitored by uv absorption at 481 nm. BUNKER and DAVIDSON 1958 (20)	Values for $k_1(M=H_2)$ and $k_1(M=D_2)$ taken from graph - authors quote only ratio of these values. Arrhenius expressions and expression for $k_1(M=I_2)$ are least-squares fits given by authors. Alternative expression for $k_1(M=n\text{-}C_4H_{10})$ also given: $7.73\times10^{21}T^{-2.16}$ cm^6 mol^{-2} s^{-1}. Least-squares fit to k_1(M=Ar) also given, using shock tube data of (17) at T=1285 K, as $k_1(M=Ar)=5.82\times10^{18}T^{-1.33}$ cm^6 mol^{-2} s^{-1} (298-1600 K). Listed by (40). $k_1(M=I_2)$ used by (37, 60 and 71). Expression $k_1(M=Ar)=3.5\times10^{14}\exp(640/T)$ cm^6 mol^{-2} s^{-1} used by (60), derived from this work and that of CHRISTIE _et al_. (16), which agrees within 11% over the range 300-1100 K with expression of KONDRATIEV (59).
$2.29\times10^{15}\exp(830/T)$	M=n-C_4H_{10}	305-493		
4.4×10^{15}	M=H_2	326		
3.9×10^{15}	M=D_2	326		
$4.47\times10^{10}T^{1.5}\exp(2680/T)$	M=I_2	302-548		

$I + I + M \rightarrow I_2 + M$



$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
	$3.15x10^{15}$	M=Ar	323	Flash photolysis study. Method as for (20). Range of third bodies enlarged to include Ar,He,H_2,C_6H_6, CH_3I,C_2H_5I,HI,CO and NO. ENGLEMAN and DAVIDSON 1960 (25)	k_1 determined from slope of $1/[I]$ plots early in reaction. Values (a) and (b) for $k_1(M=I_2)$ derived from Ar and He mixtures respectively, and are subject to considerable experimental error at higher temperatures due to decreasing relative efficiency of I_2. Correction made to $k_1(M=H_2)$ at 423 K using $k_1(M=I_2)$ determined from I_2/He mixtures, and to other data (M≠Ar,He (except k_1(M=He) at 548 K)) using $k_1(M=I_2)$ from (20). Reaction 1 with M=NO found to be very rapid, presumed due to catalysis via $I + NO \rightleftarrows NOI$ $I + NOI \rightarrow I_2 + NO$ Authors presented alternative expressions $k_1(M=He)=4.8x10^{14}exp(330/T)$ or $1.35x10^{17}T^{-0.8}$ $cm^6\ mol^{-2}\ s^{-1}$, $k_1(M=C_6H_6)=3.9x10^{15}exp(990/T)$ or $1.82x10^{23}T^{-2.53}$ $cm^6\ mol^{-2}\ s^{-1}$, $k_1(M=CH_3I)=2.3x10^{15}exp(1280/T)$ or $1.56x10^{25}T^{-3.24}$, $k_1(M=H_2)=6.6x10^{14}exp(610/T)$ or $2.26x10^{19}T^{-1.48}$ $cm^6\ mol^{-2}\ s^{-1}$ (latter using $k_1(M=H_2)$ at 326 K from (20)). Listed by (41). $k_1(M=CH_3I)$ used by (71). $k_1(M=H_2)$ used by (37).
	$1.84x10^{15}$		423		
	$(1.33 \pm 0.06)x10^{15}$	M=He	323		
	$(1.04 \pm 0.03)x10^{15}$		423		
	$(8.7 \pm 1.0)\ x10^{14}$		548		
	$(2.84 \pm 0.1)\ x10^{15}$	$M=H_2$	423		
	$(2.03 \pm 0.13)x10^{15}$		548		
	$(8.12 \pm 0.44)x10^{16}$	$M=C_6H_6$	323		
	$(5.72 \pm 0.38)x10^{16}$		373		
	$(3.1 \pm 0.13)\ x10^{16}$		473		
	$(1.18 \pm 0.05)x10^{17}$	$M=CH_3I$	323		
	$(6.97 \pm 0.29)x10^{16}$		373		
	$(3.4 \pm 0.21)\ x10^{16}$		473		
	$(2.38 \pm 0.23)x10^{17}$	$M=C_2H_5I$	323		
	$(2.81 \pm 0.18)x10^{16}$	M=HI	323		
	$(5.42 \pm 0.16)x10^{15}$	M=CO	323		
	$>4.8x10^{20}$	M=NO	323		
(a)	$1.2x10^{18}$	$M=I_2$	323		
(b)	$(9.73 \pm 1.0)\ x10^{17}$		323		
(a)	$1.90x10^{17}$		423		
(b)	$(2.27 \pm 0.53)x10^{17}$		423		
			298	Pulsed flash photolysis study. $I_2(6.5x10^{-9}\ mol\ cm^{-3})/Ar(2.4x10^{-5}\ mol\ cm^{-3})$ mixture. Uv absorption at 521 nm used to monitor $[I_2]$. KRAMER, HANES and BAIR 1961 (27)	Variation of flash energy used to obtain different initial values of $[I]$. Results showed non-linear behaviour, which was not understood by authors.
	$3.08x10^{14}exp(650/T)$	M=Ar	293-523	Flash photolysis study. I_2 (∿0.02%)/Ar,He,O_2 or CO_2 mixtures. Also mixtures of $I_2/He/C_2H_5I,C_6H_6,C_6H_5CH_3$, $C_6H_3(CH_3)_3$. No explicit description of monitoring method given. PORTER and SMITH 1961 (28)	Good linear fits of data found not only for log k_1 but also for $log(k_1/T)$ vs. T^{-1}, giving alternative expressions $k_1(M=Ar)=3.27x10^{11}T\ exp(1010/T)$, $k_1(M=He)=4.72x10^{11}T\ exp(705/T)$, $k_1(M=O_2)=5.25x10^{11}\ T\ exp(1110/T)$, $k_1(M=CO_2)=7.45x10^{11}T\ exp(1210/T)$, $k_1(M=C_6H_6)=4.35x10^{12}T\ exp(1210/T)$, $k_1(M=C_6H_5CH_3)=2.0x10^{12}T\ exp(1710/T)$, $k_1(M=C_2H_5I)=4.35x10^{12}T\ exp(1560/T)$, and $k_1(M=C_6H_3(CH_3)_3)=3.63x10^{11}T\ exp(2420/T)$ $cm^6\ mol^{-2}\ s^{-1}$. These
	$7.62x10^{14}exp(200/T)$	M=He	293-523		
	$5.08x10^{14}exp(760/T)$	$M=O_2$	293-523		
	$6.71x10^{14}exp(880/T)$	$M=CO_2$	293-523		
	$4.32x10^{15}exp(860/T)$	$M=C_6H_6$	293-523		
	$1.87x10^{15}exp(1360/T)$	$M=C_6H_5CH_3$	293-523		
	$4.23x10^{15}exp(1210/T)$	$M=C_2H_5I$	293-523		
	$3.45x10^{14}exp(2060/T)$	$M=C_6H_3(CH_3)_3$	295,427		

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
			PORTER and SMITH 1961 (28) continued.	expressions reported in earlier work by these authors (24). Listed by (41). $k_1(M=CO_2)$ and $k_1(M=I_2)$ used by (64). $k_1(M=He)$ used by (71). $k_1(M=I_2)$ quoted by (45).
$1.9x10^{15}$ $3.0x10^{19}$	M=Ne M=NO	333 333	Flash photolysis study. I_2 (∿0.03 mm Hg; 4 Pa)/NO(∿0.4 mm Hg; 53.2 Pa)/Ne (∿300 mm Hg; 40 kPa) mixtures. I_2 followed by uv absorption spectroscopy at 520 nm. PORTER, SZABO and TOWNSEND 1962 (31)	Measurements made at several temperatures, but authors only give apparent activation energies $E_1(M=Ne)$ and $E_1(M=NO)$ as -6.3 kJ mol^{-1} (-1.5 kcal mol^{-1}) and -9.2 kJ mol^{-1} (-2.2 kcal mol^{-1}) respectively. Transient spectrum at 430 nm (for p_{NO}≥20 mm Hg; 2.7 kPa) attributed to NOI.
		373	Static system. $^{131}I_2$(1.14-8.58x10^{-9} mol cm^{-3})/CF_3I (2.07-8.83x10^{-6} mol cm^{-3}) mixtures illuminated by Hg lamp at 546.1 nm. Fractional exchange measured by condensing out I_2 and using scintillation counter for CF_3I. Light absorption also monitored. LAURENCE 1967 (35)	Absorbed light intensity varied by rotating sector, over range 30 to 1. Mean life-time of I atoms calculated from rotating sector function, and yields k_1, believed value for second order under conditions of this study. Author gives k_1' $I + I \rightarrow I_2$ 1' of (5.1±2.0)x10^{10} cm^3 mol^{-1} s^{-1}. Used by (46) to derive $k_1(M=CF_3I)$ = 1.57x10^{16} cm^6 mol^{-2} s^{-1} at room temperature.
		418-520	Static photolysis system. H_2(1.77x10^{-6}-1.19x10^{-5} mol cm^{-3})/I_2(5.67x10^{-8}-2.31x10^{-7} mol cm^{-3}) mixtures photolysed at 566-599 nm. Resulting HI distilled off and pressure determined. Transmitted light intensity measured. SULLIVAN 1967 (37)	Corrections made for small amount of HI formed by thermal reaction alone. From graphical analysis of HI and absorbed light intensity ratio $k_1(M=I_2)/k_1(M=H_2)$ obtained as 79(417.9 K), 44(480.7 K), and 38(520.1 K). Uncertainty in these values ±15%.
$2.74x10^{15}$ $1.49x10^{15}$ $1.61x10^{15}$ $5.99x10^{15}$ $1.09x10^{18}$	M=Ar M=He M=Ne $M=CH_4$ $M=I_2$	298 298 298 298 298	Flash photolysis study. I_2 (200-300 μ Hg; 26.7-40 Pa) /He,Ne,Ar or CH_4 (34-204 mm Hg; 4.53-27.2 kPa) mixtures. I_2 followed by absorption at 499.5 nm. YAMANASHI and NOWAK 1968 (39)	Values of k_1 obtained from profiles of $[I]^{-1}$. Uncertainties due to random errors given as ±20% for $k_1(M=Ar,He,Ne$ and $CH_4)$, and ±100% for $k_1(M=I_2)$.

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
2.6×10^{16}	M=SO_2	293	Flash photolysis study. I_2/SO_2 mixtures, with $[I_2]/[SO_2] < 10^{-2}$. Uv absorption at 487 nm used to monitor $[I_2]$. BROWN and BURNS 1970 (43)	Expected change in properties of SO_2 over this temperature range did not appear. Rate expression not defined. Values taken from graph - authors only quote k_1 at 293 K.
1.4×10^{16}	M=SO_2	344		
8.9×10^{15}	M=SO_2	370		
5.7×10^{15}	M=SO_2	477		
3.7×10^{15}	M=SO_2	507		
4.2×10^{15}	M=SO_2	541		
2.6×10^{15}	M=SO_2	582		
2.4×10^{15}	M=SO_2	613		
2.6×10^{15}	M=SO_2	668		
$(2.4\pm0.1)\times10^{15}$	M=Ar	298	Flash photolysis study. I_2 (6.7×10^{-10}-8.23×10^{-9} mol cm^{-3})/Ar (1.67-8.01×10^{-5} mol cm^{-3}) mixtures. $[I_2]/[Ar]$ ratios $< 10^{-3}$. I_2 followed by uv absorption at 487 nm. BURNS, LeROY, MORRISS and BLAKE 1970 (44)	Observed rate constant becomes non-linear in $[I_2]/[M]$ for values of this ratio $\leqslant 10^{-4}$ (cf.16). Authors explain this by mechanism $I + M \rightleftharpoons IM$ 2 $IM + I \rightarrow I_2 + M$ 3
$(1.9\pm0.1)\times10^{15}$	M=Ar	323		
$(1.6\pm0.1)\times10^{15}$	M=Ar	423		
$(1.4\pm0.2)\times10^{18}$	M=I_2	298		
$(1.0\pm0.1)\times10^{18}$	M=I_2	323		
$(3.8\pm2.0)\times10^{17}$	M=I_2	423		
5.0×10^{16}	M=C_6F_6	298	*Flash photolysis study. No details given.* DeGRAFF and LANG 1970 (46)	*Presented as unpublished work.*
$(2.4\pm0.1)\times10^{15}$	M=Ar	298	Flash photolysis study. I_2(<1%)/Ar mixtures, $[I_2]/[Ar]$ 2×10^{-4}-8.4×10^{-3}. $[Ar]$ typically 10^{-5} mol cm^{-3}. Uv absorption at 487 nm used to follow $[I_2]$. BLAKE and BURNS 1971 (50)	Corrections made for thermal effects. Without thorough drying of apparatus consistently high values of k_1 obtained. High temperature values for $k_1(M=I_2)$ calculated assuming $k_1(M=I) \ll k_1(M=I_2)$. 'Radical-molecule complex' mechanism, reactions 2+3, produced satisfactory fit to flash photolysis data of this study and of (16,19,20 and 28).
$(8.7\pm0.3)\times10^{14}$	M=Ar	473		
$(6.6\pm0.5)\times10^{14}$	M=Ar	573		
$(4.8\pm0.3)\times10^{14}$	M=Ar	864		
$(4.1\pm0.2)\times10^{14}$	M=Ar	1064		
$(4.4\pm0.5)\times10^{14}$	M=Ar	1164		
$(1.4\pm0.21)\times10^{18}$	M=I_2	298		
$(1.1\pm0.09)\times10^{17}$	M=I_2	473		
$(6\pm1)\times10^{16}$	M=I_2	573		
$(9\pm5)\times10^{15}$	M=I_2	864		
$(6\pm30)\times10^{14}$	M=I_2	1064		
		295	Static system. I_2/Ar,He, Ne,H_2,N_2,CO,CO_2 or C_3H_8 mixtures photolysed by Ar laser at 488 nm. [I] monitored by absorption at 183 *nm*. HARADA, MORI and TANAKA 1971 (51)	Authors only presented relative rate constants for quoted diluent gases and I_2, i.e. $k_1(M= He:Ne:H_2:N_2:CO:CO_2:C_3H_8:I_2:Ar) = 0.5:0.4:0.8:0.4:3.8:6.8:27:400:1$.
$(5.5\pm2.5)\times10^{14}$	M=N_2	$\sim$1000	Shock tube study. I_2(0.8-2%) in Ar or N_2 dissociated behind incident shock, and recombination initiated by steady Prandtl-Mayer expansion. $[I_2]$ monitored by uv absorption at 492.5 nm. SLACK,BRAY,EAST and PRATT 1971 (53)	Boundary layer effects minimised by isolating core of recombining gas flow. Data are scattered over factor 5, over range 870-1280 K.

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
1.81×10^{16}	M=CF_3I	298	Flash photolysis study. CF_3I and CF_3I/NO mixtures, CF_3I at 0.1 atm (10.1 kPa) and CF_3I:NO ratios 1:0.3, 1:1 and 1:2. Photolysis performed using two values of flash intensity, both with and without laser cavity surrounding cell. I_2 monitored by uv absorption at 465 nm, and final product yield by iodometry (for I_2) and by chromatography/mass spectrometry. ANDREEVA, KUZNETSOVA, MASLOV, SOBEL'MAN and SOROKIN 1972 (55)	CF_3I decomposition <1.5%, such that temperature change <100 K. Presence of NO used to prevent recombination of CF_3 and I, in order to account for reactions of excited I. Value of k_1 obtained by matching computed $[I_2]$ profiles. Study using only one flash intensity reported by these authors in (49).
1.4×10^{15}	M=He	298	Flash photolysis study. I_2/He,Ar,Xe,N_2 and CO mixtures. Method as for (50). IP and BURNS 1972 (58)	Improved I_2 monitoring system and correction for thermal effects (>1000 K) over those of (50). k_1 $I + I + M \rightarrow I_2 + M$ 1 obtained by integrating simultaneous differential equations for $[I_2]$ and T to obtain calculated $[I_2]$ profiles. $[I_2]/[M]$ range ($\geqslant 3 \times 10^{-4}$) not low enough to cause k_1 to deviate from theoretical behaviour (see Discussion). Authors give error limits as ±15% and ±30% at low and high temperatures respectively. Expressions given by authors to these data are $\log(k_1(M{=}He)/\ cm^6\ mol^{-2}\ s^{-1}) = 15.136 - 1.716 \log(T/300) + 0.794 \log^2(T/300)$; $\log(k_1(M{=}Ar)/cm^6\ mol^{-2}\ s^{-1}) = 15.439 - 2.418 \log(T/300) + 1.911 \log^2(T/300)$; $\log(k_1(M{=}Xe)/cm^6\ mol^{-2}\ s^{-1}) = 15.652 - 2.787 \log(T/300) + 1.678 \log^2(T/300)$; $\log(k_1(M{=}N_2)/cm^6\ mol^{-2}\ s^{-1}) = 15.641 - 2.645 \log(T/300) + 1.88 \log^2(T/300)$ $\log(k_1(M{=}CO)/cm^6\ mol^{-2}\ s^{-1}) = 15.729 - 2.606 \log(T/300) + 1.457 \log^2(T/300)$ (298-1173 K). Using values for $k_1(M{=}I_2)$ from (50) authors give $\log(k_1(M{=}I_2)/cm^6\ mol^{-2}\ s^{-1}) = 18.122 - 5.844 \log(T/300) + 2.163 \log^2(T/300)$ (298-864 K).
7.6×10^{14}		423		
5.8×10^{14}		573		
4.1×10^{14}		723		
3.6×10^{14}		873		
3.1×10^{14}		1023		
3.0×10^{14}		1173		
2.7×10^{15}	M=Ar	298		
1.4×10^{15}		423		
8.4×10^{14}		573		
5.9×10^{14}		723		
5.2×10^{14}		873		
4.8×10^{14}		1023		
5.0×10^{14}		1173		
4.6×10^{15}	M=Xe	298		
1.8×10^{15}		423		
1.1×10^{15}		573		
6.6×10^{14}		723		
4.9×10^{14}		873		
4.6×10^{14}		1023		
3.9×10^{14}		1173		
4.3×10^{15}	M=N_2	298		
2.1×10^{15}		423		
1.1×10^{15}		573		
7.6×10^{14}		723		
6.4×10^{14}		873		
6.1×10^{14}		1023		
5.4×10^{14}		1173		
5.4×10^{15}	M=CO	298		
2.4×10^{15}		423		
1.3×10^{15}		573		
8.6×10^{14}		723		
6.7×10^{14}		873		
5.9×10^{14}		1023		
4.9×10^{14}		1173		
1.3×10^{18}	M=I_2	298		
2.4×10^{17}		423		
3.3×10^{16}		573		
1.3×10^{16}		723		

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})		Temperature (K)	Method and Reference	Comments
$5.68 \times 10^{22} T^{-2.627}$	M=CF_4	300-810	Flash photolysis study. I_2/CF_4,SF_6,Ne,Kr, and CO_2 mixtures. Method as for (50 and 58). CHANG and BURNS 1973 (61)	Authors also fitted following expressions to their data: log(k_1(M=Ne)/cm^6 mol^{-2} s^{-1})=15.19-1.898 log(T/300)+1.294 log^2(T/300) (300-960 K); log(k_1(M=Kr)/cm^6 mol^{-2} s^{-1})=15.572-2.654 log(T/300) +1.85 log^2(T/300) (300-1000 K); and log(k_1(M=CO_2)/cm^6 mol^{-2} s^{-1})= 16.224-3.274 log(T/300)+1.867 log^2(T/300) (300-980 K). Mechanism believed to vary between light, inert gases and heavier diluents. Data for M=CF_4 fitted by (68) to expression of (67).
$5.38 \times 10^{22} T^{-2.59}$	M=SF_6	300-810		
$5.94 \times 10^{20} T^{-2.054}$	M=H_2	300-593	Flash photolysis study. I_2/H_2,HD and D_2 mixtures. Method as described in (50 and 58). CHANG and BURNS 1973 (62)	HD purity given as 95%.
$8.31 \times 10^{19} T^{-1.737}$	M=HD	300-573		
$8.64 \times 10^{19} T^{-1.772}$	M=D_2	300-573		
		298	Flash photolysis study. I_2/He or Xe mixtures, p_{He} = 551 mm Hg (73.5 kPa) and p_{Xe}= 200 mm Hg (26.7 kPa). Reaction followed by absorption of I_2 at 495 nm. ERSHOV, ZALESKII and KOKUSHKIN 1973 (63)	Correction for thermal effect negligibly altered results. Authors corrected data for k_1(M=I_2) using value of CHRISTIE, et al (16,29), deriving k_1(M=He)=(1.22±0.2)x10^{15} cm^6 mol^{-2} s^{-1}, and k_1(M=Xe)=(5.8±0.9)x10^{15} cm^6 mol^{-2} s^{-1}.
1.27×10^{15}	M=He	300	Laser flash photolysis study. I_2/He,Ne,Ar,Kr,Xe, H_2,N_2,O_2,CO_2,CH_4,C_2H_6 and C_3H_8 mixtures. All samples fell in range 5×10^{-6}-3×10^{-2} mol cm^{-3}. I_2 followed by uv absorption at 492 nm. HIPPLER, LUTHER and TROE 1973 (64)	I_2/Ar mixtures also studied by conventional flash photolysis at high pressure, 160 atm (16.2 MPa).
1.2×10^{15}		314		
1.18×10^{15}	M=Ne	300		
1.05×10^{15}		314		
2.18×10^{15}	M=Ar	300		
1.95×10^{15}		314		
3.36×10^{15}	M=Kr	300		
5.26×10^{15}	M=Xe	300		
3.60×10^{15}	M=H_2	300		
4.37×10^{15}	M=N_2	300		
4.40×10^{15}	M=O_2	300		
1.23×10^{16}	M=CO_2	300		
7.2×10^{15}	M=CH_4	300		
1.23×10^{16}	M=C_2H_6	300		
1.8×10^{16}	M=C_3H_8	300		
$(1.09 \pm 0.04) \times 10^{18}$	M=I_2	300		
8.9×10^{17}		314		

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
$(1.09\pm0.2)x10^{18}$	M=ICl	300	Flash photolysis study. Mixtures (a) $ICl/I_2/CO_2$, (b) I_2/CO_2 (300-600 mm Hg; 40-80 kPa), (c) ICl (∿16 mm Hg; 2 kPa)/N_2 (∿600 mm Hg; 80 kPa). $[I_2]$ and [ICl] followed by uv absorption at 520 (or 570) and 470 nm. MAIER and LAMPE 1973 (65)	Photodissociation of ICl in mixtures (a) prevented by $K_2Cr_2O_7$ filter. Corrections made for CO_2 and I_2 as third body, using $k_1(M=CO_2)$ and $k_1(M=I_2)$ from (28), to give k_1(M=ICl). Mixture (b) used to confirm accuracy of technique, value $k_1(M=CO_2)$ being ±5% of that of (28).
$(9.0\ \pm1.8)x10^{17}$		325		
$(1.35\pm0.06)x10^{16}$	$M=CO_2$	300		
$(1.45\pm0.7)x10^{16}$	$M=CF_4$	296	Flash photolysis study. I_2 mixtures in CF_4, C_3F_8, CF_3Br and SiF_3I at total pressures 20-700 mm Hg (2.7-93.3 kPa). $[I_2]$ monitored by absorption at 500 nm. DYMOV and SKOROBOGATOV 1974 (67).	Initial temperature after photolysis flash calculated assuming 40.6 kJ mol^{-1} (9.7 kcal mol^{-1}) energy released by dissociation of I_2. Authors fit Arrhenius expressions to average values of k_1 in each temperature range, giving $k_1(M=CF_4)=(6.17\pm1.6)x10^{14}exp(1000\pm100/T)$, $k_1(M=C_3F_8)=(6.35\pm1.6)x10^{14} exp(1200\pm100/T)$, $k_1(M=CF_3Br)=(1.09\pm0.2)x10^{15} exp(1000\pm100/T)$, and $k_1(M=SiF_3I)=(4.00\pm0.9)x10^{14} exp(1500\pm200/T)\ cm^6\ mol^{-2}\ s^{-1}$, for the range 295-405 K.
$(1.51\pm0.5)x10^{16}$		297		
$(2.36\pm0.4)x10^{16}$		297		
$(2.21\pm0.9)x10^{16}$		302		
$(1.11\pm0.3)x10^{16}$		306		
$(9.07\pm1.8)x10^{15}$		309		
$(7.62\pm1.5)x10^{15}$		373		
$(1.51\pm0.3)x10^{16}$		373		
$(6.35\pm2.2)x10^{15}$		377		
$(5.26\pm1.3)x10^{15}$		403		
$(7.98\pm1.5)x10^{15}$		403		
$(9.79\pm2.9)x10^{15}$		403		
$(6.89\pm2.4)x10^{15}$		405		
$(3.28\pm0.7)x10^{16}$	$M=C_3F_8$	295		
$(4.28\pm0.7)x10^{16}$		296		
$(2.67\pm0.4)x10^{16}$		297		
$(3.99\pm0.9)x10^{16}$		297		
$(3.19\pm0.8)x10^{16}$		299		
$(1.81\pm0.3)x10^{16}$		350		
$(2.14\pm0.7)x10^{16}$		350		
$(2.27\pm0.5)x10^{16}$		352		
$(9.79\pm1.5)x10^{15}$		403		
$(1.07\pm0.2)x10^{16}$		403		
$(1.61\pm0.6)x10^{16}$		403		
$(3.63\pm0.4)x10^{16}$	$M=CF_3Br$	302		
$(2.78\pm0.6)x10^{16}$		305		
$(2.79\pm0.6)x10^{16}$		309		
$(1.69\pm0.3)x10^{16}$		350		
$(2.00\pm0.4)x10^{16}$		350		
$(2.18\pm0.5)x10^{16}$		351		
$(1.36\pm0.2)x10^{16}$		403		
$(1.51\pm0.2)x10^{16}$		403		
$(1.23\pm0.3)x10^{16}$		404		
$(3.45\pm0.9)x10^{16}$	$M=SiF_3I$	300		
$(8.52\pm3.6)x10^{16}$		300		
$(1.09\pm0.3)x10^{16}$		373		
$(3.08\pm0.9)x10^{16}$		373		
$3.99x10^{16}$	$M=C_3F_6$	299	Flash photolysis study. I_2/C_3F_6 (C_7F_{16} or C_8F_{18}) mixtures, $[C_3F_6]$ $2.7x10^{-6}$-$2x10^{-5}$ mol cm^{-3}, $[C_7F_{16}]$ $3.9x10^{-7}$-$2.2x10^{-6}$ mol cm^{-3}, $[C_8F_{18}]$ $1.5x10^{-7}$-$1.2x10^{16}$ mol cm^{-3}. Method as for (67). DYMOV and SKOROBOGATOV 1974 (68)	Authors give expressions $k_1(M=C_3F_6)=(1.09\pm0.2)x10^{15} exp(1100\pm100/T)\ cm^6\ mol^{-2}\ s^{-1}$, $k_1(M=C_7F_{16})=(1.81\pm0.4)x10^{15} exp(1330\pm90/T)\ cm^6\ mol^{-2}\ s^{-1}$, and $k_1(M=C_8F_{18})=(1.72\pm0.4)x10^{15} exp(1400\pm50/T)\ cm^6\ mol^{-2}\ s^{-1}$, over range 290-450 K. These together with data for $k_1(M=C_3F_8)$ (67) and $k_1(M=CF_4)$ (61, 67) used to interpolate expressions for $k_1(M=C_2F_6, C_4F_{10}, C_5F_{12}$ and $C_6F_{14})$.
$4.35x10^{16}$		302		
$3.63x10^{16}$		304		
$3.99x10^{16}$		304		
$1.81x10^{16}$		350		
$2.90x10^{16}$		350		
$1.27x10^{16}$		403		
$1.51x10^{16}$		403		
$1.98x10^{16}$		403		
$1.25x10^{17}$	$M=C_7F_{16}$	298		
$1.32x10^{17}$		300		
$1.78x10^{17}$		301		
$1.49x10^{17}$		302		
$1.51x10^{17}$		302		
$1.78x10^{17}$		302		
$8.52x10^{16}$		350		
$6.35x10^{16}$		351		
$6.89x10^{16}$		351		
$9.61x10^{16}$		351		
$4.53x10^{16}$		352		
$9.79x10^{16}$		352		
$2.72x10^{16}$		403		

$I + I + M \rightarrow I_2 + M$ 1

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
5.62×10^{16}	$M=C_7F_{16}$	403	DYMOV and SKOROBOGATOV 1974 (68) continued.	
4.53×10^{16}		404		
4.72×10^{16}		404		
6.53×10^{16}		404		
5.44×10^{16}		405		
1.38×10^{17}	$M=C_8F_{18}$	299		
1.31×10^{17}		301		
1.58×10^{17}		301		
2.14×10^{17}		301		
2.76×10^{17}		302		
1.67×10^{17}		303		
1.81×10^{17}		303		
5.62×10^{16}		351		
6.35×10^{16}		351		
7.98×10^{16}		351		
5.80×10^{16}		352		
8.89×10^{16}		352		
1.49×10^{17}		353		
1.29×10^{17}		355		
3.45×10^{16}		403		
4.72×10^{16}		403		
6.53×10^{16}		403		
4.90×10^{16}		404		
6.89×10^{16}		404		
5.26×10^{16}		405		
6.53×10^{16}		408		
$(3.63\pm1.8)\times10^{16}$	$M=CF_3I$	293	Flash photolysis study. I_2/CF_3I (25-640 mm Hg; 3.3-85.3 kPa) mixtures photolysed at wavelengths >350 nm. $[I_2]$ monitored by absorption at 500 nm. DYMOV and SKOROBOGATOV 1974 (69)	Cl_2 filter used to prevent photolysis <350 nm. Temperatures are those quoted at the end of the photolysis pulse, calculated by thermodynamic considerations. Authors quote average values of $(5.44\pm0.2)\times10^{16}$ and $(1.63\pm0.4)\times10^{16}\ cm^6\ mol^{-2}\ s^{-1}$ at 297 and 374 K respectively, to which expression $k_1(M=CF_3I)=(2.54\pm0.7)\times10^{14}\ \exp(1600\pm400/T)\ cm^6\ mol^{-2}\ s^{-1}$ was fitted.
$(7.98\pm2.0)\times10^{16}$		294		
$(4.72\pm2.2)\times10^{16}$		295		
$(4.17\pm1.5)\times10^{16}$		298		
$(5.44\pm2.0)\times10^{16}$		300		
$(8.71\pm2.7)\times10^{16}$		300		
$(4.53\pm1.6)\times10^{16}$		301		
$(1.81\pm0.5)\times10^{16}$		373		
$(1.56\pm0.5)\times10^{16}$		375		
$(3.95\pm0.3)\times10^{15}$	$M=Ne$	298	Laser photolysis study. I_2/Xe or Ne mixtures ($[I_2]/[Ne]$ (or $[Xe]$)$=5\times10^{-5}$) photolysed at 531 nm. I_2 followed by absorption at 495 nm. FILIUKOV, MITROFANOV and MISHCHENKO 1974 (70)	Values of k_1 obtained by computer matching of recombination profiles, using model including $k_1(M=I_2, I$ and Xe or Ne). $I + I + M \rightarrow I_2 + M \qquad 1$
$(1.09\pm0.03)\times10^{16}$	$M=Xe$	298		
$(1.48\pm0.7)\times10^{18}$	$M=I_2$	298		
$(2.36\pm0.8)\times10^{18}$	$M=I$	298		
$(2.4\pm1.4)\times10^{19}$	$M=NO$	300	Flash photolysis study. $CH_3I/NO/Kr/He$ mixtures at total pressures 15.4-32.1 mm Hg (2.05-4.28 kPa). $NO:CH_3I$ ratios 1 and 9.2. Reaction vessel of black glass, wetted by H_3PO_4. T.o.f. mass spectrometry used to follow I_2. MEYER 1974 (72)	Excited I atoms effectively quenched by NO. Quoted value is average of 11 experimental results. Result also reported in (47).

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

	Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)		Temperature (K)	Method and Reference	Comments
	$2.17x10^{19}T^{-1.56}$	M=Ar	500-1450	Shock tube study. I_2 (in Ar) dissociated by incident shock, and I atom recombination followed in unsteady expansion. Absorption at 493 nm used to monitor recombination. BECK and MACKIE 1976 (74)	Experimental data could not be fitted by expressions $k_1=k_1(298\ K)\ (T/298)^{-1.83}$, where $k_1(298\ K)$ used as $3x10^{15}\ cm^6\ mol^{-2}\ s^{-1}$ (attributed to (20)), or k_1 of BURNS et al. (50,58). Authors interpreted failure of fit to competition from slow vibrational relaxation of I_2. Allowance for vibrational non-equilibrium changed exponent in first expression to -1.56, i.e. giving expression presented here.
	$(7.86\pm0.99)x10^{15}$ $(2.77\pm0.80)x10^{15}$ $(1.57\pm0.22)x10^{16}$ $(7.78\pm1.25)x10^{15}$ $(7.72\pm0.92)x10^{15}$ $(1.12\pm0.17)x10^{17}$ $2.9x10^{16}$	M=Ar M=He M=Xe $M=H_2$ $M=D_2$ M=HI M=HI	206 206 206 206 206 206 293	Flash photolysis study. HI ($1.29x10^{-6}\ mol\ cm^{-3}$)/Ar,He, Xe,$H_2$,$D_2$ or HI mixtures at total pressures 0.5-1 atm (50.7-101.3 kPa). $0.02<[HI]/[M]<0.08$. Reaction followed by I_2 absorption at 487 nm. CHANG and BURNS 1976 (75)	Observed rate constant contains contributions from $k_1(M)$, $k_1(M=HI)$, $k_1(M=I_2)$, and $k_1(M=I)$. Data analysed as in (50). Approximation made that $k_1(M=I)=0$, and $k_1(M=I_2)$ extrapolated from data of (58). Using value of $k_1(M=HI)$ determined by (25), authors derive $k_1(M=HI)=1.38x10^{25}T^{-3.5}\ cm^6\ mol^{-2}\ s^{-1}$ (206-300 K).
(a) (b)	$(1.5\pm0.7)x10^{18}$ $(1.3\pm1.0)x10^{18}$ $5.72x10^{14}$ $1.0\ x10^{15}$ $1.09x10^{15}$ $8.58x10^{14}$ $9.03x10^{14}$ $9.50x10^{14}$ $7.23x10^{14}$ $7.40x10^{14}$ $5.87x10^{14}$	$M=I_2$ $M=I_2$ M=Ar $M=O_2$ $M=O_2$ $M=O_2$ $M=O_2$ $M=O_2$ $M=O_2$ $M=O_2$ $M=O_2$	300 300 723 573 573 723 723 723 873 1023 1173	Flash photolysis study. I_2 ($1x10^{-8}$-$3x10^{-8}\ mol\ cm^{-3}$)/O_2 ($1x10^{-5}$-$4x10^{-5}\ mol\ cm^{-3}$) mixtures. $[I_2]$ followed by absorption spectroscopy at 487 nm. ANTRIM, BURNS and IP 1977 (76)	Irregularity in absorption traces between 723 and 873 K explained by removal of I_2 by reaction $I_2 + O_2(^1\Delta g) \rightarrow I + I + O_2$ This irregularity not observed when O_2 replaced by Ar, giving $k_1(M=Ar)$ in agreement with previous measurements (58). Values of apparent recombination rate constant between 300 and 573 K found to be lower with NH_3 or pyrex filters. At 300 K apparent rate constants gave $k_1(M=I_2)$ only slightly different (a) with, and (b) without filters. $I + I + M \rightarrow I_2 + M$ 1 Difference between apparent k_1 with and without filters explained by additional recombination, with no filter, via $I + I + O_3 \rightleftharpoons I_2 + O_3$ $I + I + O_2(^1\Delta g) \rightleftharpoons I_2 + O_2(^1\Delta g)$ At highest temperatures (573-1173 K) no interference from side reactions apparent, and $k_1(M=O_2)$ obtained. Values of latter taken

$I + I + M \rightarrow I_2 + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^6 mol^{-2} s^{-1})	Temperature (K)	Method and Reference	Comments
		ANTRIM, BURNS and IP 1977 (76) continued.	from graph: authors give $k_1(M=O_2)=9.08x10^{16}T^{-0.71}$ cm^6 mol^{-2} s^{-1}.
		REVIEW ARTICLES	
$5.0x10^{18}T^{-1.3}$ M=Ar $2.1x10^{15}\exp(2060/T)$ $M=I_2$	300-1300	Evaluation. $k_1(M=Ar)$ based upon room temperature values of (19 and 20) and shock tube value at 1300 K of (12 and 17). $k_1(M=I_2)$ based on (20). DAVIDSON 1961 (26)	Author admits to some personal bias in this evaluation. Temperature dependence of $k_1(M=I_2)$ $I + I + M \rightarrow I_2 + M$ 1 suggested as being too low.
		Review. PORTER 1962 (30)	Data of (19,20,24,25 and 28) used to show good agreement with radical-molecule complex theory rather than with energy transfer theory (see Discussion).
$\sim 3.3x10^{14}\exp(700/T)$ M=Ar	280-470	Review. KIM 1967 (34)	Given expression, or alternative $k_1(M=Ar) \approx 3.1x10^{20}T^{-2}$ cm^6 mol^{-2} s^{-1}, is match between theory (K_2 derived assuming Lennard-Jones potential between I and M, and k_3 from collision rate between IM and I assuming Sutherland potential $I + M \rightleftarrows IM$ 2 $IM + I \rightarrow I_2 + M$ 3) and experimental results of (19, 20,25 and 28). Used by (36).
(a) $4.39x10^{19}T^{-1.68}$ M=Ar (b) $(7.08 \pm 1.6)x10^{31}T^{-5.5}$ $M=I_2$	300-1900 300-4000	Expression (a) derived from k_{-1} data obtained in this study and k_1 data of (19, 20 and 28). Expression (b) from combination of data of (20 and 33), using K_1 to convert latter. SLACK 1967 (36)	
$(3.0 \pm 0.16)x10^{15}$ M=Ar $(1.0 \pm 0.09)x10^{18}$ $M=I_2$	298 298	Review. Data of (16,19 and 44) fitted to expression for observed recombination rate, allowing for influence of I_2 as collision partner. BURNS, LeROY, MORRISS and BLAKE 1970 (44)	Standard error quoted as ±10%. Fit obtained assuming steric factors for $k_3(M=I_2)$ and $k_3(M=Ar)$ $IM + I \rightarrow I_2 + M$ 3 to be 1 and 0.5 respectively.

$I + I + M \rightarrow I_2 + M$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.7\pm0.4)\times10^{19}T^{-1.51}$ M=Ar, N_2	298-2000	Review. Fit to data of (17,19,20,28,38 and 50). SLACK, BRAY, EAST and PRATT 1971 (53)	Good agreement between directly measured high temperature k_1 data and those derived from $k_{-1}K_1$ seen as justification for this relationship under non-equilibrium conditions. Quoted expression in good agreement with theoretical prediction by SHUI et al. (48, 52).
(a) $3.77\times10^{19}T^{-1.6}$ M=Ar (b) $2.62\times10^{19}T^{-1.6}$ M=Ar	850-1600 302- 548	Review. WAGNER 1971 (54) and TROE and WAGNER 1973 (66)	Single temperature exponent of -1.6 used to fit k_1 derived from both (a) dissociation (38) and (b) recombination data (20).
$2.24\times10^{18}T^{-1.27\pm0.2}$ M=He $4.68\times10^{18}T^{-1.3\pm0.09}$ M=Ar $2.04\times10^{20}T^{-1.82\pm0.03}$ M=N_2 $1.68\times10^{26}T^{-4.04\pm0.26}$ M=CO_2 $4.47\times10^{10}T^{1.5}\exp(2680/T)$ M=I_2	290-1600 290-1570 400-1860 300-1600 302- 548	Evaluation. KONDRATIEV 1972 (59)	k_1(M=He) least squares fit to data of (17,25 and 28); k_1(M=Ar) from data of (16,17,19,20 and 28); k_1(M=N_2) from data of (11,12 and 17); k_1(M=CO_2) from data of (17 and 28). Expression for k_1(M=I_2) is that of (20).
$7.48\times10^{28}T^{-4.375}$ M=I_2	Undefined	Derived from data of (16, 25 and 58), together with authors' own data. HIPPLER, LUTHER and TROE 1973 (64)	
(a) $2.2\times10^{14}\exp(755/T)$ (b) $3.97\times10^{18}T^{-1.3}$ (c) $8\times10^{14}\sinh(570/T)$ } M=Ar	300-1600 300-1600 300-1600	Expressions fitted to low and high temperature data (authors quote (38 and 58)). SNIDER and LEAIST 1977 (77)	Function (c) found to give best fit to quoted data. Theoretical justification provided by authors.

$I + I + M \rightarrow I_2 + M$

THIRD BODY COLLISION EFFICIENCIES

INORGANIC THIRD BODIES

M= Ar	He	Ne	Kr	Xe	I_2	N_2	H_2	O_2	CO_2	CO	NO	H_2O	ICl	HI	Temperature (K)	Reference
1	5.2					18.5	11.2	29.2	50.8						298	Rabinowitch and Wood 1936 (3).
1	0.72	0.77	1.41	1.42	≤8.27										293	Christie et al. 1953 (9).
1	0.47	0.5				1.25	1.3	1.9	3.9			13.8			293	Russell and Simmons 1953 (11).
1	0.61					1.3			3.9						400	
1						1.02									1060-1860	Britton et al. 1954 (12).
1					286										293	Christie et al. 1954 (13).
1	0.37	0.5	1.22	1.62	255										294	Christie et al. 1955 (16).
1	0.5					0.99		1.2	11.8						1275	Britton et al. 1956 (17).
1					363		1.64								326	Bunker and Davidson 1958 (20).
1	0.42				309					1.72	$>1.5\times10^5$			8.92	323	Engleman and Davidson 1960 (25).
1	0.57				123		1.54								423	
1	0.53							2.4	4.8						293	Porter and Smith 1961 (28).
1	1.05							2.0	3.4						523	
		1									$1.6\times10^{4\,a}$				333	Porter et al.1962 (31).
1	0.54	0.59			398										298	Yamanashi and Nowak 1968 (39).
1					583										298	Burns et al. 1970 (44).
1					238										423	
1					<10										>1000	Blake and Burns 1971 (50).
1	0.5	0.4			400	0.4	0.8		6.8	3.8					295	Harada et al. 1971 (51).
1	0.5			1.7	482	1.6				2.0					298	Ip and Burns 1972 (58).
1	0.7			1.1	22	1.3				1.5					723	
1	0.6			0.8		1.1				1.0					1173	
1	0.6	0.5	1.5	2.4	500	2.0	1.65	2.0	5.6						300	Hippler et al. 1973 (64).
									1				80^b		300	Maier and Lampe 1973 (65).
1	0.35			2.0			0.99							14.2	206	Chang and Burns 1976 (75).
1								1.6							723	Antrim et al. 1977 (76).
1	0.5				510	1.5									300	This evaluation.
1	0.7				20	1.2									1000	

a: Efficiency relative to Ne

b: Efficiency relative to CO_2

$I + I + M \rightarrow I_2 + M$

THIRD BODY COLLISION EFFICIENCIES - CONTINUED

ORGANIC THIRD BODIES

M=	Ar	CH_4	C_2H_6	C_3H_8	$\underline{n}$-C_4H_{10}	C_5H_{12}	$\underline{n}$-C_5H_{12}	$\underline{neo}$-C_5H_{12}	$\underline{c}$-C_6H_{12}	CCl_4	CH_3OH	CH_2Cl_2	C_2H_4	C_2F_4	$\underline{c}$-C_3H_6	Temperature (K)	Reference
	1	33.9														298	(3)
	1					15.5		13.8								298	(10)
	1	2.5		8.5			13.1	12.1	15.1	14.1	18.0	13.3	4.8	5.8	11.0	293	(11)
	1									2.0						298	(14)
	1				11.5											305	(20)
	1				8.3											493	
	1	2.2														298	(39)
	1			27												295	(51)
	1	3.3	5.6	8.3												300	(64)

M=	Ar	C_6H_6	$C_6H_5CH_3$	$\underline{p}$-$C_6H_4(CH_3)_2$	$C_6H_3(CH_3)_3$	$C_6H_3F_3$	CH_3I	CH_3Br	CH_3Cl	CH_3NO_2	C_2H_5I	$(CH_3)_2O$	Temperature (K)	Reference
	1	269.2											298	(3)
	1	23.9	58,3	92.2	113.9	24.4		22.3	13.3	52	69.4	17.2	293	(11)
	1	20											400	
	1	25.8					37.5				75.6		323	(25)
	1	28.7	68.5		137.8		92.9				92.9		293	(28)
	1	21.0	23.6				40.1				40.1		523	

Discussion

The recombination of iodine atoms has been studied experimentally since 1936 [3], although theoretical analyses of this reaction have been made since 1911 [1]. The recombination is in its third order region, as given by reaction 1, up to pressures of ~ 100 atm (10.1 MPa) [38,56].

$$I + I + M \rightarrow I_2 + M \qquad (1)$$

Measurements of the recombination rate by photolysis are influenced by errors resulting from the "thermal effect," which is associated with the heat released by the strongly exothermic reaction 1($\Delta H^\circ_{298} = -151.25$ kJ mol^{-1}; -36.15 kcal mol^{-1}). Absorption of this heat by the reaction cell walls causes the gas density close to the walls to increase, with a corresponding gas density decrease at the centre of the reaction cell. If $[I_2]$ is monitored by absorption spectroscopy (as in the bulk of the photolysis studies) and the analysing beam only samples the centre of the gas volume, the subsequent overestimation of [I] results in values of k_1 that are too low. The thermal effect may be largely eliminated by employing low initial $[I_2]/[M]$ ratios [14,16,19,20,27,28,31,35,39,44,50,58,61,62,70,75] *or be neglected* by using only measurements made early in the recombination process [20,25].

A second effect upon the recombination rate is the relatively high efficiency of iodine molecules as collision partners at room temperature, and therefore in dilute mixtures the overall recombination rate constant k_1 must be taken as the sum of two components:

$$k_1 = k_1(M) + k_1(M = I_2)[I_2]/[M] \qquad (A)$$

Although $[I_2]/[M]$ may be small, the high value of $k_1(M = I_2)$ relative to $k_1(M)$ means that the second term cannot be ignored. The large contribution of iodine molecules to the reaction was not however recognised until 1954 [13], and therefore all those studies in which the correction for $k_1(M = I_2)$ has been omitted have not been used in this evaluation [3,8,9,10,11,12].

At room temperature the large variation in k_1 with the collision partner M has been shown to correlate well with such properties of M as the boiling point [11], critical temperature [11,29] and ionisation potential, i.e., with parameters that reflect the *intermolecular*, van der Waal's, forces. The influence of these forces is also shown by the fact that the small negative temperature dependence of k_1 increases with increasing (low temperature) effectiveness of M [41].

Theoretical arguments for these variations with M have produced two mechanisms for the overall recombination reaction. For light and inert collision partners [61] the energy transfer (ET) mechanism [26,30,56]

$$I + I \rightleftharpoons I_2^*$$

$$I^*_2 + M \rightarrow I_2$$

and for large and heavy, or chemically active, third bodies [61] the radical-molecule complex (RMC) mechanism [5,17,21,26,28,30,31,44,50,56,73]

$$I + M \rightleftharpoons IM \qquad (2)$$

$$IM + I \rightarrow I_2 + M \qquad (3)$$

For example, Davidson [26] has shown that both mechanisms can be used to give good agreement with data for $k_1(M = Ar)$, but that only the RMC mechanism will give comparable agreement for the $k_1(M = C_4H_{10})$ data. For $M = I_2$, Bunker and Davidson [21] and Blake and Burns [50] have both shown that the RMC mechanism is required. Moreover, Burns et al. [44] have shown that the latter mechanism also explains the deviation of k_1 from the value given by expression A, observed at very low ($\leqslant 2 \times 10^{-4}$) values of $[I_2]/[M]$.

In the case of M=NO, which has a very high collision efficiency ($(k_1(M = NO)/k_1(M = Ar,Ne) > 10^4$ [25,31]), the radical-molecule complex NOI is sufficiently stable to permit observation [31].

Of those investigations considered in this evaluation, the principal method used has been flash photolysis [14,16,18,19,25,28,31,39,43,44,50,55,58,61,62,63,65,68,69,72,75], up to temperatures of about 1200 K [58], and there are three shock tube studies [17,53,74] which have extended the range up to 1800 K.

Of these latter studies, Britton et al. [17] analysed their data, relating essentially to dissociation rates, in terms of recombination rate constants, using $k_1 = k_{-1}K_1$. However the possibility of non-equilibrium of the vibrational states of I_2 [40,74], and consequent overestimation of k_{-1} (and hence k_1) leads us to attach little weight to these data [17].

Several authors have defined the rate of recombination of I atoms by the expression

$$-d[I]/dt = k'_1[I]^2[M]$$

where $k'_1 = 2k_1$. The values presented in these works [3,4,5,9,11,13,16,24,28,51,67,68,69] have accordingly been halved before being presented in the table.

The data for $k_1(M = Ar)$ [14,16,17,18,19,20,25,28,39,44,50,58,64,74] lie within a factor of 2 over the range 290–1250 K, and are fitted to within $< 30\%$ by the recommended expression

$$k_1(M = Ar) = 2.36 \times 10^{14} \exp(754/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

For $k_1(M = I_2)$ there is good agreement over the range 290–1000 K, such that we recommend the expression

$$k_1(M = I_2) = 1.27 \times 10^{15} \exp(2120/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

which fits the data [16,18,20,25,39,44,50,58,64] to within a factor of 2. Alternatively these data may be fitted by the non-Arrhenius form (cf. that of Slack [36]).

$$k_1(M = I_2) = 3.2 \times 10^{30} T^{-5.0} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

which gives a better fit at higher temperatures. The error limits are again a factor of 2.

For He as third body, we recommend the expression

$$k_1(M = He) = 2.0 \times 10^{14} \exp(575/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the range 290–1250 K, based on the data of [16,25,28,39,58,63 and 64]. Error limits of $\pm 50\%$ should be considered.

The few data for $k_1(M=N_2)$ show little scatter [53,58,64] and a least squares fit gives

$$k_1(M=N_2) = 2.5\times10^{14} \exp(863/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

for temperatures 290–1200 K, within uncertainty limits of ±10%.

The values of k_1 for M=Ar and N_2 given by the appropriate expressions above agree to within 10% with those calculated using the reverse rate constant k_{-1} (see section D1) and the equilibrium constant, for temperatures <1250 K. Above this temperature, values of $k_1(M=Ar,N_2)$, as given by these expressions, are increasingly higher than those given by $k_{-1}K_1$ (e.g., values are 50% too high at 2000 K). Therefore we consider that above ~1250 K k_1 is best derived via the equilibrium constant.

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D3 $I + H_2 \rightarrow HI + H$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	137.595	9.841	-23.592
300	137.595	9.841	-23.443
500	137.641	9.958	-13.859
1000	138.553	11.117	- 6.657
1500	140.131	12.393	- 4.233
2000	141.336	13.096	- 3.007
2500	141.913	13.360	- 2.267
3000	141.896	13.355	- 1.773
3500	141.373	13.201	- 1.420
4000	140.419	12.945	- 1.157
4500	139.097	12.640	- 0.955
5000	137.474	12.293	- 0.794

RECOMMENDED RATE CONSTANT

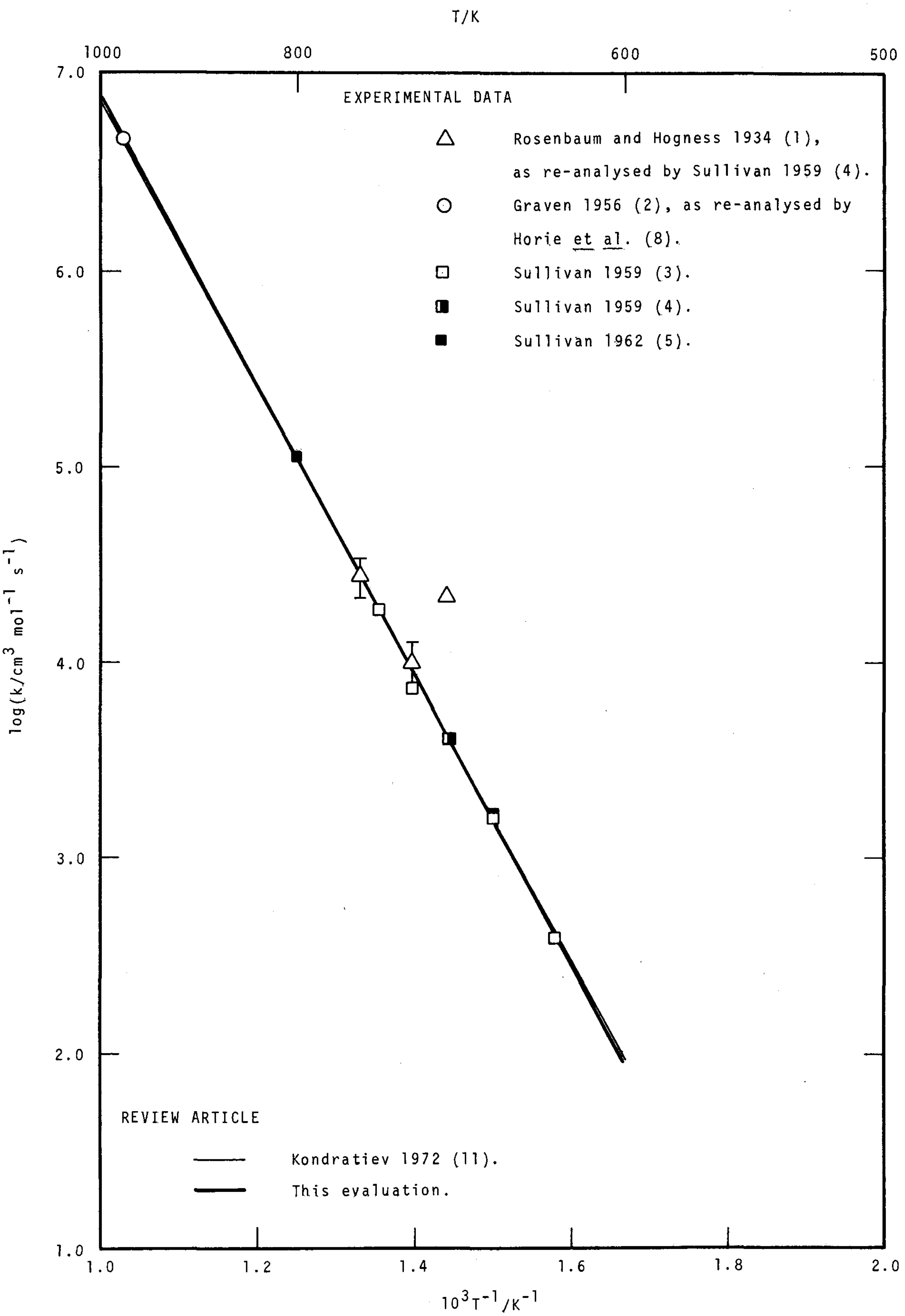
k_1 = 1.69 x 10^{14} exp(-16 930/T) cm^3 mol^{-1} s^{-1}
= 2.81 x 10^{-10}exp(-16 930/T) cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 600-1000 K

Suggested Error Limits for Calculated Rate Constant: ±20% over the whole temperature range.

Rate Parameters: log(A/cm^3 mol^{-1} s^{-1}) = 14.23 ± 0.08
log(A/cm^3 $molecule^{-1}$ s^{-1}) = -9.55 ± 0.08
E/J mol^{-1} = 140 750 ± 5 400
E/cal mol^{-1} = 33 640 ± 1 290

$I + H_2 \rightarrow HI + H$



$I + H_2 \rightarrow HI + H$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(2.2\pm3)\times10^4$ $(1.02\pm0.25)\times10^4$ $(2.75\pm0.6)\times10^4$	693 716 753	Static system. $H_2^o/H_2^p/I_2$ ($0-1.04\times10^{-6}$ mol cm^{-3}) mixtures, with 1:1 $[H_2^o]/[H_2^p]$ ratios. After quenching reaction and freezing out HI and I_2, residual $[H_2]$ determined by thermal conductivity. ROSENBAUM and HOGNESS 1934 (1)	Original purpose of this study to determine rate of para-ortho conversion of H_2 in mixtures of equilibrium $[H_2]$, [HI] and $[I_2]$. Data re-analysed by SULLIVAN (4) to give k_1 and k_2. $I + H_2 \rightarrow HI + H$ 1 $H_2 + I_2 \rightarrow HI + HI$ 2 Precision of k_1 and k_2 values at 693 K is low, presumably due to small number of data points: using his own value of k_2 (5), SULLIVAN calculates $k_1=(7.5\pm2.0)\times10^3$ $cm^3\ mol^{-1}\ s^{-1}$ at 693 K.
	873-1048	Flow system. (a) HI ($8.11\times10^{-7} - 5.67\times10^{-6}$ mol cm^{-3}) and HI (3.19×10^{-6} and 3.21×10^{-6} mol cm^{-3})/H_2 ($2\times10^{-7} - 4.79\times10^{-6}$ mol cm^{-3}) mixtures, ratios $[H_2]$:[HI] in range 0.67-16.1, (b) H_2 ($4.07\times10^{-7} - 4.54\times10^{-6}$ mol cm^{-3})/I_2 ($1.10\times10^{-6} - 5.01\times10^{-6}$ mol cm^{-3}) mixtures, ratios $[H_2]$:$[I_2]$ in range 0.08-4.01. N_2 diluent used to bring total concentrations to $\sim1.25\times10^{-5}$ mol cm^{-3}. Gravimetric analysis of products by (a) sublimation of I_2 at 273 K, (b) absorption of HI in ascarite. GRAVEN 1956 (2)	Original analysis considered only reactions 2 and -2 $H_2 + I_2 \rightleftharpoons HI + HI$ 2,-2 Re-analysis by HORIE <u>et al</u>. (8) according to steady state treatment of mechanism of reactions 2,-2 plus $I_2 + M \rightleftharpoons I + I + M$ 3 $I + H_2 \rightleftharpoons HI + H$ 1,-1 $H + I_2 \rightleftharpoons HI + I$ 4,-4 gave k_1 as functions of k_{-1}/k_4 for both HI decomposition and HI synthesis. Intersection of these functions gave $k_1=4.6\times10^6 cm^3\ mol^{-1}\ s^{-1}$ at 973 K.
	633-738	Static system. H_2 ($4.2\times10^{-7} - 2.9\times10^{-6}$ mol cm^{-3})/I_2 ($5.6\times10^{-7} - 2.4\times10^{-6}$ mol cm^{-3}) mixtures, with $0.33 \leqslant [H_2]:[I_2] \leqslant 2.62$. Reaction quenched, HI and I_2 condensed, and residual H_2 pressure measured. SULLIVAN 1959 (3)	Steady state treatment of mechanism $I_2 + M \rightleftharpoons I + I + M$ 3 $H_2 + I_2 \rightleftharpoons HI + HI$ 2 $I + H_2 \rightleftharpoons HI + H$ 1,-1 $H + I_2 \rightleftharpoons HI + I$ 4,-4 gave differential equation for $[I_2]$ in terms of $k_2, k_1K_3/k_2$, and k_{-1}/k_4. Computed best fits to experimental data gave $k_1= (3.86\pm0.07)\times10^2$ (633.21 K), $(1.605\pm0.01)\times10^3$ (666.79 K), $(7.54\pm0.04)\times10^3$ (710.33 K), and $(1.893\pm0.02)\times10^4$ $cm^3\ mol^{-1}\ s^{-1}$ (737.93 K). Author gave value at 633 K only ¼ weight

$I + H_2 \rightarrow HI + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		SULLIVAN 1959 (3) continued	of other values, and presented least squares fit as $k_1=5.62\times10^{12}$ $T^{\frac{1}{2}}$ exp{-(16 830±180)/T} cm^3 mol^{-1} s^{-1}, with uncertainty in A factor of ±30%. FETTIS and KNOX (7) quote Arrhenius expression for this work as $k_1=2.4\times10^{14}$ exp{-(17 170±350)/T} cm^3 mol^{-1} s^{-1}.
4.13×10^3	693	Static system. H_2/I_2 mixtures, with $[H_2]$ and $[I_2]$ each varied by factor 3. Method as for (3). SULLIVAN 1959 (4)	Experiments made to determine possible wall effects upon para-ortho H_2 conversion study of ROSENBAUM and HOGNESS (1). Data analysed as in (3).
$(1.67\pm0.04)\times10^3$, $(1.11\pm0.025)\times10^5$	666.79 799.77	Static system. $H_2(1.05\times10^{-8}$ - 4.59×10^{-6} mol $cm^{-3})$ $/I_2(4.0\times10^{-9}$ - 5.72×10^{-6} mol $cm^{-3})$ mixtures, $[H_2]$:$[I_2]$ ratios 0.12 to 4.51. Method as for (3). SULLIVAN 1962 (5)	HI synthesis allowed to proceed to low and high values of $[HI]/[I_2]$. Improved analysis of differential equation in $[I_2]$, generated as in (3), gave k_1 and k_2 at 667 K from I_2-rich mixtures, these values then being used to obtain k_{-1}/k_4 in H_2-rich mixtures. At 800 K low dependence on k_2 (value obtained from (3)) gave k_1 in I_2-rich mixtures, value then used to give k_{-1}/k_4 in H_2-rich mixtures. Computed best fits obtained as presented here. No wall effects found, by using reaction vessel with larger surface/volume ratio. Author gives least squares fit to these data and to values at 710 K and 738 K (3) as $k_1=3.55\times10^{12}T^{\frac{1}{2}}$ exp{-(16 510±130)/T} cm^3 mol^{-1} s^{-1}. WILSON and ARMSTRONG (10) give Arrhenius form to these data as $k_1=1.69\times10^{14}$ exp{-(16 870±130)/T} cm^3 mol^{-1} s^{-1}. WHITE (12) quotes $k_1=(2.51\pm0.5)\times10^{14}$ exp{-(16 900±150)/T} cm^3 mol^{-1} s^{-1} for this work and (3 and 4).

$I + H_2 \rightarrow HI + H$

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$1.38 \times 10^{14} \exp\{-(16\,780 \pm 120)/T\}$	600-1000	Evaluation. Least squares analysis based on data of (3,5,7,8). KONDRATIEV 1972 (11)	Error limits on A factor given as ±17.5%.
ISOTOPIC REACTION $I + D_2 \rightarrow DI + D$			
1.10×10^2	633.21	Static system. D_2(1.21×10^{-8} - 3.0×10^{-5} mol cm^{-3})/I_2(2.42×10^{-8} - 2.82×10^{-5} mol cm^{-3}) mixtures, ratios $[D_2]:[I_2]$ in range 0.26 to 2.98. Reaction quenched, DI and I_2 condensed, and residual D_2 pressure measured. SULLIVAN 1963 (6)	Steady state approximation made for [D], according to $I_2 + M \rightleftharpoons I + I + M$ 3 $D_2 + I_2 \rightleftharpoons DI + DI$ 2D $I + D_2 \rightleftharpoons DI + D$ 1D,-1D $D + I_2 \rightleftharpoons DI + I$ 4D,-4D giving differential equation in $[I_2]$, as for (3) under reaction 1. Analysis as in (5) gave k_{1D},k_{2D}, and k_{-1D}/k_{4D}. Author gives k_{1D}=(2.57 ± 0.6)$\times 10^{12} T^{\frac{1}{2}} \exp\{-(16\,990 \pm 150)/T\}$ cm^3 mol^{-1} s^{-1} (667-800 K). WHITE (12) quotes k_{1D}=(1.12 ± 0.3)$\times 10^{14} \exp\{-(17\,400 \pm 150)/T\}$ cm^3 mol^{-1} s^{-1} for this study.
5.79×10^2	666.79		
2.72×10^3	710.33		
6.87×10^3	737.93		
4.38×10^4	799.77		

Discussion

Following Sullivan's study [9] of the photochemical formation of HI from H_2 and I_2 (see the Discussion on the reaction between H_2 and I_2, section D6) it was apparent that above ~750–800 K the predominant mechanism for thermal production of HI was

$$I_2 + M \rightarrow I + I + M \qquad (3)$$
$$I + H_2 \rightarrow HI + H \qquad (1)$$
$$H + I_2 \rightarrow HI + I \qquad (4)$$
$$H + HI \rightarrow H_2 + I \qquad (-1)$$
$$I + HI \rightarrow H + I_2 \qquad (-4)$$

rather than the "molecular mechanism" of

$$H_2 + I_2 \rightleftharpoons HI + HI \qquad (2,-2)$$

Consequently all the available data for k_1 have been obtained in thermal systems, at temperatures above 600 K.

In a series of static thermal studies of H_2/I_2 mixtures, Sullivan [3,4,5] was able to separate k_1 and k_2 by varying the $[H_2]$:$[I_2]$ ratio over an order of magnitude. He also reanalysed [4] the data of Rosenbaum and Hogness [1] for the I_2 and I catalysed para-ortho conversion of hydrogen, giving values of k_1 in good agreement with his own. The high temperature flow system data of Graven [2] were also reanalysed (Graven's original interpretation was in terms of reactions 2 and -2 only) by Horie et al. [8] and gave a value of k_1 at 973 K in good agreement with the extrapolated data of Sullivan [3,4,5].

Because of this good agreement between results obtained in static H_2/I_2 systems [3,4,5], the static system para-ortho H_2 conversion by iodine [1,4], and the flow system HI synthesis/decomposition [2,8], we recommend the rate constant expression

$$k_1 = 1.69 \times 10^{14} \exp(-16\,930/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 600–1000 K. Error limits of ±20% should be considered. As may be seen from the Arrhenius plot, this expression is very close to that of Kondratiev [11], based on the same data except those of Rosenbaum and Hogness [1].

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D4 $H + HI \rightarrow H_2 + I$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-137.595	- 9.841	23.592
300	-137.595	- 9.841	23.443
500	-137.641	- 9.958	13.859
1000	-138.553	-11.117	6.657
1500	-140.131	-12.393	4.233
2000	-141.336	-13.096	3.007
2500	-141.913	-13.360	2.267
3000	-141.896	-13.355	1.773
3500	-141.373	-13.201	1.420
4000	-140.419	-12.945	1.157
4500	-139.097	-12.640	0.955
5000	-137.474	-12.293	0.794

RECOMMENDED RATE CONSTANT

$k_1 = 4.74 \times 10^{13} \exp(-330/T)$ cm^3 mol^{-1} s^{-1}

$= 7.87 \times 10^{-11} \exp(-330/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 600-1000 K

Suggested Error Limits for Calculated Rate Constant: ±20% in the temperature range quoted.

Note: this expression is based on equilibrium data and $k(I+H_2)$.

Rate Parameters: log(A/cm^3 mol^{-1} s^{-1}) = 13.68 ± 0.08

log(A/cm^3 $molecule^{-1}$ s^{-1}) = -10.10 ± 0.08

E/J mol^{-1} = 2740 ± 460

E/cal mol^{-1} = 656 ± 110

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Static photolysis system. HI(0.5-0.8 μ Hg; 66.7-106.6 mPa)/I_2 (up to 15%) mixtures. Products condensed to remove HI and I_2, H_2 pressure measured. BONHOEFFER and FARKAS 1928 (2)	HI decay completely inhibited by 15% I_2. Therefore authors estimated $k_2/k_1>100$, by comparison with HBr decay results of BODENSTEIN and LÜTKEMEYER (1). $H + HI \rightarrow H_2 + I$ 1 $H + I_2 \rightarrow HI + I$ 2
	273	Static photolysis system. HI(49.9-112.3 mm Hg; 6.65-15.1 kPa)/O_2(101.2-611.6 mm Hg; 13.5-81.5 kPa) mixtures. Products analysed for I_2 by titration with $Na_2S_2O_3$, for O_2 by absorption by pyrogallol, for H_2 by pressure difference, and for H_2O_2. BATES and LAVIN 1933 (3)	Steady state treatment of mechanism $HI + h\nu \rightarrow H + I$ $H + HI \rightarrow H_2 + I$ 1 $H + O_2 \rightleftarrows HO_2$ 3,-3 $HO_2 + HI \rightarrow H_2O_2 + I$ 4 gave differential equation for H_2 production. Integrated form of this equation solved graphically to give average $k_3/k_1=0.095$, if $[H_2]$ obtained from total pressure and p_{O_2}, or $k_3/k_1=0.085$ if $[H_2]$ from total pressure decrease and final p_{HI}. Both values obtained assuming k_{-3} insignificant. Authors also quote $k_3/k_1=0.097$. Despite more than twofold variation in total pressure, no systematic variation in k_3/k_1.
	273	Static photolysis system. HI(24.7-200.6 mm Hg; 3.3-26.8 kPa)/O_2(150.3-702.4 mm Hg; 20-93.6 kPa)/N_2 (0,388.4 and ∼474 mm Hg; 51.8 and ∼63.2 kPa) mixtures. Method as for (3) except for H_2, determined by combustion of sample of known volume. COOK and BATES 1935 (5)	Authors analysed data according to mechanism used in (3), and with three-body reaction 3' in place of reaction 3 $H + O_2 + M \rightarrow HO_2 + M$ 3' Values of k_3/k_1 obtained in first analysis dependent upon k_{-3}/k_4, for which authors assumed value 0 $HO_2 \rightarrow H + O_2$ -3 $HO_2 + HI \rightarrow H_2O_2 + I$ 4 and showed variation with added N_2. No such variation found for $k_{3'}/k_1$ obtained in second analysis, leading authors to prefer three-body mechanism for HO_2. Slight variation in $k_{3'}/k_1$ with ratio $[HI]:[O_2]$ seen as effect of higher collision efficiency for M=HI. Authors found $k_{3'}(M=HI)\approx 2k_{3'}(M=O_2)$, and assumed $k_{3'}(M=N_2)=k_{3'}(M=O_2)$. Overall value for $k_{3'}/k_1$ quoted

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		COOK and BATES 1935 (5) continued.	as $(2.11 \pm 0.29) \times 10^3$ cm^3 mol^{-1}. Using authors' tabulated data, we calculate $k_{3'}(M=O_2)/k_1 = (1.83 \pm 0.25) \times 10^3$ cm^3 mol^{-1}, and using our expression for $k_{3'}(M=O_2)$ (Volume 1, p.377), we obtain $k_1 = (6.82 \pm 0.8) \times 10^{12}$ cm^3 mol^{-1} s^{-1} (273 K).
	381	Static photolysis system. HI(50-150 mm Hg; 6.67-20 kPa)/I_2(0-20 mm Hg; 2.67 kPa) mixtures photolysed at 253.7 nm. H_2 yield measured by unspecified method, probably as in (8). OGG and WILLIAMS 1943 (6)	Experimental results agreed with mechanism $HI + h\nu \rightarrow H + I$ $H + I_2 \rightarrow HI + I$ 2 $H + HI \rightarrow H_2 + I$ 1 $I + I + M \rightarrow I_2 + M$ 5 giving $k_2/k_1 = (4.9 \pm 0.3)$ at 381 K. No systematic variation in this value over 50 K temperature range.
	375-463	Static photolysis system. HI(∿200 mm Hg; 26.7 kPa)/I_2/C_6H_{12} mixtures photolysed at 253.7 nm. Method probably as for (8). OGG and WILLIAMS 1945 (7)	Mechanism as used in (6) expanded to include 'hot' hydrogen atoms H* $HI + h\nu \rightarrow H^* + I$ $H^* + I_2 \rightarrow HI + I$ 2* $H^* + HI \rightarrow H_2 + I$ 1* $H^* + M \rightarrow H + M$ $H + I_2 \rightarrow HI + I$ 2 $H + HI \rightarrow H_2 + I$ 1 $I + I + M \rightarrow I_2 + M$ 5 Ratio k_2/k_1 given as $\leqslant (7.0 \pm 0.4)$, and hot atom ratio k_{2*}/k_{1*} given as (3.8 ± 0.4) at 428 K.
	375-462	Static photolysis system. HI(166.4-202.8 mm Hg; 22.2-27.0 kPa)/I_2(6.55-12.2 mm Hg; 0.87-1.63 kPa) mixtures photolysed at 253.7 nm. Absorbed light intensity and H_2 pressure measured. WILLIAMS and OGG 1947 (8)	Steady state treatment gave integrated rate expression for $[H_2]$ in terms of k_2/k_1. In absence of inert moderator, observed reactions considered those of H*. Tabulated results give $k_{2*}/k_{1*} = 2.4$ to 3.9 at 375 K, and 3.0 to 3.9 at 462 K. Authors quote $k_{2*}/k_{1*} = (3.5 \pm 0.3)$, independent of T. Incomplete light absorption given as reason for earlier, higher, value (6). Hot atom ratio used by (19).

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	387-471	Static photolysis system. HI(160 mm Hg; 21.3 kPa), and HI(160 mm Hg; 21.3 kPa)/H_2,He or Ar mixtures. [HI]:[H_2] ratios in range 0.12 to 0.5, [HI]:[He] = 0.15-1.4, and average [HI]:[Ar]= 0.244. Final [I_2] determined by addition of KI solution, followed by titration with $Na_2S_2O_3$, and actinometry used to determine absorbed light intensity. SCHWARZ, WILLIAMS and HAMILL 1952 (9)	Steady state treatment gave integrated rate expression for [I_2], giving k_2/k_1. For unmoderated mixtures, this ratio in fact k_{2*}/k_{1*}, found experimentally as (4.2±0.2), independent of T. Variation of ratio R (=(I_2 removal rate constant)/(HI removal rate constant)) with [HI]/[M] extrapolated to give R_o (at [M]=0) = k_{2*}/k_{1*}=5.3 (over whole temperature range), and R_∞(at [HI]/[M]= 0) = k_2/k_1=(13.5±1.0) at 387 K, (9.0±0.8) at 427 K, and (4.7±0.5) at 471 K. Authors quote Arrhenius fit to these data as $k_2/k_1=4x10^{-2}$ exp(2270/T).
	973	Flow system. (a) HI(8.11x10^{-7}-5.67x10^{-6} mol cm^{-3}) and HI(3.19x10^{-6} and 3.21x10^{-6} mol cm^{-3})/H_2(2x10^{-7}-4.79x10^{-6} mol cm^{-3}) mixtures, with 0.67< [H_2]:[HI] <16.1, and (b) H_2(4.07x10^{-7}-4.54x10^{-6} mol cm^{-3})/I_2 (1.10x10^{-6}-5.01x10^{-6} mol cm^{-3}) mixtures, ratios [H_2]:[I_2] 0.08 to 4.01. N_2 diluent added to give total concentrations ∿1.25x10^{-5} mol cm^{-3}; products analysed gravimetrically, after (a) I_2 sublimation at 273 K, and (b) absorption of HI in ascarite. GRAVEN 1956 (11)	Original analysis considered only reactions 6 and -6 $H_2 + I_2 \rightleftarrows HI + HI$ 6,-6 Re-analysis by HORIE et al.(16) used steady state treatment of reactions 5 and -5 plus sequence $I_2 + M \rightleftarrows I + I + M$ -5,5 $I + H_2 \rightleftarrows HI + H$ -1,1 $H + I_2 \rightleftarrows HI + I$ 2,-2 giving k_{-1} as functions of k_1/k_2 for both (a) HI decomposition and (b) HI synthesis. Intersection of these functions, displayed graphically, gave $k_1/k_2 \approx 0.06$ at 973 K.
	633-738	Static system. H_2(4.2x10^{-7}-2.9x10^{-6} mol cm^{-3})/I_2 (5.6x10^{-7}-2.4x10^{-6} mol cm^{-3}) mixtures, with [H_2]:[I_2] range 0.33-2.62. Reaction quenched and residual H_2 pressure measured after freezing out HI and I_2. SULLIVAN 1959 (12)	Steady state assumption for [H], according to mechanism for HI synthesis $I_2 + M \rightleftarrows I + I + M$ -5,5 $H_2 + I_2 \rightleftarrows HI + HI$ 6,-6 $I + H_2 \rightleftarrows HI + H$ -1,1 $H + I_2 \rightleftarrows HI + I$ 2,-2 gave rate equation for [I_2] in terms of k_6, k_{-1}/K_5k_6, and k_1/k_2. Best fits to data computed as k_1/k_2 = (0.07±0.04) at 633.21 K, (0.082±0.005) at 666.79 K, (0.117 ±0.007) at 710.33 K, and (0.125±

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		SULLIVAN 1959 (12) continued.	0.008) at 737.93 K. Least-squares fit to k_{-1}, found above, used with K_1 to give $k_1=1.6x10^{12}\ T^{\frac{1}{2}}\ exp\{-(240\pm180)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
	693	Static system. H_2/I_2 mixtures, with $[H_2]$ and $[I_2]$ each varied by factor 3. Method as for (12). SULLIVAN 1959 (13)	Experiments performed to determine possible wall effect in para-ortho H_2 conversion study of ROSENBAUM and HOGNESS (4). Analysis as for (12). Best fit to experimental results given by $k_1/k_2=0.09$ at 693 K.
	667,800	Static system. $H_2(1.05x10^{-8}-4.59x10^{-6}\ mol\ cm^{-3})/I_2(4.0x10^{-9}-5.72x10^{-6}\ mol\ cm^{-3})$ mixtures, with $0.12 \leqslant [H_2]:[I_2] \leqslant 4.51$. Method as for (12). SULLIVAN 1962 (14)	Rate equation for $[I_2]$ generated as in (12). For mixtures quenched at low values of $[HI]/[I_2]$, improved analysis showed rates dependent upon k_{-1} and k_6, but largely independent of k_1/k_2. For mixtures reacting to give large $[HI]/[I_2]$, strong dependence upon k_1/k_2 enabled this ratio to be evaluated using k_{-1} and k_6 determined above. Best fits given by $k_1/k_2=(0.07\pm0.02)$ at 666.79 K, and (0.082 ± 0.012) at 799.77 K. Using values of k_{-1} obtained in this study and (12), and K_1, author quotes $k_1=1.12x10^{12}\ T^{\frac{1}{2}}\ exp\{-(0\pm130)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. Surface reactions shown to be irrelevant by using reaction vessel of larger surface/volume ratio. Expression for k_1 used by (18 and 27), and recommended by (24). WHITE (25) quotes $k_1=(1.59\pm1.0)x10^{15}\ exp\{-(0\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ for this work and (12 and 13).
	298	Static photolysis system. $HI(10^{-7}-1.3x10^{-6}\ mol\ cm^{-3})/C_2H_3Cl(1.1x10^{-6}-6.4x10^{-6}\ mol\ cm^{-3})$ mixtures. $[C_2H_3Cl]:[HI]$ ratio in range 3.3-43. Products analysed manometrically, giving $[H_2]$, and by gas chromatography, giving $[C_2H_4]$ and $[C_2H_5Cl]$.	Steady state treatment of mechanism $HI + h\nu \rightarrow H + I$ $H + HI \rightarrow H_2 + I$ 1 $H + C_2H_3Cl \rightarrow C_2H_4Cl^*$ 7a $\rightarrow C_2H_3 + HCl$ 7b $\rightarrow C_2H_2Cl + H_2$ 7c $C_2H_4Cl^* + M \rightarrow C_2H_4Cl + M$ 8 $C_2H_4Cl + HI \rightarrow C_2H_5Cl + I$ $C_2H_3 + HI \rightarrow C_2H_4 + I$ 9

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		RENNERT and WIJNEN 1967 (17) and 1968 (21)	$C_2H_3 + C_2H_3Cl \rightarrow C_4H_6Cl$ 10 gave ratios k_1/k_{7a}=28, k_{7b}/k_{7a}=1.49, k_{7c}/k_{7a}=2.1, amd k_{10}/k_9=0.034. Results consistent with total de-activation of $C_2H_4Cl^*$ via reaction 8. Overall ratio k_1/k_7=6.0 at 298 K.
	326-473	Static photolysis system. HI(2.6x10^{-7}-8.5x10^{-7} mol cm^{-3})/I_2(2.5x10^{-8}-6.3x10^{-8} mol cm^{-3})/He, Ar, or H_2 mixtures photolysed 248-266 nm. [He]/[HI] ratios varied 1.5-67.7, [Ar]/[HI] ratios 19.9-35.2, and [H_2]/[HI] ratios 27.3 and 31.0. HI/I_2 mixtures, with same initial [HI] as for HI/I_2/moderator mixtures, used to determine absorbed light intensity, using actinometry. [H_2] measured manometrically, and final [HI] and [I_2] determined by adding KI, then KIO_3 solutions, following each by $Na_2S_2O_3$ titration. HOLMES and RODGERS 1968 (19)	'Hot atom' ratio k_2^*/k_1^* taken as (3.5±0.3) (8) $H^* + HI \rightarrow H_2 + I$ 1* $H^* + I_2 \rightarrow HI + I$ 2* Variation of H_2 yield ΦH_2 plotted vs. extent of reaction, enabling absorbed light intensity to be converted to [I_2], for ΦH_2=1. Substituting this value of [I_2] for absorbed light integrated rate equation for [I_2] gave k_2/k_1 (= ratio R (9) at infinite dilution) in range 11-13 over temperature range 323-473 K. Authors quote E_1-E_2=(0±1.5) kJ mol^{-1} (0±350) cal mol^{-1}). $H + HI \rightarrow H_2 + I$ 1 $H + I_2 \rightarrow HI + I$ 2
	303-533	Static photolysis system. HI(1.131-18.65 mm Hg; 0.15 -2.49 kPa)/I_2 (0.146-0.192 mm Hg; 19.5-25.6 Pa)/CO_2 (150-196.5 mm Hg; 20-26.2 kPa) mixtures, with [I_2]:[HI] range 0.008 to 0.13. H_2 yield measured by unspecifield method. PENZHORN and DARWENT 1968 (20)	Large excess of CO_2 effectively eliminated hot H-atoms, giving constant ΦH_2 for given [I_2]/[HI] ratio. Considering only reactions 1 and 2, plot of ΦH_2 vs. [I_2]/[HI] gave gradient k_2/k_1. From authors' tabulated data we calculate average k_2/k_1 values as 14.18 (303 K), 10.81 (415 K), 9.88 (478 K), and 8.84 (533 K). Authors give Arrhenius fit to these data as k_2/k_1=4.95 exp(320/T), and consider E_2=0.

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Static photolysis system. HI/C_2H_4, or C_2FH_3, or C_2F_4, or I_2/CO_2(0 and 250 mm Hg; 33.3 kPa) mixtures. $[HI]:[C_2F_xH_y]$ ratios 0.05 -1.0, and $[I_2]:[HI]$ ratio 0.01-0.13. H_2 yield measured manometrically. LETELIER, SANDOVAL and PENZHORN 1971 (22)	From plots of $1/\Phi H_2$ vs. $[C_2F_xH_y]/[HI]$, and $[I_2]/[HI]$, authors derived $k_{11}/k_1=(5.93\pm0.74)\times10^{-2}$, $k_{12}/k_1=(5.12\pm0.41)\times10^{-2}$, $k_{13}/k_1=(1.06\pm0.03)\times10^{-1}$, and $k_2/k_1=(14.05\pm0.92)$ at 298 K. $H + HI \rightarrow H_2 + I$ 1 $H + I_2 \rightarrow HI + I$ 2 $H + C_2H_4 \rightarrow C_2H_5$ 11 $H + C_2FH_3 \rightarrow C_2FH_4$ 12 $H + C_2F_4 \rightarrow C_2F_4H$ 13
	298-478	Static photolysis system. HI(~1 mm Hg; 133.3 Pa)/ C_2H_4(2.2 mm Hg; 293.5 Pa)/ CO_2(0-400 mm Hg; 53.3 kPa), and HI(0.78-8.02 mm Hg; 0.104-1.07 kPa)/C_2D_4 (1.0-10.1 mm Hg; 0.133-1.35 kPa) /CO_2(0-600 mm Hg; 80 kPa) mixtures. H_2 yield measured manometrically. PENZHORN and DARWENT 1971 (23)	H_2 yield ΦH_2 independent of CO_2 pressure for $p_{CO_2} \geqslant 100$ mm Hg (13.3 kPa) and low pressures of HI and C_2H_4 (or C_2D_4), indicating > 90% deactivation of hot H* atoms. Analysis as for (20) gave $k_{11}/k_1=(5.6\pm0.9)\times10^{-2}$ at 298 K $H + HI \rightarrow H_2 + I$ 1 $H + C_2H_4 \rightarrow C_2H_5$ 11 and $k_{11D}/k_1=(7.5\pm0.6)\times10^{-2}$ (303 K), $(1.05\pm0.04)\times10^{-1}$(417 K), and $(1.25\pm0.08)\times10^{-1}$ (478 K). Arrhenius fit to latter 3 values given as $k_{11D}/k_1=0.30\exp(-430/T)$. $H + C_2D_4 \rightarrow C_2D_4H$ 11D
	300	Static photolysis study. HI/CD_3CH_2I (~3-4 mm Hg; 400-533 Pa)/He(0 and ~100 mm Hg; 13.3 kPa) mixtures, ratio $[HI]:[CD_3CH_2I]$ in range 0-3; $HI/n\text{-}C_3H_7I/He$ (0 and ~100 mm Hg; 13.3 kPa) mixtures ($n\text{-}C_3H_7I$+HI pressure ~7 mm Hg; 935 Pa), ratio $[HI]:[n\text{-}C_3H_7I]$ 0 to 2.0; and $HI/sec\text{-}C_3H_7I/He$ (0 and ~100 mm Hg; 13.3 kPa) mixtures ($sec\text{-}C_3H_7I$+ HI pressure ~7 mm Hg; 935 Pa), ratio $[HI]:[sec\text{-}C_3H_7I]$ 0 to 3.0. Photolysis at 147 nm. Actinometry used to determine absorbed light intensity, and products analysed by mass spectrometry. REBBERT, LIAS and AUSLOOS 1973 (26)	Data analysed according to mechanism $RI + h\nu \rightarrow R + I$ $H + RI \rightarrow R + HI$ 14 $R + HI \rightarrow RH + I$ $H + HI \rightarrow H_2 + I$ 1 Deuterised C_2H_5I used solely for mass spectral identification. From variation of RH (C_2H_6 or C_3H_8) yields with $[RI]/[HI]$, authors obtain ratios $k_{14}/k_1 = (0.44\pm0.04)$ for C_2H_5I, (0.575 ± 0.06) for $n\text{-}C_3H_7I$, and (0.95 ± 0.1) for $sec\text{-}C_3H_7I$. Preliminary data for C_2H_5Br given as $k_{14}/k_1=(2.4\pm1.0)\times10^{-2}$.

$H + HI \rightarrow H_2 + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		ISOTOPIC REACTION $D + DI \rightarrow D_2 + I$	
	273,293	Static photolysis system. DI(25.1-201.4 mm Hg; 3.4 -26.9 kPa)/O_2 (297.3-688.1 mm Hg; 39.6-91.7 kPa)/N_2 (0, 369.3 and 391.8 mm Hg; 49.2 and 52.2 kPa) mixtures. Method as for reaction 1. COOK and BATES 1935 (5)	Steady state treatment of mechanism $DI + h\nu \rightarrow D + I$ $D + DI \rightarrow D_2 + I$ 1D $D + O_2 + M \rightarrow DO_2 + M$ 3D' $DO_2 + DI \rightarrow D_2O_2 + I$ 4D gave H_2 rate equation. Solution obtained as for reaction 1. Authors quote $k_{3D'}/k_{1D} = (3.98 \pm 0.75) \times 10^3\ cm^3\ mol^{-1}$ at 273 K, and from table we find $k_{3D'}/k_{1D} = (3.65 \pm 0.27) \times 10^3\ cm^3\ mol^{-1}$ at 293 K.
	298,373	Static photolysis system. DI/H_2 mixtures ([DI]:[H_2] ratios 0.05-1.3), and DI/H_2/He mixtures ([DI]:[H_2]:[He] ratios 1:1:1.7 and 0.69:1:1:18). Non-condensable products analysed by mass spectrometry. CARTER, HAMILL and WILLIAMS 1955 (10)	From relative yields of D_2 and HD, according to steady state treatment of [D] in mechanism $DI + h\nu \rightarrow D^* + I$ $D^* + DI \rightarrow D_2 + I$ 1D* $D^* + H_2 \rightarrow HD + H$ 1S authors obtained ratio $k_{1D^*}/k_{1S} = 5.64$, with no temperature dependence.
	800	Static system. D_2(1.21×10^{-8}-3.98×10^{-8} mol cm^{-3})/I_2(8.52×10^{-9}-4.63×10^{-8} mol cm^{-3}) mixtures, ratio [D_2]:[I_2] in range 0.36-3.54. Reaction quenched, DI and I_2 frozen out, and residual D_2 pressure measured. SULLIVAN 1963 (15)	Steady state approximation for [D], according to mechanism $I_2 + M \rightleftharpoons I + I + M$ -5,5 $D_2 + I_2 \rightleftharpoons DI + DI$ 6D,-6D $I + D_2 \rightleftharpoons DI + D$ -1D,1D $D + I_2 \rightleftharpoons DI + I$ 2D,-2D gave [I_2] rate equation, as for reaction 1 (12). Analysis as in (14), giving k_{1D}/k_{2D}, k_{-1D}, and with less precision k_{6D}. Best fit given by $k_{1D}/k_{2D} = 0.073$ at 799.77 K.

Discussion

There are no absolute data for the rate of reaction of hydrogen atoms with hydrogen iodide

$$H + HI \rightarrow H_2 + I \qquad (1)$$

and in the only study [5] in which k_1 is obtained relative to a well-known rate constant ($k_{3'}$)

$$H + O_2 + M \rightarrow HO_2 + M \qquad (3')$$

Cook and Bates were unaware of the effects of "hot" hydrogen atoms (H*) formed by the photolysis of HI

$$HI + h\nu \rightarrow H^* + I$$

and their resulting value of $k_1 = (6.82 \pm 0.8) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ (273 K) must be considered to be of doubtful validity.

Because of the rapid sequence

$$H + I_2 \rightarrow HI + I \qquad (2)$$

$$H + HI \rightarrow H_2 + I \qquad (1)$$

all of the data from HI/I_2 or H_2/I_2 systems are expressed in terms of the ratio k_2/k_1, which is considered under reaction 2 (section D5).

Consequently, in the absence of reliable data for k_1, we have used our recommended expression for k_{-1} (section D3)

$$I + H_2 \rightarrow HI + H \qquad (-1)$$

together with the equilibrium constant to obtain the expression

$$k_1 = 4.74 \times 10^{13} \exp(-330/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

which is valid for the temperature interval 600–1000 K. Values of k_1 obtained from this expression are within uncertainty limits of ±20%.

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D5 $H + I_2 \rightarrow HI + I$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-147.319	11.970	26.434
300	-147.335	11.920	26.276
500	-148.904	7.912	15.969
1000	-152.042	3.439	8.121
1500	-153.854	1.937	5.459
2000	-154.850	1.356	4.115
2500	-155.293	1.159	3.305
3000	-155.335	1.142	2.765
3500	-155.097	1.209	2.378
4000	-154.695	1.322	2.089
4500	-154.201	1.431	1.865
5000	-153.674	1.544	1.686

RECOMMENDED RATE CONSTANT

$k_1 = 4.31 \times 10^{14} \exp(-217/T)$ cm^3 mol^{-1} s^{-1}

$= 7.16 \times 10^{-10} \exp(-217/T)$ cm^3 molecule^{-1} s^{-1}

Temperature Range: 600-800 K

Suggested Error Limits for Calculated Rate Constant: ±60% over quoted temperature range

Rate Parameters:

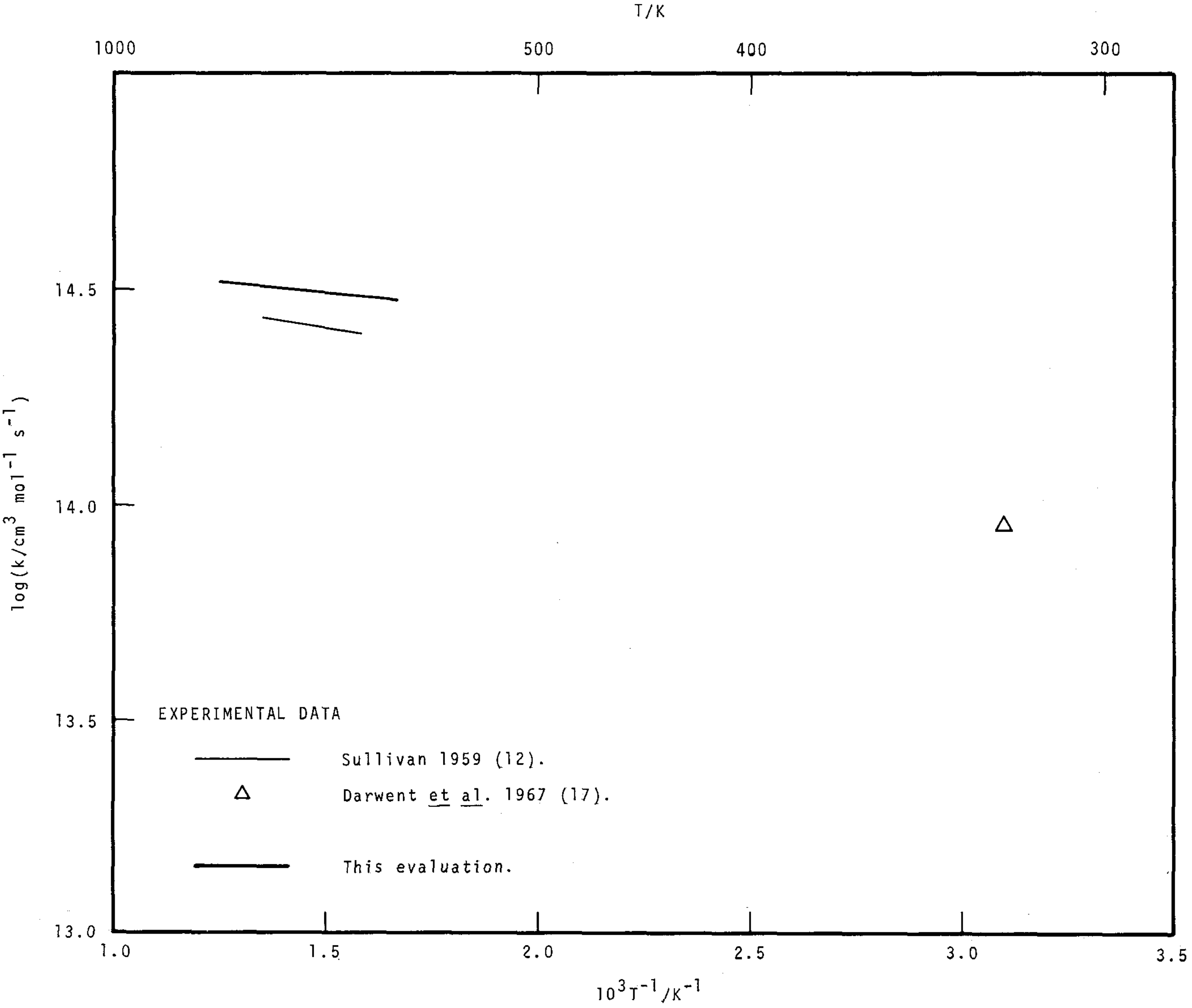
log(A/cm^3 mol^{-1} s^{-1}) = 14.64 ± 0.2

log(A/cm^3 molecule^{-1} s^{-1}) = -9.15 ± 0.2

E/J mol^{-1} = 1803 ±18 410

E/cal mol^{-1} = 431 ± 4 400

$H + I_2 \rightarrow HI + I$

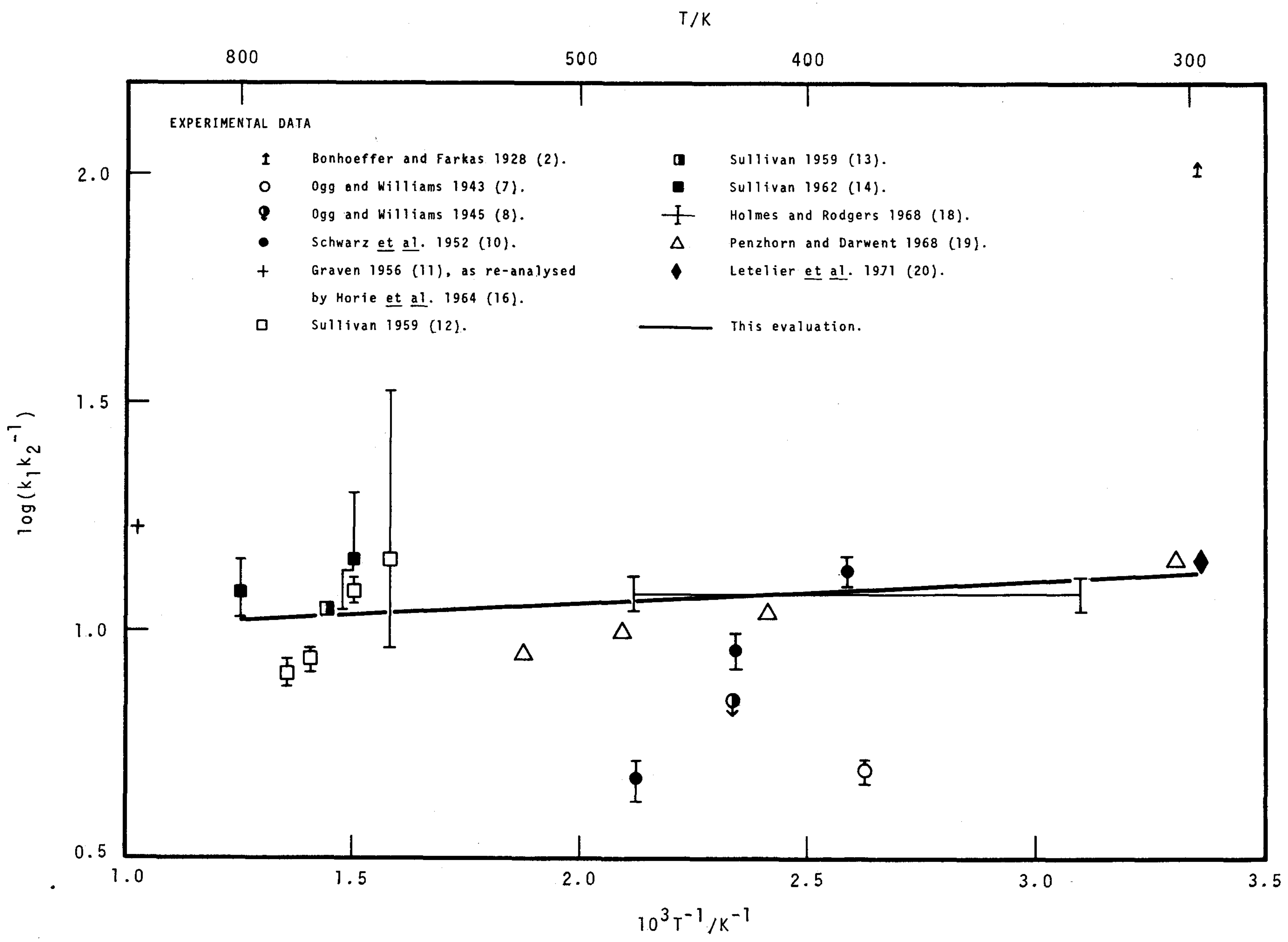


$H + I_2 \rightarrow HI + I$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	298	Static photolysis system. HI (0.5-0.8 μ Hg; 66.7-106.6 mPa)/I_2 (up to 15%) mixtures. H_2 pressure in products determined after condensing out HI and I_2. BONHOEFFER and FARKAS 1928 (2)	Complete inhibition of HI decay by 15% I_2 led authors to estimate k_1/k_2>100, by comparison with HBr decay results of BODENSTEIN and LÜTKEMEYER (1). $H + I_2 \rightarrow HI + I$ 1 $H + HI \rightarrow H_2 + I$ 2 Data quoted by (3,5,6).
	381	Static photolysis system. HI (50-150 mm Hg; 6.67-20 kPa)/I_2 (0-20 mm Hg; 2.67 kPa) mixtures photolysed at 253.7 nm. H_2 yield measured by unspecified method, probably as in (9). OGG and WILLIAMS 1943 (7)	Experimental results suggested mechanism $HI + h\nu \rightarrow H + I$ $H + I_2 \rightarrow HI + I$ 1 $H + HI \rightarrow H_2 + I$ 2 $I + I + M \rightarrow I_2 + M$ 3 giving $k_1/k_2=(4.9\pm0.3)$ at 381 K. No systematic variation in this value over 50 K temperature change.
	375-463	Static photolysis system. HI (∿200 mm Hg; 26.7 kPa) /I_2/C_6H_{12} mixtures photolysed at 253.7 nm. Method probably as for (9). OGG and WILLIAMS 1945 (8)	Mechanism of (7) expanded to include 'hot' hydrogen atoms H* $HI + h\nu \rightarrow H^* + I$ $H^* + I_2 \rightarrow HI + I$ 1* $H^* + HI \rightarrow H_2 + I$ 2* $H^* + M \rightarrow H + M$ $H + I_2 \rightarrow HI + I$ 1 $H + HI \rightarrow H_2 + I$ 2 $I + I + M \rightarrow I_2 + M$ 3 Hot atom effect given as $k_{1*}/k_{2*}=(3.8\pm0.4)$, and ratio $k_1/k_2<(7.0\pm0.4)$ at 428 K.
	375-462	Static photolysis system. HI (166.4-202.8 mm Hg; 22.2-27.0 kPa)/I_2(6.55-12.2 mm Hg; 0.87-1.63 kPa) mixtures photolysed at 253.7 nm. Absorbed light intensity and H_2 pressure measured. WILLIAMS and OGG 1947 (9)	Steady state analysis gave integrated rate expression for $[H_2]$ in terms of k_1/k_2. In absence of inert moderator (e.g. C_6H_{12} in (8)), observed reactions probably those of H*. Tabulated results give $k_{1*}/k_{2*}=2.4$ to 3.9 at 375 K, and 3.0 to 3.9 at 462 K. Authors give $k_{1*}/k_{2*}=(3.5\pm0.3)$, independent of T. Incomplete light absorption given as reason for earlier, higher, value (7). Hot atom ratio used by (18).

$H + I_2 / H + HI$


T/K
800
500
400
300
EXPERIMENTAL DATA
↥ Bonhoeffer and Farkas 1928 (2).
○ Ogg and Williams 1943 (7).
Ogg and Williams 1945 (8).
● Schwarz et al. 1952 (10).
+ Graven 1956 (11), as re-analysed by Horie et al. 1964 (16).
□ Sullivan 1959 (12).
Sullivan 1959 (13).
■ Sullivan 1962 (14).
Holmes and Rodgers 1968 (18).
△ Penzhorn and Darwent 1968 (19).
◆ Letelier et al. 1971 (20).
This evaluation.
$\log(k_1 k_2^{-1})$
2.0
1.5
1.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
$10^3 T^{-1} / K^{-1}$

$H + I_2 \rightarrow HI + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	387-471	Static photolysis system. HI (160 mm Hg; 21.3 kPa), and HI (160 mm Hg; 21.3 kPa)/H_2, He or Ar mixtures. $[HI]:[H_2]$=0.12-0.5, [HI]:[He]=0.15-1.4, and average [HI]:[Ar]= (0.244±0.01). Final $[I_2]$ measured by adding KI solution, followed by $Na_2S_2O_3$ titration, and absorbed light by actinometry. SCHWARZ, WILLIAMS and HAMILL 1952 (10)	Steady state analysis gave integrated rate expression for $[I_2]$, giving k_1/k_2. For mixtures containing only HI, this ratio in fact k_{1*}/k_{2*}, found experimentally as (4.2±0.2), independent of T. Variation of ratio R(=(I_2 removal rate constant)/(HI removal rate constant)) with [HI]/[M] extrapolated to give R_0(at [M]=0)=k_{1*}/k_{2*}=5.3, and R_∞ (at [HI]/[M]=0)= k_1/k_2 = (13.5±1.0) at 387 K, (9.0 ±0.8) at 427 K, and (4.7±0.5) at 471 K. Authors give Arrhenius fit to these data as $k_1/k_2=4\times10^{-2}$ exp (2270/T).
	973	Flow system. (a) HI(8.11×10^{-7}-5.67×10^{-6} mol cm^{-3}) and HI(3.19×10^{-6} and 3.21×10^{-6} mol cm^{-3})/H_2(2×10^{-7}-4.79×10^{-6} mol cm^{-3}) mixtures, in ratios $[H_2]:[HI]$ of 0.67 to 16.1, and (b) H_2 (4.07×10^{-7}-4.54×10^{-6} mol cm^{-3})/I_2 (1.10×10^{-6}-5.01×10^{-6} mol cm^{-3}) mixtures, ratios $[H_2]:[I_2]$ in range 0.08-4.01. N_2 diluent added to give total concentrations of ~1.25×10^{-5} mol cm^{-3}. Products analysed gravimetrically, after (a) I_2 sublimation at 273 K, and (b) absorption of HI in ascarite. GRAVEN 1956 (11)	Original analysis considered only reactions 4 and -4 $H_2 + I_2 \rightleftharpoons HI + HI$ 4,-4 Re-analysis by HORIE et al. (16) according to steady state treatment of these reactions plus $I_2 + M \rightleftharpoons I + I + M$ -3,3 $I + H_2 \rightleftharpoons HI + H$ -2,2 $H + I_2 \rightleftharpoons HI + I$ 1,-1 gave k_{-2} as functions of k_2/k_1 for both (a) HI decomposition and (b) HI synthesis. Intersection of these functions gave $k_2/k_1 \approx 0.06$ at 973 K.
	633-738	Static system. H_2(4.2×10^{-7} -2.9×10^{-6} mol cm^{-3})/I_2 (5.6×10^{-7}-2.4×10^{-6} mol cm^{-3}) mixtures, with $[H_2]:[I_2]$ range 0.33-2.62. Reaction quenched and residual H_2 pressure measured after freezing out HI and I_2. SULLIVAN 1959 (12)	Steady state assumption for [H], according to mechanism $I_2 + M \rightleftharpoons I + I + M$ -3,3 $H_2 + I_2 \rightleftharpoons HI + HI$ 4,-4 $I + H_2 \rightleftharpoons HI + H$ -2,2 $H + I_2 \rightleftharpoons HI + I$ 1,-1 gave differential equation for $[I_2]$ in terms of k_4, k_{-2}/K_3k_4, and k_2/k_1. Best fits to data computed as k_2/k_1=(0.07±0.04) at 633.21 K, (0.082±0.005) at 666.79 K, (0.117±0.007) at 710.33 K, and (0.125±0.008) at 737.93 K.

$H + I_2 \rightarrow HI + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		SULLIVAN 1959 (12) continued.	Using least-squares fit to k_{-2} found from above ratios, with K_2, author obtained expression for k_2. Using best fits to k_{-2} and k_4, author calculated 'more reliable' values for k_2/k_1. These values, together with k_2 as found above, used to give $k_1=10^{13}T^{\frac{1}{2}}\exp\{-(0\pm250)/T\}$ cm^3 mol^{-1} s^{-1}, to within ±50%.
	693	Static system. H_2/I_2 mixtures, with $[H_2]$ and $[I_2]$ each varied by factor 3. Method as for (12). SULLIVAN 1959 (13)	Experiments performed to determine possible wall effect in para-ortho H_2 conversion study of ROSENBAUM and HOGNESS (4). Analysis as for (12). Best fit to experimental results given by $k_2/k_1=0.09$ at 693 K.
	667,800	Static system. H_2 (1.05×10^{-8}-4.59×10^{-6} mol cm^{-3})/ I_2(4.0×10^{-9}-5.72×10^{-6} mol cm^{-3}) mixtures, with $0.12 \leq [H_2]:[I_2] \leq 4.51$. Method as for (12). SULLIVAN 1962 (14)	Differential equation in $[I_2]$ generated as for (12). For mixtures allowed to react to low values of $[HI]/[I_2]$, improved analysis showed rates dependent upon k_4 and k_{-2}, but largely independent of k_2/k_1. For mixtures reacting to give large $[HI]/[I_2]$, strong dependence on k_2/k_1 enabled this ratio to be evaluated using k_4 and k_{-2} previously determined. Best fits given by $k_2/k_1=(0.07\pm0.02)$ at 666.79 K, and (0.082 ± 0.012) at 799.77 K. Small variation of k_2/k_1 with T led author to quote $E_1=E_2=0$. Negligible effect of surface reactions showed by using reaction vessel of larger surface/volume ratio.
	323	Static photolysis system. H_2S(9.5 mm Hg; 1.27 kPa)/ I_2(0.2mm Hg; 26.7 Pa)/CO_2 (0 and 689 mm Hg; 91.84 kPa) mixtures photolysed at 253.7 nm. Products analysed for H_2. DARWENT, WADLINGER and ALLARD 1967 (17)	Yield of H_2 decreased in CO_2-moderated mixtures, suggesting de-activated H* atoms react more strongly with I_2 than H_2S. Assuming all H atoms thermalised by CO_2, authors quote $k_1/k_5=166$ $H + I_2 \rightarrow HI + I$ 1 $H + H_2S \rightarrow H_2 + HS$ 5 Using our expression for k_5 (Volume 3, p.445) we obtain $k_1=9.03\times10^{13}$ cm^3 mol^{-1} s^{-1} (323 K).

$H + I_2 \rightarrow HI + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	326-473	Static photolysis system. HI($2.6x10^{-7}$-$8.5x10^{-7}$ mol cm^{-3})/I_2($2.5x10^{-8}$-$6.3x10^{-8}$ mol cm^{-3})/He, Ar, or H_2 mixtures photolysed 248-266 nm. [He]/[HI] ratios varied 1.5-67.7, [Ar]/[HI] ratios 19.9-35.2, and [H_2]/[HI] ratios 27.3 and 31.0. HI/I_2 mixtures, with same initial [HI] as for HI/I_2/moderator mixtures, used to determine absorbed light intensity, using actinometry. Non-condensable product (H_2) pressure measured, and final [HI] and [I_2] determined using KI and KIO_3 solutions, each being followed by titration against $Na_2S_2O_3$. HOLMES and RODGERS 1968 (18)	Assuming 'hot atom' ratio k_{1^*}/k_{2^*} =(3.5±0.3) (9) $H^* + I_2 \rightarrow HI + I$ 1* $H^* + HI \rightarrow H_2 + I$ 2* variation of H_2 yield ΦH_2 plotted vs extent of reaction. Absorbed light intensity thereby converted to [I_2] for ΦH_2=1. Substitution of [I_2] for absorbed light in integrated rate equation for [I_2], derived from steady state treatment of [H] and [H*], gave k_1/k_2(=ratio R (10) at infinite moderation) in range 11-13 for temperatures 323-473 K. Authors quote E_2-E_1=(0±1.5) kJ mol^{-1} (0±350) cal mol^{-1}): $H + I_2 \rightarrow HI + I$ 1 $H + HI \rightarrow H_2 + I$ 2
	303-533	Static photolysis system. HI(1.131-18.65 mm Hg; 0.15-2.49 kPa)/I_2(0.146-0.192 mm Hg: 19.5-25.6 Pa)/CO_2 (150-196.5 mm Hg; 20-26.2 kPa) mixtures, with [I_2]/[HI] range 0.008 to 0.13, and 8<[CO_2]/[HI]<133. Yield of H_2 measured by unspecified method. PENZHORN and DARWENT 1968 (19)	Large excess of CO_2 effectively eliminated hot H-atoms, giving constant ΦH_2 for given [I_2]/[HI] ratio. Considering only reactions 1 and 2, plot of 1/ΦH_2 vs. [I_2]/[HI] gave k_1/k_2. From authors' tabulated data we calculate average k_1/k_2 values as 14.18 (303 K), 10.81 (415 K), 9.88 (478 K), and 8.84 (533 K). Authors give Arrhenius expression for these data as k_1/k_2= 4.95 exp(320/T), and assume E_1=0.
	298	Static photolysis system. I_2/HI (or HBr)/CO_2(0 and 250 mm Hg; 33.3 kPa) mixtures. [I_2]/[HI] (or [I_2]/[HBr]) varied 0.01-0.13. H_2 yield measured manometrically. LETELIER, SANDOVAL and PENZHORN 1971 (20)	From plots of 1/ΦH_2 vs [I_2]/[HI] and [I_2]/[HBr], authors derive k_1/k_2=(14.05±0.92) and k_1/k_6= (19.05±0.63) respectively. $H + HBr \rightarrow H_2 + Br$ 6 In absence of CO_2, authors obtain k_{1^*}/k_{6^*}=2.8 $H^* + I_2 \rightarrow HI + I$ 1* $H^* + HBr \rightarrow H_2 + Br$ 6*

$H + I_2 \rightarrow HI + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
ISOTOPIC REACTION $D + I_2 \rightarrow DI + I$			
	800	Static system. D_2(1.21×10^{-8}-3.98×10^{-8} mol cm^{-3})/I_2(8.52×10^{-9}-4.63×10^{-8} mol cm^{-3}) mixtures, with $[D_2]/[I_2]$ ratio in range 0.36-3.54. After quenching reaction residual D_2 pressure measured after condensing out DI and I_2. SULLIVAN 1963 (15)	Steady state approximation for [D], using mechanism $I_2 + M \rightleftharpoons I + I + M$ -3,3 $D_2 + I_2 \rightleftharpoons DI + DI$ 4D,-4D $I + D_2 \rightleftharpoons DI + D$ -2D,2D $D + I_2 \rightleftharpoons DI + I$ 1D,-1D gave differential equation for $[I_2]$, as for (12) under reaction 1. Analysis as in (14), giving k_{2D}/k_{1D}, k_{-2D}, and with less precision, k_{4D}. Best fit given by $k_{2D}/k_{1D} = 0.073$.

Discussion

The reaction between iodine and atomic hydrogen is the more important of the chain propagating steps 1 and 2 in the photo or thermal synthesis of HI above ~600 K.

$$H + I_2 \rightarrow HI + I \qquad (1)$$

$$H + HI \rightarrow H_2 + I \qquad (2)$$

Because of the competition between these two reactions, all of the data retrieved from H_2/I_2 [12,13,14] and HI/H_2 or I_2 [2,7,8,9,10,11,18,19,20] mixtures have been in terms of the ratio k_1/k_2. In those studies in which reaction was initiated by photolysis (of HI [2,7,8,9,10,18,19,20] or H_2S [17]) the reaction mechanism must be enlarged to account for the reactions of "hot" hydrogen atoms (H*) produced in the primary act

$$HI + h\nu \rightarrow H^* + I$$

Sufficiently high pressures of moderator gases must be added in such systems to thermalise the H* atoms—otherwise the removal of I_2 and HI are the overall reactions (1+1*) and (2+2*), respectively

$$H^* + I_2 \rightarrow HI + I \qquad (1^*)$$

$$H^* + HI \rightarrow H_2 + I \qquad (2^*)$$

The early photolysis studies [2,7] contained no allowance for this factor and have not been considered in this evaluation. In the case of the study by Schwarz et al. [10] moderator gas pressures were not high enough relative to the HI pressure ($[M]:[HI] \ngtr 8$) and the resulting values of k_1/k_2 were too low (cf. the work of Penzhorn and Darwent [19] in which $8 < [M]:[HI] < 133$). The re-analysis by Horie et al. [16] of Graven's work [11] unfortunately only gave an approximate value for k_1/k_2, but it does indicate that there is no great variation of this ratio with temperature.

We consider the later work of Sullivan [14] to be the most accurate of his studies [12,13,14], but even so, when taken with the remaining reliable data for k_1/k_2 [19,20] we find little difference between the fit to [12,19,20] and the fit including in addition Sullivan's earlier results [12,13]. There is no improvement to be gained by making an empirical fit of the form $\log(k_1/k_2T^n)$ vs T^{-1} as for the ratio $k(H+Br_2)/k(H+HBr)$ (see section C6). Our assessment therefore, of the data of [12,13,14,19,20], yields the expression

$$k_1/k_2 = 9.09 \exp(114/T)$$

for the temperature range 298-800 K, within uncertainty limits of ±30%.

Combined with our recommended expression for k_2 (section D4) this ratio gives

$$k_1 = 4.31 \times 10^{14} \exp(-217/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for temperatures 600-800 K. Uncertainty limits of ±60% must be considered.

Rate of the Reverse Reaction

There are no data available on the rate of the reverse reaction

$$I + HI \rightarrow H + I_2 \qquad (-1)$$

By extrapolating our recommended rate constant expression for k_1 to 1000 K, slightly above the upper limit to this recommendation, and using the equilibrium constant, we obtain a value for k_{-1} of only 2.63×10^6 cm^3 mol^{-1} s^{-1}. Such a small value therefore means that in most H_2/I_2 systems, reaction −1 may be ignored relative to reaction −2

$$I + H_2 \rightarrow HI + H \qquad (-2)$$

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D6 $H_2 + I_2 \rightarrow HI + HI$

THERMODYNAMIC DATA ($H_2 + I_2 \rightarrow HI + HI$)

T (K)	ΔH^o ($kJ\ mol^{-1}$)	ΔS^o ($J\ K^{-1}\ mol^{-1}$)	log K
298	- 9.724	21.811	2.842
300	- 9.740	21.761	2.833
500	-11.096	17.870	2.110
1000	-13.489	14.556	1.464
1500	-13.724	14.330	1.226
2000	-13.514	14.452	1.108
2500	-13.380	14.518	1.038
3000	-13.439	14.498	0.992
3500	-13.724	14.410	0.958
4000	-14.276	14.267	0.932
4500	-15.104	14.071	0.910
5000	-16.200	13.836	0.892

RECOMMENDED RATE CONSTANT

$$k = 1.94 \times 10^{14} \exp(-20\ 620/T)\ cm^3\ mol^{-1}\ s^{-1}$$

$$= 3.22 \times 10^{-10} \exp(-20\ 620/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

(k is defined by $d[HI]/dt = 2k[H_2][I_2] = -2d[H_2]/dt$)

Temperature Range: 400-800 K

Suggested Error Limits for Calculated Rate Constant: ±30% over the quoted temperature range.

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.29 \pm 0.12$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -9.49 \pm 0.12$

$E/J\ mol^{-1} = 171\ 440 \pm 3\ 680$

$E/cal\ mol^{-1} = 40\ 980 \pm 880$

$H_2 + I_2 \rightarrow HI + HI$

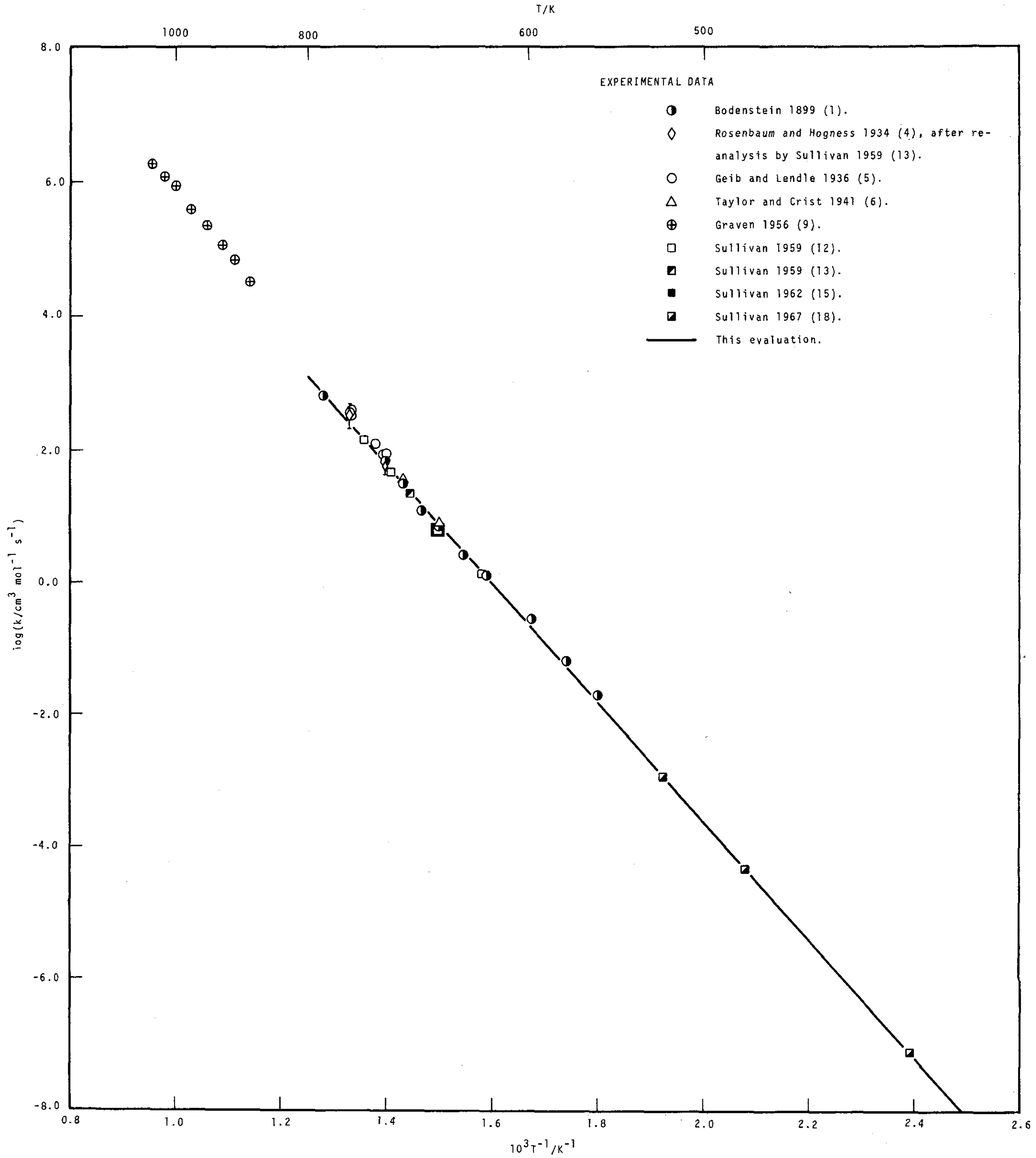
THERMODYNAMIC DATA ($H_2 + 2I \rightarrow HI + HI$)

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-118.968	-78.952	24.048
300	-118.993	-79.032	23.916
500	-163.059	-85.161	8.384
1000	-167.385	-91.169	3.980
1500	-169.435	-92.868	1.047
2000	-171.142	-93.847	- 0.432
2500	-173.218	-94.763	- 1.330
3000	-175.787	-95.701	- 1.938
3500	-178.816	-96.625	- 2.378
4000	-182.205	-97.529	- 2.714
4500	-185.862	-98.391	- 2.982
5000	-189.703	-99.249	- 3.200

RECOMMENDED RATE CONSTANT

(No recommendation specifically for this reaction: see Discussion and Recommended Rate Constant for $H_2 + I_2 \rightarrow HI + HI$)

$H_2 + I_2 \rightarrow HI + HI$

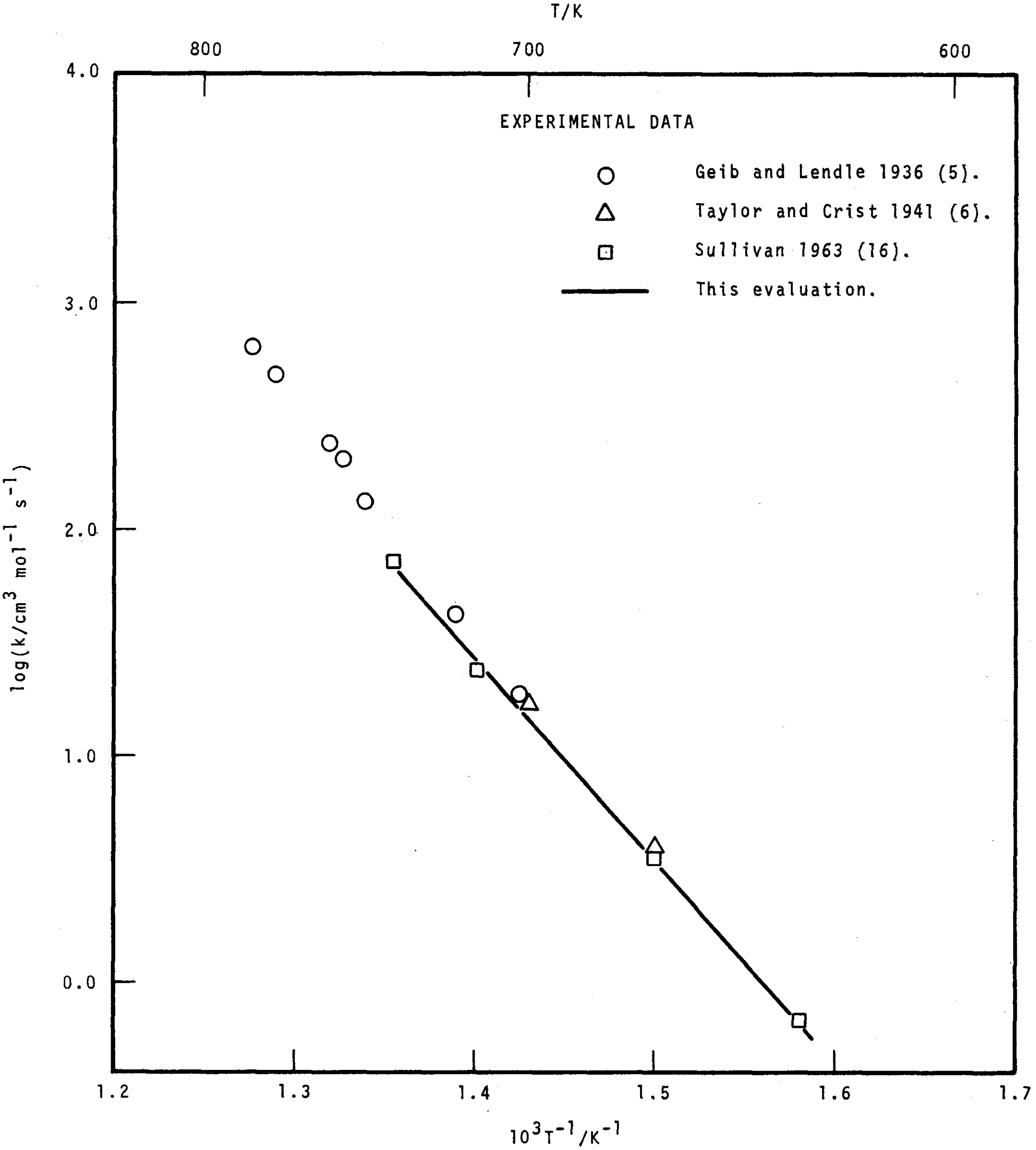


$H_2 + I_2 \rightarrow HI + HI$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.22×10^{-2}	556	Static system. H_2(7.05×10^{-6}-4.06×10^{-5} mol cm^{-3})/I_2 (7.0×10^{-6}-1.0×10^{-4} mol cm^{-3}) mixtures, with [H_2]:[I_2] ratios 0.23-4.33. Reaction products analysed for H_2, I_2 and HI. BODENSTEIN 1899 (1)	Reverse reaction expressed in terms of k_1 and K_1 $H_2 + I_2 \rightarrow HI + HI$ 1 to allow for incomplete reaction. To correspond to our definition of k_1, we have halved the values of k_1 as presented by KASSEL (2, 3) and PEASE (7) following conversion to cm^3, mol, s units. BODENSTEIN originally expressed these data as $2k_1=4.44 \times 10^{46} T^{-12.872} \exp(1.751 \times 10^{-2} T).\exp(-21\,830/T)$ $cm^3\ mol^{-1}\ s^{-1}$. KASSEL (2,3) demonstrated no simple Arrhenius T dependence, and quoted $2k_1=3.3 \times 10^{12} T^{\frac{1}{2}} \exp(-19\,570/T)$ and $1.07 \times 10^{-20} T^{10.5} \exp(-13\,080/T)$ $cm^3\ mol^{-1}\ s^{-1}$, the former showing systematic deviations from experimental data, latter showing random deviations. GEIB and LENDLE (5) quote E_1 for this work as 169.5 kJ mol^{-1} (40.5 kcal mol^{-1}). PEASE (7) expresses these data in form $2k_1=1.57 \times 10^{13} T^{\frac{1}{2}} \exp(-20\,590/T)$ $cm^3\ mol^{-1}\ s^{-1}$, whereas WHITE (20) quotes expression $2k_1=5.96 \times 10^{13} \exp(-19\,370/T)$ $cm^3\ mol^{-1}\ s^{-1}$ for these data.
6.59×10^{-2}	575		
2.725×10^{-1}	599		
1.262	629		
2.61	647		
7.08	666		
12.30	683		
32.15	700		
70.0	716		
6.68×10^{2}	781		
(0 ±150)	693	Static system. $H_2^o/H_2^p/I_2$ (0-1.04×10^{-6} mol cm^{-3}) mixtures, with 1:1 [H_2^o]:[H_2^p] ratios. After reaction quenched, HI and I_2 frozen out and residual [H_2] determined by thermal conductivity. ROSENBAUM and HOGNESS 1934 (4)	Original purpose of this study to determine rate of para-ortho conversion of H_2 in equilibrium mixtures of [H_2],[HI]and [I_2]. Data re-analysed by SULLIVAN (13) in terms of k_1/K_3 and k_2, giving values of k_1 presented here. $H_2 + I_2 \rightarrow HI + HI$ 1 $I + H_2 \rightarrow HI + H$ 2 $I_2 + M \rightarrow I + I + M$ 3 Low precision of k_1 at 693 K due to small number of data points.
(60 ± 17)	716		
$(3.5 \pm 1.4) \times 10^{2}$	753		

$D_2 + I_2 \rightarrow DI + DI$



$H_2 + I_2 \rightarrow HI + HI$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
90.0 86.5 $1.25x10^2$ $3.60x10^2$ $4.00x10^2$ $3.75x10^2$	715.2 717.2 724.4 749 749.2 751.5	Static system. H_2/I_2(20-150 mm Hg; 2.7-20 kPa) mixtures at total pressures 159-280 mm Hg (21.2-37.3 kPa). $[I_2]$ followed photometrically and overall $[HI+I_2]$ in products determined by iodometry. GEIB and LENDLE 1936 (5)	Authors quote E_1 as 181.2 kJ mol^{-1} (43.3 kcal mol^{-1}). Broad radiation band used to monitor $[I_2]$ necessitated large corrections to authors' calibration curves. Precision of these data considered low (6,20). These values of k_1 are half those presented by authors, to agree with our definition of k_1.
(7.80±0.06) (33.5 ±1.4)	666.8 698.6	Static system. $H_2(1.09x10^{-5}-1.11x10^{-5}$ mol $cm^{-3})/I_2(9.7x10^{-6}-1.29x10^{-5}$ mol cm^{-3}) mixtures. [HI] in products determined by iodometry. TAYLOR and CRIST 1941 (6)	Values of k_1 obtained using same analysis as BODENSTEIN (1), and K_1 determined in this study. These values are half those presented by authors, to correspond to our definition of k_1.
$3.15x10^4$ $6.90x10^4$ $1.15x10^5$ $2.17x10^5$ $3.80x10^5$ $8.75x10^5$ $1.20x10^6$ $1.81x10^6$	871 895 919 944 973 997 1020 1047	Flow system. $H_2(4.07x10^{-7}-4.54x10^{-6}$ mol $cm^{-3})/I_2(1.1x10^{-6}-5.71x10^{-6}$ mol cm^{-3}) mixtures, with $[H_2]:[I_2]$ ratios 0.25-12.0. Unreacted I_2 frozen out and [HI] determined by gravimetric analysis after absorption in ascarite. GRAVEN 1956 (9)	Integration of HI rate equation, using K_1 to convert contribution of k_{-1} $H_2 + I_2 \rightleftharpoons HI + HI$ 1,-1 used to derive these values of k_1, taken from graph of log $(k_1T^{-\frac{1}{2}})$ vs. T^{-1}. Author represents these data by $k_1=1.23x10^{15}$ exp(-20 630/T) $cm^3\ mol^{-1}\ s^{-1}$ (despite form of above plot). We have halved the values from the author's graph, to agree with our definition of k_1. These data re-analysed by HORIE et al. (17).
(1.313±0.002) (6.68±0.01) (46.9±0.15) $(1.387±0.0055)x10^2$	633.21 666.79 710.33 737.93	Static system $H_2(4.2x10^{-7}-2.9x10^{-6}$ mol $cm^{-3})/I_2(5.6x10^{-7}-2.4x10^{-6}$ mol cm^{-3}) mixtures, with $0.33 \leq [H_2]:[I_2] \leq 2.62$. Reaction quenched, HI and I_2 condensed and residual H_2 pressure measured. SULLIVAN 1959 (12)	Steady state treatment of mechanism $I_2 + M \rightleftharpoons I + I + M$ 3,-3 $H_2 + I_2 \rightleftharpoons HI + HI$ 1,-1 $I + H_2 \rightleftharpoons HI + H$ 2,-2 $H + I_2 \rightleftharpoons HI + I$ 4,-4 gave rate equation for $[I_2]$ in terms of k_1, k_2K_3/k_1, and k_{-2}/k_4. Computed best fits to experimental data gave values of k_1 shown here. Least squares fit, with k_1 at 633 K assigned ¼ weight of other values, given as $k_1=(6.03±1.0)x10^{12}T^{\frac{1}{2}}$ exp{-(20 500±130)/T} $cm^3\ mol^{-1}\ s^{-1}$. Slightly higher values of k_1 obtained in silica-packed reaction cells. Expression for k_1 used by (13,15).

$H_2 + I_2 \rightarrow HI + HI$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
21.99	693	Static system. H_2/I_2 mixtures, with $[H_2]$ and $[I_2]$ each varied by factor 3. Method as for (12). SULLIVAN 1959 (13)	Experiments performed to investigate possible wall effects upon para-ortho H_2 conversion study of ROSENBAUM and HOGNESS (4). Computer integration of I_2 rate equation, as for (12), used to determine k_1.
(6.60±0.09)	666.79	Static system. $H_2(2.49\times10^{-7}-4.59\times10^{-6}\ mol\ cm^{-3})/I_2(5.94\times10^{-7}-5.72\times10^{-6}\ mol\ cm^{-3})$ mixtures, $[H_2]:[I_2]$ ratios varied 0.12-3.22. Final $[H_2]$ measured as in (12). SULLIVAN 1962 (15)	HI synthesis allowed to proceed to low and high values of $[HI]/[I_2]$. Improved analysis of I_2 rate equation, generated as in (12), gave k_1 and k_2 from I_2-rich mixtures, these values then being used to give k_{-2}/k_4 in H_2-rich mixtures. In similar experiments at 800 K, low contribution from reaction 1 prevented measurement of k_1 - value derived from (12) used in analysis of k_2 and k_{-2}/k_4. WHITE (20) quotes $k_1=(2.63\pm0.3)\times10^{14}\exp\{-(20\ 830\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ for data of this work and (12 and 13).

REACTION $H_2 + 2I \rightarrow HI + HI$

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.12\pm0.02)\times10^{11}$	417.9	Static photolysis system. $H_2(1.77\times10^{-6}-1.19\times10^{-5}\ mol\ cm^{-3})/I_2(5.67\times10^{-8}-2.25\times10^{-7}\ mol\ cm^{-3})$ mixtures photolysed at 578 nm. [HI] measured manometrically after separation from H_2 and I_2 and absorbed light intensity measured. SULLIVAN 1967 (18)	Values of $k_{1'}$, obtained from integrated HI rate equation $H_2 + 2I \rightarrow HI + HI$ 1' Blank runs (i.e. with zero photolysis) at 418 and 481 K showed small thermal reaction - corrections made to allow for this. Values of $k_{-3}(M=H_2)$ and $k_{-3}(M=I_2)$ $I + I + M \rightarrow I_2 + M$ -3 taken from (14) and (11) respectively used to calculate k_1. Least-squares analysis of data of $k_{1'}$, and k_1 (converted to $k_{1'}$, according to $k_{1'}=k_1/K_3$) gave $k_{1'}=(6.66\pm0.5)\times10^{13}\exp\{-(2670\pm40)/T\}\ cm^6\ mol^{-2}\ s^{-1}$. We have reversed the above conversion and calculated k_1 from these values of $k_{1'}$, and a straight line fit to current JANAF data for K_3, to give $k_1=(7.75\pm0.14)\times10^{-8}$, $(4.66\pm0.3)\times10^{-5}$, and $(1.17\pm0.04)\times$
$(2.60\pm0.17)\times10^{11}$	480.7		
$(3.96\pm0.15)\times10^{11}$	520.1		

$H_2 + I_2 \rightarrow HI + HI$

REACTION $H_2 + 2I \rightarrow HI + HI$ – CONTINUED

Rate Constant k ($cm^6\ mol^{-2}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		SULLIVAN 1967 (18) continued.	$10^{-3}\ cm^3\ mol^{-1}\ s^{-1}$ at 417.9, 480.7 and 520.1 K respectively.

ISOTOPIC REACTION $D_2 + I_2 \rightarrow DI + DI$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
19.0 42.5 $1.35x10^2$ $2.05x10^2$ $2.40x10^2$ $4.85x10^2$ $6.40x10^2$	701 719 746.5 753.5 757.7 774.4 783	Static system. D_2/I_2 (20-150 mm Hg; 2.7-20 kPa) mixtures at total pressures 103-287 mm Hg (13.7-38.3 kPa). $[I_2]$ followed by absorption spectrometry and overall $[DI+I_2]$ in products measured by iodometry. GEIB and LENDLE 1936 (5)	Purity of D_2 given as 90%, remaining 10% being HD. E_{1D} quoted by authors as 195.0 kJ mol^{-1} (46.6 kcal mol^{-1}). $D_2 + I_2 \rightarrow DI + DI$ 1D We have halved authors' tabulated values to correspond with our definition of k_1.
(3.98±0.031) (17.24±0.23)	666.8 698.6	Static system. D_2($1.097x10^{-5}$-$1.109x10^{-5}$ mol cm^{-3})/I_2($9.39x10^{-6}$-$1.26x10^{-5}$ mol cm^{-3}) mixtures. Iodometry used to measure [DI] in products. TAYLOR and CRIST 1941 (6)	Analysis as for reaction 1 (see Comments column under (6)). Tabulated values halved to agree with our definition of k_1.
0.681 3.47 24.44 72.4	633.21 666.79 710.33 737.93	Static system. D_2($2.6x10^{-7}$-$3.0x10^{-5}$ mol cm^{-3})/I_2($6.9x10^{-7}$-$2.82x10^{-5}$ mol cm^{-3}) mixtures, ratios $[D_2]:[I_2]$ in range 0.26 to 2.98. Reaction quenched, DI and I_2 frozen out, and remaining D_2 pressure measured. SULLIVAN 1963 (16)	Steady state treatment of mechanism $I_2 + M \rightleftharpoons I + I + M$ 3,-3 $D_2 + I_2 \rightleftharpoons DI + DI$ 1D,-1D $I + D_2 \rightleftharpoons DI + D$ 2D,-2D $D + I_2 \rightleftharpoons DI + I$ 4D,-4D gave rate equation for $[I_2]$, as in (12) under reaction 1. Analysis as in (15) gave k_{1D},k_{2D} and k_{-2D}/k_{4D}. Author gives k_{1D}=(3.16±0.5)$x10^{12}T^{\frac{1}{2}}$ exp{-(20 530±100)/T} $cm^3\ mol^{-1}\ s^{-1}$ (633-738 K) for these data, whereas WHITE (20) quotes k_{1D}=(4.17±0.6)$x10^{14}$ exp{-(20 880±100)/T} $cm^3\ mol^{-1}\ s^{-1}$.

$H_2 + I_2 \rightarrow HI + HI$

ISOTOPIC REACTION $HD + I_2 \rightarrow HI + DI$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	678	Static system. H_2/HD/I_2 mixtures. Thermal reaction quenched and HI and DI reduced to H_2 and HD by hot Zn. Mass spectrometry used to determine ratio [HI]:[DI]. MAGEE 1957 (10)	Reaction allowed to proceed to 5-10% consumption of H_2 and HD. From integrated rate equation for H_2 and HD, author obtained values of k_1/k_{1HD} $H_2 + I_2 \rightarrow HI + HI$ 1 $HD + I_2 \rightarrow HI + DI$ 1HD This ratio approached lower limiting value with successive experiments, indicating wall effect. Final value of k_1/k_{1HD} given as 1.548 at 678 K.

Discussion

Until very recently the reaction between hydrogen and iodine

$$H_2 + I_2 \rightarrow HI + HI \qquad (1)$$

has been considered as a classic example of a biomolecular four-centre reaction, and one in which the identity between the equilibrium constant and the ratio of the experimentally measured forward and reverse rate constants was obeyed (see [19]). However, following Benson and Srinavansan's calculations [8], Sullivan [12] showed that under some circumstances the simple interpretation was incorrect, and that the above relationship was merely fortuitous. Thermal HI formation could be more satisfactorily described by the mechanism.

$$I_2 + M \rightleftharpoons I + I + M \qquad (3,-3)$$

$$H_2 + I_2 \rightleftharpoons HI + HI \qquad (1,-1)$$

$$I + H_2 \rightleftharpoons HI + H \qquad (2,-2)$$

$$H + I_2 \rightleftharpoons HI + I \qquad (4,-4)$$

Above 600 K this complete mechanism predominates, but at lower temperatures reactions 2 and 4 (and their reverses) are negligible [12]. At still lower temperatures (420–520 K), where the thermal production of HI is very slow, Sullivan [18] found the rate of HI production following the photolysis of H_2/I_2 mixtures to be consistent with the reaction

$$H_2 + 2I \rightarrow HI + HI \qquad (1')$$

In thermal systems reactions 1 and 1′ are kinetically indistinguishable because I and I_2 are in thermal equilibrium, and k_1 and $k_{1'}$ are related by $k_1 = k_{1'}K_3$.

Upon treating his earlier data for k_1 [12] in terms of $k_{1'}$, Sullivan [18] found the Arrhenius parameters for the thermal data [12] to be the same as those for the photochemical data [18]. He therefore concluded that the actual reaction responsible for thermal HI formation was in fact reaction 1′ and not reaction 1. Further considerations of the H_2–I_2 reaction [21,22], although critical of Sullivan's interpretation, have failed to show how reactions 1 and 1′ may be kinetically separated.

We have evaluated the rate constant data in terms of k_1 (as being the form in which most of the data have been expressed) and because of the indistinguishable nature of the two HI production paths, have included the data for $k_{1'}$ of Sullivan [18] by making the conversion $k_1 = k_{1'}K_3$. In the event that the reaction is subsequently proved to be that of 1′, our recommended expression for k_1 should merely be converted by reversing the above procedure.

The data of Bodenstein [1] and Taylor and Crist [6] have been shown by Sullivan [12] to demonstrate the fortuitous elimination of the radical mechanism (reactions 2 and 4) terms from the HI production rate equation, giving for example [6] measured values of k_1 only 1–2% lower than those calculated according to the complete mechanism. Such cancellation of terms is also likely in the study of Geib and Lendle [5], the data of which are allegedly [6,20] subject to considerable error owing to the variation of the extinction coefficient of I_2 over the broad radiation band used. Nevertheless these values are in good agreement with those of other studies.

The data of Graven [9] at higher temperatures, where the radical mechanism (reactions 3,2 and 4) is particularly dominant, show a higher activation energy than any of the other results. Graven's data [9] were re-analysed by Horie et al. [17] in terms of the complete mechanism, but the analysis led only to the equilibrium constant K_1.

The only values of k_1 based on the full HI production mechanism are those of Sullivan [12,13,15,18] and those of Rosenbaum and Hogness [4], as re-analysed by Sullivan [13].

From these data we obtain our recommended expression

$$k_1 = 1.94 \times 10^{14} \exp(-20\,620/T)\ cm^3\ mol^{-1}\ s^{-1}$$

for the temperature interval 400–800 K. The data scatter is sufficiently small to allow error limits of ±30%.

$D_2 + I_2 \rightarrow DI + DI$

As for reaction 1, the only study to interpret the data for the reaction between deuterium and iodine

$$D_2 + I_2 \rightarrow DI + DI \qquad (1D)$$

according to the complete mechanism (in this case the deuterised equivalents of reactions 1,2 and 4, plus reaction 3) is that of Sullivan [16]. A least squares fit to these data gives $k_{1D}=1.32\times10^{14}\ \exp(-20\,840/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ for 630–740 K. Error limits are ±20%.

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D7 $HI + HI \rightarrow H_2 + I_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	9.724	-21.811	-2.842
300	9.740	-21.761	-2.833
500	11.096	-17.870	-2.110
1000	13.489	-14.556	-1.464
1500	13.724	-14.330	-1.226
2000	13.514	-14.452	-1.108
2500	13.380	-14.518	-1.038
3000	13.439	-14.498	-0.992
3500	13.724	-14.410	-0.958
4000	14.276	-14.267	-0.932
4500	15.104	-14.071	-0.910
5000	16.200	-13.836	-0.892

RECOMMENDED RATE CONSTANT

$k = 2.55 \times 10^{13} \exp(-22\ 020/T)\ cm^3\ mol^{-1}\ s^{-1}$

$= 4.23 \times 10^{-11} \exp(-22\ 020/T)\ cm^3\ molecule^{-1}\ s^{-1}$

(k is defined by $-d[HI]/dt = 2k[HI]^2 = 2d[I_2]/dt$)

Temperature Range: 400-800 K.

Suggested Error Limits for Calculated Rate Constant: ±30% over quoted temperature range.

Note: this expression is based on equilibrium data and $k(H_2+I_2)$

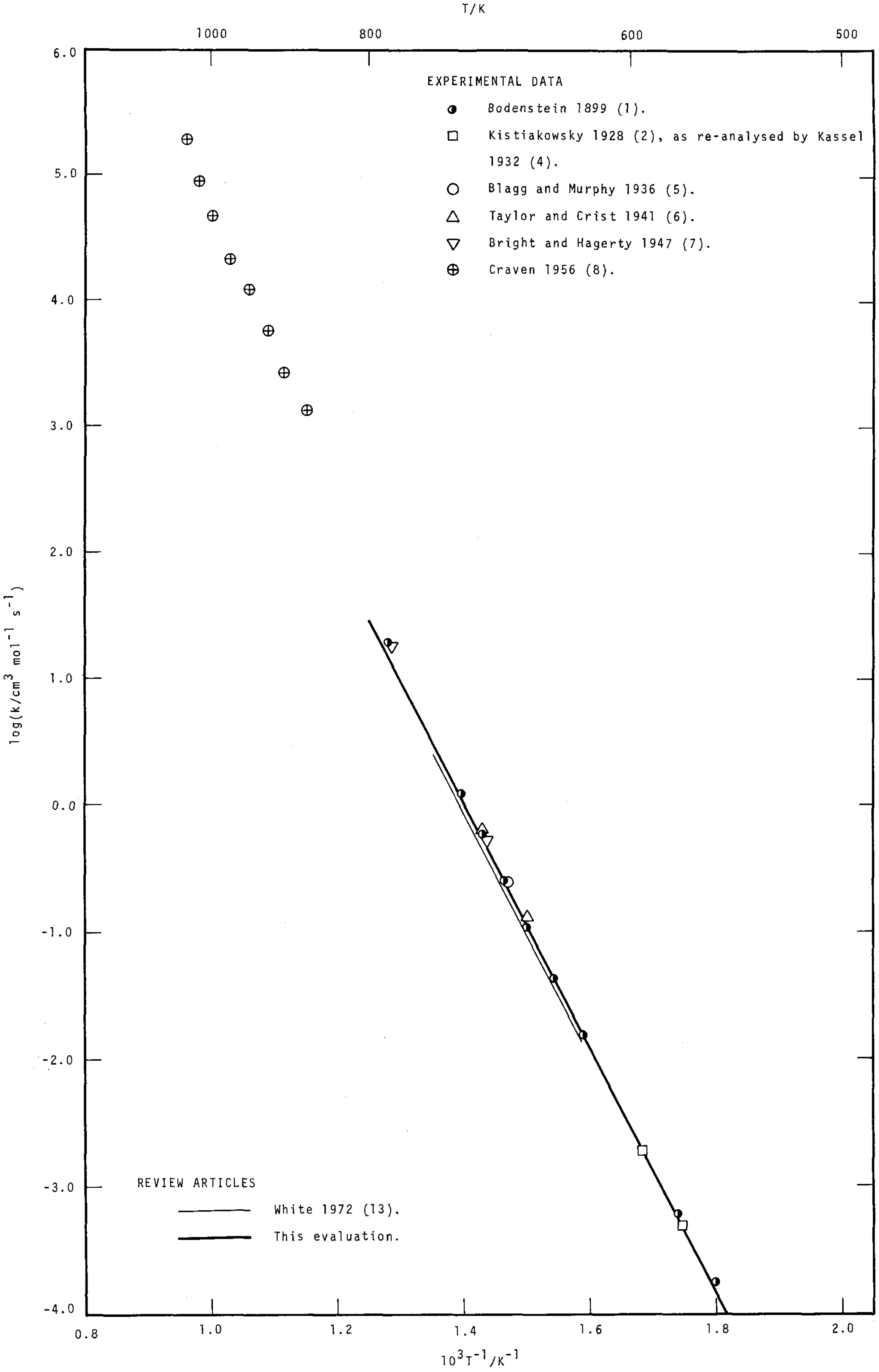
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.41 \pm 0.12$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -10.37 \pm 0.12$

$E/J\ mol^{-1} = 183\ 050 \pm 3680$

$E/cal\ mol^{-1} = 43\ 750 \pm 880$

$HI + HI \rightarrow H_2 + I_2$

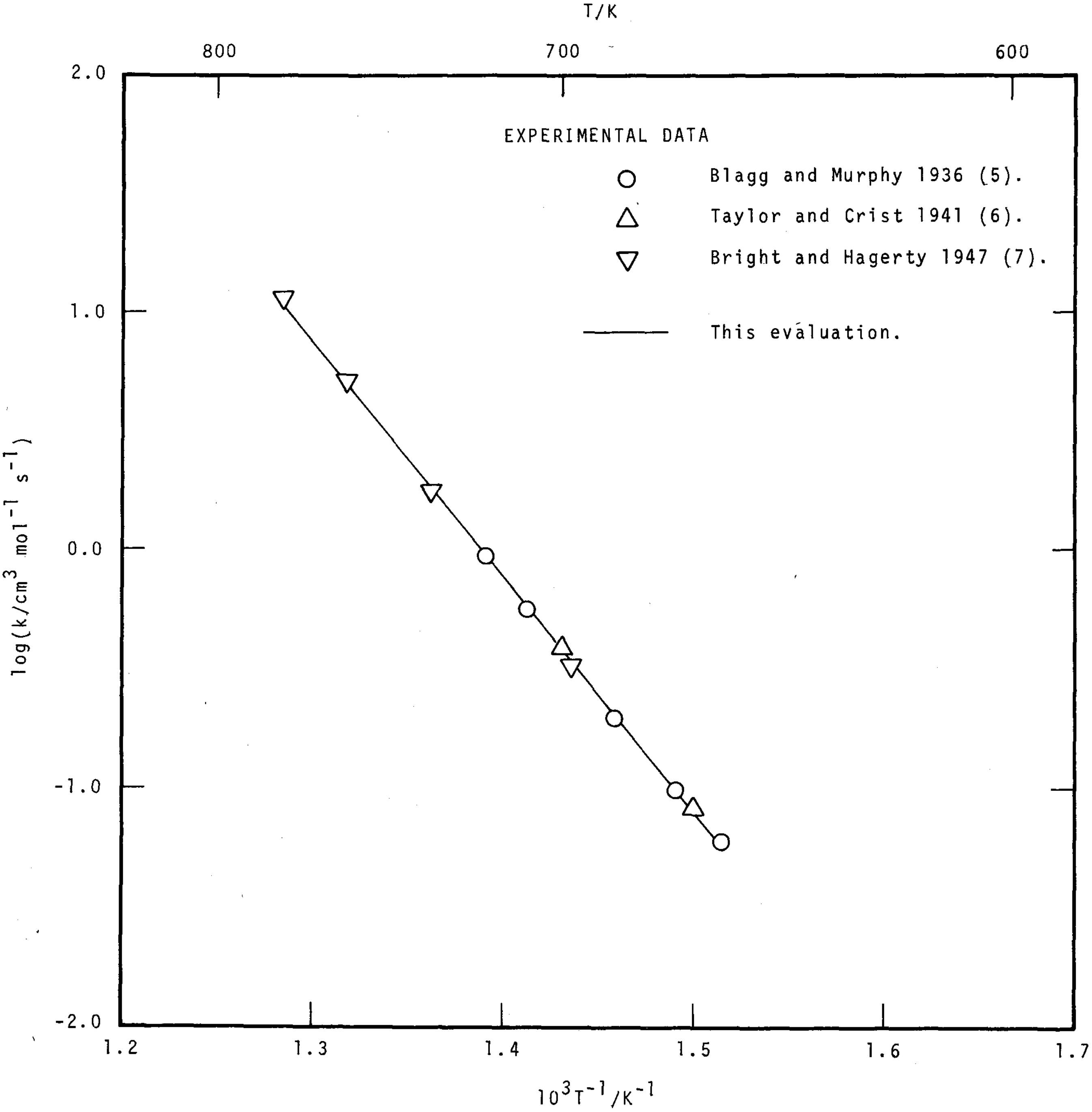


$HI + HI \rightarrow H_2 + I_2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1.76×10^{-4}	556	Static system. HI samples (∿4.2×10^{-5} mol cm^{-3} (2): original data tabulated in terms of degree of reaction). Reaction products analysed for H_2, I_2 and HI. BODENSTEIN 1899 (1)	Values of k_1 obtained from integrated form of rate equation, allowing for reverse reaction by means of K_1 $HI + HI \rightarrow H_2 + I_2$ 1 Values of k_1 presented by KASSEL (3,4) halved to correspond to our definition of k_1. BODENSTEIN gives two empirical expressions for these data, $2k_1=2.67\times10^{-38} T^{15.865}\exp(-12\ 090/T)$ and $2k_1= 6.59\times10^{47}T^{-14.468}\exp(-21\ 920/T)\cdot\exp(2.31\times10^{-2}T)$ $cm^3\ mol^{-1}\ s^{-1}$, the latter being preferred. KASSEL (3,4) fits expressions $2k_1=2.05\times10^{12}T^{\frac{1}{2}}\exp(-22\ 010/T)$ and $2k_1=9.29\times10^{-39}T^{16}\exp(-11\ 970/T)$ $cm^3\ mol^{-1}\ s^{-1}$ to these data. WHITE (13) quotes expression $2k_1= 1.4\times10^{14}\exp(-22\ 600/T)$ $cm^3\ mol^{-1}\ s^{-1}$ for these data.
6.08×10^{-4}	575		
1.51×10^{-2}	629		
4.30×10^{-2}	647		
1.10×10^{-1}	666		
2.56×10^{-1}	683		
5.78×10^{-1}	700		
1.25	716		
19.77	781		
5.90×10^{-4}	573	Static system. HI(2.34×10^{-5}-7.13×10^{-3} mol cm^{-3}) samples thermally decomposed. Reaction quenched and $[I_2]$ and [HI] in products determined by iodometry. KISTIAKOWSKY 1928 (2)	k_1 determined using analysis of BODENSTEIN (1). Several experiments performed with particularly pure HI to observe influence of impurities. Possible systematic errors in titration and cooling time considered to give only ∿1.5% and 2% error, respectively, in k_1. Values presented here are half average of author's data, to agree with our definition of k_1. These values, together with those of BODENSTEIN (1) for T>575 K gave author $E_1'=185.4$ kJ mol^{-1} (44.3 kcal mol^{-1}), when $\log(k_1T^{-\frac{1}{2}})$ plotted vs. T^{-1}. KASSEL (4) reanalysed these data to give $k_1= 4.88\times10^{-4}$ $cm^3\ mol^{-1}\ s^{-1}$ at 573 K and $k_1=1.94\times10^{-3}$ $cm^3\ mol^{-1}\ s^{-1}$ at 594.4 K, as presented on Arrhenius plot.
1.98×10^{-3}	594.4		
2.42×10^{-1}	681	Static system. HI(1.82×10^{-5} -2.16×10^{-5} mol cm^{-3}) samples. Reaction quenched and $[I_2]$ and remaining [HI] determined by iodometry. BLAGG and MURPHY 1936 (5)	Integrated form of HI removal equation used (as in (1)) to obtain values of k_1 $HI + HI \rightarrow H_2 + I_2$ 1 (Authors' tabulated value halved to agree with our definition of k_1).

$DI + DI \rightarrow D_2 + I_2$



EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.30\pm0.04)\times10^{-1}$	666.8	Static system. HI ($1.20\times10^{-5}-1.68\times10^{-5}$ mol cm^{-3}) samples. Reaction quenched and products dissolved in KI solution. $[I_2]$ in products determined by starch titrations. TAYLOR and CRIST 1941 (6)	Values of k_1 obtained from integrated HI rate equation, as for (1). To correspond with our definition of k_1, authors' tabulated values halved.
$(6.21\pm0.14)\times10^{-1}$	698.6		
5.25×10^{-1}	696.4	Static sytem. HI (∿92-415 mm Hg; 12.3-55.3 kPa) samples. $[I_2]$ followed by absorption at $\lambda>580$ nm. Reaction quenched when no further variation in I_2 absorption detectable, and products dissolved in H_2O. Product $[I_2]$ determined by $Na_2S_2O_3$ titration, and similarly [HI] after extraction of I_2 by oxidation by H_2O_2 and separation by CCl_4. BRIGHT and HAGERTY 1947 (7)	BODENSTEIN (1) equation used to obtain k_1 $HI + HI \rightarrow H_2 + I_2$ 1 with final $[I_2]$ as determined photometrically used in preference to analytical method. Small corrections made to allow for vessel filling and sealing time. Over 80% of decomposition period values of k_1 constant to ±2%. Authors' values halved to agree with our definition of k_1. Expression $2k_1=1.00\times10^{13}T^{\frac{1}{2}}\exp(-23\,100/T)$ $cm^3\ mol^{-1}\ s^{-1}$ given by authors for these data. WHITE (13) represents these data by $2k_1=4.6\times10^{14}\exp(-23\,500/T)$ $cm^3\ mol^{-1}\ s^{-1}$.
18.6	778.8		
1.32×10^3	870	Flow system. HI($8.11\times10^{-7}-5.67\times10^{-6}$ mol cm^{-3}) and HI(3.2×10^{-6} mol cm^{-3})/H_2 ($2.0\times10^{-7}-4.8\times10^{-6}$ mol cm^{-3}) mixtures. I_2 condensed at 273 K and $[I_2]$ determined gravimetrically. GRAVEN 1956 (8)	Integrated rate expression used to give k_1. Values of k_1 taken from graph of $\log(k_1T^{-\frac{1}{2}})$vs. T^{-1} and halved to correspond to our definition of k_1. Author quotes $2k_1=3.59\times10^{15}\exp(-24\,760/T)$ $cm^3\ mol^{-1}\ s^{-1}$ as fit to these data, *despite above form of graph.* Author's quoted value of $k_1=1.6\times10^4$ $cm^3\ mol^{-1}\ s^{-1}$ at 973 K matches this expression but not the data presented here. These data re-analysed by HORIE *et al.* (12).
2.69×10^3	897		
5.75×10^3	919		
1.21×10^4	945		
2.22×10^4	973		
4.35×10^4	997		
8.91×10^4	1021		
1.94×10^5	1047		

REVIEW ARTICLE

$(2.0\pm0.3)\times10^{13}\exp\{-(22000\pm150)/T\}$	630-740	Review. WHITE 1972 (13)	Expression based on reverse rate constant expression, derived from data of SULLIVAN (9,10,11).

$HI + HI \rightarrow H_2 + I_2$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
ISOTOPIC REACTION $DI + DI \rightarrow D_2 + I_2$			
5.95×10^{-2} 9.90×10^{-2} 1.96×10^{-1} 5.56×10^{-1} 9.17×10^{-1}	660 671 686 708 719	Static system. DI(1.66×10^{-5} - 1.97×10^{-5} mol cm^{-3}) samples. Reaction quenched and $[I_2]$ and remaining [DI] determined by iodometry. BLAGG and MURPHY 1936 (5)	Integrated form of DI removal equation used (as in (1)) to obtain values of k_{1D} $DI + DI \rightarrow D_2 + I_2$ 1D Values presented here are half those tabulated by authors, to correspond with our definition of k_{1D}. Collision theory invoked to give fit to these data as $2k_{1D} = 6.30 \times 10^{11} T^{\frac{1}{2}} \exp(-21\,490/T)$ $cm^3\ mol^{-1}\ s^{-1}$. WHITE (13) fits expression $2k_{1D} = 1.30 \times 10^{14} \exp(-21\,340/T)$ $cm^3\ mol^{-1}\ s^{-1}$ to these data.
$(8.39 \pm 0.13) \times 10^{-2}$ $(3.89 \pm 0.09) \times 10^{-1}$	666.8 698.6	Static system. DI(1.38×10^{-5} - 2.17×10^{-5} mol cm^{-3}) samples. Reaction quenched and products dissolved in KI solution. $[I_2]$ in products determined by $Na_2S_2O_3$ titrations. TAYLOR and CRIST 1941 (6)	Analysis of results as for reaction 1 (see Comments column). Values of k_{1D} as tabulated by authors halved to agree with our definition.
3.20×10^{-1} 1.74 5.05 11.45	696.4 734.2 759.3 778.8	Static system. DI(∼60-307 mm Hg; 8-40.9 kPa) samples. $[I_2]$ followed by absorption at $\lambda > 580$ nm. Reaction quenched when no further variation in I_2 absorption detectable, and products dissolved in H_2O. Free $[I_2]$ determined by $Na_2S_2O_3$ titrations, and [HI] similarly after extraction of I_2 by oxidation by H_2O_2 and separation by CCl_4. BRIGHT and HAGERTY 1947 (7)	Results analysed as for reaction 1 (see Comments column). Authors' values halved to correspond to our definition of k_{1D}. Authors represent these data by $2k_{1D} = 8.20 \times 10^{12} T^{\frac{1}{2}} \exp(-23\,330/T)$ $cm^3\ mol^{-1}\ s^{-1}$. WHITE (13) expresses these data by $2k_{1D} = 3.54 \times 10^{14} \exp(-23\,600/T)$ $cm^3\ mol^{-1}\ s^{-1}$.

Discussion

Data on the rate of the decomposition of hydrogen iodide

$$HI + HI \rightarrow H_2 + I_2 \qquad (1)$$

have been obtained principally in static pyrolysis systems, except for the results at the highest temperatures [8], which were obtained using a flow system. Apart from the latter results, there is good agreement between all the available data [1,2,5,6,7] spanning a time gap of nearly fifty years.

Our recommended expression for k_1 is based on our recommended expression for the reverse reaction

$$H_2 + I_2 \rightarrow HI + HI \qquad (-1)$$

which has been derived from a greater number of results, covering a wider temperature range, than are available for k_1 itself.

$$k_1 = 2.55 \times 10^{13} \exp(-22\,020/T)\ cm^3\ mol^{-1}\ s^{-1}$$

is recommended for the temperature interval 400–800 K, within uncertainty limits of ±30% over the whole interval.

The agreement between this expression and the measured data for k_1 is well within these limits.

$DI + DI \rightarrow D_2 + I_2$

The isotopic reaction 1D

$$DI + DI \rightarrow D_2 + I_2 \qquad (1D)$$

has not received quite as much attention as reaction 1, and all the data for k_{1D} have been obtained in static systems. Nevertheless these data are in good agreement, and our recommended expression is $k_{1D}=4.73\times10^{13}\ \exp(-22\,690/T)$ $cm^3\ mol^{-1}\ s^{-1}$, for temperatures in the range 660–780 K. Uncertainty limits of ±20% should be considered. We have not used k_{-1D}, as for reaction 1, as there are no more data for the reverse than for the forward reaction, and reliable high temperature thermodynamic data for DI (and hence K_{1D}) are unavailable.

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Miscellaneous Reactions Involving I Atoms

D8 $OH + HI \rightarrow H_2O + I$

There are only two determinations of the rate of reaction of OH radicals with HI—those of Takacs and Glass [1] and Smith and Zellner [2].

$$OH + HI \rightarrow H_2O + I \qquad (1)$$

$$\Delta H^\circ_{298}=-201.05\ kJ\ mol^{-1}(-48.05\ kcal\ mol^{-1})$$

Using a fast flow system with a wall coating of fluorinated halocarbon wax, and generating OH by the reaction of H atoms (from a microwave discharge in an H_2/Ar mixture) and NO_2, Takacs and Glass [1] determined k_1 at 295 K and at pressures 0.5 to 1.5 mm Hg (66.7-200 Pa). They monitored the e.p.r. spectrum of OH, and compared the experimental [OH] profiles with those generated by a computer program which accounted for OH removal by reactions 2–4.

$$OH + OH \rightarrow H_2O + O \qquad (2)$$

$$OH + O \rightarrow H + O_2 \qquad (3)$$

$$OH \rightarrow wall \qquad (4)$$

An excess of HI enabled the effects of reactions 2–4 to be reduced so that initial estimates of k_1 could be taken from the experimental decay of OH. Their final value, averaged over 6 results, was $k_1=(7.83\pm3.0)\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$.

Reaction 1 was studied by Smith and Zellner [2] by flash photolysing mixtures of H_2O, or N_2O and H_2, and HI, at total pressures of about 10–20 mm Hg (1.3–2.7 kPa). Resonance radiation from a microwave powered OH source was used to follow [OH]. The authors consider their result of $k_1=(5.4\pm2.4)\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ at 298 K as preliminary, but nevertheless it is in good agreement with that of [1]. Consequently we recommend at 298 K, $k_1=(6.9\pm3.9)\times10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$.

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D9 $I + CH_4 \rightarrow CH_3 + HI$

The only determination of the rate constant for the reaction

$$I + CH_4 \rightarrow CH_3 + HI \qquad (1)$$

$$\Delta H^\circ_{298}=140.2\ kJ\ mol^{-1}\ (33.50\ kcal\ mol^{-1})$$

is that of Goy and Pritchard [4] who studied the reaction between CH_4 (~25 mm Hg; 3.3 kPa) and I_2 in a static system over the temperature range 548–618 K. The reaction was not allowed to proceed by more than 10% toward equilibrium. Gas chromatography was used to determine the rate of formation of CH_3I. The reaction mechanism was found to describe the observed dependence of the

$$I_2 + M \rightleftharpoons I + I + M \qquad (2)$$

$$I + CH_4 \rightarrow CH_3 + HI \qquad (1)$$

$$CH_3 + I_2 \rightarrow I + CH_3I \qquad (3)$$

CH_3I formation rate upon I_2 and CH_4, according to $d[CH_3I]/dt=k_1K_2^{1/2}[CH_4][I_2]^{1/2}$. Obtaining K_2 from JANAF Tables, the authors quoted $k_1=8.91\times10^{14}$ $\exp\{-(17\,630\pm550/T)\ cm^3\ mol^{-1}\ s^{-1}$. From measurements of the equilibrium concentrations of CH_3I and HI, the authors found the overall equilibrium constant K_T for CH_3I and HI production from CH_4 and I_2 as 5.74 $\exp\{-(6380\pm100)/T\}$, over the temperature range 585-748 K. According to the above reaction scheme $K_T=k_1k_3/k_{-1}k_{-3}$ and using the values of k_{-3} and k_{-1}/k_3 as determined by Flowers and Benson [3], Goy and Pritchard derive $k_1=5.01\times10^{14}\ \exp\{-(17\,160\pm760)/T\}\ cm^3\ mol^{-1}$ s^{-1}, in good agreement with their directly derived expression. In the abstract to this work, k_1 is quoted with $A_1=10^{15}\ cm^3$ $mol^{-1}\ s^{-1}$, and this value is quoted by Golden and Benson [5], and Kerr [6].

The only other expressions for k_1 have been those of Benson et al. [1,3], derived from the reverse rate constant k_{-1}.

However, since we are unable to reconcile adequately the expressions of [4] with the data on k_{-1} and the JANAF thermodynamic data (see discussion of the reverse reaction below), we make no recommendation.

Rate of the Reverse Reaction

The data for the rate constant k_{-1}

$$CH_3 + HI \rightarrow I + CH_4 \qquad (-1)$$

have been summarised and evaluated by Kerr and Parsonage [7], who preferred the rate constant expression of O'Neal and Benson [2]: $k_{-1} = 4.17 \times 10^{12} \exp(-650/T)$ cm^3 mol^{-1} s^{-1} (350–600 K), within error limits of ±50%.

Using this expression and JANAF thermodynamic data to determine K_1, we derive for k_1 the value 65.4 at 600 K, which is a factor of ~3 below that derived from the expressions of [4]. On the other hand if it is assumed that $\Delta H^\circ_{f,600}(CH_3)$ is ~4.7 kJ mol^{-1} (1.1 kcal mol^{-1}) less than that given by the JANAF tables, for which there is other evidence (see Discussion section B7), this leads to a value of K_1 which when combined with the expression of [7] gives a value of 170 for k_1 at 600 K, in good agreement with the expression of [4]. Clearly more work is required to decide whether the discrepancy is due to defects in the results of [4] or in the thermodynamic data.

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D10 $CH_3 + I_2 \rightarrow CH_3I + I$

The rate constant for the reaction between molecular iodine and methyl radicals

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad (1)$$

(no thermodynamic data available for CH_3I)

has frequently been used as a reference in the estimation of k_2

$$CH_3 + HI \rightarrow I + CH_4 \qquad (2)$$

[1,8,9,10], but only two determinations of k_1 have been made, neither being absolute measurements but made with reference to k_3 and k_4

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (3)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (4)$$

Flash photolysis was used by Davidson and Carrington [3] to produce CH_3 radicals from CH_3I (26 mm Hg; 3.5 kPa) mixed with I_2 (2 μm Hg; 0.27 Pa) and Ar (600 mm Hg; 80 kPa) at 333 K. The mixtures could be circulated through the system to prevent I_2 accumulation. After repeated flashing, the I_2 present was determined using a spectrophotometer, and in one experiment the products were analysed by mass spectrometry. From an analysis of the production of CH_3, leading to an expression relating $d[C_2H_6]/dt$ ($=d[I_2]/dt$, as confirmed experimentally) to the number of flashes, these authors obtained $k_3 = 0.6k_1$, and also an estimate for k_1 of 1.1×10^{13} cm^3 mol^{-1} s^{-1}. From these values they derived $k_3 = 7 \times 10^{12}$ cm^3 mol^{-1} s^{-1} (333 K). However they considered the ratio to be more reliable than the individual rate constant values, and so we derive $k_1 = 4.02 \times 10^{13}$ cm^3 mol^{-1} s^{-1} (333 K) using our recommended value of k_3 (Volume 5, to be published). At 600 mm Hg pressure (80 kPa) reaction 3 is in its high pressure region.

Christie [7] photolysed mixtures of CH_3I (1–9 mm Hg; 133.3–1200 Pa), O_2 (1.0–6.1 mm Hg; 133.3–813.1 Pa), and CO_2, in a static system at total pressures 50–300 mm Hg (6.7–40 kPa), between 240 and 320 nm. The production of I_2 was followed by u.v. absorption at 490–570 nm, and likewise the disappearance of CH_3I, at 240–320 nm. From a steady state treatment of the mechanism

$$CH_3I + h\nu \rightarrow CH_3 + I$$

$$CH_3 + O_2 \rightarrow \text{products} \qquad (5)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (4)$$

$$CH_3 + I_2 \rightarrow CH_3\,I + I \qquad (1)$$

$$CH_3 + I \rightarrow CH_3I$$

$$I + I + M \rightarrow I_2 + M$$

the author obtained the ratios k_4/k_1 and k_5/k_1 at 293 K. By considering previous determinations of k_4 relative to k_3

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (3)$$

[2,5,6], adjusting the originally quoted values of k_4 according to $k_3 = 3.7 \times 10^{13}$ cm^3 mol^{-1} s^{-1} (4), the value for $k_4(M=CO_2)$ was estimated as 10^{15}–10^{16} cm^6 mol^{-2} s^{-1} at 293 K. From the ratio $k_4(M=CO_2)/k_1 = 5.4 \times 10^2$ cm^3 mol^{-1}, k_1 was derived as 2×10^{12}–2×10^{13} cm^3 mol^{-1} s^{-1}. Golden and Benson [11] quoted this work as giving $k_1 = 10^{13}$ cm^3 mol^{-1} s^{-1} at 293 K, and used Flowers and Benson's value for k_{-1} [10] together with the equilibrium constant for reaction

$$CH_3\,I + I \rightarrow CH_3 + I_2 \qquad (-1)$$

1 to derive $k_1 = 10^{13}$ cm^3 mol^{-1} s^{-1} at 560 K. They therefore concluded that $E_1 \cong 0.0$. This temperature independent value was used by Kerr and Parsonage [12] as a reference in their evaluation of k_2. Flowers and Benson [10] themselves derived k_1 from k_{-1} and K_1, and obtained $k_1 = 10^{13} \exp(-755/T)$ cm^3 mol^{-1} s^{-1}. At 293 K this gives a value $k_1 =$

7.6×10^{11} cm^3 mol^{-1} s^{-1}, which is considerably below the range for k_1 quoted by Christie [7]. Even if we adjust this range using our recommended value for k_3 (Volume 5, to be published) giving $1.3\times10^{12}\leqslant k_1\leqslant1.3\times10^{13}$ cm^3 mol^{-1} s^{-1} the value of [10] is still amost a factor of 2 below the lower limit.

Although it seems from the data of [3 and 7], and the calculation of [11] that $k_1\cong10^{13}$ cm^3 mol^{-1} s^{-1} over a wide temperature range, there is insufficient precision for us to make any recommendation.

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Miscellaneous Reactions Involving I/O Species

D11 I + O_3 → IO + O_2

The reactions in the IO_x system have received less attention than reactions involving other halogen oxides, being of comparatively little interest in atmosphere or combustion problems. Reaction 1 has been studied by Clyne and Cruse [2] in a flow system.

$$I + O_3 \rightarrow IO + O_2; \qquad (1)$$

thermodynamic data unavailable for IO.

I atoms were produced by adding HI downstream of a Cl_2 $(Br_2)/Ar$ discharge, and O_3 added further downstream. No details of pressures are given, but HI was used in excess of Cl atoms to avoid interference from ICl. [IO] was monitored by time-resolved absorption spectroscopy at 430 nm. A value of $k_1=5.0\times10^{11}$ cm^3 mol^{-1} s^{-1} at 293 K was obtained, higher than the value obtained by the same authors for the corresponding reaction of Br atoms [1], but much less than the values for F or Cl [3,4]. The authors believe that 25% of the IO is formed in excited vibrational states.

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D12 IO + IO → IOO + I

IO radicals are believed to disproportionate in an analogous manner to BrO [2], giving IOO as an intermediate.

$$IO + IO \rightarrow IOO + I \rightarrow 2I + O_2 \qquad (1)$$

Clyne and Cruse [2] found this mechanism fitted their data obtained from observations of the decay of [IO] at 430 nm. IO was produced in a flow system by adding ozone to a stream of I atoms, produced by adding HI to the products of a $Cl_2(Br_2)/Ar$ discharge. No details of pressures given. Assuming that the extinction coefficient ϵ_1 is slightly less than that for BrO [1], they obtained $k_1=3.1\times10^{12}$ cm^3 mol^{-1} s^{-1} at 293 K, roughly half the value obtained for BrO decay (k_1 defined by $-d[IO]/dt = k_1[IO]^2$).

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D13 HI + O_2 → I + HO_2

The use of hydrogen halides as catalysts in hydrocarbon oxidation reactions has been mentioned elsewhere (sections B25 and C11). HI has not been so widely used as HBr, and there has been less work undertaken on its oxidation as a result.

$$HI + O_2 \rightarrow I + HO_2; \qquad (1)$$

$$\Delta H^\circ_{298}=101.32 \text{ kJ mol}^{-1} \ (24.217 \text{ kcal mol}^{-1})$$

Ioffe et al. [1] studied the reaction over the temperature range 673–823 K in a stirred flow reactor. HI($<1\%$)/O_2($<50\%$) mixtures were diluted to 1 atm pressure with Ar, CO_2, N_2, He or H_2O. The reaction was followed by periodic wet chemical analysis of samples from the reaction vessel. No evidence was found for HI decomposition in the absence of O_2. The apparent rate constant was found to increase by over an order of magnitude as the reaction proceeded. The authors attributed this to experimental error, and used only the results from the initial stages of the oxidation to give $k_1=1.7\times10^{14}\exp(-14\,700/T)$ cm^3 mol^{-1} s^{-1}.

Kochubei and Moin [2] used a static system with HI (4–80%)/O_2(0.35–4%)/He or N_2 mixtures at 1 atm pressure over the temperature range 373–473 K. Analysis of O_2 consumption was by gas chromatography. They assumed a similar mechanism to that for HBr oxidation, with reaction 1 as the rate-determining initial step, and obtained $k_1=1.4\times10^{12}\exp(-10\,100/T)$ cm^3 mol^{-1} s^{-1}.

As Ioffe et al. gave no consideration to the reaction mechanism, the accuracy of their expression must be considered doubtful. In view of the lack of direct information on the reaction mechanism and the few results available, no recommendation can be made.

References

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Miscellaneous Reactions Involving I/N/O Species

D14 $N + I_2 \rightarrow NI + I$

Phillips [2] has studied the disappearance of nitrogen atoms in an active N_2/I_2 flame. Active nitrogen was produced by a discharge through 100% N_2 at 667 Pa pressure, and an $I_2(\sim5\%)/Ar$ mixture at 14.0 Pa added downstream. The decay of the nitrogen afterglow was monitored at 625 nm. Under the reaction conditions, the author believed that N atoms could not be lost by a termolecular reaction, and felt that reaction 1 could be the only process removing them.

$$N + I_2 \rightarrow NI + I; \qquad (1)$$

thermodynamic data unavailable for NI.

Measurements of [N] were delayed for a sufficient length of time so that [N] was very low, thus ruling out any contribution from reaction 2, which tended to produce excited $N_2(A^3\Sigma_u^+)$ molecules, unlike the corresponding chlorine and bromine reactions [1].

On this scheme, he obtained $k_1 = 1.4\times10^{10}$ cm^3 mol^{-1} s^{-1} at 288 K, and $k_1 = 1.6\times10^{10} \exp(-35/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 283–323 K.

$$N + NI \rightarrow N_2 + I \qquad (2)$$

References

[1] Raxworthy, K. S., and Phillips, L. F., Can. J. Chem. **42**, 2928 (1964).

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D15 $NO + I + M \rightarrow NOI + M$

Interest in the reaction between nitric oxide and iodine atoms has developed following observance of the strong catalytic effect exerted by NO during iodine atom recombination (section D2).

$$NO + I + M \rightarrow NOI + M; \qquad (1)$$

$$\Delta H^\circ_{298} = -84.923 \text{ kJ mol}^{-1} \ (-20.297 \text{ kcal mol}^{-1})$$

The catalysed recombination was first studied by Engleman and Davidson [1] by flash photolysis, in which I_2 was photolysed in the presence of NO (0.13–58.9 kPa) and Ar (0–16.3 kPa). The apparent recombination proceeded too fast to be measured, and the authors concluded that NOI was probably formed as an intermediate. In a similar study, Porter et al. [2] used a wide range of NO pressures (<0.1–60.0 kPa) added to a mixture of I_2 (4.00–480 Pa) and Ne (26.6 kPa) at 333 K. [NOI] was monitored by absorption of light at 430 nm, and [I_2] at 520 nm. For [NO]<0.1 kPa, there was normal three-body iodine recombination independent of [NO]; for 0.1<[NO]<5.33 kPa, the apparent second-order observed rate constant was proportional to [NO], and for [NO]>5.33 kPa, this rate constant was proportional to [NO]$^{-1}$, although for the latter conditions, the authors obtained a wide scatter on their results. They proposed that the NOI intermediate decayed by three paths, reactions –1, 2 and 3.

$$NOI + I \rightarrow NO + I_2 \qquad (2)$$

$$2NOI \rightarrow 2NO + I_2 \qquad (3)$$

Using their own value for k_2, they were able to isolate the equilibrium constant $K_1 = 6\times10^6$ cm^3 mol^{-1}, but were unable to separate forward and back reactions.

van den Bergh and Troe [3,4] used a Q-switched ruby laser as their flash source, flashing I_2 (63.9–234 Pa)/He (0–27.8 MPa) mixtures in the presence of NO(0.03–135 kPa). [NOI] was followed by absorption at 420 nm, and [I_2] at 492 nm. They used the same reaction scheme as Porter et al., but were able to show that I_2 is formed in two stages, initially by reaction 2 and in the later stages by reaction 3. Although they were able to study the reaction to very high pressures, they did not attain the limiting high pressure rate constant, and quote a lower limit of $k_1^\infty \geqslant 10^{13}$ cm^3 mol^{-1} s^{-1} at 330 K. Below 100 kPa, a satisfactory value of the low pressure limit of the rate constant was obtained, $k_1^\circ = (2\pm0.5)\times10^{15}$ cm^6 mol^{-2} s^{-1} at 330 K. Data on the temperature dependence were admitted by the authors to be not very good, although they do report $k_1^\circ \propto T(-1\pm0.5)$.

In view of the lack of confirmatory data, no recommendation is made for k_1.

References

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Note Added in Proof

Two further studies of this reaction have been reported. van den Bergh et al. (Int. J. Chem. Kin. **9**, 223 (1977)), in experiments similar to those described in [3] and [4], measured values of k_1° at 330 K for the bath gases M = He,Ne,Ar,Xe,H_2,N_2,CO, N_2O, CO_2,CH_4,C_3H_8,i–C_4H_{10} and neo–C_5H_{12}.

Basco and Hunt (Int. J. Chem. Kin. **10**, 773 (1978)) flash photolysed mixtures of I_2(4–17 Pa), NO(0.014–107 kPa) and Ar(0–60 kPa). [I_2] was followed by absorption at 500 nm and [INO] over the ranges 251–310 nm and 360–460 nm. For [NO]⩽65 Pa the reappearance of I_2 obeyed a third order rate law, the recombination becoming too fast to measure for NO pressures in the range 65–650 Pa but becoming measurable again at higher NO pressures.

These results could be interpreted in terms of the occurrence of reactions 1,–1,2 and 3 and yielded values of $k_1^\circ/\mathrm{cm}^6\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$ of $3.73 \pm 0.25 \times 10^{15}$ at 298 K and $3.34 \pm 0.36 \times 10^{15}$ at 328 K. The latter value is in excellent agreement with the value obtained by van den Bergh et al. at the same temperature and leads us to recommend a value of $k_1^\circ(\mathrm{M}=\mathrm{Ar}) = 3.4 \pm 0.5 \times 10^{15}\ \mathrm{cm}^6\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$ at 330 K.

D16 NOI + NOI → 2NO + I$_2$

This alternative means of NOI removal in the flash photolysis of I_2/NO mixtures was not considered by Engleman and Davidson [1]. In Porter's system [2], reaction 1 was considered, and thought to be particularly important when a large excess of NO was present. In these cases the observed bimolecular rate constant for I_2 formation$=$ $k_2/K_3[\mathrm{NO}]+k_1$.

$$\mathrm{NOI} + \mathrm{NOI} \rightarrow 2\mathrm{NO} + \mathrm{I_2}; \tag{1}$$

$$\Delta H^\circ_{298} = -18.761\ \mathrm{kJ\ mol^{-1}}\ (-4.484\ \mathrm{kcal\ mol^{-1}})$$

$$\mathrm{NOI} + \mathrm{I} \rightarrow \mathrm{NO} + \mathrm{I_2} \tag{2}$$

$$\mathrm{NO} + \mathrm{I} + \mathrm{M} \rightarrow \mathrm{NOI} + \mathrm{M} \tag{3}$$

For $[\mathrm{NO}] > 5.33$ kPa, Porter's results for k_{bimol} scattered badly and they could only give an upper limit for k_1, $\leqslant 4 \times 10^{10}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ at 333 K.

van den Bergh and Troe [3,4] assumed that reaction 1 must be responsible for fresh production of I_2 in their flash photolysis system, several ms after the initial I_2 production, assumed due to reaction 2. From the rate of production of this secondary iodine, they obtained $k_1 = 5.0 \times 10^{13}\ \exp(-2600/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$ over the temperature range 310–450 K. The activation energy agrees well with Porter's estimate [2] and continues the trend of decreasing activation energy for the reaction $2\mathrm{NOX} \rightarrow 2\mathrm{NO} + \mathrm{X_2}$ shown through X$=$Cl and Br. At 333 K, $k_1 = 2.0 \times 10^{10}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$, below Porter's upper limit.

We thus accept the expression of van den Bergh and Troe over the stated temperature range, and suggest error limits of ±75%.

References

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[4] van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

Note Added in Proof

Basco and Hunt (Int. J. Chem. Kin. **10**, 773 (1978)) in a flash photolysis study on I_2/NO/Ar mixtures (see Note Added in Proof, section D15) obtained values of $k_1/\mathrm{cm^3\ mol^{-1}\ s^{-1}}$ of $2.05 \pm 0.03 \times 10^{10}$ at 298 K and $3.10 \pm 0.08 \times 10^{10}$ at 328 K. The latter value is some 50% higher than that calculated from the recommended expression of van den Bergh and Troe but within the error limits suggested.

D17 NOI + I → NO + I$_2$

First proposed by Engleman and Davidson [1] to account for iodine production in the flash photolysis of iodine in the presence of NO, a rate constant was determined by Porter et al. in their flash photolysis system [2].

$$\mathrm{NOI} + \mathrm{I} \rightarrow \mathrm{NO} + \mathrm{I_2}; \tag{1}$$

$$\Delta H^\circ_{298} = -66.162\ \mathrm{kJ\ mol^{-1}}\ (-15.813\ \mathrm{kcal\ mol^{-1}})$$

They flashed I_2 (0.1–2%)/Ne mixtures at 26.6 kPa pressure in the presence of NO($<$0.1–60.0 kPa), at 333 K. [NOI] was monitored by absorption spectroscopy at 430 nm and $[I_2]$ at 520 nm. They obtained values for k_1K_2 and k_1/K_2, from which they obtained $k_1 = 4.0 \times 10^{12}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$. This leads to $K_2 = 6 \times 10^6\ \mathrm{cm^3\ mol^{-1}}$, about 10^6 lower than that given by JANAF.

$$\mathrm{NO} + \mathrm{I} + \mathrm{M} \rightarrow \mathrm{NOI} + \mathrm{M} \tag{2}$$

van den Bergh and Troe [3,4] studied this system in more detail over a large pressure range (100 Pa–27.8 MPa). They found that iodine molecules reformed in two stages, initial formation being directly after the flash by means of reaction 1. From this rapid recombination they obtained $k_1 = 1.7 \times 10^{14}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$, over the temperature range 330–400 K with temperature having little effect. This is a factor of 40 higher than Porter's value, while their value of K_2 agrees well with that of JANAF. Consequently we prefer Troe's k_1, but choose not to make a recommendation at this time.

References

[1] Engleman, R., Jr., and Davidson, N. R., J. Amer. Chem. Soc. **82**, 4770 (1960).

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[4] van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

D18 NO$_2$ + I + M → NO$_2$I + M

The recombination of iodine atoms in the presence of nitrogen dioxide has not received the same attention as the NO/I_2 system. van den Bergh and Troe [1] used the same flash photolysis system as for the NO/I_2 reactions, using a Q-switched ruby laser as light source, and a large range of concentrations of both NO_2 and I_2/He. (NO_2 at 0.03–4.49 kPa; I_2 at 63.9–234 Pa; He at 0–27.8 MPa). I_2 formation was followed at 492 and 498 nm. It was not possible to observe any NO_2I spectrum, as it was masked by that of NO_2, but the results were compatible with a similar mechanism to that of the NO/I_2 system.

$$\mathrm{NO_2} + \mathrm{I} + \mathrm{M} \rightarrow \mathrm{NO_2I} + \mathrm{M}; \tag{1}$$

thermodynamic data unavailable for NO_2I.

$$\mathrm{NO_2I} + \mathrm{I} \rightarrow \mathrm{NO_2} + \mathrm{I_2} \tag{2}$$

$$2\mathrm{NO_2I} \rightarrow 2\mathrm{NO_2} + \mathrm{I_2} \tag{3}$$

Iodine was again formed in two stages, and from its formation in the initial stage, with low $[\mathrm{NO_2}]$, a value of $k_1^\circ=$

5.0×10^{16} cm^6 mol^{-2} s^{-1} was found at 330 K, with temperature dependence again uncertain. In contrast to the NO/I_2 results, a limiting second order rate constant was obtained, $k_1^{\infty}=4.0\times10^{13}$ cm^3 mol^{-1} s^{-1} at 330 K.

Reference

[1] van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

Note Added in Proof

van den Bergh et al. (Int. J. Chem. Kin. **9**, 223 (1977)) have used the same technique as in their previous study [1] to obtain values of k_1°/cm^3 mol^{-2} s^{-1} at 330 K for the bath gases M = He, Ne, Ar, Xe, H_2, D_2, N_2, CO, O_2, N_2O, CO_2, CH_4, CF_4, C_4H_4, SF_6, C_2H_6, C_2F_6, C_3H_8, C_3F_8, n–C_4H_{10}, i–C_4H_{10}, neo–C_5H_{12}; 2,2–dimethylbutane; 2,4–dimethylpentane; 2,2,4–trimethyl pentane.

D19 $NO_2I + I \rightarrow NO_2 + I_2$

The reactions for the removal of the NO_2I complex in the NO_2/I_2 system are similar to those in the NO/I_2 system, and their rate constants have been determined from the two separate phases of I_2 formation. van den Bergh and Troe [1] obtained $k_1=5.0\times10^{13}$ cm^3 mol^{-1} s^{-1} at 330 K, but found no appreciable variation with temperature up to 450 K.

$$NO_2I + I \rightarrow NO_2 + I_2 \qquad (1)$$

Reference

[1] van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

D20 $NO_2I + NO_2I \rightarrow 2NO_2 + I_2$

The rate constant for reaction 1 was determined by van den Bergh and Troe [1] from the second phase of iodine formation following the flash photolysis of NO_2/I_2 mixtures.

$$NO_2I + NO_2I \rightarrow 2NO_2 + I_2 \qquad (1)$$

They found $k_1=1.0\times10^{10}$ cm^3 mol^{-1} s^{-1} at 350 K. It was not possible to establish any temperature dependence over the small temperature range studied (300–400 K), but using the same *A*-factor as obtained for reaction 2, an activation energy $E_1=25$ kJ mol^{-1} (6 kcal mol^{-1}) is obtained.

$$2NOI \rightarrow 2NO + I_2 \qquad (2)$$

Reference

[1] van den Bergh, H., and Troe, J., J. Chem. Phys. **64**, 736 (1976).

D21 $N_2O + I \rightarrow N_2 + IO$

This reaction shows many similar characteristics to that of the reaction between N_2O and Br atoms, and has been studied by the same workers [1,2,3].

$$N_2O + I \rightarrow N_2 + IO \qquad (1)$$

Musgrave and Hinshelwood [1] used i–C_3H_7I (0–3.07 kPa) as their source of I atoms, allowing it to decompose at 898–973 K in the presence of N_2O (40.0–53.3 kPa). The derived second-order rate constant varies with [I], and the activation energy of 215.5 kJ mol^{-1} (51.5 kcal mol^{-1}) again includes E_2.

$$I_2 + M \rightarrow I + I + M \qquad (2)$$

Volmer and Bogdan [2] used I_2 (2.65–26300 Pa)/N_2O (20.0–61.3 kPa) mixtures over the temperature range 723–917 K, and found excellent proportionality between the apparent first order rate constant and $[I_2]^{1/2}$ over the entire pressure range. From their data we obtain $k_1K_2^{1/2}=1.1\times10^{14}$ exp(–26 500/T) cm$^{3/2}$ mol$^{-1/2}$ s^{-1} over the given temperature range and, using JANAF thermodynamic data to calculate K_2, we derive $k_1=9.7\times10^{13}$ exp(–17 800/T) cm^3 mol^{-1} s^{-1}.

Kaufman et al. [3] obtained I atoms from C_2H_5I (5.33–106.7 Pa), allowing it to decompose in the presence of N_2O (13.3 kPa). Correcting for the effects of reactions 2 and 3, they obtained $k_1=2.8\times10^{14}$ exp(–19 100/T) cm^3 mol^{-1} s^{-1} over the temperature range 876–973 K.

$$N_2O + M \rightarrow N_2 + O + M \qquad (3)$$

Their activation energy, $E_1=159.0$ kJ mol^{-1} (38 kcal mol^{-1}) is again in good agreement with that of Volmer and Bogdan, although the latter authors's k_1 is ~50% higher at 870 K.

References

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D22 $NO + HI \rightarrow HNO + I$

There has been just one study of reaction 1 by Holmes [1].

$$NO + HI \rightarrow HNO + I; \qquad (1)$$

$$\Delta H^{\circ}_{298}=89.859 \text{ kJ mol}^{-1} \ (21.477 \text{ kcal mol}^{-1})$$

A static system was used, with NO at 5.33–66.7 kPa and HI at 16.0–100 kPa pressure, over the temperature range 363–573 K. The reaction was followed by analysing samples chemically for NO, HI, NH_4I and I_2. The latter two products were found, with H_2O, to be overall products of the reaction. The reaction vessel was coated with a "carbonaceous deposit" in order to prevent any heterogeneous reactions, but the reaction mechanism was not elucidated. The author assumed reaction 1 to be the rate determining initial step, and obtained $k_1=2.7\times10^{11}$ exp(–11 100/T) cm^3 mol^{-1} s^{-1}.

Reference

[1] Holmes, J. L., Proc. Chem. Soc. 75 (1962).

D23 $HNO + HI \rightarrow H_2 + NOI$

Reaction 1 is thought to occur following the photolysis of HI in the presence of NO.

$$HNO + HI \rightarrow H_2 + NOI; \qquad (1)$$

$$\Delta H^{\circ}_{298}=-13.807 \text{ kJ mol}^{-1} \ (-3.300 \text{ kcal mol}^{-1})$$

Holmes and Sunderam [1,2] photolysed HI at 313 and 366 nm, adding NO between 253 and 298 K to observe the inhibition in a static system. At 298 K [1] with HI at a pressure of 9.02 kPa, and NO added so that the NO:HI ratio varied from 0.5 to 8.6, $[H_2]$, measured mass-spectrometrically after the other products had been condensed at 58 K, decreased with increasing [NO] to a limiting value. This led the authors to believe that HNO radicals were being formed and reacting according to the following scheme.

$$HI + h\nu \rightarrow H + I \tag{2}$$

$$H + NO + M \rightarrow HNO + M \tag{3}$$

$$HNO + HI \rightarrow H_2 + NOI \tag{1}$$

$$HNO + I_2 \rightarrow HI + NOI \tag{4}$$

Since $[H_2]_{\text{limit}}$ was independent of [NO], then $[H_2]_{\text{limit}} = 1/(1+k_4[I_2]/k_1[HI])$. Assuming $[I_2]$=S.V.P. of iodine at 298 K, this gave $k_4/k_1 = 79.9$.

At lower temperatures, $[I_2]$ is much reduced, and hence reaction 4 becomes unimportant. Photolysing HI (3.42–12.9 kPa) with added NO(14.9–61.2 kPa) as before at 253 and 279 K [2], authors obtained increased nitrogen yields, believed due to reactions between HNO and NO.

$$HNO + NO \rightleftharpoons H(NO)_2 \tag{5}$$

$$H(NO)_2 + NO \rightarrow HNO_3 + N_2 \tag{6}$$

At low [NO], $[H_2]/[N_2] \propto k_1/K_5k_6$. At high [NO], $[H_2]/[N_2] \propto k_1/k_5$. The following ratios were obtained:

T (K)	k_1/K_5k_6 (mol cm^{-3})	k_1/k_5
253	7.27×10^{-4}	~18
279	1.0×10^{-3}	73
298		237

The temperature dependences yield $E_1-(E_6+(\Delta H_5^\circ)_{298}) =$ 8.0 kJ mol^{-1} (1.9 kcal mol^{-1}) and $E_1-E_5 = 35.6\pm6.3$ kJ mol^{-1} (8.5 ± 1.5 kcal mol^{-1}).

References

[1] Holmes, J. L., and Sunderam, E. V., Trans. Faraday Soc. **62**, 910 (1966).

[2] Holmes, J. L., and Sunderam, E. V., Trans. Faraday Soc. **62**, 1822 (1966).

D24 $HNO + I_2 \rightarrow HI + NOI$

In the photolysis of hydrogen iodide at room temperature in the presence of nitric oxide, reaction 1 competes with reaction 2 for consumption of HNO.

$$HNO + I_2 \rightarrow HI + NOI; \tag{1}$$

$$\Delta H_{298}^\circ = 38.911 \text{ kJ mol}^{-1} \text{ (9.300 kcal mol}^{-1}\text{)}$$

$$HNO + HI \rightarrow H_2 + NOI \tag{2}$$

Holmes and Sunderam [1] photolysed HI (9.02 kPa) at 313 and 366 nm and 298 K, with NO added so that [NO]:[HI]=0.5 to 8.6. $[H_2]$ was measured mass-spectrometrically, and found to be independent of [NO]. Assuming $[I_2]$=S.V.P. of iodine at 298 K, this gave the rate constant ratio $k_1/k_2 = 79.9$. In this system the reaction is expected to be unimportant at lower temperatures as the S.V.P. of iodine falls [2].

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E1 $F + Cl_2 \rightarrow ClF + Cl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	- 8.414	1.305	1.542
300	- 8.418	1.289	1.532
500	- 8.732	0.435	0.935
1000	- 8.606	0.577	0.479
1500	- 8.368	0.766	0.331
2000	- 8.226	0.854	0.259
2500	- 8.167	0.874	0.216
3000	- 8.251	0.849	0.188
3500	- 8.548	0.761	0.167
4000	- 9.021	0.632	0.150
4500	- 9.615	0.490	0.137
5000	-10.247	0.360	0.125

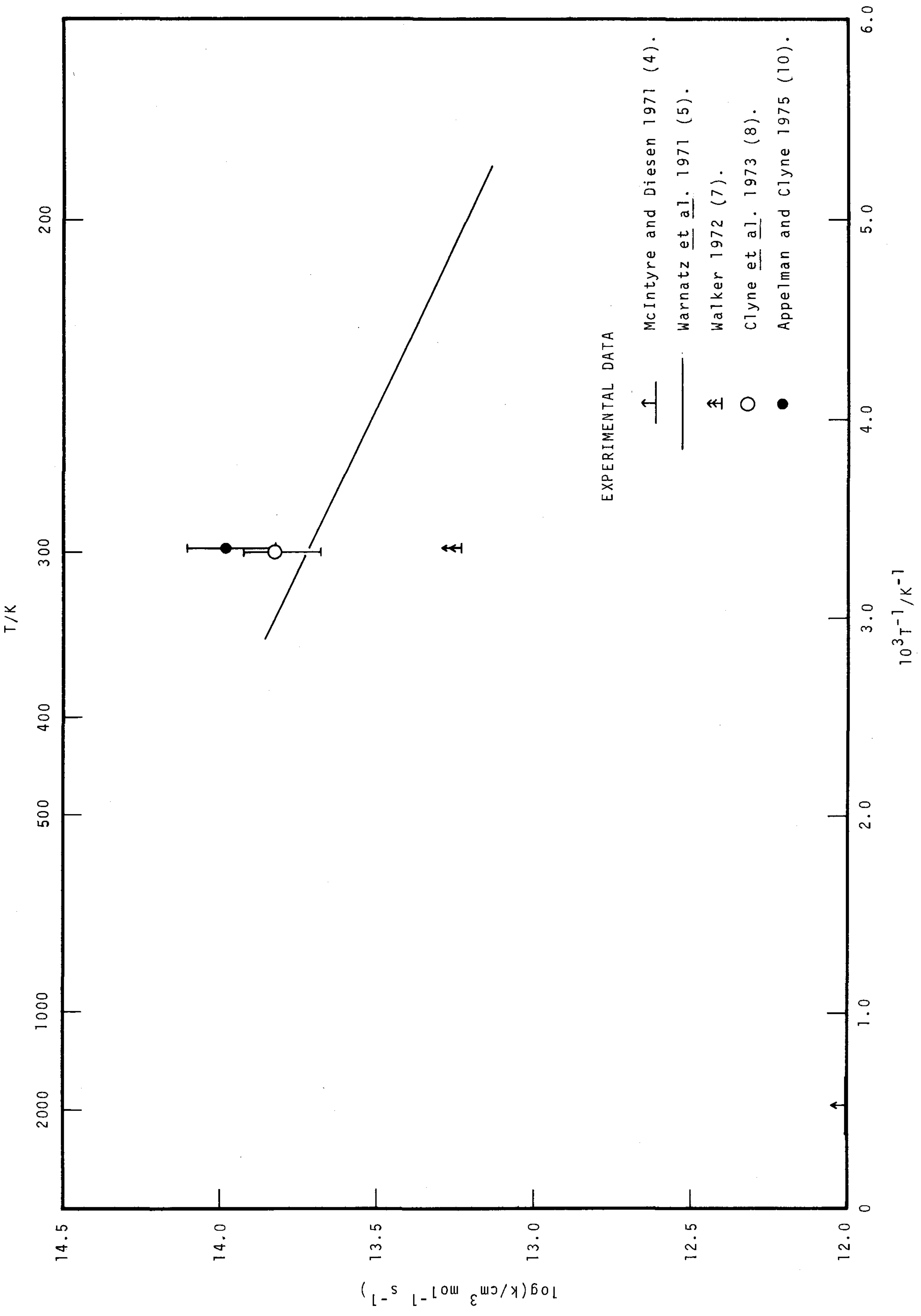
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$\geq 10^{12}$	1450-2700	Shock tube study. Cl_2(0.5%)/F_2(0.5%)/Ar(0.25%)/Ne mixtures behind reflected shocks. Reaction followed by mass spectrometry. McINTYRE and DIESEN 1971 (4)	ClF production displayed induction period, variation of which with $[Cl_2]$ gave lower limit for k_1.
$5.5 \times 10^{14} \exp(-705/T)$	190-345	Discharge flow system. N_2/He mixtures passed through discharge, and thermally dissociated N_2F_4 added downstream. Cl_2 added in excess ($[Cl_2] \simeq 5[F]$) through moveable inlet, total pressures 3.5 mm Hg (467 Pa). Mass spectrometry used to	F atom production via reaction $N + NF_2 \rightarrow N_2 + 2F$ Values of k_1 obtained from profiles of [F], [Cl] and [ClF] $F + Cl_2 \rightarrow ClF + Cl$ 1

$F + Cl_2 \rightarrow Cl + ClF$



$F + Cl_2 \rightarrow ClF + Cl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		monitor F, ClF and Cl. WARNATZ, WAGNER and ZETZSCH 1971 (5)	
$>1.7\times10^{13}$	298	Discharge flow system. CF_4 (3%)/Ar mixtures through discharge, Cl_2 added downstream. $8\times10^{-12} \leq [Cl_2] \leq 1\times10^{-11}$ mol cm^{-3}. $[Cl_2]$ followed by mass spectroscopy. WALKER 1972 (7)	Complete consumption of Cl_2 when $[F]=5\times10^{-11}$ mol cm^{-3}. Lower limit only for k_1 owing to low sensitivity to Cl_2.
$(6.6\pm1.8)\times10^{13}$	300	F_2-discharge flow system. Cl_2 added downstream such that $4.2\times10^{-12} \leq [Cl_2] \leq 1.05\times10^{-11}$ mol cm^{-3}. [F] range 4.9×10^{-12}-1.13×10^{-11} mol cm^{-3}. Total pressures 118-132 Pa. Cl_2 removal rate measured using mass spectrometry. CLYNE, McKENNEY and WALKER 1973 (8)	Values of [F] obtained from $[Cl_2]$ consumption, as verified by ClF formation. k_1 determined from $[Cl_2]$ decay.
$(9.64\pm3.0)\times10^{13}$	298	F_2-discharge flow system. F_2/He mixtures in discharge, Cl_2 added downstream. $1.58\times10^{-12} \leq [F] \leq 2.4\times10^{-12}$ mol cm^{-3}, and $8.1\times10^{-13} \leq [Cl_2] \leq 1.88\times10^{-12}$ mol cm^{-3}. Mass spectrometry used to follow [ClF] and $[Cl_2]$. APPELMAN and CLYNE 1975 (10)	ClF only product detected. Equating [ClF] produced to [F], pseudo-first order analysis used to give k_1. Authors believe this measurement to be more accurate than that of (8). Authors attribute value $k_1=5.18\times10^{13}$ cm^3 mol^{-1} s^{-1} to (9).

Discussion

Prior to any experimental investigation, rate constants for reaction 1

$$F + Cl_2 \rightarrow ClF + Cl \qquad (1)$$

were estimated by Mayer and Schieler [1]: $k_1 = 10^{14} \exp(-252/T)$ cm^3 mol^{-1} s^{-1} (as used by [6]); and [2], $k_1 = 6.2 \times 10^{12}\ T^{0.68} \exp(-252/T)$ cm^3 mol^{-1} s^{-1}, and also by Fletcher and Dahneke [3], $k_1 = 10^{13} \exp(-1510/T)$ cm^3 mol^{-1} s^{-1}.

All of the low temperature measurements of k_1 have been made using discharge flow systems and mass spectrometry, although the production of F atoms was achieved by a variety of means, e.g., simple F_2 discharge [8,10], CF_4 discharge [7] and N_2 discharge followed by addition of NF_2 [5], and the progress of the reaction has been followed by detection of both reactants, F [5] and Cl_2 [7,8,10], and products, Cl [5] and ClF [5,10].

The only high temperature investigation of k_1 is that of McIntyre and Diesen [4], again using mass spectroscopy, behind reflected shocks. But this study only provided a lower limit for k_1, over a very wide temperature range.

From the Arrhenius plot for k_1 it can be seen that the measured value of k_1 at room temperature has increased with successive determinations, but until independent confirmation has been made of the highest values so far obtained (Appelman and Clyne [10]) we make no recommendation for k_1.

References

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E2 $F + HCl \rightarrow HF + Cl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-137.854	-6.694	23.802
300	-137.859	-6.699	23.653
500	-137.867	-6.676	14.050
1000	-137.767	-6.573	6.853
1500	-138.235	-6.950	4.451
2000	-138.842	-7.297	3.245
2500	-139.373	-7.535	2.518
3000	-139.804	-7.694	2.033
3500	-140.164	-7.803	1.684
4000	-140.453	-7.883	1.422
4500	-140.695	-7.945	1.218
5000	-140.913	-7.983	1.055

RECOMMENDED RATE CONSTANT

$$k = 7.0 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$$
$$= 1.16 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

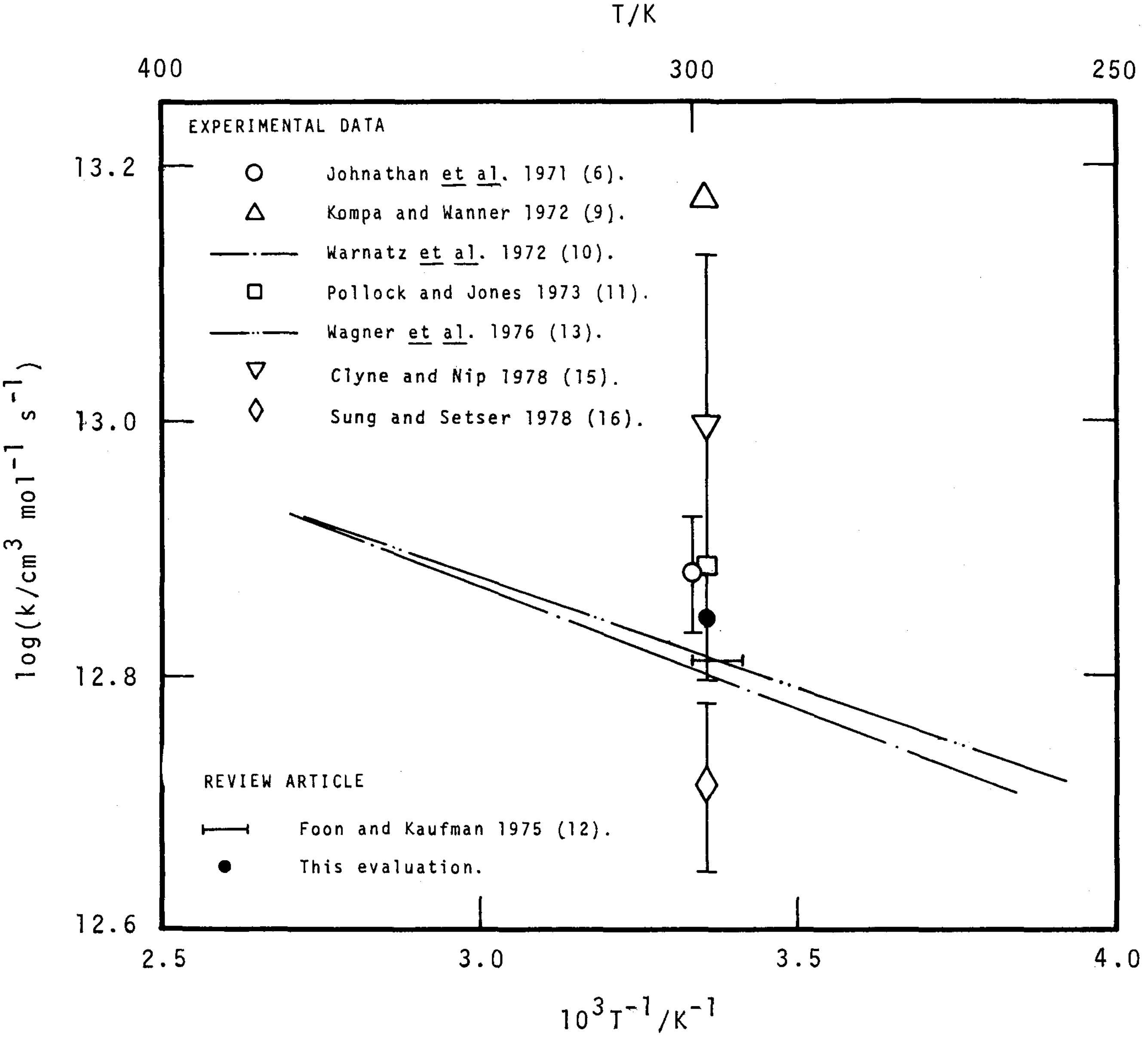
Temperature Range: 298-300 K.

Suggested Error Limits: ±20%

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	300	Discharge flow system. CF_4 (∿1%)/Ar mixtures passed through discharge. HCl or CH_4 added downstream at partial pressures ∿1% and 10%. Total pressures 80-100 μ Hg (10.7-13.3 Pa). Emission from HF* monitored over range 350-420 nm. JONATHAN, MELLIAR-SMITH, OKUDA, SLATER and TIMLIN 1971 (6)	Rate constants for population of various HF vibrational levels derived from measured peak intensities, with extrapolation to zero time to correct for varying rates of collisional deactivation. HF spectra produced by reactions 1 and 2 compared $F + HCl \rightarrow HF + Cl$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 with allowance for HF (v=0) production. Hence ratio k_1/k_2= (0.19±0.02). Using our recommended value of k_2 (this Volume, section A6) we obtain k_1=(7.6±

$F + HCl \rightarrow Cl + HF$



F + HCl → HF + Cl

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		JONATHAN, MELLIAR-SMITH, OKUDA, SLATER and TIMLIN 1971 (6) continued.	0.8)$\times10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ at 300 K. Estimate for E_1 of 10.63 kJ mol^{-1} (2.54 kcal mol^{-1}) also given, derived from data for k_2 amd k_3 given by (3). $F + H_2 \rightarrow HF + H$ 3 These data also reported in (7).
1.5×10^{13}	298	Flash photolysis study. WF_6 (0.25 mm Hg; 33.3 Pa) /HCl mixtures, total pressures 0.5 mm Hg (66.7 Pa). HF emission followed. KOMPA and WANNER 1972 (9)	Authors assumed negligible vibrational de-activation of HF. Value independent of [F], which authors could only estimate.
$2.8\times10^{13}\exp(-443/T)$	260-370	Discharge flow system. N_2/He stream passed through discharge, and added to thermally dissociated N_2F_4. HCl added downstream, such that F atoms in excess. Decay of HCl and production of Cl and HF followed by mass spectrometry. WARNATZ, WAGNER and ZETZSCH 1972 (10)	F atoms generated by reaction $N + NF_2 \rightarrow N_2 + F + F$ Good agreement obtained for k_1 between values derived from F atom decay, and from HF and Cl production. $F + HCl \rightarrow HF + Cl$ 1
	298	Flow system. NO and HCl added downstream to flow of F_2 in Ar ([Ar]:[F_2] ratio 1.67×10^{3}). Total pressures 3.7 mm Hg (494 Pa). Pale yellow emission intensity measured. POLLOCK and JONES 1973 (11)	Reaction sequence for emission taken to be $F_2 + NO \rightarrow F + NOF$ $F + NO + M \rightarrow NOF^* + M$ 4 $NOF^* \rightarrow NOF + h\nu$ Addition of HCl caused reaction 1 to compete for F atoms with reaction 4 $F + HCl \rightarrow HF + Cl$ 1 affecting emission intensity. Variation in intensity gave $k_4[M]/k_1=(7.8\pm0.7)\times10^{-4}$. Using k_4 from (8) authors reported k_1 as 7.3×10^{12} $cm^3\ mol^{-1}\ s^{-1}$. Using our recommended value for k_4 (this Volume, section A22) we derive $k_1=7.7\times10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$.

F + HCl → HF + Cl

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$2.5\times10^{13}\exp\{-(400\pm140)/T\}$	255-367	Discharge flow system. F_2/He mixture (with He in > 1000-fold excess) passed through discharge. HCl added downstream, giving $0.2<[HCl]/[F]<50$. Total pressures 3.2×10^{2}-4.3×10^{2} Pa. Mass spectrometry used to follow HCl and F atom decays, and HF and Cl atom production. WAGNER, WARNATZ and ZETZSCH 1976 (13)	From removal of F and HCl, compared with production of HF, authors found stoichiometry of 1.0. Values of k_1 derived from product formation and reactant decay rates in good agreement. Correction for diffusion estimated to be ∿2%, i.e. less than experimental error in determination of [F], so correction ignored.
$(9.88\pm3.6)\times10^{12}$	298	Discharge flow system. (F_2 +He) (4%)/Ar mixtures passed through discharge. CH_4 added in excess downstream. Total pressures 150 Pa. [F] decay followed by vacuum uv resonance fluorescence at 94.58 nm. CLYNE and NIP 1978 (15)	Value of k_1 derived from pseudo first order decay of [F]. $F + HCl \rightarrow HF + Cl$ Authors also measured product branching ratio for excited Cl atoms. Authors recommended value $k_1=(8.13\pm2.1)\times10^{12}$ cm^3 mol^{-1} s^{-1}, as mean of this work and result of (10,13).
	298	Discharge flow system. CF_4/Ar mixtures passed through discharge, giving typically $[F]= 1.7\times10^{-12}$ mol cm^{-3}, $[Ar]=4.0\times10^{-8}$ mol cm^{-3}. HCl added downstream at typical concentrations 6.6×10^{-13}-5.0×10^{-11} mol cm^{-3}. Vibrationally excited HF spectra recorded. SUNG and SETSER 1978 (16)	Relative total emission intensities of HF* obtained when HCl or CH_4 added to F/Ar stream. Hence $k_1/k_2=(0.13\pm0.02)$ $F + HCl \rightarrow HF + Cl$ 1 $F + CH_4 \rightarrow HF + CH_3$ 2 Using our recommended value for k_2 (this Volume, section A6) we derive $k_1=(5.2\pm0.8)\times10^{12}$ cm^3 mol^{-1} s^{-1}. These data also reported in (14).

REVIEW ARTICLE

6.5×10^{12}	293-300	Review. Expression of WARNATZ *et al.* (10) used to derive this value. FOON and KAUFMAN 1975 (12)	

Discussion

The generation of HF laser emission by the reaction

$$F + HCl \rightarrow HF + Cl \tag{1}$$

has provoked studies of the rate constant k_1. Previous to any experimental data Tunder et al. [1] had estimated $k_1 = 1.9\times10^{12}\ T^{0.68}\ \exp(-300/T)\ cm^3\ mol^{-1}\ s^{-1}$ by the Johnston-Parr method, as quoted by [2], and Mayer and Schieler [4] had estimated $k_1 = 9.3\times10^{11}\ T^{0.5}\ \exp(-300/T)\ cm^3\ mol^{-1}\ s^{-1}$, by the same method. This latter expression was used by [5].

There is good agreement between the room temperature values obtained in discharge flow [6,10,13] and simple flow systems [11] indicating a recommended value of

$$k_1 = (7.0\pm1.4)\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$$

at room temperature (298–300 K). The value of Kompa and Wanner [9], obtained by flash photolysis, is a factor of 2 higher than this recommendation. We note that while these authors' value for k_3

$$F + H_2 \rightarrow HF + H \tag{3}$$

is also relatively high (see section A4), their value for k_2 is in good agreement with other data for reaction 2.

$$F + CH_4 \rightarrow HF + CH_3 \tag{2}$$

We are unable to explain this difference.

The value of k_1 of Sung and Setser [16] is the lowest determined so far, and we note that it is separated from the other data for k_1 by a factor similar to that which separates these authors' determinations of the rate constants for reactions 5 and 6

$$F + HBr \rightarrow HF + Br \tag{5}$$

$$F + HI \rightarrow HF + I \tag{6}$$

from other data for k_5 and k_6 (see sections E3 and E4).

As the only information regarding the temperature variation of k_1 has been obtained in the same laboratory, using the same technique [10,13], in the absence of independent data we make no recommendation for the temperature coefficient of k_1.

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Note Added in Proof

An absolute measurement of k_1 has been reported by Wurzberg et al. (Chem. Phys. Letts. **57**, 373 (1978)) obtained by monitoring the rise time of HF vibrational fluorescence following multiphoton dissociation of SF_6 (CO_2 laser radiation) in mixtures with HCl and argon. The value of k_1 so obtained, (presumably at ≅300 K) is $(5.0\pm0.5)\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ which is lower than, and outside the error limits of, our recommended value. The values of the rate constants for reactions of F atoms with the other hydrogen halides reported in this paper also appear to be low by a similar amount.

Miscellaneous Inter-Halogen Reactions Involving F Atoms

E3 F + HBr → HF + Br

There have been no absolute determinations of the rate constant for reaction 1

$$F + HBr \rightarrow HF + Br \tag{1}$$

$$(\Delta H^\circ_{298} = -203.15\ kJ\ mol^{-1};\ -48.56\ kcal\ mol^{-1})$$

Mayer and Schieler [1] estimated k_1 as $9.5\times10^{11}\ T^{0.5}\ \exp(-200/T)\ cm^3\ mol^{-1}\ s^{-1}$, using the rigid-sphere collision model of the Johnston-Parr method, for the temperature range 298–2500 K.

Jonathan et al. [2] passed a CF_4 (∼1%)/Ar mixture through a discharge and added HBr or CH_4 downstream, at total pressures of 80–100 μm Hg (10.7–13.3 Pa). The emission spectrum of the vibrationally excited HF product was recorded at 320–420 nm. The ratios of intensity peaks of this spectrum gave relative rate constants for the population of various vibrational levels of HF, after extrapolation to zero time to correct for varying rates of collisional deactivation. By comparing the spectra produced by reactions 1 and 2

$$F + CH_4 \rightarrow HF + CH_3 \tag{2}$$

the authors gave $k_1/k_2 = (0.87\pm0.14)$ at 300 K.

Using our value at 300 K for k_2 (see section A6) we obtain $k_1 = (3.48\pm0.6)\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$.

The same method was used by Sung and Setser [3] whose conditions were typically [F]$=1.7\times10^{-12}$ mol cm^{-3}, [Ar]$=4.0\times10^{-8}$ mol cm^{-3}, and [HBr] 6.6×10^{-13} to 5.0×10^{-11} mol cm^{-3}. These authors compared the relative total emission intensities of vibrationally excited HF obtained in reactions 1 and 2, and found $k_1/k_2=(0.68\pm0.07)$ at room temperature. With our value for k_2 (section A6) we obtain $k_1=(2.72\pm0.28)\times10^{13}$ cm^3 mol^{-1} s^{-1}. These authors also report that they directly compared the emission intensities from reaction 1 and reaction 3

$$F + HI \rightarrow HF + I \qquad (3)$$

and quote $k_3/k_1=(1.1\pm0.1)$. Using our tentative recommendation for k_3 (section E4) we derive $k_1=(3.73\pm1.5)\times10^{13}$ cm^3 mol^{-1} s^{-1}.

On the basis of the latter value, and that of Jonathan et al. [2], noting that the value of [3] derived from k_2 is low, as are their values for the rate constants of the reactions of F atoms with the hydrogen halides HCl and HI, we tentatively recommend the value for the overall rate constant of reaction 1 as $(3.3\pm1.5)\times10^{13}$ cm^3 mol^{-1} s^{-1} at 300 K.

References

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Note Added in Proof

In a recent paper (J. Phys. Chem. **81**, 898 (1977)) the value of k_1/k_2 obtained by Sung and Setser [3] has been corrected for differences in the vibrational distribution in HF derived from the two reactions. The corrected value of 0.81 leads to a value of k_1 in good agreement with our recommendation.

An absolute measurement of k_1 has been carried out by Wurzberg et al. (see Note Added in Proof, section E2). The value obtained of $(2.03\pm0.13)\times10^{13}$ cm^3 mol^{-1} s^{-1} which, like other rate constants reported in this work, is substantially lower than our recommendation.

E4 F + HI → HF + I

No absolute determination of the rate constant of reaction 1 has been made:

$$F + HI \rightarrow HF + I \qquad (1)$$

$$(\Delta H^\circ_{298}=-271.05 \text{ kJ mol}^{-1}; -64.78 \text{ kcal mol}^{-1})$$

Prior to any experimental studies, Mayer and Schieler [2] used the rigid-sphere collision model of the Johnston/Parr method to estimate $k_1=1.1\times10^{12}\ T^{0.5}\ \exp(-200/T)$ cm^3 mol^{-1} s^{-1}, for 298–2500 K.

Jonathan et al. [3] measured k_1 relative to k_2 at 300 K using

$$F + CH_4 \rightarrow HF + CH_3 \qquad (2)$$

a discharge flow system in which CF_4($\sim$1%)/Ar mixtures were passed through the discharge, and HI or CH_4 added downstream. Total pressures were 80–100 μm Hg (10.7–13.3 Pa). The emission spectrum of the vibrationally excited HF product was recorded at 310–420 nm, and the relative peak heights of this spectrum gave relative rate constants for the population of the various vibrational levels of HF. Allowing for variation in rates of collisional deactivation, by extrapolating back to zero time, comparison of the HF spectra produced by reactions 1 and 2 gave $k_1/k_2=(1.2\pm0.1)$. These authors also gave an estimate for E_1 of 5.95 kJ mol^{-1} (1.42 kcal mol^{-1}), using data for k_2 and k_3 given by (1).

$$F + H_2 \rightarrow HF + H \qquad (3)$$

Relative measurements of k_1 have also been made by Williams and Rowland [4,5] using ^{18}F produced by neutron irradiation of mixtures of SF_6 (370–3040 mm Hg; 49.3–406 kPa)/C_2H_2 (14-587 mm Hg; 1.87–78.3 kPa)/HI (4–260 mm Hg; 0.53–34.7 kPa) at total pressures of $\sim$3000 mm Hg (400 kPa). The products were analysed by radio gas chromatography. The yields of $CH_2=CH^{18}F$, resulting from the reaction sequence 4 and 5.

$$^{18}F + C_2H_2 \rightarrow CH^{18}F=CH \qquad (4)$$

$$CH^{18}F=CH + HI \rightarrow CH_2=CH^{18}F + I \qquad (5)$$

were compared with the total available ^{18}F atoms to give the ratio $(k_{1'}+k_{1''})/k_4=(0.37\pm0.05)$ at 298 K [5]. (A slightly different value is quoted in the earlier report [4] for a temperature of 283 K.)

$$^{18}F + HI \rightarrow H^{18}F + I \qquad (1')$$

$$\rightarrow {}^{18}FI + H \qquad (1'')$$

The alternative reaction 1″ was indistinguishable from reaction 1′. Further experiments were performed in which the $CH_2=CH^{18}F$ yield was reduced by the addition of CH_4 or H_2, and the authors quote $k_{2'}/k_4$ and $k_{3'}/k_4$

$$^{18}F + CH_4 \rightarrow H^{18}F + CH_3 \qquad (2')$$

$$^{18}F + H_2 \rightarrow H^{18}F + H \qquad (3')$$

Therefore we derive the ratios $(k_{1'}+k_{1''})/k_{2'}=(0.90\pm0.2)$ and $(k_{1'}+k_{1''})/k_{3'}=(2.64\pm0.9)$. There is evidence (see Discussions for reactions 2 and 3, sections A6 and A4, respectively) that the ^{18}F atoms used in this study were effectively thermalised, therefore direct comparison between the isotopic and non-isotopic reactions is possible. Using our values for k_2 and k_3 (sections A6 and A4) we obtain $k_1=(3.6\pm0.8)\times10^{13}$ cm^3 mol^{-1} s^{-1} and $(3.96\pm1.4)\times10^{13}$ cm^3 mol^{-1} s^{-1}, respectively, at 298 K. Bearing in mind that these values may contain a contribution from reaction 1″, there is still agreement to within 30% with the value $k_1=(4.8\pm0.4)\times10^{13}$ cm^3 mol^{-1} s^{-1} derived from the k_1/k_2 ratio of Jonathan et al. [3].

Sung and Setser [6] also used a discharge flow system, generating F atoms by passing CF_4/Ar mixtures through the discharge, giving [F] typically$=1.7\times10^{-12}$ mol cm^{-3}, and $[Ar]=4.0\times10^{-8}$ mol cm^{-3}. They added HI or CH_4 downstream, at concentrations between 6.6×10^{-13} and 5×10^{-11} mol cm^{-3}. By comparing the relative total emission intensities from the vibrationally excited HF produced, they derived a value for the ratio k_1/k_2 of (0.74±0.08). Using our recommended value for k_2 (section A6) we obtain $k_1=(2.96\pm0.32)\times10^{13}$ cm^3 mol^{-1} s^{-1} at room temperature.

Because this value and those for the rate constants of reactions of F atoms with the other hydrogen halides obtained in the same study [6] are low, we consider the results of Jonathan et al. [3] and Williams and Rowland [4,5] to be more reliable, and tentatively recommend the value $k_1=(4.1\pm1.3)\times10^{13}$ cm^3 mol^{-1} s^{-1} (300±3 K).

References

[1] Trotman-Dickenson, A. F., and Milne, G. S., National Bureau of Standards, NSRDS-NBS 9 (1967).

[2] Mayer, S. W., and Schieler, L., J. Phys. Chem. **72**, 236 (1968).

[3] Jonathan, N., Melliar-Smith, C. M., Okuda, S., Slater, D. H., and Timlin, D., Molecular Physics **22**, 561 (1971).

[4] Williams, R. L., and Rowland, F. S., J. Phys. Chem. **75**, 2709 (1971).

[5] Williams, R. L., and Rowland, F. S., J. Phys. Chem. **77**, 301 (1973).

[6] Sung, J. P., and Setser, D. W., Chem. Phys. Lett. **48**, 413 (1977).

Note Added in Proof

In a recent paper (J. Phys. Chem. **81**, 898 (1977)) the value of k_1/k_2 obtained by Sung and Setser [6] has been corrected for differences in the vibrational distribution in HF derived from the two reactions. The corrected value of 0.90 leads to a value of k_1 in good agreement with our recommendation.

An absolute measurement of k_1 has been carried out by Wurzberg et al. (see Note Added in Proof, section E2). The value obtained of $(1.6\pm0.4)\times10^{13}$ cm^3 mol^{-1} s^{-1} which, like other rate constants reported in this work, is substantially lower than our recommendation.

E5 $F + Br_2 \rightarrow Br + BrF$

Appelman and Clyne [1] have studied the reactions of fluorine atoms with a series of halogens in a flow system, using mass spectrometric detection. The reactions all display the characteristics of inter-halogen reactions.

$$F + Br_2 \rightarrow Br + BrF; \qquad (1)$$

$$\Delta H^\circ_{298}=-56.421 \text{ kJ mol}^{-1} \ (-13.485 \text{ kcal mol}^{-1})$$

Appelman and Clyne [1] used F_2(<5%)/Ar mixtures at 130 Pa, following the reaction mass spectrometrically, with $[F]>[Br_2]$. When $[F]>>[Br_2]$, BrF_5 could be detected as a product after 100 ms, otherwise reaction 1 was the only process observed. They obtained $k_1=1.9\times10^{14}$ cm^3 mol^{-1} s^{-1} at 298 K, almost equal to the calculated hard sphere collision frequency.

Bemand and Clyne [2] have made two determinations of k_1, both in a discharge flow system, producing F atoms from a discharge through F_2(4%)/He or Ar mixtures at around 200–250 Pa total pressure. The major impurity, O atoms, was not expected to be important compared with the fast inter-halogen reaction. Br_2 was added downstream in excess at 10.4–36 mPa. [F] was monitored by resonance fluorescence between 95–98 nm. Assuming the fluorescence intensity $I_F\propto[F]$, they obtained $k_1=5.4\times10^{13}$ cm^3 mol^{-1} s^{-1} at 300 K. However, because of self-reversal of the $^2P_{3/2}$–$^2P_{3/2}$ transition at 95.48 nm, $I_F \not\propto [F]$, but to f[F]. Measurements of I_F were made over a range of [F], and k_1 recalculated at 8.4×10^{13} cm^3 mol^{-1} s^{-1}, in better agreement with [1]. Clyne combines the two results to give $k_1=1.3\times10^{14}$ cm^3 mol^{-1} s^{-1} at 298–300 K. We recommend this value, with error limits of a factor of three.

References

[1] Appelman, E. H., and Clyne, M. A. A., JCS Faraday I **71**, 2072 (1975).

[2] Bemand, P. P., and Clyne, M. A. A., JCS Faraday II **72**, 191 (1976).

E6 $F + I_2 \rightarrow I + IF$

Unlike the F + Br_2 reaction, the reaction between fluorine atoms and iodine rapidly yields IF_5 as a product, even at reaction times as short as 2 ms. Appelman and Clyne [1] believe this to be due to a heterogeneous reaction involving IF and F atoms, a theory supported by solid deposits on the wall of their flow tube.

$$F + I_2 \rightarrow I + IF; \qquad (1)$$

$$\Delta H^\circ_{298}=-129.35 \text{ kJ mol}^{-1} \ (-30.915 \text{ kcal mol}^{-1})$$

Reaction conditions were the same as those used in the $F+Br_2$ reaction, with $[F]>[I_2]$. A value of $k_1=2.6\times10^{14}$ cm^3 mol^{-1} s^{-1} was obtained at 298 K. Thus the expected trend is shown in the rate constants for $F+X_2$, with $k(I_2)>k(Br_2)>k(Cl_2)$.

Reference

[1] Appelman, E. H., and Clyne, M. A. A., JCS Faraday I **71**, 2072 (1975).

E7 $ClF + M \rightarrow F + Cl + M$

The apparently straight forward decomposition of chlorine fluoride is in fact a process involving several complicating secondary reactions, and its kinetics have not been easy to characterise

$$ClF + M \rightarrow F + Cl + M; \qquad (1)$$

$$\Delta H^\circ_{298}=250.99 \text{ kJ mol}^{-1} \ (59.989 \text{ kcal mol}^{-1})$$

Fletcher et al. have studied the reactions of Cl_2/F_2 mixtures in a static pyrolysis system [4,8]. They found that ClF was formed as a product, but were only able to obtain an overall rate constant for its formation from Cl_2 and F_2. In their chosen mechanism, they initially ignored reaction 1 [4] taking a value of $\sim 10^{17}$ cm^6 mol^{-2} s^{-1} for k_{-1} at 373 K from comparison with k_2 [2] and k_3 [3].

$$F + F + M \rightarrow F_2 + M \qquad (2)$$

$$Cl + Cl + M \rightarrow Cl_2 + M \qquad (3)$$

In a later study [8], reaction 1 was added, and from the measured rate of formation of ClF, by comparison with k_{-3} from [1], a value of 10^{-14} cm^3 mol^{-1} s^{-1} for k_1 was obtained at 423 K.

McIntyre and Diesen [6] investigated the decomposition of ClF in a shock tube over the temperature range 2000–2950 K, anticipating simpler kinetics under these conditions. They shocked ClF (0.5%)/Ne mixtures, following the reaction behind reflected shocks by mass spectrometry. No details of pressure are given. The results led to an apparent rate constant $k_a=7.9\times10^{12}$ exp(-20 900/T) cm^3 mol^{-1} s^{-1}. However, this rate constant is very similar to the rate constant obtained from measurements of Cl_2 dissociation by the same authors, who also found no decrease in [Cl_2] when Cl_2(3–5%)/ClF mixtures were shocked. This led them to believe that the kinetics were being complicated by reaction 4, and they could only recommend $k_1 \cong k_{-3}$.

$$Cl + ClF \rightarrow F + Cl_2 \qquad (4)$$

Blauer et al. [5] also investigated the decomposition in a shock tube, shocking ClF (2.03–5.33%)/Ar mixtures at total pressures of 0.31–2.32 MPa over the temperature range 1718–2167 K. [Cl] was followed by emission spectroscopy at 500 nm. By considering only the initial reaction, the authors claimed to be able to ignore all secondary reactions and obtained k_1(M=Ar)$=1.0\times10^{14}$ exp(-30 900/T) cm^3 mol^{-1} s^{-1}. However, a determination of k_{-4} by Warnatz et al. [7] prompted the authors to re-examine the reaction using a reaction scheme of 1,3,4 and 5.

$$F + ClF \rightarrow Cl + F_2 \qquad (5)$$

Keeping k_{-4} constant, they obtained $k_1=3.0\times10^{14}$ exp(-28 900/T) cm^3 mol^{-1} s^{-1} from a computer fit to the data.

Although the two shock-tube studies agree to within a factor of three over the investigated temperature ranges, there is considerable disagreement in the activation energies obtained. Blauer et al. attribute this to the scatter typically obtained from shock tube experiments. However, because of the uncertainties in the mechanism of the decomposition we make no recommendation.

References

[1] Jacobs, T. R., and Giedt, R. R., J. Chem. Phys. **39**, 749 (1963).

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[4] Fletcher, E. A., and Dahneke, B. E., J. Amer. Chem. Soc. **91**, 1603 (1969).

[5] Blauer, J. A., Solomon, W. C., and Engleman, V. S., J. Phys. Chem. **75**, 3939 (1971).

[6] McIntyre, J. A., and Diesen, R. W., J. Phys. Chem. **75**, 1765 (1971).

[7] Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Ber. Bunsenges. Phys. Chem. **75**, 119 (1971).

[8] Wiersma, S. J., and Fletcher, E. A., J. Phys. Chem. **75**, 867 (1971).

E8 F + ICl → products

Appelman and Clyne [2] have obtained mass-spectrometric evidence for both reactions 1a and 1b.

$$F + ICl \rightarrow Cl + IF; \qquad (1a)$$

$$\Delta H^\circ_{298}=-69.885 \text{ kJ mol}^{-1} \ (-16.703 \text{ kcal mol}^{-1})$$

$$F + ICl \rightarrow I + ClF; \qquad (1b)$$

$$\Delta H^\circ_{298}=-40.447 \text{ kJ mol}^{-1} \ (-9.667 \text{ kcal mol}^{-1})$$

Reaction 1a predominates, ClF forming just 20% of the total products. The authors rejected the possibility of ClF formation via reactions 2 and 3 since $k_2 << k_{1a}$, and [Cl_2] only becomes large when [F] is small. Also $k_3 < k_{1a}$.

$$Cl + ICl \rightarrow I + Cl_2 \qquad (2)$$

$$F + Cl_2 \rightarrow Cl + ClF \qquad (3)$$

The reaction conditions were the same again as for their other studies of the inter-halogen reactions, with [F]>[ICl]. An overall value of $k_1=3\times10^{14}$ cm^3 mol^{-1} s^{-1} was obtained at 298 K. Using their data on product formation, their own value of k_3, and taking k_2 from [1] they obtain $k_{1a}/k_{1b}=3.3\pm0.7$, and hence, using k_1, give $k_{1a}=2.3\times10^{14}$ cm^3 mol^{-1} s^{-1} and $k_{1b}=7.2\times10^{13}$ cm^3 mol^{-1} s^{-1}.

References

[1] Clyne, M. A. A., and Cruse, H. W., JCS Faraday II **68**, 1377 (1972).

[2] Appelman, E. H., and Clyne, M. A. A., JCS Faraday I **71**, 2072 (1975).

E9 F_2 + ClO_2 → F + $FClO_2$

The reaction between fluorine and chlorine dioxide has been investigated only by Aymonino et al. [1].

$$ClO_2 + F_2 \rightarrow FClO_2 + F; \qquad (1)$$

thermodynamic data unavailable for $FClO_2$.

They used a static system with F_2/ClO_2 mixtures at total pressures of 6.67–66.7 kPa, the F_2:ClO_2 ratio being varied by about a factor of 10. In some experiments N_2, O_2 or $FClO_2$ were added as inert gases, but no third body effect was observed. No details given as to how the reaction was followed. Over the temperature range 227–247 K, the authors obtained $k_1=3.5\times10^{10}$ exp(-4300/T) cm^3 mol^{-1} s^{-1}.

Reference

[1] Aymonino, P. J., Sicre, J. E., and Schumacher, H. J., J. Chem. Phys. **22**, 756 (1954).

E10 F + NOCl → products

Two paths are available for the reaction of fluorine atoms with nitrosyl chloride, but there have been no studies of the reaction, and the ratio of the products is unknown.

$$\mathrm{NOCl} + \mathrm{F} \rightarrow \mathrm{NO} + \mathrm{FCl} \qquad (1a)$$

$$\mathrm{NOCl} + \mathrm{F} \rightarrow \mathrm{NOF} + \mathrm{Cl} \qquad (1b)$$

Homann et al. [1] used the reaction as a titration reaction to determine F atom concentrations. They found a 1:1 stoichiometry, following the reaction both mass spectroscopically and by pressure changes in the flow tube. By analogy with reaction 2, they assumed $k_1 > 10^{12}$ cm^3 mol^{-1} s^{-1} at 300 K. Thermodynamic considerations excluded contributions from reactions 3 and 4.

$$\mathrm{NOCl} + \mathrm{Cl} \rightarrow \mathrm{NO} + \mathrm{Cl_2} \qquad (2)$$

$$\mathrm{NOCl} + \mathrm{F} \rightarrow \mathrm{NCl} + \mathrm{FO} \qquad (3)$$

$$\mathrm{NOCl} + \mathrm{F} \rightarrow \mathrm{NF} + \mathrm{ClO} \qquad (4)$$

Reference

[1] Homann, K. H., Solomon, W. C., Warnatz, J., Wagner, H. Gg., and Zetzsch, C., Ber. Bunsenges. Phys. Chem. **74**, 585 (1970).

E11 ClF$_3$ + M → ClF$_2$ + F + M

The dissociation of chlorine trifluoride in shock waves has been studied by Blauer et al. [1]

$$\mathrm{ClF_3} + \mathrm{M} \rightarrow \mathrm{ClF_2} + \mathrm{F} + \mathrm{M}; \qquad (1)$$

thermodynamic data unavailable for ClF$_2$.

ClF$_3$($<2\%$)/Ar mixtures at 0.23–3.19 MPa were shocked. In a number of cases trace quantities of F$_2$ or ClF were added. [ClF$_3$] decay was monitored by u.v. absorption spectroscopy at 220 nm behind incident shocks. From consideration of the initial reaction rates the authors obtained $k_1 = 3.1 \times 10^{13} \exp(-14\,200/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 660–1144 K. No evidence of first order kinetics was seen.

A computer analysis was then made of a six-step reaction mechanism. The most important of the subsequent reactions was reaction 2.

$$\mathrm{F} + \mathrm{ClF_3} \rightarrow \mathrm{ClF_2} + \mathrm{F_2} \qquad (2)$$

Adjusting an assumed value of k_2 until the experimental data were fitted gave $k_2 = 7.5 \times 10^{10} \exp(-1300/T)$ cm^3 mol^{-1} s^{-1} and $k_1 = 7.0 \times 10^{13} \exp(-15\,000/T)$ cm^3 mol^{-1} s^{-1}, in good agreement with the value determined from the initial rate.

Reference

[1] Blauer, J. A., McMath, H. G., and Jaye, F. C., J. Phys. Chem. **73**, 2683 (1969).

E12 H + ClF$_3$ → products

Hydrogen atoms can abstract fluorine from chlorine trifluoride to yield three different sets of products, the predominating route not being clear [6].

$$\mathrm{H} + \mathrm{ClF_3} \rightarrow \mathrm{HF} + \mathrm{ClF_2}; \qquad (1a)$$

No thermodynamic data available for ClF$_2$

$$\mathrm{H} + \mathrm{ClF_3} \rightarrow \mathrm{HF} + \mathrm{ClF} + \mathrm{F}; \qquad (1b)$$

$$\Delta H^\circ_{298} = -303.56 \text{ kJ mol}^{-1} \ (-72.553 \text{ kcal mol}^{-1})$$

$$\mathrm{H} + \mathrm{ClF_3} \rightarrow \mathrm{HF} + \mathrm{Cl} + 2\mathrm{F}; \qquad (1c)$$

$$\Delta H^\circ_{298} = -52.568 \text{ kJ mol}^{-1} \ (-12.564 \text{ kcal mol}^{-1})$$

Jaye and Blauer [1] assumed reaction 1a to be the predominating path, and obtained $k_{1a} = 1.5 \times 10^{12}$ cm^3 mol^{-1} s^{-1} over the temperature range 350–525 K. Few details are available of these experiments, but they appear to have used a flow system producing H atoms in an excess of H$_2$ from a discharge, and followed the reaction by t.o.f. mass spectrometry.

Krogh and Pimentel [2] believed reaction 1c to be important in the HF laser where flash photolysis of ClF$_3$/H$_2$ mixtures was used as the initiation step. If it occurred, reaction 1c would be chain branching. Rabideau [4] investigated reaction 1c to this end, producing H atoms from an H$_2$/He discharge in a flow system at 267 Pa pressure. ClF$_3$ was added in small amounts downstream and the reaction followed by t.o.f. mass spectrometry. No evidence of HF formation was found between 300 and 650 K, and the author concluded that reaction 1c was unimportant under the conditions chosen.

However, in a molecular beam study at 2700 K, Cross [3] fired beams of D atoms at beams of ClF$_3$, and observed DF as a product in a mass spectrometer, attributing this to reaction 1d

$$\mathrm{D} + \mathrm{ClF_3} \rightarrow \mathrm{DF} + \mathrm{ClF_2} \qquad (1d)$$

A similar result was obtained by Haberland and Schmidt [5].

Rabideau [4] attributed the difference between these results to those of his own study to the temperature difference. None of these authors attempted to obtain a rate constant.

The most exhaustive study of reaction 1 has been by Pak et al. [6]. They used a flow system, producing H atoms from a discharge through H$_2$ (0.025%)/He mixtures at 0.53–1.06 kPa pressure with ClF$_3$ added in excess downstream. [H] was followed by e.p.r. spectroscopy. Over the temperature range 243-313 K, they found $k_{\mathrm{exp}} = 7.9 \times 10^{11} \exp(-750/T)$ cm^3 mol^{-1} s^{-1}. Assuming all three reactions 1a–1c possible, and that H atoms could be regenerated by reaction 2, they concluded that $k_{\mathrm{exp}} = k_{1a} - k_{1c}$

$$\mathrm{F} + \mathrm{H_2} \rightarrow \mathrm{HF} + \mathrm{H} \qquad (2)$$

and therefore $k_{1a} \geqslant 7.9 \times 10^{11} \exp(-750/T)$ cm^3 mol^{-1} s^{-1} which is compatible with the value obtained in [1].

In view of the uncertainty in the mechanism of this reaction, no recommendation is made for k_1.

References

[1] Jaye, F. C., and Blauer, J. A., Air Force Rocket Propulsion Lab., Technical Report No. AFRPL-TR-69-62 (1969).
[2] Krogh, O. D., and Pimentel, G. C., J. Chem. Phys. **56**, 969 (1972).
[3] Cross, J. B., J. Chem. Phys. **59**, 966 (1973).
[4] Rabideau, S. W., J. Chem. Phys. **59**, 1533 (1973).
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[6] Pak, S. J., Krech, R. H., MacFadden, D. L., and Maclean, D. I., J. Chem. Phys. **62**, 3419 (1975).

E13 $Cl + Br_2 \rightarrow Br + BrCl$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-25.694	4.347	4.728
300	-25.698	4.335	4.701
500	-26.167	3.155	2.898
1000	-27.083	1.820	1.510
1500	-27.175	1.728	1.037
2000	-26.690	2.000	0.802
2500	-25.958	2.322	0.664
3000	-25.175	2.611	0.574
3500	-24.426	2.837	0.513
4000	-23.753	3.025	0.468
4500	-23.146	3.163	0.414
5000	-22.615	3.272	0.408

RECOMMENDED RATE CONSTANT

$k = 1 \times 10^{14}$ cm^3 mol^{-1} s^{-1}

$= 1.7 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}

Temperature: 298 K

Suggested Error Limits for Calculated Rate Constant: One order of magnitude.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2.3×10^{11}	293	Static photolysis of Br_2 (5-7.5%) at 430 nm in the presence of Cl_2(5-7.5%) and CO_2 at total pressures of 30.7 kPa. [Br_2] monitored by actinometry at 440 nm. CHRISTIE, ROY and THRUSH 1959 (2)	The system was designed to measure the rate of reaction 2. $Br + Cl_2 \rightarrow Cl + BrCl$ 2 Using their k_2 and k_3 from (1) they were able to determine k_1 at 293 K. $Cl + Br_2 \rightarrow Br + BrCl$ 1 $Br + Br + M \rightarrow Br_2 + M$ 3 Because of the high value obtained for k_1, the authors deduced that reaction 1 must have a low activation energy, and by analogy with reaction 2, give the expression $k_1 = 4.5 \times 10^{12}$ exp(-860/

$Cl + Br_2 \rightarrow Br + BrCl$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		CHRISTIE, ROY and THRUSH 1959 (2) continued.	T) cm^3 mol^{-1} s^{-1}. Quoted by (3, 4,9,12 and 13).
7.2×10^{13}	298	Discharge flow system. Cl_2(0.1%)/Ar mixtures at 60 Pa pressure. Br_2 added in excess downstream. [Cl] and [Br] followed by resonance fluorescence at 138 and 157 nm respectively. CLYNE and CRUSE 1972 (12)	Reactant concentrations kept very low as reaction very rapid (∿0.5 of hard sphere bimolecular collision frequency). The result is also in good agreement with reaction cross-sections obtained from molecular beam work (5,6,7,8,10), and also with results for k_4 (11). $F + Cl_2 \rightarrow ClF + Cl$ 4 Authors suspect contribution from heterogeneous recombination of Br atoms for low value in (2). Quoted by (15,16 and 17).
1.1×10^{14}	298	Discharge flow system. Cl_2 (0.1%)/Ar mixtures at 60 Pa pressure. Br_2 added in excess downstream. [Cl] followed by resonance fluorescence at 138 nm. BEMAND 1973 (14) BEMAND and CLYNE 1975 (18)	Conditions similar to those used in (12), except that silicone oil flowmeters were not used to measure the Br_2 flow, since the authors found that Br_2 is removed from dilute Br_2/Ar mixtures by the oil. This, they reason, accounts for the slightly low value of k_1 in (12). Quoted by (19).

Discussion

Amongst the inter-halogen reactions, the reaction between chlorine atoms and bromine has probably received the most attention. It is extremely fast at room temperature, the most recent estimate putting the rate at ~0.7 times the hard sphere bimolecular collision frequency.

$$Cl + Br_2 \rightarrow Br + BrCl \qquad (1)$$

Agreement between the three determinations of k_1 is not good. Of these, that from the Br_2/Cl_2 photochemical system (Christie et al. [2]) is most likely to be in error. k_1 was determined indirectly and required the rates of reactions 2 and 3 for its calculation.

$$Br + Cl_2 \rightarrow Cl + BrCl \qquad (2)$$

$$Br + Br + M \rightarrow Br_2 + M \qquad (3)$$

There are few data available on reaction 2, and the authors neglected the heterogeneous component of reaction 3. The two studies of Clyne et al. [12,18] give a value higher by nearly three orders of magnitude. Owing to its rapid rate, reaction 1 is difficult to study conventionally, but Clyne's results are in good agreement with reaction cross-sections from molecular beam work [5,6,7,8,10].

We consider Clyne's work to be the most accurate and recommend $k_1 = 10^{14}$ cm^3 mol^{-1} s^{-1} at 298 K, with error limits of an order of magnitude.

Rate of the Reverse Reaction

There has been no direct determination of the rate of the reverse reaction -1.

$$Br + BrCl \rightarrow Cl + Br_2 \qquad (-1)$$

Christie et al. [2] calculated $k_{-1} = 3.1 \times 10^6$ cm^3 mol^{-1} s^{-1} at 293 K from their value of k_1 and the equilibrium constant. By comparison with reactions 2 and -2 they obtained $k_{-1} = 2.0 \times 10^{12} \exp(-4000/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 293-333 K. We recommend $k_{-1} = 2 \times 10^9$ cm^3 mol^{-1} s^{-1} at 298 K, derived from Clyne's k_1 and the equilibrium constant, with error limits of an order of magnitude.

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E14 $Cl + HBr \rightarrow HCl + Br$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-65.30	-1.97	11.34
300	-65.30	-1.98	11.27
500	-65.64	-2.81	6.71
1000	-66.66	-4.26	3.26
1500	-67.05	-4.59	2.10
2000	-66.82	-4.46	1.51
2500	-66.28	-4.23	1.17
3000	-65.66	-4.00	0.93
3500	-65.03	-3.81	0.77
4000	-64.45	-3.65	0.65
4500	-63.94	-3.53	0.56
5000	-63.48	-3.44	0.48

RECOMMENDED RATE CONSTANT

$k = (4.70 \pm 0.7) \times 10^{12}$ cm^3 mol^{-1} s^{-1}

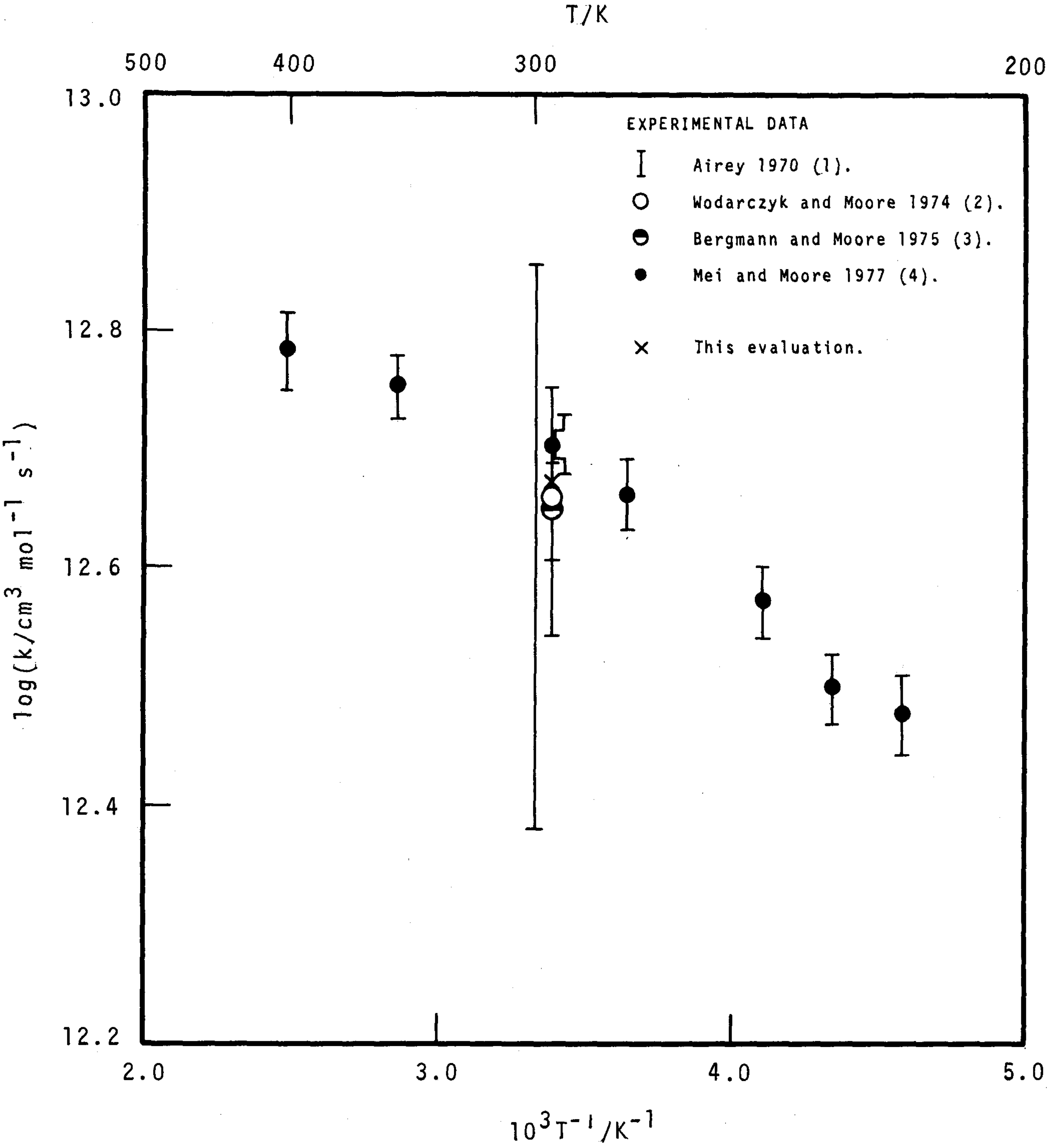
$= (7.81 \pm 1.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}

Temperature: 295 K

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$\geqslant 2.4\times10^{12}$ $\leqslant 7.2\times10^{12}$	300 300	Flash photolysis flow system. Cl_2/HBr mixtures at total pressures ∿8 mm Hg (1.07 kPa) in laser cavity. Laser emission monitored at 4 μm. AIREY 1970 (1)	Theoretical analysis of production of laser pulse compared with observed pulse profile, giving $k_1(v=1)-k_1(v=0) \simeq 2.4\times10^{12}$ cm^3 mol^{-1} s^{-1} $Cl + HBr \rightarrow HCl(v) + Br$ 1 Calculations of profile shapes found to be similar with either $k_1(v=0)=0$, $k_1(v=1)=2.4\times10^{12}$ cm^3 mol^{-1} s^{-1}, or $k_1(v=0)=2.4\times10^{12}$, $k_1(v=1)=4.8\times10^{12}$ cm^3 mol^{-1} s^{-1}. Taking overall rate constant k_1 as $(k_1(v=0)+k_1(v=1))$, these values give limits as shown.

$Cl + HBr \rightarrow HCl + Br$



Cl + HBr → HCl + Br

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.58 \pm 1.1) \times 10^{12}$	295	Laser photolysis flow system. Cl_2/HBr/Ar mixtures, at ratios ∿1:2:15, total pressures 20 mm Hg (2.7 kPa), photolysed by 347.1 nm laser pulse. HCl chemiluminescence monitored over range 3.5-4.3 μm. WODARCZYK and MOORE 1974 (2)	Rates of reaction 1 and HCl vibrational energy transfer to HBr are comparable, so equation governing emission intensity could not be simplified by ingoring latter. However as most of HCl emission from v=1, intensities for v>1 neglected, leaving expression for emission intensity as sum of exponential rise and exponential decay. Extrapolation of linear semi-logarithmic decay enabled correction to be made to rise of fluorescence. Value of k_1 obtained from resulting reaction time for HBr pressures 0.1-4.5 mm Hg (13.3-600 Pa).
$(4.46 \pm 0.4) \times 10^{12}$	295±2	Laser photolysis flow system. Cl_2/HBr/Ar mixtures, with $[Cl_2]$:[HBr]:[Ar] ratios in range 0.5:1:150 to 10:1:150, at total pressures 15 mm Hg (2 kPa). Photolysis by N_2 laser pulse at 337 nm. HCl chemiluminescence monitored in region 3.39-4.82 μm. BERGMANN and MOORE 1975 (3)	Signal averaged emission profiles compared with computed profiles, allowing for quenching of excited HCl by HBr, giving best fit to k_1 as shown. Cl + HBr → HCl + Br 1 Reaction 1D also investigated, under same conditions, and value $k_{1D} = (2.99 \pm 0.3) \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ obtained. Cl + DBr → DCl + Br 1D
$(3.00 \pm 0.2) \times 10^{12}$ $(3.16 \pm 0.2) \times 10^{12}$ $(3.73 \pm 0.3) \times 10^{12}$ $(4.61 \pm 0.3) \times 10^{12}$ $(5.06 \pm 0.3) \times 10^{12}$ $(5.67 \pm 0.4) \times 10^{12}$ $(6.08 \pm 0.5) \times 10^{12}$	218 230 243 274.5 294.5 349 402	Laser photolysis flow system. Cl_2(0.07-0.38 mm Hg; 9.3-50.7 Pa)/HBr(0.06-0.46 mm Hg; 8-61.3 Pa)/Ar (9.8-15.5 mm Hg; 1.3-2.1 kPa) mixtures, with $[Cl_2]$:[HBr]:[Ar] ratios ranging from 0.3:1:100 to 3:1:100, photolysed by N_2 laser at 337 nm. Chemiluminescence from HCl monitored 3.2-4.2 μm. MEI and MOORE 1977 (4)	Pre-reaction between Cl_2 and HBr minimised by low [HBr] showed to be successful by absence of dependence of rates upon $[Cl_2]$/[HBr] ratio. Values of k_1 derived from fluorescence profiles as in (3).

Discussion

The high exothermicity of the reaction between Cl atoms and HBr leads to excited state HCl (v⩾0) which produces chemiluminescence. This can be usefully used to produce a chemical laser.

$$Cl + HBr \rightarrow HCl + Br \qquad (1)$$

Reaction 1 has been studied in all cases by using the emission intensity-governing equation to match the observed fluorescence profiles. Allowance has been made for the quenching of excited HCl by HBr. The reaction has been studied extensively by Moore et al. [2,3,4], whose room temperature measurements of k_1 fall within the limits previously determined by Airey [1]. Although there is no independent confirmation of Moore's data, his room temperature values are within 15% of each other, and their error limits become successively smaller. We therefore recommend a value at 295 K of $(4.7 \pm 0.7) \times 10^{12}$ cm^3 mol^{-1} s^{-1}.

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E15 $Cl + HI \rightarrow HCl + I$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-133.20	-4.09	23.12
300	-133.20	-4.10	22.98
500	-133.56	-4.99	13.69
1000	-135.02	-6.99	6.69
1500	-136.28	-8.02	4.33
2000	-137.05	-8.47	3.14
2500	-137.36	-8.61	2.42
3000	-137.29	-8.59	1.94
3500	-136.93	-8.49	1.60
4000	-136.41	-8.35	1.35
4500	-135.77	-8.19	1.15
5000	-135.09	-8.05	0.99

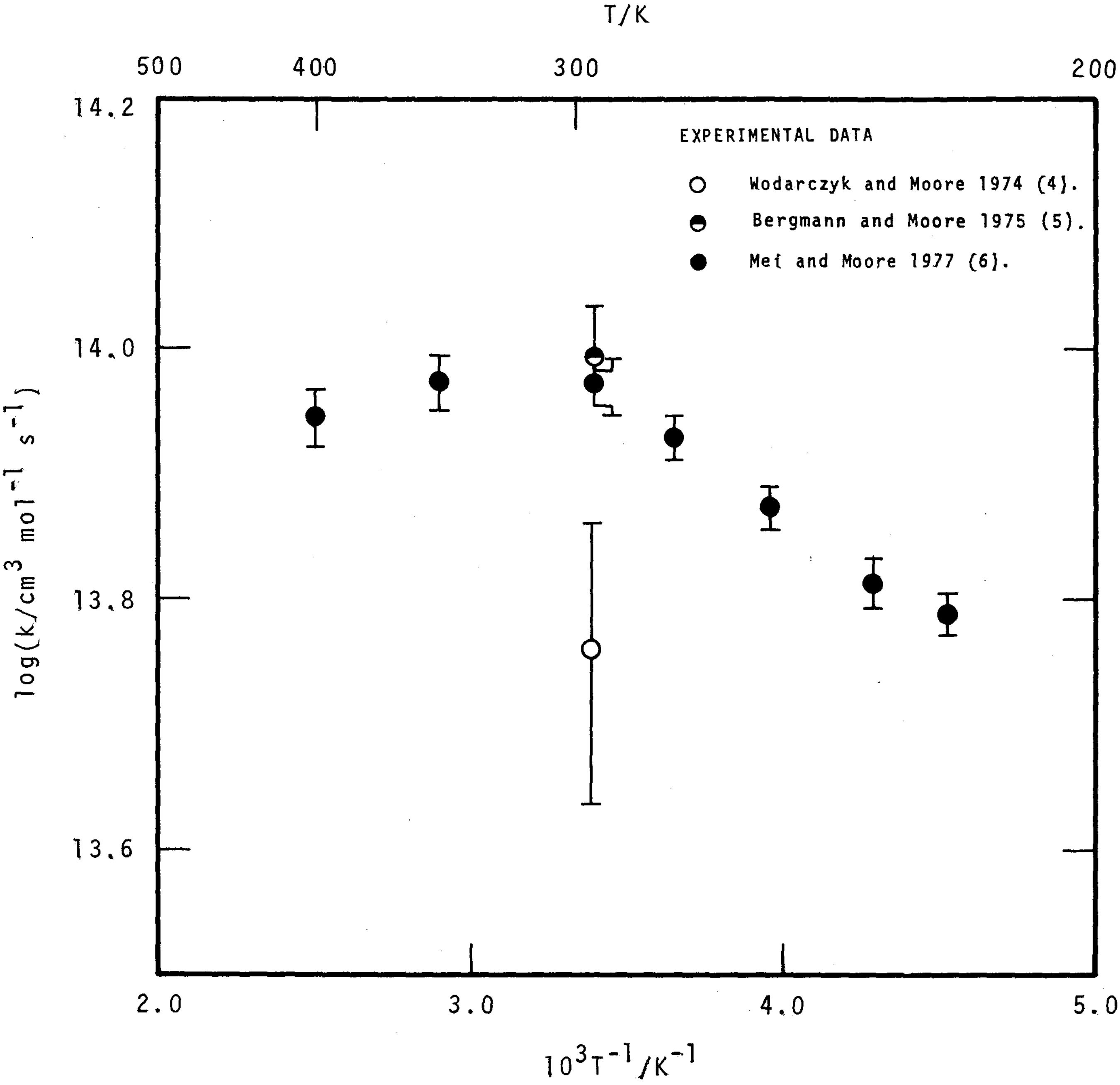
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(5.78 \pm 1.5) \times 10^{13}$	295	Laser photolysis flow system. Cl_2/HI/Ar mixtures (ratios ∿1:1:30) at total pressures 20 mm Hg (2.7 kPa), photolysed by laser pulse at 347.1 nm. HCl ir chemiluminescence monitored at 3.5-4.3 μm. WODARCZYK and MOORE 1974 (4)	Relaxation of excited HCl ∿2 orders of magnitude slower than reaction rate, so governing equation for emission intensity simplified, giving k_1 directly from rise time of chemiluminescence $Cl + HI \rightarrow HCl + I$ 1 For HI pressures 0.1-0.75 mm Hg (13.3-100 Pa) value of k_1 found as given here. Error limits due to ∿15% uncertainty in HI pressure and ∿10% uncertainty in gradients of semi-logarithmic intensity plots.

$Cl + HI \rightarrow HCl + I$



$Cl + HI \rightarrow HCl + I$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(9.88^{+1.0}_{-0.4})x10^{13}$	295±2	Laser photolysis flow system. $Cl_2/HI/Ar$ mixtures, with $0.5{:}1{:}150 \leqslant [Cl_2]{:}[HI]{:}[Ar] \leqslant 10{:}1{:}150$, photolysed by N_2 laser pulse at 337 nm. Total pressures 15 mm Hg (2 kPa), Cl_2 and HI partial pressures $\not>$0.4 mm Hg (53.3 Pa). HCl chemiluminescence monitored at 3.39-4.82 μm. BERGMANN and MOORE 1975 (5)	Values of k_1 derived from rise time of signal averaged intensity profiles. Larger upper error limit attributed to possible slight influence of pre-reaction $Cl_2 + HI \rightarrow HCl + ClI$ as an increase in k_1 was observed with decreasing $[Cl_2]$. No comment made on 70% increase in k_1 over value from (4).
$(6.14\pm0.2)x10^{13}$ $(6.50\pm0.3)x10^{13}$ $(7.47\pm0.3)x10^{13}$ $(8.49\pm0.4)x10^{13}$ $(9.33\pm0.5)x10^{13}$ $(9.40\pm0.5)x10^{13}$ $(8.79\pm0.5)x10^{13}$	221 233 253 274.5 294.5 345 400	Laser photolysis flow system. Cl_2 (0.03-0.15 mm Hg; 4-20 Pa)/HI(0.03-0.14 mm Hg; 4-18.7 Pa)/Ar(10.3-13.4 mm Hg; 1.4-1.8 kPa) mixtures photolysed by N_2 laser pulse at 337 nm. $[Cl_2]{:}[HI]{:}[Ar]$ ratios varied 0.3:1:100 to 3:1:100. Fluorescence from excited HCl monitored over range 3.2-4.2 μm. MEI and MOORE 1977 (6)	k_1 derived from rise of emission profiles as in (5). Pre-reaction minimised by low Cl_2 and HI pressures, shown successful by absence of effect on rates of $[Cl_2]/[HI]$ ratios. k_{1D} was also measured in this system, under the same conditions as for k_1 $Cl + DI \rightarrow DCl + I$ 1D giving $k_{1D}=(5.35^{+0.8}_{-0.4})x10^{13}\ cm^3\ mol^{-1}\ s^{-1}$.

Discussion

Theoretical studies of the relative rates of production of HCl in excited vibrational states by the reaction of Cl atoms and hydrogen iodide have been made by Polanyi et al. [3], and studied experimentally by [1 and 2] using molecular beams. However there have only been three studies of the absolute rate of reaction 1

$$Cl + HI \rightarrow HCl + I \qquad (1)$$

all by Moore et al. [4,5,6] in a pulsed laser photolysis system. No explanation was given for the first of their room temperature measurements [4] being ~70% lower than the subsequent values [5,6]. Although the results at 295 K of [5 and 6] are within 6% of each other, because the values of k_1 fall above 300 K [6], and because of the lack of independent corroboration of these results, we make no recommendation for k_1.

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Miscellaneous Inter-Halogen Reactions Involving Cl Atoms

E16 $Cl + F_2 \rightarrow ClF + F$

Prior to any measurements of k_1

$$Cl + F_2 \rightarrow ClF + F \qquad (1)$$

$$\Delta H^\circ_{298} = -93.2 \text{ kJ mol}^{-1} \ (-22.27 \text{ kcal mol}^{-1})$$

estimates of 10^{13} and 10^{14} cm^3 mol^{-1} s^{-1} were used ([2] and [5], respectively), the latter being derived from Mayer and Schieler's [1] estimated Arrhenius expression. However Schatz and Kaufman [6] found in their study of F-atom reactions that k_1 was considerably smaller than these estimates.

Bemand [7] found in his flow system investigation that $k_1 < 2.41 \times 10^{13}$ cm^3 mol^{-1} s^{-1} (as reported by [11]). Further study in the same laboratory [10] using the same flow system gave $k_1 < 3 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 298 K.

In a footnote to their discharge flow system investigation Ganguli and Kaufman [8] quote that they used molecular beam analysis to show that $k_1 < 10^9$ cm^3 mol^{-1} s^{-1} at 295 K.

Apart from these room temperature upper limits to k_1 there has been a low pressure (77 mm Hg; 10.3 kPa) flame study of the reaction between F_2 and CCl_2F_2 by Homann and Maclean [4]. Stoichiometric mixtures of F_2 and CCl_2F_2 were burnt, quasi-premixed, on a multidiffusion burner, and the concentration profiles across the reaction zone were measured by a molecular beam sampling technique using a time-of-flight mass spectrometer. The authors interpreted their data according to the simple reaction mechanism

$$F + CCl_2F_2 \rightarrow Cl + CClF_3 \qquad (2)$$

$$Cl + F_2 \rightarrow ClF + F \qquad (1)$$

$$F + CClF_3 \rightarrow Cl + CF_4 \qquad (3)$$

$$ClF + Cl \rightleftharpoons F + Cl_2$$

and from the $[CClF_3]$ maximum, and the simultaneous values of $d[F_2]/dt$ and $d[CCl_2F_2]/dt$, they obtained respectively $k_2/k_3 = 7$ at 1600 K, and $k_1/k_2 = 50$ at 1500 K. Taking $k_3 = 6.31 \times 10^{13} \exp(-10\,510/T)$ cm^3 mol^{-1} s^{-1} from the review by Foon and Kaufman [9] we obtain a value for k_1 in the region of 10^{13} cm^3 mol^{-1} s^{-1}. However Foon and Kaufman [9] point out that at similar temperatures, in Cl_2/F_2 flames, Ambs and Fletcher [3] observed light emission similar to that due to Cl-atom recombination in H_2/Cl_2 flames, even with excess F_2. The inference is that reaction 1 is still insufficiently fast at flame temperatures, and that an alternative mechanism is in operation [9].

Although we make no recommendation for k_1, we consider reaction 1 to be sufficiently slow that it may be ignored in most Cl_2/F_2 systems.

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E17 $Cl + BrCl \rightarrow Br + Cl_2$

Chlorine atoms react rapidly with bromine monochloride in a typical inter-halogen reaction

$$Cl + BrCl \rightarrow Br + Cl_2; \qquad (1)$$

$$\Delta H^\circ_{298} = -24.075 \text{ kJ mol}^{-1} \ (-5.754 \text{ kcal mol}^{-1})$$

Christie et al. studied both reaction 1 and its reverse in a photolytic system [3]. They photolysed Br_2 (5–7.5%) at 430 nm in the presence of Cl_2 (5–7.5%) and CO_2 at total pressures of ~30.7 kPa. $[Br_2]$ was monitored by actinometry at 440 nm. The authors concluded that following the photodissociation of the bromine, only reactions -1 and 2 occurred in the initial period.

$$Br + Br + M \rightarrow Br_2 + M \qquad (2)$$

Taking k_2 from [1] they obtained $k_{-1}=4.5\times10^{12}$ exp(-3500/T) cm^3 mol^{-1} s^{-1} over the temperature range 293–333 K. Using thermodynamic data from [2] they calculated $k_1=2.0\times10^{12}$ exp(-560/T) cm^3 mol^{-1} s^{-1}. Using the most recent JANAF data we obtain $k_1=2.5\times10^{11}$ cm^3 mol^{-1} s^{-1} at 298 K, compared with their value of 3.0×10^{11} cm^3 mol^{-1} s^{-1}. Another potential source of error is heterogeneous recombination of Br atoms which was not considered by Christie et al.[4].

Clyne and Cruse [4] studied reaction 1 in a flow system. Cl atoms were produced in a discharge through Cl_2 (0.1%)/Ar mixtures at 60 Pa pressure. BrCl was added downstream, and [Cl] and [Br] followed by resonance fluorescence at 138 and 157 nm, respectively. Under these conditions, reaction -1 is unimportant at 298 K, and the authors obtained $k_1=8.7\times10^{12}$ cm^3 mol^{-1} s^{-1}. In a similar study of reaction 3, Clyne made refinements to the experimental technique and produced a slightly higher value of k_3 some years later [5]. In view of this, no recommendation is made for k_1.

$$Cl + Br_2 \rightarrow Br + BrCl \qquad (3)$$

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E18 Cl + ICl → I + Cl_2

There has been only one absolute determination of the rate of reaction 1

$$Cl + ICl \rightarrow I + Cl_2 \qquad (1)$$

$$(\Delta H^\circ_{298}=-32.03 \text{ kJ mol}^{-1};\ -7.66 \text{ kcal mol}^{-1})$$

Clyne and Cruse [3] used a discharge flow system in which the pseudo first order decay of Cl atoms (initially at 2×10^{-12} mol cm^{-3}) was followed by Cl resonance fluorescence at 138 nm. The values of [ICl] varied from 4.8×10^{-12} to 3.3×10^{-11} mol cm^{-3}. They obtained the value $k_1=(4.82\pm0.6)\times10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K. A few measurements of the I atom production rate, using I resonance fluorescence at 183 nm, gave values of k_1 generally in agreement with this value, despite scattering of data due to interference from I emission produced by the photolysis of ICl.

In an earlier static photolysis study by Christie et al. [2] I_2 absorption at 570 nm was monitored following the photolysis of ICl (5 mm Hg; 666.5 Pa)/Ne (210 and 510 mm Hg; 28 and 68 kPa), or N_2 (120–450 mm Hg; 16–60 kPa), or CO_2 (300 and 600 mm Hg; 40 and 80 kPa) mixtures. The variation of I_2 production with [M] showed the mechanism for ICl decomposition to be

$$ICl + h\nu \rightarrow I + Cl$$

$$Cl + ICl \rightarrow I + Cl_2 \qquad (1)$$

$$I + I + M \rightarrow I_2 + M \qquad (2)$$

$$I + Cl + M \rightarrow ICl + M \qquad (3)$$

$$Cl + Cl + M \rightarrow Cl_2 + M \qquad (4)$$

Using the steady-state approximation, k_1 was given as the roots of a quadratic equation involving k_2, k_3 and k_4. Taking $k_4=k_3/2=k_2$, this equation was simplified to give $k_1 \propto k_2^{1/2}$. We have little data for k_4 over a wide variety of third bodies (see section B2) but it appears that $k_4 \cong 2k_2$, and hence the above derivation of k_1 is incorrect. Because of the complicated nature of the solution for k_1, and the uncertainty in the values for k_3 and k_4, we can only comment that the values $k_1=1.05\times10^8$ (303 K) and 2.05×10^8 cm^3 mol^{-1} s^{-1} (333 K) quoted by Christie et al. [2] appear to be much too low. Although the temperature range of this study was only 30 K, the authors expressed k_1 as 5×10^{11} exp(-2270/T) cm^3 mol^{-1} s^{-1}.

Burns and Dainton [1] used a semi-empirical method to estimate k_1, using potential energy surfaces based on the London model. They derived the expression $k_1=1.6\times10^{13}$ exp(-1180/T) cm^3 mol^{-1} s^{-1}. At 298 K this gives a value of k_1 an order of magnitude below that of Clyne and Cruse [3].

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E19 Cl + I + M → ICl + M

The only study of the combination of iodine and chlorine atoms has been by Maier and Lampe [5], investigating reactions following the flash photolysis of ICl.

$$I + Cl + M \rightarrow ICl + M; \qquad (1)$$

$$\Delta H^\circ_{298}=-210.55 \text{ kJ mol}^{-1}\ (-50.322 \text{ kcal mol}^{-1})$$

ICl was flash photolysed alone or in ICl (1.7–5%)/N_2 or CO_2 mixtures, at total pressures of 40.0–80.0 kPa. [I_2] and [ICl] were monitored by absorption spectroscopy at 520 and 470 nm, respectively. The reaction scheme proposed by Christie et al. [2] was adopted.

$$ICl + h\nu \rightarrow I + Cl$$

$$\mathrm{Cl + ICl \rightarrow I + Cl_2} \qquad (2)$$

$$\mathrm{I + I + M \rightarrow I_2 + M} \qquad (3)$$

$$\mathrm{I + Cl + M \rightarrow ICl + M} \qquad (1)$$

$$\mathrm{Cl + Cl + M \rightarrow Cl_2 + M} \qquad (4)$$

Reaction 2 was ignored, as [ICl] increased in a similar manner to [I_2]. Assuming $[I]_0=[Cl]_0$, and taking $k_3(M=CO_2)$ and $k_3(M=N_2)$ from [1 and 3], $k_1(M=CO_2,N_2)$ could be determined. Separate experiments were performed by the authors to give $k_3(M=ICl)$, which agreed well with $k_3(M=I_2)$ as determined by [3]. The final values obtained at 325 K were $k_1(M=N_2)=6.1\times10^{16}$ cm^6 mol^{-2} s^{-1}; $k_1(M=CO_2)=1.6\times10^{17}$ cm^6 mol^{-2} s^{-1}; $k_1(M=ICl)=4.4\times10^{17}$ cm^6 mol^{-2} s^{-1}. The value for $k_1(M=ICl)$ was much as expected, falling midway between $k_3(M=I_2)$ [3] and $k_4(M=Cl_2)$ [4].

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[4] Clyne, M. A. A., and Stedman, D. H., Trans. Faraday Soc. **64**, 2698 (1968).

[5] Maier, H. N., and Lampe, F. W., J. Phys. Chem. **77**, 430 (1973).

E20 $\mathrm{Cl + NF_2 + M \rightarrow NF_2Cl + M}$

The third order combination reactions of the difluoramino radical with halogen atoms have been studied by Clyne et al. [1,2]. A steady decrease in rate is seen in the order F>Cl>Br.

$$\mathrm{NF_2 + Cl + M \rightarrow NF_2Cl + M;} \qquad (1)$$

thermodynamic data unavailable for NF_2Cl.

Reaction 1 was studied by Clyne and Connor [1], in a flow system, Cl atoms being produced by a discharge through Cl_2 at 8.1 Pa pressure and added to a flow of NF_2 radicals in Ar at total pressures of 162–324 Pa, NF_2 radicals being formed by thermal decomposition of N_2F_4. Concentrations of [NF_2] and [Cl] were approximately equal. [Cl] was followed by observing the chlorine afterglow at 525 nm after titration with NOCl. Although the Cl concentration was seen to fall away, *no* change was noticed in [NF_2], which was followed by u.v. absorption spectroscopy at 260 nm. This led the authors to postulate a rapid subsequent reaction 2, regenerating NF_2.

$$\mathrm{Cl + NF_2Cl \rightarrow NF_2 + Cl_2} \qquad (2)$$

On this basis, they obtained $k_1=9.7\times10^{16}$ cm^6 mol^{-2} s^{-1} at 293 K.

References

[1] Clyne, M. A. A., and Conner, J., JCS Faraday II **68**, 1220 (1972).

[2] Clyne, M. A. A., and Watson, R. T., JCS Faraday I **70**, 1109 (1974).

E21 $Br + F_2 \rightarrow BrF + F$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-91.412	9.904	16.532
300	-91.408	9.929	16.433
500	-90.789	11.535	10.087
1000	-90.199	12.439	5.362
1500	-90.596	12.142	3.789
2000	-91.575	11.581	2.996
2500	-92.830	11.029	2.516
3000	-94.190	10.531	2.190
3500	-95.575	10.100	1.954
4000	-96.964	9.732	1.775
4500	-98.358	9.406	1.632
5000	-99.751	9.109	1.518

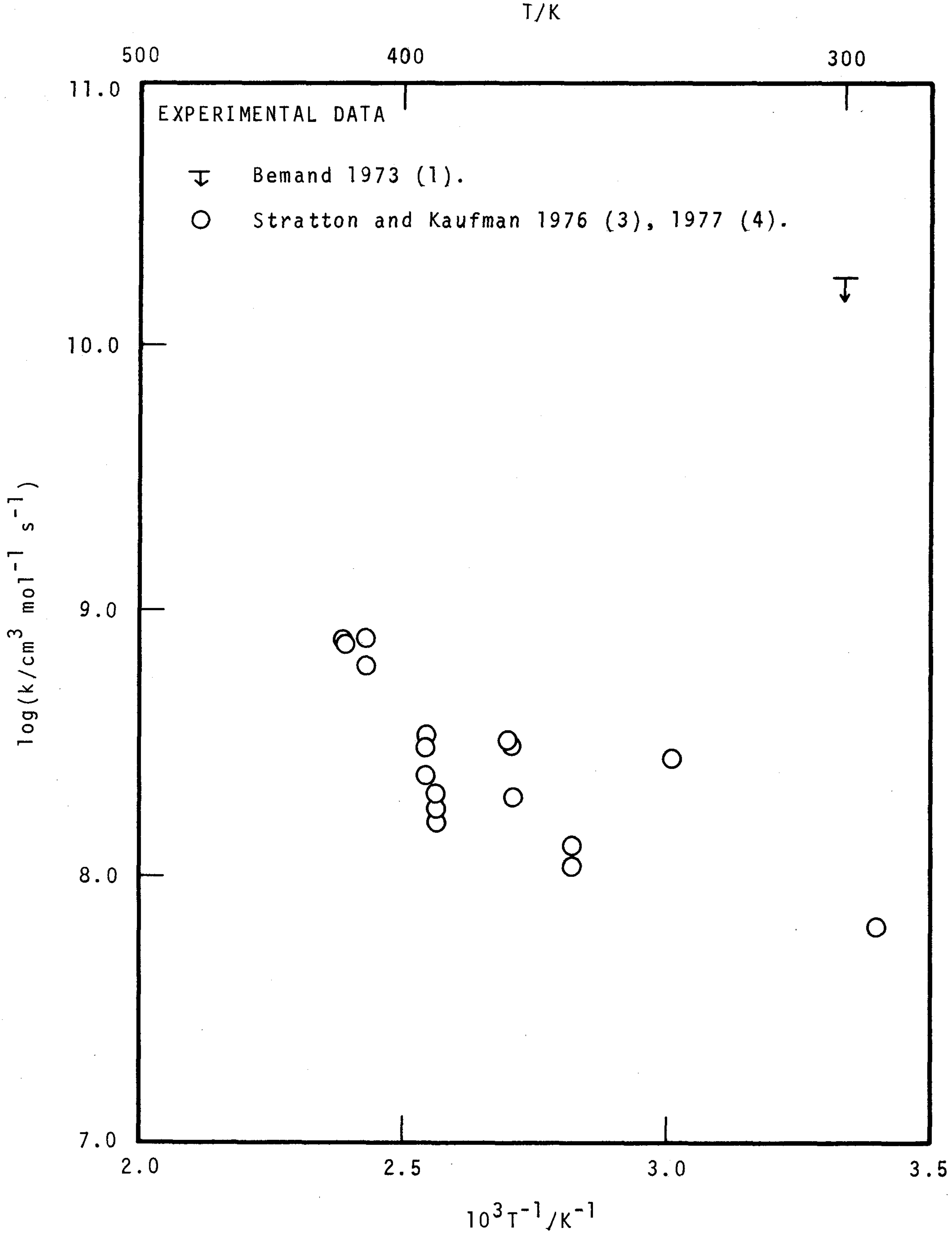
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$<1.81 \times 10^{10}$	∿300	Flow system. Few details. Resonance fluorescence of either Br or F atoms used to follow reaction. BEMAND 1973 (1)	Upper limit obtained as secondary result in study of F atom reactions. Value reported by (2).
6.38×10^{7} 2.73×10^{8} 1.07×10^{8} 1.28×10^{8} 1.97×10^{8} 3.07×10^{8} 3.18×10^{8} 1.58×10^{8} 1.75×10^{8} 2.02×10^{8} 2.38×10^{8} 3.01×10^{8} 3.37×10^{8} 6.13×10^{8} 7.84×10^{8} 7.45×10^{8} 7.66×10^{8}	296 332 354 354 369 369 370 390 390 390 393 393 393 411 411 418 418	Discharge flow system. Br_2 (∿1-2%)/He mixtures passed through discharge, giving $1.2 \times 10^{-10} \leqslant [Br] \leqslant 6.03 \times 10^{-10}$ mol cm^{-3}. F_2 added downstream via moveable inlet. Total pressures 0.38-0.84 mm Hg (50.7-112.0 Pa). Production of BrF monitored by mass spectrometry. STRATTON and KAUFMAN 1976 (3) and 1977 (4)	Stoichiometry of 2 assumed, owing to further BrF production by reaction 2 $F + Br_2 \rightarrow BrF + Br$ 2 k_1 derived from [BrF] at fixed reaction time as function of $[F_2]$, assuming [Br] constant. No systematic variation of k_1 with pressure or [Br], nor did packing tube affect k_1. Least squares fit to these data given as $k_1 = 7.89 \times 10^{10} \exp(-2150/T)$ cm^3 mol^{-1} s^{-1}. $Br + F_2 \rightarrow BrF + F$

$Br + F_2 \rightarrow BrF + F$



Discussion

There are insufficient data on the rate of this inter-halogen reaction to make a recommendation. Stratton and Kaufman's discharge flow results [3,4] are below Bemand's upper limit [1], but show considerable scatter (almost a factor of 2).

References

[1] Bemand, P. P., Ph. D. Thesis, University of London (1973).

[2] Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., Int. J. Chem. Kinet. **8**, 425 (1976).

[3] Stratton, L. W., and Kaufman, M., Emory University, Report TR 12 (1976).

[4] Stratton, L. W., and Kaufman, M., J. Chem. Phys. **66**, 4963 (1977).

Miscellaneous Inter-Halogen Reactions Involving Br Atoms

E22 Br + ICl → I + BrCl

Of the exothermic inter-halogen reactions, that between bromine and iodine monochloride is anomalously slow. The reason is not clear, but Lee et al. [1], in a crossed molecular beam study, report that the collision complex BrClI is long-lived.

$$\mathrm{Br} + \mathrm{ICl} \rightarrow \mathrm{I} + \mathrm{BrCl}; \qquad (1)$$

$$\Delta H^\circ_{298} = -31.330 \text{ kJ mol}^{-1} \ (-7.488 \text{ kcal mol}^{-1})$$

The alternative reaction path to Cl + IBr is not energetically favourable.

Clyne and Cruse [2] studied the reaction in their flow system, producing Br atoms by a discharge through Br_2 (0.1%)/Ar mixtures at 60 Pa pressure, and adding ICl downstream so that [Br]>[ICl]. [I] was followed by resonance fluorescence at 183 nm, and [Br] measured by NOCl titration. A value of $k_1 = 1.8 \times 10^{10}$ cm^3 mol^{-1} s^{-1} was obtained at 298 K.

References

[1] Lee, Y. T., McDonald, J. D., LeBreton, P. R., and Herschbach, D. R., J. Chem. Phys. **49**, 2447 (1968).

[2] Clyne, M. A. A., and Cruse, H. W., JCS Faraday II **68**, 1377 (1972).

E23 Br + IBr → I + Br_2

The reaction between bromine and iodine monobromide is difficult to study due to the position of equilibrium of reaction 2, allowing appreciable concentrations of IBr, I_2 and Br_2 to co-exist at 298 K.

$$\mathrm{Br} + \mathrm{IBr} \rightarrow \mathrm{I} + \mathrm{Br_2}; \qquad (1)$$

$$\Delta H^\circ_{298} = -15.067 \text{ kJ mol}^{-1} \ (-3.601 \text{ kcal mol}^{-1})$$

$$\mathrm{IBr} \rightleftharpoons \tfrac{1}{2}\mathrm{I_2} + \tfrac{1}{2}\mathrm{Br_2} \qquad (2)$$

Clyne and Cruse [3] studied the reaction in a flow system, producing Br atoms by a discharge through Br_2 (0.1%)/Ar mixtures at 60 Pa pressure, and adding IBr downstream. [I] was monitored by resonance fluorescence at 183 nm in an excess of Br atoms. Under these conditions the problem of IBr dissociation was not important. A value of $k_1 = 2.1 \times 10^{13}$ cm^3 mol^{-1} s^{-1} was obtained at 298 K. When measurements were made with [IBr]>[Br], and following [Br] at 157 nm, a value of $k_1 = 1.6 \times 10^{13}$ cm^3 mol^{-1} s^{-1} was obtained, lower as expected due to the incorrect estimation of [IBr].

Donovan et al. [2] considered reaction 1 to be an important source of ground state $I(^2P_{3/2})$ atoms following reactions -1′ and 3′ in a study of the reactions of excited $I(^2P_{5/2})$ atoms.

$$\mathrm{I}(^2P_{1/2}) + \mathrm{Br_2} \rightarrow \mathrm{Br} + \mathrm{IBr} \qquad (-1')$$

$$\mathrm{I}(^2P_{1/2}) + \mathrm{IBr} \rightarrow \mathrm{Br} + \mathrm{I_2} \qquad (3')$$

To test this possibility, they photolysed Br_2 to give Br atoms in the presence of IBr, so that [Br]>[IBr]. Assuming photolysis of 15% of the Br_2 and neglecting bromine recombination, the authors followed [I] by u.v. absorption spectroscopy at 178.3 nm and obtained $k_1 = 2.3 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 300 K. No further details are available. The low value is probably reasonable in view of the approximations made. Using thermodynamic data from [1] they obtained $k_{-1} = 1.6 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 300 K. Using the most recent JANAF data, we obtain $k_{-1} = 1.3 \times 10^{10}$ cm^3 mol^{-1} s^{-1}.

In view of the lack of agreement we make no recommendation, but prefer Clyne's value for k_1 in view of his success in determining rate constants of other inter-halogen reactions with this same system.

References

[1] Herzberg, G., "Spectra of Diatomic Molecules" (Van Nostrand, New York, 1961).

[2] Donovan, R. J., Hathorn, F. G. M., and Husain, D., Trans. Faraday Soc. **64**, 1228 (1968).

[3] Clyne, M. A. A., and Cruse, H. W., JCS Faraday II **68**, 1377 (1972).

E24 Br + ClO_2 → BrO + ClO

The exact mechanism of the reaction of bromine atoms with chlorine dioxide is uncertain, as stated above.

$$\mathrm{Br} + \mathrm{ClO_2} \rightarrow \mathrm{BrO} + \mathrm{ClO} \qquad (1)$$

Clyne and Coxon [1] studied the reaction in a flow system, producing Br atoms by a discharge through dilute Br_2/Ar mixtures at 133–400 Pa total pressure. ClO_2 was added downstream and [ClO_2] decay followed by u.v. absorption spectroscopy at 351.5 nm. Attempts to observe ClO and BrO proved fruitless, and the authors concluded that the reaction proceeded directly to the observed products, BrCl and O_2. They obtained the rate constant $k_1 = 3.1 \times 10^{10}$ cm^3 mol^{-1} s^{-1} at 300 K.

In later experiments [2], they were able to observe the ClO radical, and thus doubted their own interpretation of the reaction. Basco and Dogra [3] were able to observe both ClO and BrO in their flash photolysis and thus characterised the decomposition mechanism as occurring by reaction 1. Later, Watson [4] re-assessed the reaction in a flow system, using mass-spectrometry to follow the reaction, and found the reverse reaction k_{-1} more important than had been considered previously. At 298 K, he obtained $k_1 = 2.5 \times 10^{11}$ $cm^3\ mol^{-1}\ s^{-1}$.

In view of the uncertainty in the mechanism of the reaction, no recommendation is made for k_1.

References

[1] Clyne, M. A. A., and Coxon, J. A., Proc. Roy. Soc. **A298**, 424 (1967).

[2] Clyne, M. A. A., and Coxon, J. A., Proc. Roy. Soc. **A303**, 207 (1968).

[3] Basco, N., and Dogra, S. K., Proc. Roy. Soc. **A323**, 417 (1971).

[4] Clyne, M. A. A., and Watson, R. T., JCS Faraday I **73**, 1169 (1977).

E25 Br + NOCl → NO + BrCl

There has been only one study of the fast reaction 1, by Clyne and Cruse [2].

$$\mathrm{Br + NOCl \rightarrow NO + BrCl;} \tag{1}$$

$$\Delta H^\circ_{298} = -58.700\ \mathrm{kJ\ mol^{-1}}\ (-14.030\ \mathrm{kcal\ mol^{-1}})$$

Br atoms were generated in a discharge through Br_2 at ~150 Pa, and NOCl added in excess downstream at 0.60–2.69 Pa. [Br] was followed by resonance fluorescence at 157.7 nm. A value of $k_1 = 6.0 \times 10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ was obtained at 298 K. A preliminary value of $k_1 = 2.0 \times 10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ is attributed to these authors by [1] and quoted by [5]. Like the better known reaction of Cl atoms with NOCl, reaction 1 can be used as a titration reaction, to estimate Br atom concentrations [3,4].

In the absence of further work on reaction 1, no recommendation for k_1 is given.

References

[1] Clyne, M. A. A., Coxon, J. A., and Woon-Fat, A. R., Faraday Disc. Chem. Soc. **53**, 82 (1972).

[2] Clyne, M. A. A., and Cruse, H. W., JCS Faraday II **68**, 1281 (1972).

[3] Clyne, M. A. A., "Physical Chemistry of Fast Reactions" **1**, 245 (1973). (Plenum, London). Ed. B. P. Levitt.

[4] Clyne, M. A. A., McKenny, D. J., and Walker, R. F., Can. J. Chem. **51**, 3596 (1973).

[5] Arnoldi, D., Kaufmann, K., and Wolfrum, J., Phys. Rev. Letts. **34**, 1597 (1975).

E26 Br + NF_2 + M → NF_2Br + M

Using identical conditions to the above, Clyne and Connor also studied the combination of NF_2 radicals and Br atoms [1].

$$\mathrm{Br + NF_2 + M \rightarrow NF_2Br + M;} \tag{1}$$

thermodynamic data unavailable for NF_2Br.

Br atoms were produced in a discharge through Br_2 at 8.1 Pa pressure, and added to a stream of NF_2 radicals in Ar at total pressures of 162–324 Pa. [Br] was followed by observing the bromine afterglow at 685 nm after titration with NOCl. The reaction proceeded in a manner identical to that between NF_2 and Cl, the authors obtaining $k_1 = 3.6 \times 10^{16}$ $cm^6\ mol^{-2}\ s^{-1}$ at 293 K.

Reference

[1] Clyne, M. A. A., and Connor, J., JCS Faraday II **68**, 1220 (1972).

Miscellaneous Inter-Halogen Reactions Involving O Species

E27 O + BrCl → Cl + BrO

The only experimental investigation of reaction 1 has been by Clyne et al. [1] using a flow system.

$$\mathrm{O + BrCl \rightarrow Cl + BrO} \tag{1}$$

They produced O atoms either from a discharge through 100% N_2 followed by addition of excess NO, or by a discharge through 99.995% He, dissociating the impurity oxygen. Total pressure ~70 Pa. BrCl was added downstream in a large excess, so that [BrCl]~10–40[O]. [O] was monitored by resonance fluorescence at 130 nm. A preliminary value of $k_1 = (1.4 \pm 0.5) \times 10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ was obtained at 298 K, and work over the temperature range 298–619 K suggested a zero activation energy ($E_1 = 0 \pm 700$ $J\ mol^{-1}$ (0 ± 170 $cal\ mol^{-1}$)).

Mass-spectrometric analysis confirmed reaction 1 to occur in preference to the energetically favoured reaction 2.

$$\mathrm{O + BrCl \rightarrow Br + ClO} \tag{2}$$

A Model was set up examining the effect of possible secondary reactions, as a result of which a final rate constant $k_1 = (1.3 \pm 0.4) \times 10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ was obtained over the temperature range 298–619 K.

Reference

[1] Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., Int. J. Chem. Kinet. **8**, 425 (1976).

E28 BrO + ClO → BrCl + O_2

The reaction between BrO and ClO radicals proceeds at a faster rate than the bimolecular decomposition of either radical [2].

$$\mathrm{BrO + ClO \rightarrow BrCl + O_2;} \tag{1}$$

thermodynamic data unavailable for BrO.

Basco and Dogra [2] suggested that reaction 1 participates in the reaction scheme for the overall reaction between Br and ClO_2.

$$\mathrm{Br + ClO_2 \rightarrow BrO + ClO} \tag{2}$$

$$\mathrm{BrO + ClO \rightarrow BrCl + O_2} \tag{1}$$

They flash photolysed Br_2(1–4%)/ClO_2 (<0.05%)/Ar or N_2 mixtures at total pressures of 13.3–66.7 kPa. Photolysis of ClO_2 was prevented by only photolysing above ~440 nm. [ClO] was followed by u.v. absorption spectroscopy at 277 nm, and [BrO] and [ClO_2] over the range 320–335 nm. They rejected any suggestion of interference from reaction 3, as it was known to be too slow (section B15), but made allowance for reaction 4 to obtain $k_1 = 1.5 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K.

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (3)$$

$$BrO + BrO \rightarrow Br_2 + O_2 \qquad (4)$$

Reaction 1 was considered a more likely pathway than reaction -2 by Clyne and Coxon [1] on energetic grounds. However, Watson [3] subsequently investigated the equilibrium in reaction 2 in a flow system. Br atoms were produced from a discharge through dilute Br_2/He mixtures and ClO_2 added downstream, the reaction being followed mass-spectrometrically. Using values for k_3 and k_4 determined by himself earlier he claimed that $k_1 = k_{-2}$, that the two routes were equally probable, with $k_1 = 4.0 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 300 K, and hence $k_1 + k_{-2} = 8.0 \times 10^{12}$ cm^3 mol^{-1} s^{-1}, totally incompatible with the result of Basco and Dogra. Unfortunately, few details are available of Watson's work, and we thus make no recommendation for k_1.

References

[1] Clyne, M. A. A., and Coxon, J. A., Proc. Roy. Soc. **A298**, 424 (1967).
[2] Basco, N., and Dogra, S. K., Proc. Roy. Soc. **A323**, 417 (1971).
[3] Watson, R. T., Ph. D. Thesis, London University (1973).

Miscellaneous Inter-Halogen Reactions Involving N Species

E29 N + ICl → products

Following his work on active N_2/I_2 flames, Phillips extended these studies to the inter-halogen compounds ICl and IBr, finding the initial reaction between N atoms and these compounds to be even slower than for I_2 [1]. Active nitrogen was produced by discharge through 100% N_2 at 400 Pa pressure, and ICl added downstream at 0.55–3.46 Pa in an Ar carrier. The reaction was followed by monitoring the nitrogen afterglow at 625 nm. The rate constant thus derived was extrapolated to zero halogen pressure to isolate the effect of wall recombination, giving $k_1 = 6.5 \times 10^5 \exp(1600/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 291–328 K, the very low value of k_1 being similar to that for reaction 2.

$$N + ICl \rightarrow NI + Cl \qquad (1a)$$

$$N + ICl \rightarrow NCl + I \qquad (1b)$$

$$N + Cl_2 \rightarrow NCl + Cl \qquad (2)$$

Reference

[1] Grigor, M. R., and Phillips, L. F., 11th Combustion Symp. 1171 (1967).

E30 N + IBr → products

Reaction 1 has also been studied by Grigor and Phillips [1] in active N_2/IBr flames. Active nitrogen was produced by discharge through 100% N_2 at 400 Pa pressure, and IBr added downstream at ~1 Pa in an Ar carrier. The reaction was followed by monitoring the nitrogen afterglow at 625 nm; thus it was not possible to distinguish between the two reaction paths 1a and 1b.

$$N + IBr \rightarrow NBr + I; \qquad (1a)$$

$$\Delta H^\circ_{298} = -106.00 \text{ kJ mol}^{-1} \ (-25.335 \text{ kcal mol}^{-1})$$

$$N + IBr \rightarrow NI + Br \qquad (1b)$$

(No thermodynamic data are available for NI).

The authors obtained $k_1 = 2.7 \times 10^{10} \exp(-350/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 291–328 K.

Reference

[1] Grigor, M. R., and Phillips, L. F., 11th Combustion Symp. 1171 (1967).

E31 $NF_2 + ClF_3 \rightarrow NF_3 + ClF_2$

The reaction between chlorine trifluoride and the difluoramino radical has been studied by von Ellenreider et al. [1] in a static system over the temperature range 453–483 K.

$$NF_2 + ClF_3 \rightarrow NF_3 + ClF_2 \qquad (1)$$

N_2F_4 (3.49–31.0 kPa)/ClF_3 (8.03–47.8 kPa) mixtures, in some cases with added N_2 or O_2 (40.0 kPa) were used. The reaction was followed manometrically. In this way, the position of the N_2F_4/NF_2 equilibrium could be ascertained, and it was found that the equilibrium position was reached much faster than the overall reaction rate, in agreement with the results of Modica and Hornig [2]. The final products were NF_3 and ClF in the ratio 2:1. The authors assumed reaction 1 to be the rate determining step, and obtained $k_1 = 1.5 \times 10^{12} \exp(-11\,800/T)$ cm^3 mol^{-1} s^{-1}. Added third bodies had no effect on the reaction rate.

References

[1] von Ellenrieder, G., Castellano, E., and Schumacher, H.-J., Z. Phys. Chem. NF **56**, 20 (1967).
[2] Modica, A. P., and Hornig, D. F., J. Chem. Phys. **49**, 629 (1968).

F1 $(CN)_2 + M \rightarrow CN + CN + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	561.200	163.599	-89.780	-94.168
300	561.200	163.607	-89.172	-93.563
500	560.669	162.394	-50.093	-54.706
1000	556.690	157.021	-20.879	-25.793
1500	551.752	153.026	-11.223	-16.313
2000	547.041	150.310	- 6.438	-11.653
2500	543.573	148.754	- 3.591	- 8.903
3000	541.874	148.130	- 1.700	- 7.091
3500	541.878	148.135	- 0.354	- 5.812
4000	543.196	148.494	0.659	- 4.857
4500	545.347	149.009	1.408	- 4.159
5000	547.920	149.570	2.083	- 3.530

SI Units: $\log(K_p/\text{Pa}) = \log(K_p/\text{atm}) + 5.006$

$\log(K_c/\text{mol m}^{-3}) = \log(K_c/\text{mol cm}^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k^o = 3.2 \times 10^{16} \exp(-47\,500/T)$ cm^3 mol^{-1} s^{-1} (M=Ar)

$= 5.3 \times 10^{-8} \exp(-47\,500/T)$ cm^3 molecule^{-1} s^{-1} (M=Ar)

(k is defined by $-d[(CN)_2]/dt = k_1[(CN)_2][M]$)

Temperature Range: 2000-4000 K.

Suggested Error Limits for Calculated Rate Constant: a factor of two.

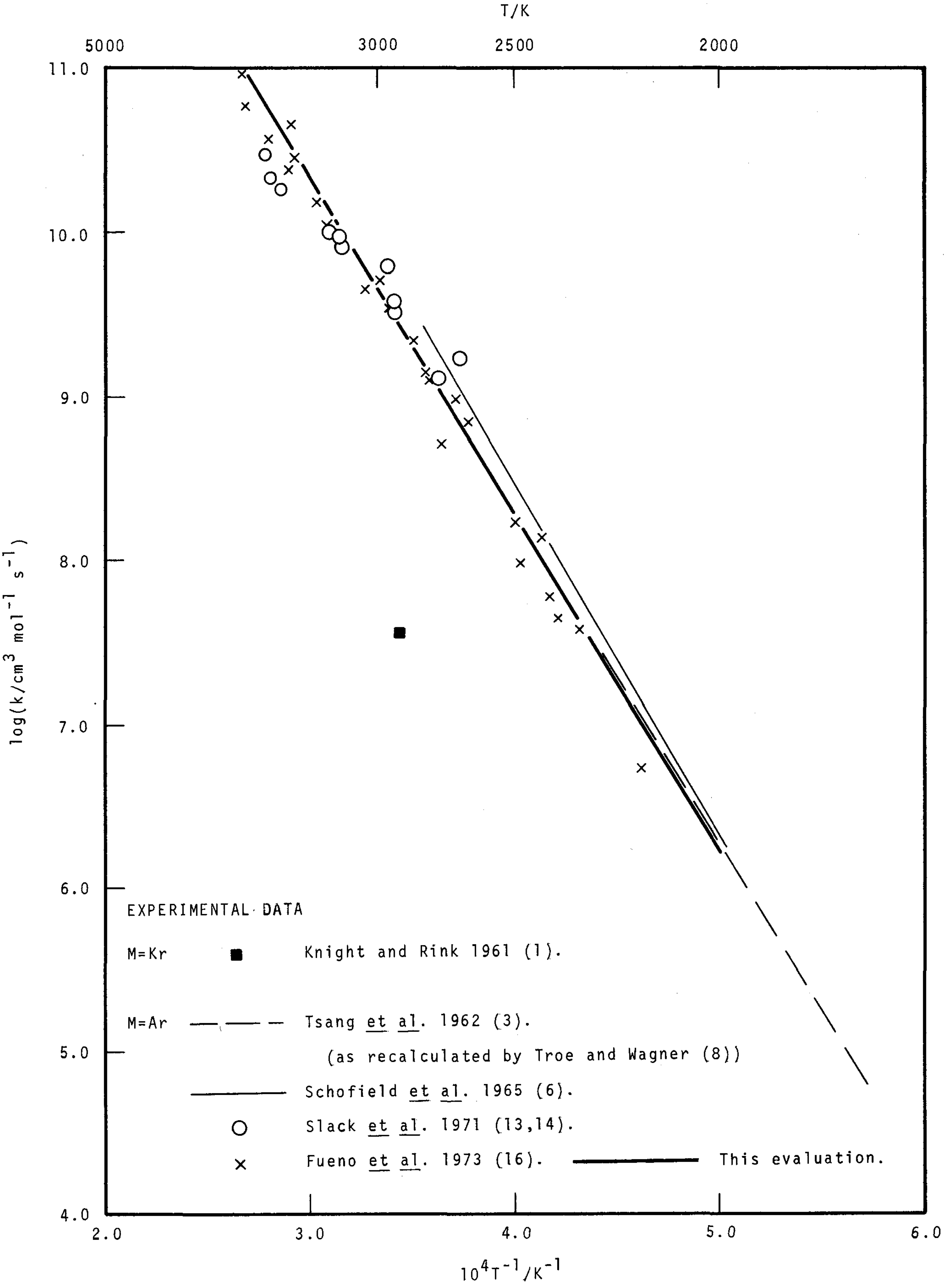
Rate Parameters: $\log(A/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 16.50 \pm 0.30$

$\log(A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -7.28 \pm 0.30$

$E/\text{J mol}^{-1} = 394\,000 \pm 42\,000$

$E/\text{cal mol}^{-1} = 94\,300 \pm 10\,000$

$(CN)_2 + M \rightarrow CN + CN + M$



$(CN)_2 + M \rightarrow CN + CN + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o			
$3.8x10^7$ M=Kr	2900	Shock tube study. $(CN)_2$ (15%)/Kr mixtures at 6.67 kPa pressure. Incident shocks. Reaction followed by X-ray densitometry. KNIGHT and RINK 1961 (1)	Investigation primarily to determine bond dissociation energy of $(CN)_2$. Assuming that E_1=D_{CN-CN}, found by the authors to be 607 kJ mol^{-1} (145 kcal mol^{-1}) at 2865 K, they were able to produce an Arrhenius expression k_1=$3.3x10^{18}$ exp(-73 000/T) $cm^3\ mol^{-1}\ s^{-1}$. $(CN)_2 + M \rightarrow CN + CN + M$ 1 Quoted by (13). Used by (7).
$1.0x10^{10}T^{\frac{1}{2}}(63\ 000/T)^{5.5}$ exp(-63 000/T) M=Ar	1700-2500	Shock tube study. $(CN)_2$ (1-10%)/Ar mixtures at total pressurs of 13.3-40 kPa. Incident and reflected shocks. $(CN)_2$ decay monitored by uv absorption spectroscopy at 219 nm. TSANG, BAUER and COWPERTHWAITE 1962 (3)	Rate expression given only in RRK form. A value for the activation energy, E_1=398 kJ mol^{-1} (95 kcal mol^{-1}) was determined from the reflected shock data when the system was in equilibrium and the effect of the recombination reaction had to be considered. Data used by (10,13,14). RRK expression quoted by (5,12,16). k_1 given as $2.8x10^{36}T^{-5}$ exp(-63 000/T) $cm^3\ mol^{-1}\ s^{-1}$ by (17, 18). Incident shock data gave E_1 ≈440 kJ mol^{-1} (106 kcal mol^{-1}), but no detailed analysis was made. No change of rate found by altering % $[(CN)_2]$. k_1 given as $4.0x10^{16}$ exp(-48 000/T) $cm^3\ mol^{-1}\ s^{-1}$ in (8). This expression plotted on the Arrhenius diagram.
$1.7x10^{17}$ exp(-50 500/T) M=Ar	2000-2800	Shock tube study. ClCN (0.5-5.0%)/Ar mixtures at total pressures of 1.00-7.00 kPa. In some experiments 0.17% Cl_2 added. Incident shocks. [CN] monitored by absorption spectroscopy at 388.3 nm. SCHOFIELD, TSANG and BAUER 1965 (6)	Considering just initial reaction rates, a six reaction mechanism was proposed for the ClCN decomposition, including reaction 1. A computer fit was then made to the results, giving the expression shown, which agrees well with that in (3). Quoted by (8). Used by (10).

$(CN)_2 + M \rightarrow CN + CN + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})		Temperature (K)	Method and Reference	Comments
1.7×10^{9}	M=Ar	2680	Shock tube study. $(CN)_2$ (0.5-1%)/Ar mixtures at total pressures of 1.33-4.00 kPa. Incident shocks. [CN] monitored by emission spectroscopy at 420 nm, and [C_2] at 516.5 nm. SLACK, FISHBURNE and JOHNSON 1971 (13) SLACK, FISHBURNE and JOHNSON 1971 (14)	Authors obtain expression $k_1=4.6\times10^{14}\exp(-34\ 700/T)$ cm^3 mol^{-1} s^{-1} for use in the temperature range 2700-4000 K. At the upper end of this range, C_2 appeared as a major product, indicating dissociation of the CN radicals. They combine their data with that from (3) to give the RRK expression $k_1=3.7\times10^6T^{\frac{1}{2}}(64\ 800/T)^8\exp(-64\ 800/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 1750-4000 K. This expression recalculated in (15) to give $k_1=5.0\times10^{19}(T/400)^{-7.5}\exp(-64\ 800/T)$ cm^3 mol^{-1} s^{-1}. There has obviously been an error in deriving or printing this expression as it gives values of k_1 six orders of magnitude too low. Original expression quoted by (15 and 16).
1.3×10^{9}		2752		
3.2×10^{9}		2922		
3.7×10^{9}		2930		
6.1×10^{9}		2955		
8.3×10^{9}		3162		
9.6×10^{9}		3171		
1.0×10^{10}		3223		
1.8×10^{10}		3498		
2.1×10^{10}		3563		
2.9×10^{10}		3588		
5.4×10^{6}		2163	Shock tube study. $(CN)_2$ (0.1-0.5%)/Ar mixtures at total pressures of 0.21-1.35 atm. (21.3-137 kPa). Incident shocks. [CN] followed by absorption and emission spectroscopy at 421.6 nm. FUENO, TABAYASHI and KAJIMOTO 1973 (16)	Results divided into two sections; those obtained from absorption measurements, and those from emission. Neither set showed the effect of any side reactions. From the absorption data, authors obtained $k_1=6.7\times10^{16}\exp(-49\ 600/T)$ cm^3 mol^{-1} s^{-1}, and from the emission, $k_1=9.3\times10^{15}\exp(-44\ 000/T)$ cm^3 mol^{-1} s^{-1}. The lower activation energy for the emission results are attributed to an inadequacy in describing the thermal equilibrium between the $CN(B^2\Sigma^+)$ and $(X^2\Sigma^+)$ states. Using a collisional de-excitation cross-section for CN $B^2\Sigma^+\rightarrow X^2\Sigma^+$ from (11) gives k_1(emission)$=7.6\times10^{16}\exp(-49\ 800/T)$ cm^3 mol^{-1} s^{-1}, essentially in agreement with the absorption results. $(CN)_2 + M \rightarrow CN + CN + M$ 1 An RRK fit to the absorption data gave $k_1=2.9\times10^{10}T^{\frac{1}{2}}(63\ 100/T)^5\exp(-63\ 100/T)$ cm^3 mol^{-1} s^{-1}. k_1 (absorption) quoted by (20). k_1 (emission) quoted by (21).
3.9×10^{7}		2312		
4.6×10^{7}		2374		
6.0×10^{7}		2397		
1.4×10^{8}		2419		
9.9×10^{7}		2476		
1.7×10^{8}		2499		
7.1×10^{8}		2649		
9.6×10^{8}		2690		
5.1×10^{8}		2742		
1.3×10^{9}		2786		
1.4×10^{9}		2801		
2.2×10^{9}		2843		
3.5×10^{9}		2950		
5.0×10^{9}		2981		
4.5×10^{9}		3041		
1.1×10^{10}		3234		
1.5×10^{10}		3287		
2.8×10^{10}		3403		
4.6×10^{10}		3422		
2.4×10^{10}		3445		
3.6×10^{10}		3566		
5.7×10^{10}		3720		
9.2×10^{10}		3743		

$(CN)_2 + M \rightarrow CN + CN + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
1st ORDER RATE CONSTANT k_1^∞			
$2.9\times10^{11}\exp(-52\ 000/T)\ s^{-1}$	All	Theoretical study, from unimolecular reaction rate theory. KECK and KALELKAR 1968 (10)	Value reported as being ∿3x the value of k_1^∞ apparently found by (3 and 6) at 2600 K.

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Review of unimolecular thermal decompositions. TROE and WAGNER 1967 (8)	Reviews (3 and 6). Data from (3) re-calculated to give $k_1=4.0\times10^{16}\exp(-48\ 000/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 1750-2200 K. From the data in both studies, the authors recommend a value for $E_1 \approx 500\ kJ\ mol^{-1}$ (120 kcal mol^{-1}).
		Review of reactions behind shock waves. WAGNER 1971 (15)	Reviews only (13). Derives alternative expression $k_1=5.0\times10^{19}(T/400)^{-7.5}\exp(-64\ 800/T)\ cm^3\ mol^{-1}\ s^{-1}$ which is obviously in error since it gives values of k_1 six orders of magnitude lower than original expression in (13).
		Review of reactions behind shock waves. TROE 1975 (21)	Considers both k_1 and D_{CN-CN} from (16). Author applies his own developments of unimolecular reaction theory to obtain $E_1=410\ kJ\ mol^{-1}$ (98 kcal mol^{-1})

Discussion

The behaviour of the cyano radical CN in many ways parallels that of the halogen atoms. It has, indeed, been referred to as a "pseudo-halogen" [9]. The dissociation of the cyanogen molecule $(CN)_2$ has not received the same attention as have the dissociations of the corresponding halogen molecules, but is important in the formation of CN radicals in combustion processes.

$$(CN)_2 + M \rightarrow CN + CN + M \qquad (1)$$

The decomposition has been studied exclusively in shock tubes, over a range of 2000 K. All investigations have been at fairly low pressures (<2 atm), and consequently only a second order reaction has been observed. So far there is no experimental evidence for a first order rate constant. Keck and Kalelkar [10] have applied Keck's unimolecular reaction rate theory to the problem and obtained a value of k_1 approximately a factor of three below first order rate constants derived from [3] and [6].

The agreement over the entire temperature range is remarkably good, only the one point of Knight and Rink [1] being substantially in error. They used Kr as a third body, which might account for some discrepancy. However, their value for the C≡N dissociation energy is considerably higher than the value of 720 kJ mol^{-1} (172 kcal mol^{-1}) currently accepted. According to Slack et al. [13], recalculation of their results using recent thermodynamic data yields a value of k_1 approximately three times higher, although still below other values.

Slack et al. themselves obtain a substantially lower activation energy than any of the other authors. Although slight errors might have been caused by using emission spectoroscopy to follow [CN] and assuming an incorrect equilibrium between $CN(B\,^2\Sigma^+)$ and $(X\,^2\Sigma^+)$, subsequent work by Fueno et al. [16] shows that the difference between absorption and emission results is not that great.

However, we feel that their activation energy is too low, and prefer a value in the region of that obtained by the other authors. In evaluating a rate constant expression, we have ignored the RRK expressions derived to fit results, and for convenience have considered only the Arrhenius expressions used. In the case of the results from [3], we have used the expression derived in [8]. We recommend the following expression, based on the results of [3,6,13,16], but ignoring the activation energy in [13]:

$$k_1(M=Ar) = 3.2\times10^{16} \exp(-47\,500/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 2000–4000 K, with error limits of a factor of two.

Comparing this with the decomposition of halogen molecules over the same temperature range, rates are comparable at 4000 K, but $k_1 << k_2$ at 2000 K.

$$X_2 + M \rightarrow X + X + M \qquad (2)$$

The reason for the large difference in activation energy is the greater strength of the C–C bond in $(CN)_2$ compared with the X–X bond in halogen molecules. Only above 4000 K does $(CN)_2$ dissociate rapidly.

Rate of the Reverse Reaction

Unlike the recombination of halogen atoms, CN radical recombination has received relatively little attention. The following values of k_{-1} have been determined from k_1 and the equilibrium constant by authors undertaking $(CN)_2$ decomposition studies:

k_{-1} ($cm^6\ mol^{-2}\ s^{-1}$)	T (K)	Reference
1×10^{15} (M=Kr)	2900	[1]
$2.3\times10^{12}(63\,000/T)^3$ (M=Ar)	1700-2500	[3]
3.0×10^{16} (M=Ar)	300-4000	[13]

$$CN + CN + M \rightarrow (CN)_2 + M \qquad (-1)$$

At room temperature the reaction mechanism is uncertain. Basco et al. [4] flash photolysed C_2N_2 (<7%)/N_2 mixtures at 1 atm (101 kPa) pressure, and monitored the decay of [CN] by absorption spectroscopy at 420 nm. CN radicals are produced in excited vibrational states up to $v=4$, and it was impossible to follow $CN_{v=0}$ until all the other vibrational states had disappeared. At this point, decay is very slow, and changes in intensity are small. The authors found that [CN] decay was best fitted by a plot second order in [CN], although a rough first order plot could also be obtained. Thus they assumed reaction -1 to be the reaction removing CN and gave $k_{-1}=1.7\times10^{16}$ $cm^6\ mol^{-2}\ s^{-1}$ at 298 K. This agrees well with [13], and, assuming a small negative activation energy similar to that for halogen recombination, extrapolates well to the value of [1] at 2900 K. However, they admit any agreement probably to be fortuitous, and it has since been shown that k_{-1} as determined in [1] is in error.

Moreover, Basco et al. are in the minority in their explanation of CN disappearance. Other studies of flash photolysis of $(CN)_2$ [2,19] find that the process of removal is clearly first order in [CN], and suggest that this must be by reaction 3.

$$CN + (CN)_2 \rightarrow \text{products} \qquad (3)$$

This reaction is discussed in detail in section F2. There have been no kinetic studies made in which it has been possible to isolate reactions -1 or 3 and measure their rate. In view of this controversy we recommend the expression

$$k_{-1}(M=Ar) = 3.8\times10^{14} \exp(15\,000/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

over the temperature range 2000–4000 K, derived from k_1 and the equilibrium constant, with error limits of a factor of two. Values of k_{-1} determined below 2000 K from this expression are very high and unreliable. Over the temperature range considered, CN recombination is seen to be at least two orders of magnitude faster than any halogen atom recombination reaction.

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F2 $CN + (CN)_2 \rightarrow$ products

THERMODYNAMIC DATA

There are no thermodynamic data available for $(CN)_3$ or the C_3N radical.

RECOMMENDED RATE CONSTANT

$k = 3.2 \times 10^{9}$ cm^3 mol^{-1} s^{-1}

$= 5.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

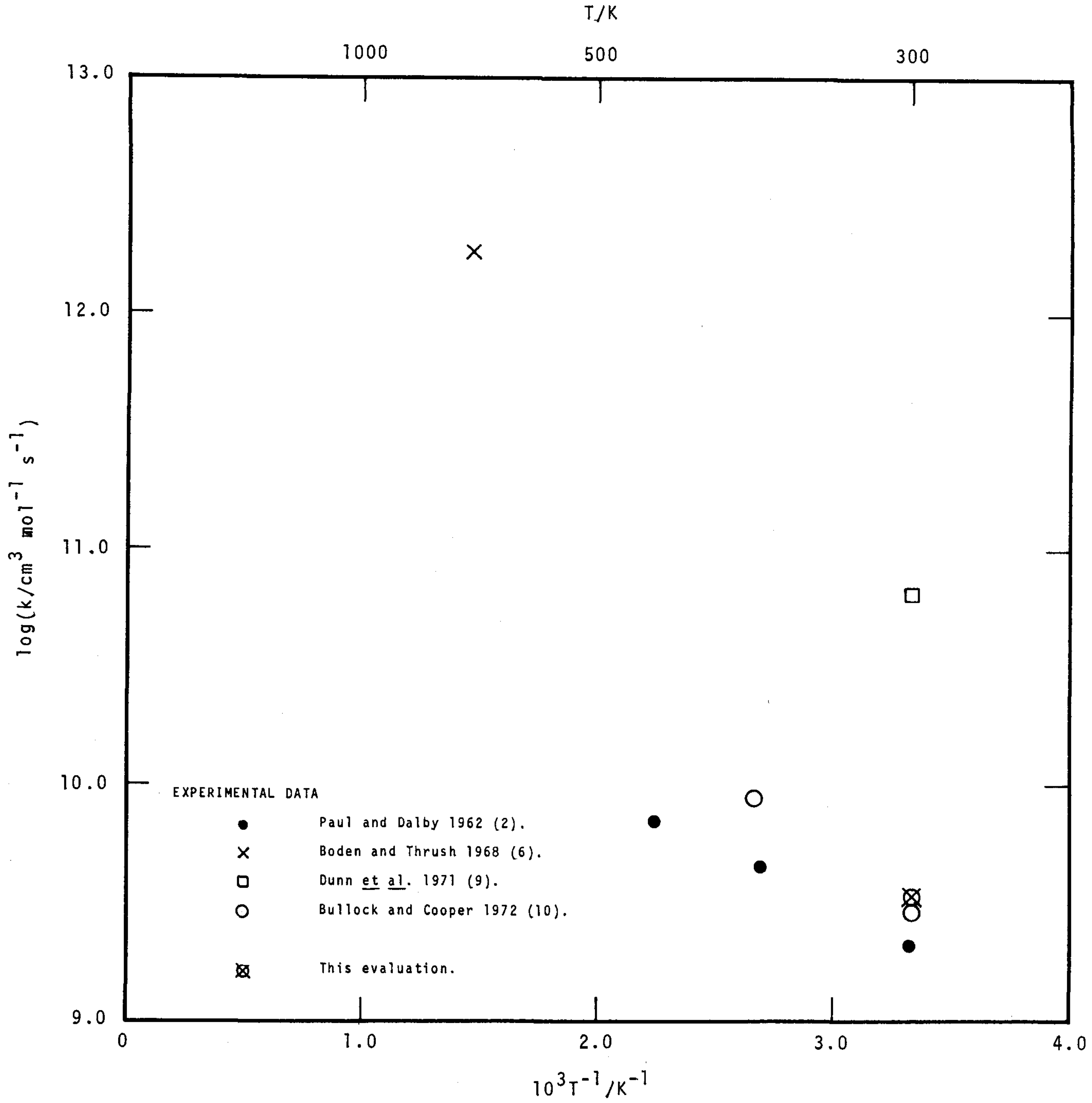
Temperature: 300 K.

Suggested Error Limits for Calculated Rate Constant: a factor of three.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2.1×10^{9}	301	Flash photolysis of $(CN)_2$ (98% pure) at pressures of 0.32-75.0 kPa. [CN] monitored by absorption spectroscopy at 388.3 nm. PAUL and DALBY 1962 (2)	No assumption made as to the reaction products. Disappearance of CN found to be entirely first order, thus reaction 1 proposed as CN removal mechanism. $CN + (CN)_2 \rightarrow$ products 1 Authors derive the expression $k_1 = 7.3 \times 10^{10} \exp(-1050/T)$ cm^3 mol^{-1} s^{-1}. Quoted by (4,5,6,8,9,10,11).
4.3×10^{9}	372		
6.9×10^{9}	447		
1.8×10^{12}	687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream. $(CN)_2$ added in large excess in the reaction cell. [O] determined in inlet and outlet gases by NO titration, monitoring the air afterglow. BODEN and THRUSH 1968 (6)	The apparent rate of reaction 2 was observed to increase with $[(CN)_2]$ in the absence of O_2. $O + (CN)_2 \rightarrow CN + CNO$ 2 Authors attributed this to a chain reaction removing O atoms, beginning with reaction 1a. $CN + (CN)_2 \rightarrow C_3N + N_2$ 1a $O + C_3N \rightarrow C_2N + CO$ $O + C_2N \rightarrow CN + CO$ i.e. no consumption of CN, as observed. Process considered to be partly heterogeneous, on account of large value of k_1 compared with that in (2). Quoted by (9).

CN + $(CN)_2 \rightarrow$ products



$CN + (CN)_2 \rightarrow$ products

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
6.5×10^{10}	300	Flame study. $(CN)_2$ (2-40%) /H_2 mixtures at pressures ∿133 Pa. [H] monitored by NO_2 titration, stable products by mass spectrometry. DUNN, FREEMAN, McEWAN and PHILLIPS 1971 (9)	When $[(CN)_2] > [H]$, cyanogen polymerisation was observed. Authors concluded that reaction 3 was competing with reaction 1b for CN. $CN + (CN)_2 \rightarrow (CN)_3$ 1b $CN + H_2 \rightarrow H + HCN$ 3 They measured concentrations of [H], $[H_2]$ and $[(CN)_2]$ at the onset of polymer formation, and equating $k_3[H_2]$ with $k_1[(CN)_2]$, obtained values of k_1, taking k_3 from (7). Using our value of k_3 (This Vol., section F5) we obtain $k_1 = 3.2 \times 10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ at 300 K. Quoted by (10).
3.0×10^9 8.6×10^9	300 377	Pulse radiolysis of $(CN)_2$ (≥500 Pa)/Ar mixtures. Total pressure ∿100 kPa. [CN] monitored by absorption spectroscopy at 388.2 nm. BULLOCK and COOPER 1972 (10)	At high $[CN]:[(CN)_2]$ ratios, complicated kinetic behaviour, with both first and second order removal of CN observed. These results were rejected. Higher temperature value corrected for relaxation of higher CN vibrational states. Authors quote expression $k_1 = 5.6 \times 10^{11} \exp(-1600/T)\ cm^3\ mol^{-1}\ s^{-1}$.

Discussion

The mechanism of removal of CN radicals derived from cyanogen decomposition is not at all clear. Three distinct possibilities exist, reactions 1a, 1b and 4.

$$CN + (CN)_2 \rightarrow C_3N + N_2 \tag{1a}$$

$$CN + (CN)_2 \rightarrow (CN)_3 \tag{1b}$$

$$CN + CN + M \rightarrow (CN)_2 + M \tag{4}$$

Reaction 4 has been considered by most authors to be the least likely path, requiring a high rate constant $\sim 10^{18}$ cm^6 mol^{-2} s^{-1} at 300 K to be of importance [6]. Only Basco et al. [3] claim it to be the main reaction removing CN. Bullock and Cooper [10], however, did observe a second order contribution to [CN] decay at low [$(CN)_2$], and explain the results of Basco et al. as being due to these conditions prevailing.

To distinguish between reactions 1a and 1b is more difficult, since in all experiments the reaction has been followed by monitoring [CN] decay. Certainly polymerisation of CN radicals has been observed under both shock tube [4] and photolysis [1] conditions, with reaction 1b being the obvious initial step. On the other hand, reaction 1a, put forward by Boden and Thrush [6] to account for enhanced [CN] decay in their $(CN)_2/O_2$ system in the absence of molecular oxygen, cannot be rejected. It accounts for the CN removal in Thrush's system and no evidence exists against it. We have combined $k_{1a}+k_{1b}$ in reaction 1, and consider all values of k_{1a} or k_{1b} determined to represent the combined rate constant k_1.

$$CN + (CN)_2 \rightarrow \text{products} \tag{1}$$

All four determinations of k_1 have used different methods, although the flash photolysis [2] and pulse radiolysis [10] studies, where reaction 1 can be investigated directly, must be considered the most reliable. Bullock and Cooper found the presence of HCN as an impurity to affect the measured k_1 considerably, increasing it by up to an order of magnitude at room temperature, an observation which must certainly affect the flame study of Dunn et al. [9]. A reduction of an order of magnitude here gives better agreement with the other room temperature work.

Boden and Thrush considered their high value due to a possible heterogeneous contribution, and it could be that at higher temperatures this is indeed the case.

We recommend the value $k_1=3.2\times10^9$ cm^3 mol^{-1} s^{-1} at 300 K, with error limits of a factor of three, based on [6 and 10]. The results in [9] agree with this when corrected for reaction 5.

$$CN + HCN \rightarrow \text{products} \tag{5}$$

An activation energy of $\sim$11 kJ mol^{-1} (2.6 kcal mol^{-1}) is indicated from the Arrhenius plot, but there are not sufficient concordant data to make any recommendation. Further work is required on the temperature dependence.

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F3 $(CN)_2 + O \rightarrow CN + CNO$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	36.305	32.234	-4.682
300	36.288	32.179	-4.642
500	34.313	27.137	-2.170
1000	30.020	21.108	-0.469
1500	26.179	17.987	0.025
2000	22.652	15.958	0.240
2500	19.799	14.682	0.350
3000	17.824	13.958	0.416
3500	16.657	13.606	0.458
4000	16.071	13.460	0.489
4500	15.816	13.410	0.512
5000	15.703	13.401	0.530

RECOMMENDED RATE CONSTANT

$k = 2.5 \times 10^{13} \exp(-5500/T)$ cm^3 mol^{-1} s^{-1}

$= 4.2 \times 10^{-11} \exp(-5500/T)$ cm^3 molecule^{-1} s^{-1}

Temperature Range: 500-700 K.

Note: Expression is that of BODEN and THRUSH (5).

Suggested Error Limits for Calculated Rate Constant: a factor of two.

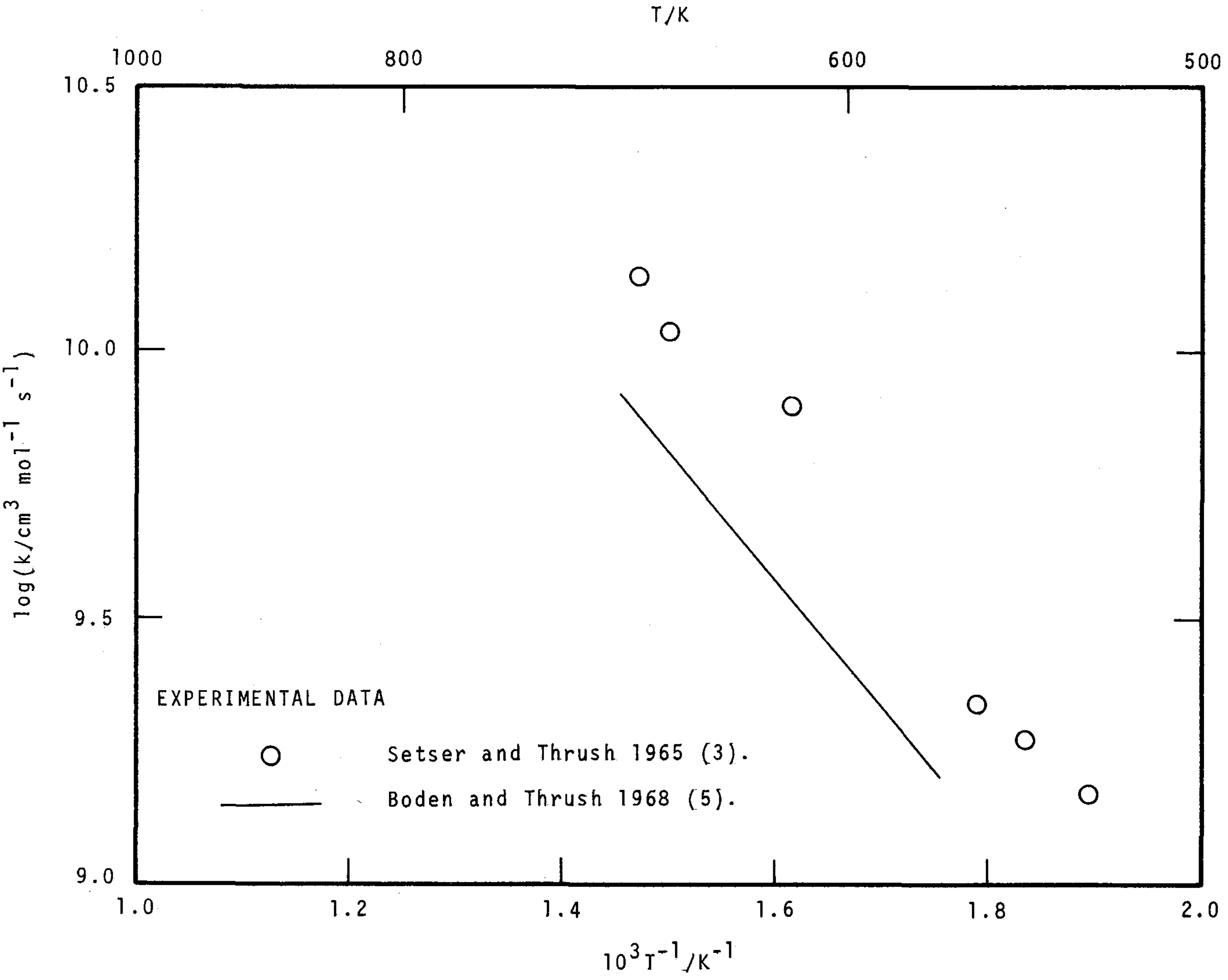
Rate Parameters: log(A/cm^3 mol^{-1} s^{-1}) = 13.40 ± 0.30

log(A/cm^3 molecule^{-1} s^{-1}) = -10.38 ± 0.30

E/J mol^{-1} = 45 700 ± 2100

E/cal mol^{-1} = 10 900 ± 500

$(CN)_2 + O \rightarrow CN + CNO$



$(CN)_2 + O \rightarrow CN + CNO$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1.5×10^9 1.9×10^9 2.2×10^9 8.0×10^9 1.1×10^{10} 1.4×10^{10}	528 545 559 619 667 679	Discharge flow system. 100% N_2 at 133-667 Pa pressure, NO added downstream, or O_2 (3%)/Ar mixtures at 107-667 Pa. $(CN)_2$ added in excess further downstream. [O] decay by titration with NO and monitoring of air afterglow. SETSER and THRUSH 1965 (3)	Data given based only on N_2 discharge figures. Those for O_2 discharge slightly higher. Reaction of active nitrogen excluded by long delay time before addition of NO. All data given are at 250 Pa pressure, for reaction found to be pressure dependent. Authors suspect heterogeneous contribution at higher pressures. Observed rate constant given as $8.0 \times 10^{13} \exp(-5500/T)$ cm^3 mol^{-1} s^{-1}. All data have been halved to agree with stoichiometry postulated. $(CN)_2 + O \rightarrow CN + CNO$ 1 $O + CNO \rightarrow NO + CO$ 2 Reaction 2 is rapid (2). No evidence was found from spectroscopic measurements for CNO, so authors also considered alternative mechanism feasible. $O + (CN)_2 \rightarrow CN_2 + CO$ 3 $O + CN_2 \rightarrow CN + NO$ 4 Quoted by (9).
	298	Flash photolysis study. NO_2 (400 Pa) in the presence of $(CN)_2$ (2.00 kPa) and Ar (1.33 kPa). [CN], [CNO] and [CN_2] followed by kinetic spectroscopy. MORROW and McGRATH 1966 (4)	No reaction observed when the photolysis performed in Pyrex apparatus. In spectrosil apparatus, CN and CNO observed immediately, followed after 15 ms by CN_2. This reaction is due to $O(^1D)$, but indicates reactions 1 and 2 as the initial steps, followed by reaction 5. $CN + CNO \rightarrow CN_2 + NO$ 5
$2.5 \times 10^{13} \exp(-5500/T)$	570-687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream, or O_2 (3-5%)/Ar mixtures at 200-667 Pa. $(CN)_2$ added in excess into the reaction cell. [O] determined in inlet and outlet gases by NO titration, monitoring the air afterglow. BODEN and THRUSH 1968 (5)	Capacity flow conditions prevailed in the reaction vessel (rate of inflow balanced by reaction rate + outflow rate). Sufficient time again allowed for excited N_2 to decay. In presence of O_2, reaction rate independent of pressure, but in absence of O_2, rate increased with [$(CN)_2$]. Authors attributed this to competition between reactions 6 and 7, the former prevailing in the presence of O_2.

$(CN)_2 + O \rightarrow \dot{C}N + CNO$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BODEN and THRUSH 1968 (5) continued.	$CN + O_2 \rightarrow CNO + O$ 6 $CN + (CN)_2 \rightarrow C_3N + N_2$ 7 k_1 obtained by extrapolating to zero $[(CN)_2]$, or taking results in the presence of excess O_2. Used by (12). Quoted by (6,8,9, 11). (10) attributes value of $k_1 < 10^7$ $cm^3\ mol^{-1}\ s^{-1}$ at room temperature to this paper.
$<10^7$	295	Discharge flow system. 100% N_2 at 66.7-667 Pa pressure, NO added downstream, $(CN)_2$ added further downstream in excess. [O] monitored by esr spectroscopy, stable products by mass spectrometry. REINHARDT, WAGNER and WOLFRUM 1969 (7)	No evidence of any reaction found. No further details given. k_1 attributed to (5) by (10).

REVIEW ARTICLE

Review of oxidation of inorganic non-metallic compounds. HEICKLEN and COHEN 1972 (9)	Quotes (3 and 5). Reaction mechanism reviewed with regard to the work of (1 and 4).

Discussion

The reaction between oxygen atoms and cyanogen plays only a minor role in cyanogen combustion systems, when CN radicals are more likely to be present in the initial stages than O atoms. At room temperature the reaction is too slow to be detected [4,7], and the only measurements of the rate constant k_1 have been at intermediate temperatures.

$$(CN)_2 + O \rightarrow CN + CNO \qquad (1)$$

The reaction mechanism is not clear, but the bulk of evidence points to reaction 1 followed by the rapid reaction 2.

$$O + CNO \rightarrow NO + CO \qquad (2)$$

This gives the observed products CN, NO and CO, and also a stoichiometry of 2. So too, does the following scheme:

$$O + (CN)_2 \rightarrow CN_2 + CO \qquad (3)$$

$$O + CN_2 \rightarrow CN + NO \qquad (4)$$

Neither CNO nor CN_2 have been observed as intermediates, due to the rapid nature of reactions 2 and 4. Reaction 3 is preferred to 1 on thermochemical grounds, but requires the breaking of a C≡N triple bond. Morrow and McGrath [4] studied the reaction of $O(^1D)$ atoms with cyanogen, and observed both CNO and CN_2 transient spectra. However, the CN_2 did not appear until 15 ms after the CNO, and those authors assumed reaction 1 to be the rate determining step, followed by reactions 2 and 5.

$$CN + CNO \rightarrow CN_2 + CO \qquad (5)$$

Of the two determinations of k_1 both agree as to activation energy, but there is a discrepancy of a factor of two in the A factor. However, the earlier data of Setser and Thrush [3] are given at one pressure only, and in both cases a pressure dependence of the observed rate constant was seen. In [5] this was corrected by extrapolating to zero $[(CN)_2]$, or working in excess O_2. This eliminates the effect of reaction 7.

$$CN + (CN)_2 \rightarrow C_3N + N_2 \qquad (7)$$

If this correction were applied to the earlier work, it is likely the agreement would be better.

We therefore recommend the expression of Boden and Thrush [5],

$$k_1 = 2.5 \times 10^{13} \exp(-5500/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 500–700 K, with error limits of a factor of two.

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F4 $CN + M \rightarrow C + N + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	752.50	108.65	-126.15	-130.54
300	752.52	108.73	-125.34	-129.73
500	754.95	114.96	- 72.858	- 77.471
1000	759.86	121.91	- 33.319	- 38.233
1500	763.33	124.76	- 20.063	- 25.153
2000	765.87	126.22	- 13.407	- 18.622
2500	767.46	126.95	- 9.402	- 14.714
3000	768.16	127.20	- 6.729	- 12.120
3500	768.16	127.20	- 4.818	- 10.726
4000	767.82	127.10	- 3.385	- 8.901
4500	767.48	127.02	- 2.271	- 7.838
5000	767.43	127.00	- 1.381	- 6.994

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$
$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

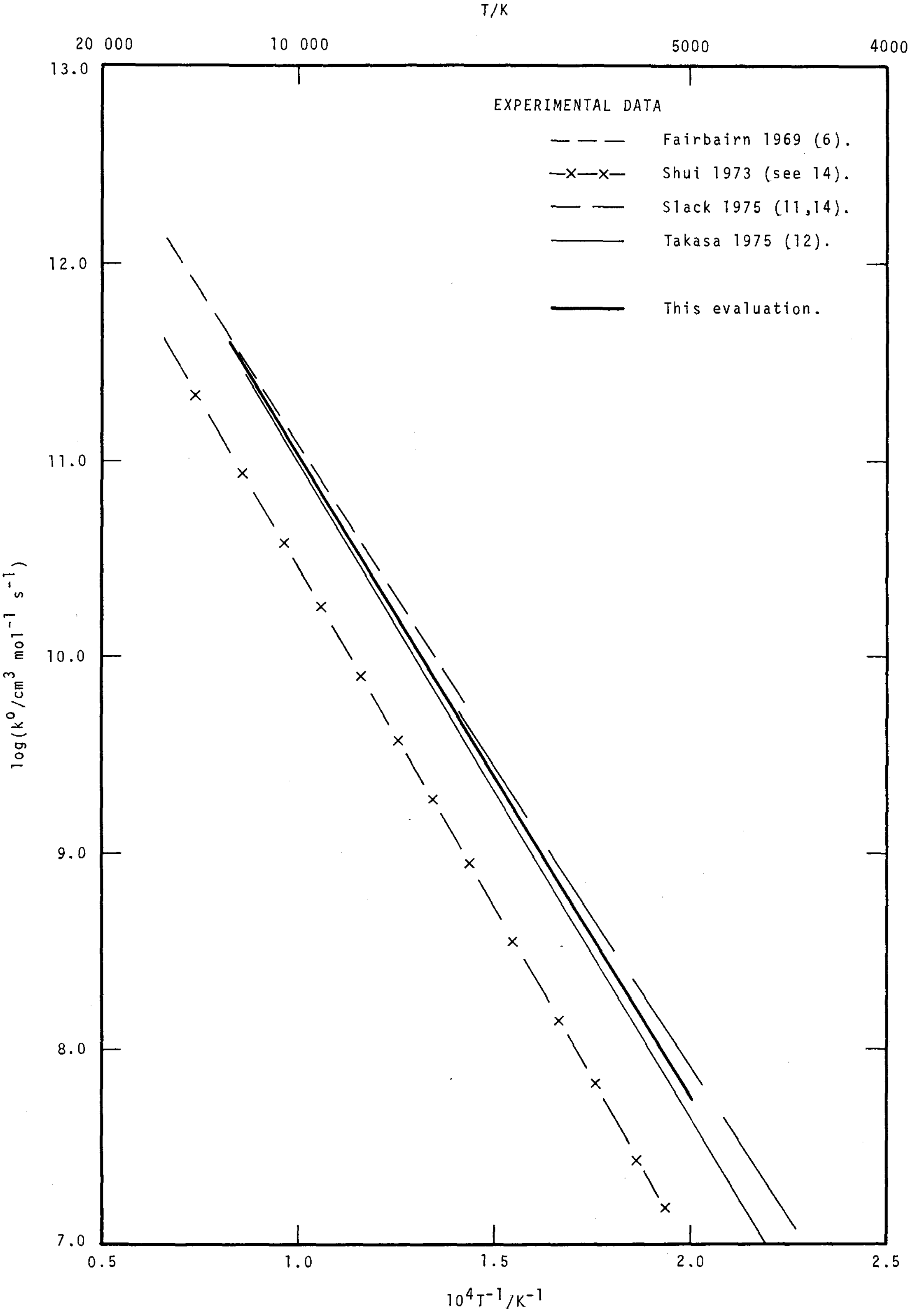
$k^o = 2.0 \times 10^{14} \exp(-75\,000/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)
$= 3.3 \times 10^{-10} \exp(-75\,000/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)

Temperature Range: 5000-12000 K.

Suggested Error Limits for Calculated Rate Constant: ±60% at 5000 K, falling to ±30% at 10 000 K.

Rate Parameters: $\log(k/cm^3\ mol^{-1}\ s^{-1}) = 14.30 \pm 0.20$
$\log(k/cm^3\ molecule^{-1}\ s^{-1}) = -9.48 \pm 0.20$
$E/J\ mol^{-1} = 625\,000 \pm 62\,500$
$E/cal\ mol^{-1} = 150\,000 \pm 15\,000$

$CN + M \rightarrow C + N + M$



$CN + M \rightarrow C + N + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	3400-4800	Shock tube study. $(CN)_2$ (0.3-5%)/Ar mixtures and $(CN)_2$ (0.66%)/N_2 mixtures at 24-44 kPa pressure. Incident shocks. [CN] and [C_2] monitored by absorption and emission spectroscopy. FAIRBAIRN 1962 (1)	Author assumed CN to decay via reaction 2, due to C_2 formed. $CN + CN \rightarrow C_2 + N_2$ 2 He gave $k_2 = 2.0 \times 10^{11}$ (3400 K), 2.2×10^{12} (4050 K) and 1.2×10^{13} $cm^3\ mol^{-1}\ s^{-1}$ at 4800 K, giving an activation energy of 402 kJ mol^{-1} (96 kcal mol^{-1}), but conceded that the mechanism could be reaction 1 followed by reaction 3. $CN + M \rightarrow C + N + M$ 1 $C + CN \rightarrow N + C_2$ 3 Quoted by (5).
	3500-7000	Shock tube study. BrCN (1-5%)/Ar mixtures at total pressures of 67-4000 Pa. Incident shocks. [CN] and [C_2] monitored by emission spectroscopy at 421.6 and 516.5 nm respectively. PATTERSON and GREENE 1962 (2)	Again, authors assumed reaction 2 to be the dominant reaction removing CN, obtaining $k_2 = 1.6 \times 10^{15} \exp(-21\ 500/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the quoted temperature range. However, in lean mixtures the authors obtained evidence that some other reaction was removing CN, becoming increasingly important at higher temperatures. They believed this to be reaction 1. Quoted by (5,8).
$1.5 \times 10^{14} \exp(-71\ 000/T)$ M=Ar	7000-15000	Shock tube study. BrCN (<0.1%)/Ar mixtures at total pressures of 0.13-1.33 kPa. Incident shocks. [CN], [C], [C_2] monitored by emission spectroscopy at 383, 516 and 247 nm respectively. FAIRBAIRN 1969 (6)	From the [CN], [C] and [C_2] profiles, author put together a five-reaction mechanism following the initial BrCN decomposition, consisting of reaction 1 and reactions 3-6. $N + CN \rightarrow C + N_2$ 4 $N_2 + M \rightarrow N + N + M$ 5 $C_2 + M \rightarrow C + C + M$ 6 From the [CN] decay, he obtained an overall rate constant $k = 2.53 \times 10^{14} \exp(-71\ 000/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Taking k_5 from (3) and k_6 from (7), and knowing [C_2] to be in steady state with respect to [CN], he corrected this expression to give the expression quoted. Quoted by (11,13,14). Used by (9,10).

$CN + M \rightarrow C + N + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1.2×10^{14} exp(-71 000/T) M=Ar	4400-13000	Shock tube study. BrCN (0.1%)/Ar, $(CN)_2$ (0.2-1%)/Ar and $(CN)_2$ (0.2%)/N_2 (4%)/Ar mixtures at total pressures of 0.13-2.67 kPa. Reflected shocks. [CN] and [C_2] monitored by emission spectroscopy at 390 and 514 nm respectively. SLACK 1975 (11) SLACK 1976 (14)	In lean mixtures author concluded he could ignore the secondary reactions 3 and 4. [CN] decay was first order, and thus he also ignored reaction 2, obtaining k_1 from [CN] decay alone. $CN + M \rightarrow C + N + M$ 1 $CN + CN \rightarrow C_2 + N_2$ 2 $C + CN \rightarrow N + C_2$ 3 $N + CN \rightarrow C + N_2$ 4 Author also quotes a private communication from SHUI, giving $k_1=10^{14}$ exp(-81 000/T) cm^3 mol^{-1} s^{-1} obtained by KECK's modified phase space theory (4).
2.3×10^{14} exp(-77 500/T)	Unknown	Shock tube study. No details available. TAKASA 1975 (12)	Author reported in (14) to have studied CN dissociation behind reflected shock waves, the results agreeing well with those of (6 and 14).

REVIEW ARTICLE

		Review of dissociation of diatomic molecules. KERN 1976 (13)	Quotes (6). Also refers to the work of (1 and 2). Notes low experimental activation energy but makes no comment.

Discussion

The cyano radical can undergo two separate decomposition reactions, reaction 1 apparently predominating at temperatures >5000 K, while below this temperature there is more evidence favouring reaction 2 [9].

$$CN + M \rightarrow C + N + M \qquad (1)$$

$$CN + CN \rightarrow C_2 + N_2 \qquad (2)$$

Disproportionation reactions involving species such as C_2N or CN_2 are not considered important at high temperatures [14]. Fairbairn [1,6] has studied the decomposition over the widest temperature range and, from the nature of the disappearance of [CN], proposed that reaction 2 predominated at lower temperatures, although both he and Slack [14] admit that the exact relationship between the two paths is not clear. Reaction 2 is dealt with further elsewhere, (section F11).

All studies of CN decomposition have been made in shock tubes, monitoring both [CN] and [C_2], and making the reasonable assumption that the CN radical source (BrCN or $(CN)_2$) is very rapidly dissociated at the high temperatures used. As might be expected, no evidence was found for first order kinetics. The simple mechanism proposed by Fairbairn [6] seems to take into account all possible reactions, and has been adopted by other authors [11,14]. However, they still found it necessary to make assumptions about the secondary reactions in order to obtain a value for k_1. Nevertheless, the agreement between the three expressions obtained is good.

We recommend the expression

$$k_1^\circ\ (M{=}Ar) = 2.0\times10^{14} \exp(-75\,000/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}},$$

based on [6,12,14], over the temperature range 5000–12000 K, with error limits of ±60% at 5000 K, falling to ±30% at 10 000 K. We feel this best represents the available data, although the activation energy may fall off at higher temperatures as in the analogous reaction 7 (Volume 3, p. 177).

$$CO + M \rightarrow C + O + M \qquad (7)$$

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F5 $CN + H_2 \rightarrow HCN + H$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-81.994	-16.782	13.489
300	-81.994	-16.790	13.400
500	-81.739	-16.230	7.691
1000	-78.864	-12.401	3.472
1500	-74.864	- 9.171	2.128
2000	-70.977	- 6.929	1.492
2500	-67.890	- 5.540	1.129
3000	-65.902	- 4.812	0.896
3500	-64.986	- 4.523	0.734
4000	-64.998	- 4.527	0.613
4500	-65.731	- 4.690	0.518
5000	-66.986	- 4.975	0.441

RECOMMENDED RATE CONSTANT

$k = 6.8 \times 10^{13} \exp(-2700/T)$ cm^3 mol^{-1} s^{-1}

$= 1.1 \times 10^{-10} \exp(-2700/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 300-1000 K.

Suggested Error Limits for Calculated Rate Constant: ±50% at 300 K, rising to a factor of three at 1000 K.

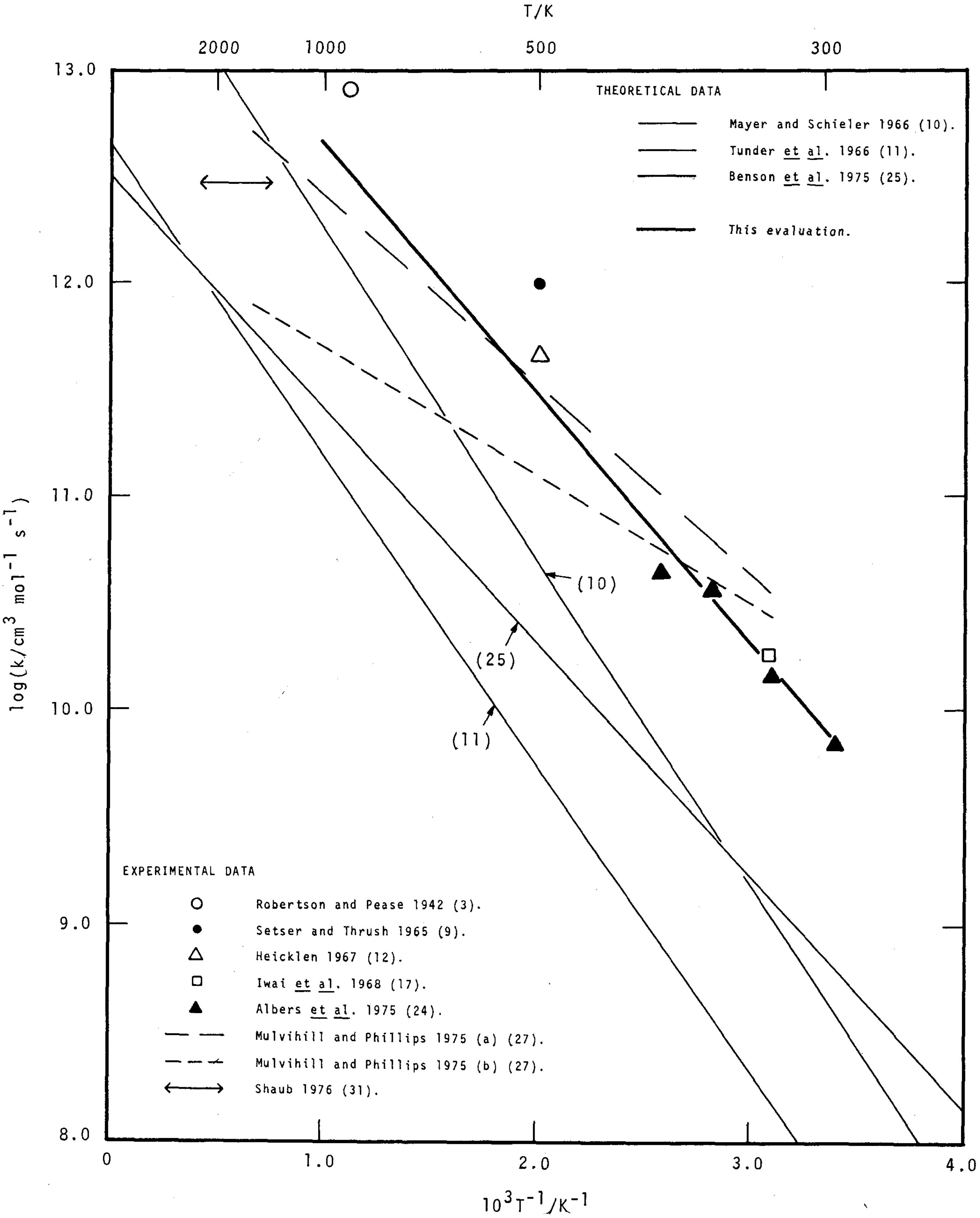
Rate Parameters: log(A/cm^3 mol^{-1} s^{-1}) = 13.83 ± 0.20

log(A/cm^3 $molecule^{-1}$ s^{-1}) = - 9.95 ± 0.20

E/J mol^{-1} = 22 600 ± 6000

E/cal mol^{-1} = 5 400 ± 1400

$CN + H_2 \rightarrow HCN + H$



$CN + H_2 \rightarrow HCN + H$

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	533-623	Flame study. Na(<0.01%)/H_2 mixtures at total pressures of 173-1200 Pa. $(CN)_2$ or ClCN added at 387-1280 Pa pressure. $[H_2]$ followed manometrically, other products being condensed after the flame. VON HARTEL and POLANYI 1930 (1)	Na reacts rapidly with $(CN)_2$ or ClCN, giving CN radicals. $[H_2]$ consumption was observed to rise rapidly with temperature. This the authors attributed to reaction 1, and obtained E_1= 29kJ mol^{-1} (7 kcal mol^{-1}). $CN + H_2 \rightarrow HCN + H$ 1 Used by (3). Expression $k_1=3.4\times10^{13}\exp(-3520/T)$ cm^3 mol^{-1} s^{-1} used by (32). Quoted by (5,7,14,15,19). Attributed to (3) by (18).
8.1×10^{12}	900	Theoretical estimate from *collision theory.* ROBERTSON and PEASE 1942 (3)	Value of E_1 taken from (1). k_1 *required for investigation of the* $H_2/(CN)_2$ reaction over the temperature range 848-948 K. Reaction 1 assumed to be main reaction producing H atoms. A value of $k_1=10^{13}$ cm^3 mol^{-1} s^{-1} attributed to this paper by (24).
	300	Flash photolysis study. H_2(0.17-33.3%)/$(CN)_2$ mixtures at total pressures of 5.33-8.00 kPa. [CN] monitored by absorption spectroscopy at 416 nm. PAUL and DALBY 1962 (6)	[CN] decay rate found to vary with total pressure. HCN definitely established as a product of the photolytic reaction but the authors were unable to elucidate a mechanism or rate constant.
	493-503	Discharge flow system, 100% N_2 at 133-667 Pa pressure, NO added downstream, $(CN)_2$ added further downstream. H_2 added near the observation point. [CN] monitored by emission spectroscopy at 388.3 nm. SETSER and THRUSH 1965 (9)	Ratio k_1/k_2 given as 0.1 at 500 K by monitoring the quenching of CN $A^2\Pi$ and $B^2\Sigma^+$ $CN + O_2 \rightarrow CNO + O$ 2 k_2/k_3 determined earlier by adding O_2 in place of H_2 and observing its effect on the decay of [CN]. $O + CN \rightarrow N + CO$ 3 Using our value of k_2 (this Volume, section F8), we obtain $k_1=9.8\times10^{11}$ cm^3 mol^{-1} s^{-1} at 500 K. Quoted by (19,22,23). HEICKLEN (12) uses k_2 from (6a) to give $k_1=4.6\times10^{11}$ cm^3 mol^{-1} s^{-1} at 500 K.

$CN + H_2 \rightarrow HCN + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$9.1\times10^{11}T^{0.56}\exp(-3200/T)$	All	Theoretical estimate based on Johnston-Parr method. MAYER and SCHIELER 1966 (10)	Quoted by (28).
$10^{11}T^{0.5}\exp(-3000/T)$	All	Theoretical estimate based on collision theory. TUNDER, MAYER, COOK and SCHIELER 1966 (11)	Quoted by (28).
$<2\times10^{11}$	687	Discharge capacity flow system. 100%N_2 at 200-667 Pa pressure, NO added downstream, $(CN)_2$ added to the reaction cell. H_2 added later to the reaction cell at <9.33 Pa pressure. [CN] monitored by absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (15)	Ratio k_1/k_2 calculated as in (9) and given as <0.05. Authors used their own value of k_2 to give an upper limit for k_1. Using our value of k_2 (this Volume, section F8), we obtain $k_1<6.2\times10^{11}$ cm^3 mol^{-1} s^{-1} at 687 K. $CN + H_2 \rightarrow HCN + H$ 1 $CN + O_2 \rightarrow CNO + O$ 2 Unlike the emission work in (9), the effect of H_2 addition on absorption was barely noticeable, hence the upper limit given. Quoted by (16,19, 21,22,23,24).
1.8×10^{10}	325	Flame study. CH_2Cl_2, CCl_4, $(CN)_2$, CH_3CN, CH_4 and C_2H_2 flames at pressure of 66.7 -2670 Pa. The products of a 100% N_2 discharge at 133 Pa added, H_2 added at <6.67 Pa to pre-flame gases. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. IWAI, PRATT and BROIDA 1968 (17)	Rate constant determined from work on $(CN)_2/H_2$/active nitrogen flames. Data on the lifetime of CN and the species $(CN)_2^+$ believed to be formed taken from early work by WHITE (2). Work on CH_2Cl_2/N_2 flames by SOBERING and WINKLER (4) also considered, from which the authors derive the ratio k_1/k_4= 0.4 at 498 K. Using this relationship in their own $CH_2Cl_2/N_2/H_2$ flames gave $k_1\simeq4\times10^{11}$ cm^3 mol^{-1} s^{-1} at 325 K. As they neglected reactions of excited CN here, they consider this to be an upper limit. $CN + Cl_2 \rightarrow ClCN + Cl$ 4 Quoted by (16,20). Used by (27).

$CN + H_2 \rightarrow HCN + H$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$7.0\text{x}10^{9}$ $1.5\text{x}10^{10}$ $3.6\text{x}10^{10}$ $4.4\text{x}10^{10}$	295 323 356 388	Flash photolysis/flow system. $(CN)_2$ at 267-1400 Pa pressure, H_2 added in excess downstream. [CN] monitored by absorption spectroscopy at 388.3 nm. ALBERS, HOYERMANN, SCHACKE, SCHMATJKO, WAGNER and WOLFRUM 1975 (24)	Authors derive the expression $k_1=6\text{x}10^{13}\ \exp(-2670/T)\ cm^3\ mol^{-1}\ s^{-1}$, and note that the value of $E_1 \approx E_5$, rather than midway between E_5 and E_6 as predicted by theory. $Cl + H_2 \rightarrow HCl + H$ 5 $F + H_2 \rightarrow HF + H$ 6 Used by (29 and 30).
$3.2\text{x}10^{12}\ \exp(-2500/T)$		Theoretical estimate from transition state theory. BENSON, GOLDEN, LAWRENCE, SHAW and WOOLFOLK 1975 (25)	No comments given.
(a) $2.0\text{x}10^{13}\ \exp(-2050/T)$ (b) $2.0\text{x}10^{12}\ \exp(-1390/T)$	325-1500 325-1500	Flame study. $H_2/N_2/O_2$ (4.5:8:1) flames, total pressure not given. $(CN)_2$ (<1%) added to the pre-flame gases. Reaction followed mass spectrometrically. MULVIHILL and PHILLIPS 1975 (27)	Both expressions are computer fits to data obtained at 1500 K, combined with the value of k_1 from (17) at 325 K. $CN + H_2 \rightarrow HCN + H$ 1
$3.0\text{x}10^{12}$	1300-2500	Shock tube study. C_2H_2 (2%)/O_2 (1%)/NO (2%)/Ar mixtures behind reflected shocks. Product analysis by gas chromatography. SHAUB 1976 (31)	Computer modelling of [CO], [N_2], [C_2H_2] and [CO_2] profiles vs. T gave best fit as given here. Initial estimate quoted as $5.28\text{x}10^{12}\ cm^3\ mol^{-1}\ s^{-1}$.

REVIEW ARTICLE

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Review of reactions of atoms and small free radicals. CLYNE 1968 (16)	Quotes (15 and 17).

Discussion

The reaction between CN radicals and hydrogen is important in $H_2/(CN)_2$ flames, but only above 1000 K where it can compete with reaction 2, or else in fuel-rich conditions where O_2 is excluded or present only in small amounts.

$$CN + H_2 \rightarrow HCN + H \quad (1)$$

$$CN + O_2 \rightarrow CNO + O \quad (2)$$

A number of authors have studied the $H_2/(CN)_2$ system [3,20,27], comparing its kinetics with that of the analogous halogen reactions. Robertson and Pease [3] reported that the kinetics at 900 K could be described by a mechanism similar to that proposed for H_2/Br_2, and their collision theory estimate of k_1 gives good agreement with lower temperature experimental work. Albers et al. [24] compared the activation energy they obtained for reaction 1 and found it $\cong E_5$, although the H–CN bond dissociation energy is midway between that for H–Cl and H–F.

$$Cl + H_2 \rightarrow HCl + H \quad (5)$$

The work of Albers et al. gives the only direct determination of k_1, other systems being complicated by the presence of oxygen atoms or molecules. As might be expected, under these conditions Boden and Thrush [15] failed to observe any reaction, while that observed in the emission studies of Setser and Thrush [9] probably includes a contribution from other excited species, although again their value of k_1 agrees well with lower temperature work. Iwai et al. [17] used active nitrogen in flames of methane and cyanogen derivatives to produce CN, and used a mechanism involving ionic species as put forward by White [2] to obtain a value of k_1. Nevertheless, this agrees well with the results of Albers et al. for k_1 and that of Sobering and Winkler [4] for k_1/k_4.

$$CN + Cl_2 \rightarrow ClCN + Cl \quad (4)$$

There have been two determinations of the activation energy E_1. Von Hartel and Polanyi [1] obtained $E_1 = 29$ kJ mol^{-1} (7 kcal mol^{-1}) from measurements of $Na/(CN)_2$ flames using H_2 as diluent. Albers et al. give $E_1 = 22.2$ kJ mol^{-1} (5.3 kcal mol^{-1}). Both values are significantly higher than the estimations of Mulvihill and Phillips [27]. The fact that they were able to vary k_1 by nearly an order of magnitude at 1500 K without affecting the kinetics of their system highlights the relative unimportance of reaction 1 in the presence of oxygen.

There are thus very few reliable data on reaction 1. As an interim measure we recommend the expression

$$k_1 = 6.8\times10^{13} \exp(-2700/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 300–1000 K, with error limits of ±50% at 300 K, increasing to a factor of 3 at 1000 K. This is essentially an extrapolation of the work of Albers et al., with consideration being given to other values in agreement. Clearly more work is required, especially around 1000 K where the reaction becomes important.

Rate of the Reverse Reaction

High temperature studies of reaction 1 have had to consider the reverse reaction –1 in the overall reaction scheme.

$$H + HCN \rightarrow CN + H_2 \quad (-1)$$

Robertson and Pease [3] allowed HCN to stand on its own for 48 hours at 898 K and showed no decomposition occurred. Mulvihill and Phillips [27] added expressions for k_{-1} to their computer fit to $H_2/N_2/O_2/(CN)_2$ flames. They obtained k_{-1} from their own expressions for k_1 and the equilibrium constant K_1 from JANAF, giving (a) $k_{-1} = 9.0\times10^{13} \exp(-10\,700/T)$ cm^3 mol^{-1} s^{-1} and (b) $k_{-1} = 9.0\times10^{12} \exp(-10\,000/T)$ cm^3 mol^{-1} s^{-1}. Johnston-Parr calculations have yielded two expressions, $k_{-1} = 2.6\times10^{11}\ T^{0.695} \exp(-9260/T)$ [8] and $k_{-1} = 2.1\times10^{11}\ T^{0.69} \exp(-9300/T)$ [13] cm^3 mol^{-1} s^{-1}. Although at $T < 2500$ K, $k_{-1} < k_1$, reaction –1 is sufficiently fast to be of importance in flame and shock tube studies involving HCN. However, because of the complexity of such systems, and the nature of the equilibrium in reaction 1, direct measurement of k_{-1} has proved difficult. Roth and Just [30] obtain an upper limit for $k_{-1} < 2\times10^{11}$ cm^3 mol^{-1} s^{-1} at 2600 K from shock tube studies of HCN dissociation, failing to detect any subsequent reaction of either H or CN in their system. Morley [26] added nitrogen-containing species to hydrocarbon/Ar flames, and monitored [HCN] decay mass spectrometrically. At 2350 K he found $k_{-1} \sim 10^{14}$ cm^3 mol^{-1} s^{-1}, assuming the rate determining reaction in the flame to be reaction 6.

$$CN + OH \rightarrow CNO + H \quad (6)$$

It is clear that there is no agreement between any of the data, experimental or theoretical. The problems posed by HCN systems at high temperatures are considerable and obtaining an accurate direct measurement of k_{-1} poses many problems. We recommend use of the expression

$$k_{-1} = 3.8\times10^{14} \exp(-12\,400/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

derived from k_1/K_1, over the temperature range 300–1000 K, with error limits of a factor of 3.

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F6 $CN + CH_4 \rightarrow HCN + CH_3$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-79.433	7.100	14.288
300	-79.412	7.159	14.202
500	-77.216	12.761	8.733
1000	-73.701	17.916	4.786
1500	-72.509	18.920	3.513
2000	-72.274	19.062	2.883
2500	-72.877	18.807	2.505
3000	-74.396	18.255	2.249
3500	-76.743	17.535	2.061
4000	-79.709	16.744	1.916
4500	-83.061	15.958	1.798
5000	-86.609	15.192	1.699

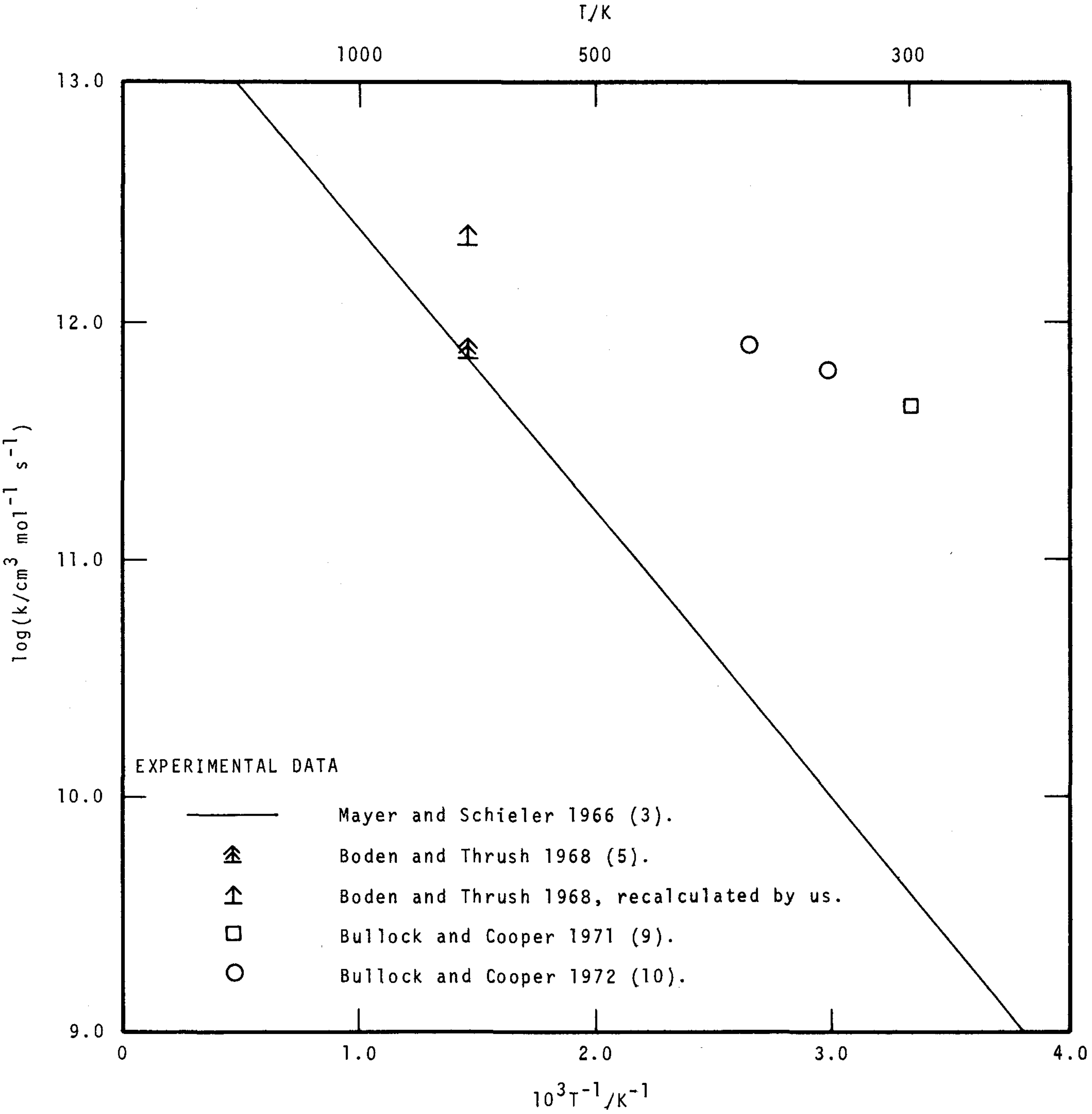
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	303-423	Static photolysis of ICN (∿133 Pa) at 253.7 nm in the presence of I_2 (0.4g, <100 Pa) and a CH_4 (∿50%) /C_2H_6 mixture at total pressures of 6.67-13.3 kPa. $[CH_3I]$, $[C_2H_5I]$ by gas chromatography. GOY, SHAW and PRITCHARD 1965 (2)	The presence of I_2 served two purposes: it helped arrest any decomposition of ICN by reaction 2, and ensured production of iodides rather than cyanides as products: $ICN + h\nu \rightarrow I + CN$ $CN + CH_4 \rightarrow HCN + CH_3$ 1 $CH_3 + I_2 \rightarrow CH_3I + I$ $CN + I_2 \rightarrow ICN + I$ $2ICN \rightleftarrows I_2 + (CN)_2$ 2 and similarly for C_2H_6. Measurement of $[CH_3I]$ gave a quantitative assessment of $[CH_3]$. Thus the authors were able to obtain the ratio k_3/k_1=20.9 (303 K); 16.2 (316 K); 14.1 (324 K); 12.3 (332 K); 10.2 (340 K); 8.71 (356 K); 7.90 (364 K); 6.17 (377 K); 4.27

$CN + CH_4 \rightarrow HCN + CH_3$



$CN + CH_4 \rightarrow HCN + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		GOY, SHAW and PRITCHARD 1965 (2) continued.	(392 K); 5.50 (423 K). $CN + C_2H_6 \rightarrow HCN + C_2H_5$ 3 Above 373 K, all results corrected for photolysis of C_2H_5I. CH_3I was unaffected. Authors derive expression $k_1/k_3=20.6 \exp(-1900/T)$. Quoted by (8,9,10,12).
$2.9\times10^{11}T^{0.657} \exp(-2400/T)$	All	Theoretical estimate based on Eyring-Polanyi transition state theory. MAYER and SCHIELER 1966 (3)	Quoted by (4,13).
$<7\times10^{11}$	687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream. CH_4 added later to reaction cell at <1.5 Pa pressure. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (5)	Attenuation of CN absorption and emission compared with that obtained when O_2 added in place of CH_4. No reduction in absorption detectable hence ratio k_1/k_4 given as <0.15. $CN + O_2 \rightarrow CNO + O$ 4 Using our value of k_4 (This Vol., section F8) we obtain $k_1<2.1\times10^{12}$ $cm^3\ mol^{-1}\ s^{-1}$ at 687 K. Quoted by (6,8,10,11). Used by (9).
4.5×10^{11}	300	Pulse radiolysis of $(CN)_2$ (2-2.7%)/Ar mixtures at a total pressure of 104 kPa, in the presence of <1% CH_4. [CN] followed by absorption spectroscopy at 388.3 nm. BULLOCK and COOPER 1971 (9)	Decay of [CN] (v=4) also observed and found to be 10% faster than the ground state. Authors report an activation energy $E_1 \approx$ 5 kJ mol^{-1} (1.20 kcal mol^{-1}), but stress that their radiolysis cell was not designed for work at elevated temperatures. $CN + CH_4 \rightarrow HCN + CH_3$ 1 Quoted by (11,14). Used by (10).
6.3×10^{11} 8.2×10^{11}	335 377	Pulse radiolysis of (CN_2)/Ar mixtures, in the presence of CH_4 (<941 Pa). No further pressure details given. [CN] followed by absorption spectroscopy at 388.3 nm. BULLOCK and COOPER 1972 (10)	Similar method used to that in (9), but radiolysis cell modified for use at higher temperatures. Combining these results with those of (9) authors obtain expression $k_1=9.1\times10^{12}\exp(-900/T)$ $cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 300-377 K. However, they do warn that the value at 377 K may be too low due to relaxation of CN^v effectively slowing down CN removal, and taking this into account give as a revised expression $k_1=1.3\times10^{13}\exp(-1000/$

$CN + CH_4 \rightarrow HCN + CH_3$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		BULLOCK and COOPER 1972 (10) continued.	T) $cm^3\ mol^{-1}\ s^{-1}$. Quoted by (14).

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Review of reactions of atoms and small free radicals. CLYNE 1968 (6)	Quotes (5).
		Review of reactions involving halogen, nitrogen and sulphur compounds. WHITE 1972 (12)	Quotes rate constant ratio expression from (2).

ISOTOPIC REACTION $CN + CD_4 \rightarrow DCN + CD_3$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2.4×10^{11}	300	Pulse radiolysis of $(CN)_2$/Ar mixtures in the presence of CD_4, no details of pressure given. [CN] followed by absorption spectroscopy at 388.3 nm. BULLOCK and COOPER 1972 (10)	Insufficient data available to make comment on isotope effect, but authors believe that H atom tunnelling is present.

Discussion

CN radicals abstract hydrogen atoms from methane in a manner analogous to halogen atoms. Evidence seems to suggest [2,9], that they react at a similar rate to Cl atoms, although the relationship between activation energies is not so clear.

$$\mathrm{CN} + \mathrm{CH_4} \rightarrow \mathrm{HCN} + \mathrm{CH_3} \qquad (1)$$

$$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{HCl} + \mathrm{CH_3} \qquad (5)$$

Safrany and Jaster [7] report that the substitution reaction 6 is also fast, but present no evidence for this, and its occurrence is not mentioned elsewhere.

$$\mathrm{CN} + \mathrm{CH_4} \rightarrow \mathrm{CH_3CN} + \mathrm{H} \qquad (6)$$

There are very little data available from direct measurements of reaction 1, and even less data on reaction 3. It is difficult to draw any conclusions from the work of Goy et al. [2]—their ratio A_1/A_3 is in considerable disagreement with that obtained for A_5/A_7, [1] and with A_1/A_3 as obtained from the individual direct determinations of Bullock and Cooper [10]. The latter authors suggest that possible side reactions may be the cause in a static photolytic system.

$$\mathrm{CN} + \mathrm{C_2H_6} \rightarrow \mathrm{HCN} + \mathrm{C_2H_5} \qquad (3)$$

$$\mathrm{Cl} + \mathrm{C_2H_6} \rightarrow \mathrm{HCl} + \mathrm{C_2H_5} \qquad (7)$$

The low activation energy E_1 found by Bullock and Cooper [10] leads to a value of k_1 at 687 K above the lower limit of Boden and Thrush [5] as recalculated by us.

As the radiolysis system used by Bullock and Cooper produced a low activation energy for the $\mathrm{CN}+\mathrm{O_2}$ reaction, this discrepancy can only be resolved by questioning Thrush's ratio k_1/k_4.

$$\mathrm{CN} + \mathrm{O_2} \rightarrow \mathrm{CNO} + \mathrm{O} \qquad (4)$$

In view of the lack of reliable, direct data, we can make *no recommendation for* k_1.

Isotopic Reaction $\mathrm{CN} + \mathrm{CD_4} \rightarrow \mathrm{DCN} + \mathrm{CD_3}$

Bullock and Cooper [10] made a determination of k_{1D} at 300 K. They were unable to comment in detail on the isotope effect due to insufficient data.

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Note Added in Proof

Schacke et al. (Ber. Bunsenges. Phys. Chem. **81**, 670 (1977)) have produced CN radicals by flash photolysis of $\mathrm{C_2N_2}$ in a flow system, and studied their rate of removal by a large excess of $\mathrm{CH_4}$. Total pressures used were in range 4–5 torr. (0.4–0.7 kPa) and temperatures of 266–397 K. The CN is produced in various vibrationally excited states the disappearance of which could be monitored by absorption spectroscopy.

For $\mathrm{CN}(V^{11}=0)$ they found $k_1=(6\pm3)\times10^{12}$ $\exp(-870/T)$ cm^3 mol^{-1} s^{-1} which, within the substantial error limits, is in agreement with the results of Bullock et al. [10].

F7 $CN + O \rightarrow CO + N$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-322.189	-12.740	55.784
300	-322.185	-12.744	55.436
500	-322.352	-13.163	32.991
1000	-322.599	-13.514	16.146
1500	-322.800	-13.673	10.527
2000	-323.227	-13.916	7.716
2500	-324.302	-14.393	6.026
3000	-326.247	-15.104	4.892
3500	-328.975	-15.949	4.078
4000	-332.210	-16.815	3.462
4500	-335.611	-17.619	2.978
5000	-338.891	-18.322	2.585

RECOMMENDED RATE CONSTANT

$k = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}

$= 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

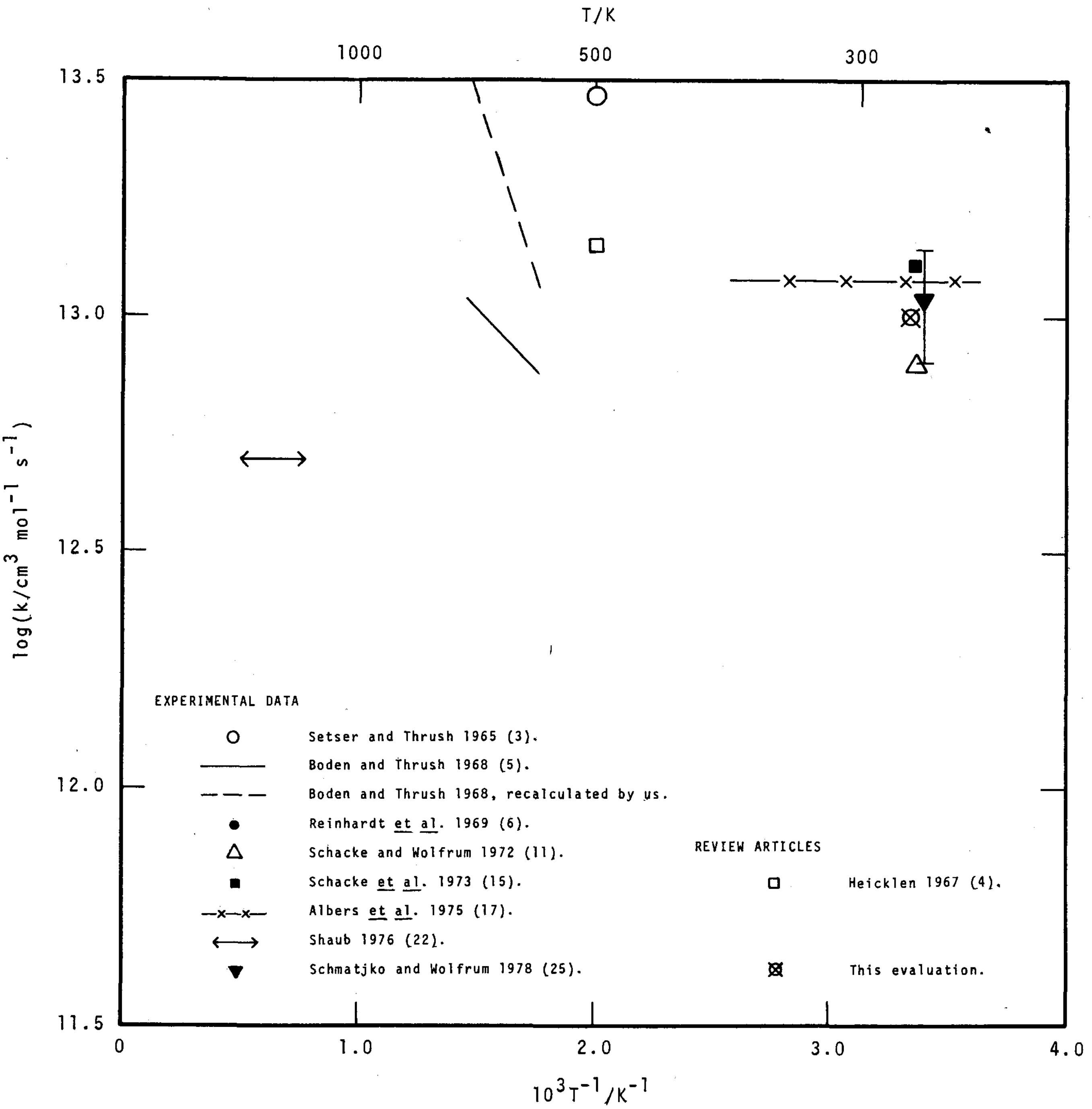
Temperature: 298 K.

Suggested Error Limits: ±50%.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	493-503	Discharge flow system. 100% N_2 at 133-667 Pa pressure, NO added downstream. $(CN)_2$ added in excess further downstream. In some experiments O_2 was added near the observation point at 0.67-4.00 Pa pressure. [CN] monitored by emission spectroscopy at 388.3 nm. SETSER and THRUSH 1965 (3)	Ratio k_1/k_2 determined as 3.1 by monitoring the quenching of CN $A^2\Pi$ and $B^2\Sigma^+$ $CN + O \rightarrow CO + N$ 1 $CN + O_2 \rightarrow CNO + O$ 2 Authors concluded the only reaction capable of exciting CN radicals was $O + O + CN \rightarrow O_2 + CN^*$ with decay following collisions with ground state CN. Reaction 2 removes ground state CN, thus attenuating the CN emission. At short reaction times reaction 1 is the only other reaction competing for CN, no dependence

$CN + O \rightarrow CO + N$



$CN + O \rightarrow CO + N$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		SETSER and THRUSH 1965 (3) continued.	being found for CN decay on $[(CN)_2]$, ruling out reaction 3. $CN + (CN)_2 \rightarrow$ products 3 Using our value of k_2 (this Volume, section F8), we obtain $k_1=3.0\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ at 500 K. An activation energy of ∿4 kJ mol^{-1} (1 kcal mol^{-1}) was deduced. Used by (4).
$6.3\times10^{13}\exp(-1200/T)$	570-687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream. $(CN)_2$ added in excess to the reaction cell. In some experiments O_2 was added later to the reaction cell at 0.33-2.50 Pa pressure. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (5)	Relative rate k_1/k_2 determined as in (3) and given as 2.56 at 687 K. The activation energy difference $E_1-E_2=10.0$ kJ mol^{-1} (2.4 kcal mol^{-1}). In this case, the authors were able to determine k_2 independently and thus give $k_1=1.1\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ at 687 K. Using our value of k_2 (this Volume, section F8), we obtain $k_1=3.2\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$. Comparison of their k_2 with those of other authors (1,2) at other temperatures led them to the conclusion that $E_2=0$, hence $E_1=10.0$ kJ mol^{-1} (2.4 kcal mol^{-1}). Used by (9). Quoted by (6,10,14,16). Attributed by (8) to (7). Using our expression for k_2 we obtain the expression $k_1=6.0\times10^{15}\exp(-3550/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 570-687 K. Both expressions plotted on Arrhenius diagram.
6.4×10^{11}	295	Discharge/flash photolysis flow system. NO/He mixtures at a total pressure of 850 Pa. CN radicals added downstream so that O atoms were in a large excess. CN produced from the flash photolysis of $(CN)_2$ at 137 Pa. [CN] monitored by absorption spectroscopy at 388.3 nm. REINHARDT, WAGNER and WOLFRUM 1969 (7)	NO dissociation used to produce high concentrations of O atoms. Energy of discharge chosen with regard to [NO] to avoid build up of N atoms or excess NO. In this way, reaction 1 monitored directly. $CN + O \rightarrow CO + N$ 1 Quoted by (10).

$CN + O \rightarrow CO + N$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$8x10^{12}$	298	Flash photolysis study. No details given, but the method is probably similar to that in (15). SCHACKE and WOLFRUM 1972 (11)	Optical pumping used to produce vibrationally excited CN up to v=6. No change in k_1 found for $v \leqslant 5$.
$1.3x10^{13}$	298	Discharge/flash photolysis flow system. N_2/He mixtures at 400-533 Pa pressure. NO added downstream, $(CN)_2$ further downstream so that $[(CN)_2] > [O]$. Entire mixture flash photolysed. [CN] monitored by kinetic absorption spectroscopy at 421.6 nm. SCHACKE, SCHMATJKO and WOLFRUM 1973 (15)	In these experiments, only CN(v=0) produced, although experiments with excited CN ($v \leqslant 6$) produced the same rate constant. $(CN)_2$ pressure chosen so that after photolysis $[O] >> [CN]$. Authors believe low value of k_1 in (7) due to presence of N atoms before photolysis, reducing $[(CN)_2]$. Quoted by (18).
$1.2x10^{13}$	275-387	Discharge/flash photolysis flow system. N_2(<0.1%)/He mixtures at 325 Pa pressure. NO added downstream, $(CN)_2$ further downstream. Entire mixture flash photolysed. In some experiments excess NO added. [CN] monitored by kinetic absorption spectroscopy at 388.3 nm. ALBERS, HOYERMANN, SCHACKE, SCHMATJKO, WAGNER and WOLFRUM 1975 (17)	Authors found that CN signal increased if $[O] > 5x10^{-10}$ mol cm^{-3}. They assumed this to be due to the increased production of N atoms in reaction 1, followed by generation of CN in reaction 4. $N + (CN)_2 \rightarrow CN + CN_2$ 4 Excess NO was added to scavenge the N atoms, and on the basis of these experiments the rate constant k_1 was obtained from first order [CN] decay. Quoted by (24). Value $1.3x10^{13}$ cm^3 mol^{-1} s^{-1} used by (21).
$5.0x10^{12}$	1300-2500	Shock tube study. C_2H_2 (2%)/O_2(1%)/NO (2%)/Ar mixtures. Reflected shocks. Products quenched by reflected expansion and analysed by gas chromatography. SHAUB 1976 (22).	Modelling of [CO], $[N_2]$, $[CO_2]$ and $[C_2H_2]$ vs. T profiles conducted initially using expression of (5). Better fit obtained using altered, temperature-independent value.

$CN + O \rightarrow CO + N$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$(1.1\pm0.3)\times10^{13}$	295	Flash photolysis/discharge flow system. $(CN)_2$ (1.4x10^{-10}-6.2x10^{-9} mol cm^{-3})/ He mixtures at total pressures 1.7-2.7 mm Hg (227-360 Pa) flash photolysed in presence of excess [O] from discharge (9x10^{-11}≤[O]≤ 3.3x10^{-9} mol cm^{-3}). [CO(v)] monitored by ir absorption and [N] by vuv absorption at 120, 149 and 174 nm. SCHMATJKO and WOLFRUM 1978 (25)	Value of k_1 obtained from [CO] profiles. No systematic $CN + O \rightarrow CO + N$ 1 variation found for levels v= 5-12.

REVIEW ARTICLES

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1.4×10^{13}	500	Review of gas phase chemistry of re-entry. HEICKLEN 1967 (4)	Value of k_1 derived from k_1/k_2 from (3), using k_2 from (2). $CN + O \rightarrow CO + N$ 1 $CN + O_2 \rightarrow CNO + O$ 2 Quoted by (20).
		Review of reactions of atoms and small free radicals. CLYNE 1968 (6)	Quotes (4).
		Review of oxidations of inorganic non-metallic compounds. HEICKLEN and COHEN 1972 (10)	Quotes (6 and 8).
		Review of pollutant formation in flames. PALMER and SEERY 1973 (14)	Quotes (5). Suggests that reaction 1 may be source of NO from fuel nitrogen in flames (12), N atoms reacting further by reaction 5 $N + O_2 \rightarrow NO + O$ 5
		Review of reactions of atoms in ground and electronically excited states. DONOVAN and GILLESPIE 1975 (18)	Quotes (15).

$CN + O \rightarrow CO + N$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1x10^{12}$	All	Selected value for use in methane/air combustion. ENGLEMAN 1976 (20)	Based on (5 and 6). Activation energy E_1 assumed to be zero. Author notes lack of experimental data and advises caution in use of his k_1.

Discussion

Reaction 1 rapidly removes CN radicals from photolytic $(CN)_2/O_2$ systems at room temperature. Its effect in cyanogen flames is not known at all, Mulvihill and Phillips [19] considering it to be unlikely to occur in fuel-rich flames where there will be few O atoms available, and CN radicals can be removed by other means. Its rate at room temperature suggests, however, that it should be important in fuel-lean conditions.

$$CN + O \rightarrow CO + N \qquad (1)$$

Appleton and Heywood [12] consider that reaction 1 followed by 5 is an important source of NO emission from flames, a view supported by Bowman [13].

$$N + O_2 \rightarrow NO + O \qquad (5)$$

The only direct determinations of k_1 are all at or around room temperature, combining discharge flow and flash photolysis techniques. The agreement would appear not to be good, but the value of Shacke and Wolfrum [11] is a preliminary one, updated in [15], while Reinhardt et al. [7] produce O atoms in high concentrations by direct dissociation of NO. Although they claim that N atoms produced *recombine before* $(CN)_2$ *is added, Schacke et al.* [15] *consider* this unlikely and believe that the low value of k_1 is due to reactions between the N atoms and $(CN)_2$ before the flash photolysis stage, thus increasing [CN]. This problem was avoided by Albers et al. [17] who added excess NO to scavenge the N atoms.

Little weight can be given to the results of Thrush et al. [3,5] and of Shaub [22].

Those values of k_1 determined using our expression for k_2 (section F8) are liable to large error limits as we cannot guarantee the accuracy of k_2 at such high temperatures. The remaining expression, of Boden and Thrush [5] was determined assuming that reaction 2 has zero activation energy.

$$CN + O_2 \rightarrow CNO + O \qquad (2)$$

We believe that evidence points to $E_2 \sim 3.6$ kJ mol^{-1} (0.9 kcal mol^{-1}). If this activation energy is used, and accepting Thrush's value of k_1 at 687 K, then we obtain at 570 K, $k_1 = 8.8 \times 10^{12}$ cm^3 mol^{-1} s^{-1}, slightly higher than plotted on the Arrhenius diagram, and giving weight to the contention of Albers et al. that $E_1 = 0$.

We suspect that reaction 1, like reaction 2, has a very small positive activation energy, but we do not have enough reliable data to make a recommendation over a temperature range. However, at 298 K we recommend $k_1 = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, with error limits of ±50%.

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F8 $CN + O_2 \rightarrow CNO + O$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-26.556	-14.506	3.896
300	-26.547	-14.481	3.866
500	-25.414	-11.678	2.045
1000	-21.317	- 6.033	0.798
1500	-17.251	- 2.724	0.458
2000	-13.824	- 0.741	0.322
2500	-11.552	0.285	0.257
3000	-10.665	0.615	0.218
3500	-11.033	0.510	0.192
4000	-12.351	0.159	0.170
4500	-14.255	- 0.289	0.150
5000	-16.422	- 0.761	0.133

RECOMMENDED RATE CONSTANT

$k = 2.4 \times 10^{13} \exp(-450/T)$ cm^3 mol^{-1} s^{-1}

$= 4.0 \times 10^{-11} \exp(-450/T)$ cm^3 $molecule^{-1}$ s^{-1}

Temperature Range: 290-400 K.

Suggested Error Limits for Calculated Rate Constant: ±30% over the whole temperature range.

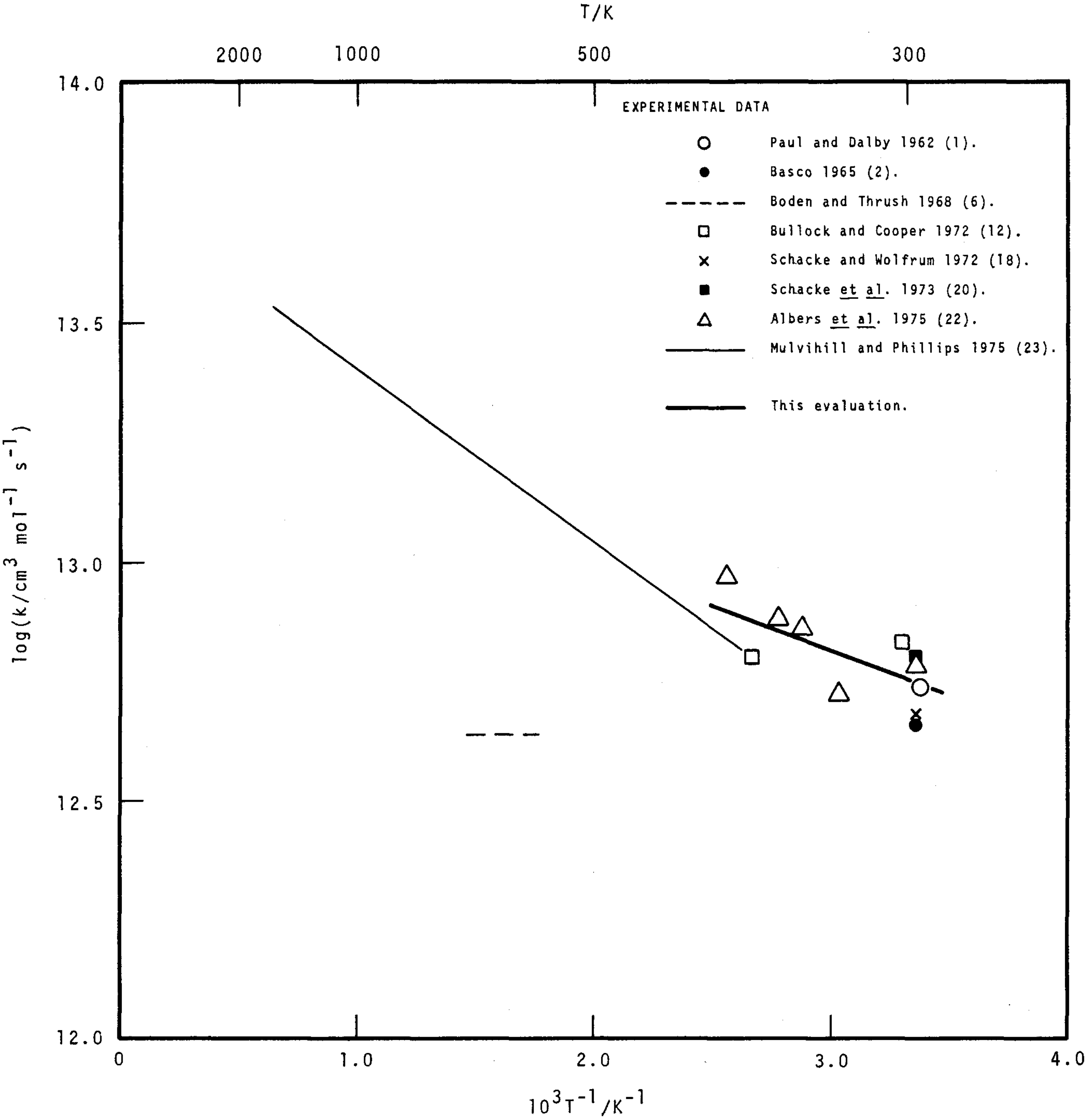
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 13.39 \pm 0.12$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -10.40 \pm 0.12$

$E/J\ mol^{-1} = 3\,700 \pm 3\,700$

$E/cal\ mol^{-1} = 890 \pm 890$

$CN + O_2 \rightarrow CNO + O$



$CN + O_2 \rightarrow CNO + O$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
5.5×10^{12}	296	Flash photolysis of $(CN)_2$ (98% pure)/O_2 mixtures. No pressure details. [CN] followed by absorption spectroscopy at 388.3 nm. PAUL and DALBY 1962 (1)	Assuming a non-chain process, authors obtained k_1 which they considered only an approximate value. $CN + O_2 \rightarrow CNO + O$ 1 Used by (6,16,17). Quoted by (2,3,8,9,10,12,14).
4.6×10^{12}	298	Flash photolysis study. $(CN)_2$ (1.7-9.0%) in the presence of O_2 (<0.1-98%) /N_2 (0-97%) mixtures at pressures of 26.7-65.0 kPa, or BrCN (3.5%) in the presence of O_2 (<0.1%)/N_2 mixtures at 40 kPa pressure. [CN] monitored by absorption spectroscopy at 388.3 and 421.6 nm. BASCO 1965 (2)	Only those data measured at low [O_2] were considered, as this increased the likelihood of reaction 1 being the only reaction removing CN. In the presence of >5% O_2, ozone formation began. Reactions removing CN in the absence of O_2 were ignored as their consideration made very little difference to k_1. From measurements of [NO] production at various [O_2], author claimed the direct reaction 1' was responsible for ∿15% of NO formation. $CN + O_2 \rightarrow CO + NO$ 1' Quoted by (5,8,9,10,12,14,19,21). Used by (4,6,11,16,17,24).
	293-503	Discharge flow system. 100% N_2 at 133-667 Pa pressure, NO added downstream. $(CN)_2$ added in excess further downstream. In some experiments O_2 was added near the observation point at 0.67-4.00 Pa pressure. [CN] monitored by emission spectroscopy at 388.3 nm. SETSER and THRUSH 1965 (3)	Ratio k_1/k_2 determined as 0.32 by monitoring the quenching of CN $A^2\Pi$ and $B^2\Sigma^+$. $O + CN \rightarrow N + CO$ 2 Authors concluded the only reaction capable of exciting CN radicals was $O + O + CN \rightarrow O_2 + CN^*$ with decay following collisions with ground state CN. Reaction 1 removes ground state CN, thus attenuating the CN emission. Addition of other quenching agents gave the following ratios: k_1/k_3=0.37; k_1/k_4=10; k_1/k_5=0.16, all at 500 K. $CN + NO \rightarrow CO + N_2$ 3 $CN + H_2 \rightarrow HCN + H$ 4 $CN + NH_3 \rightarrow HCN + NH_2$ 5 We have used k_1 determined in this evaluation to obtain values of k_2 to k_5.

$CN + O_2 \rightarrow CNO + O$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
4.4×10^{12}	570-687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream. $(CN)_2$ added in excess to the reaction cell. In some experiments O_2 was added later to the reaction cell at 0.33-2.50 Pa pressure. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (6)	Both absorption and emission results gave k_1/k_2=0.39 at 687 K, confirming mechanism in (3). The activation energy difference E_2-E_1=10.0 kJ mol^{-1} (2.4 kcal mol^{-1}). The authors used this ratio and their value of k_6 determined earlier to obtain k_1 from the observed value of [CN]. $O + (CN)_2 \rightarrow CNO + CN$ 6 Comparing their k_1 with those of (1 and 2) at room temperature, they concluded that E_1=0. Adding other quenching gases, they obtained the ratios k_1/k_3=16.7; $k_1/k_4 \geq 20$; k_1/k_5=0.83; $k_1/k_7 \geq 6.67$, at 687 K. $CN + CH_4 \rightarrow HCN + CH_3$ 7 $CN + O_2 \rightarrow CNO + O$ 1 k_1 quoted by (7,9,10,12,13,14,15, 23). Used by (11). Ratios quoted by (15).
6.8×10^{12} 6.3×10^{12}	303 375	Pulse radiolysis study. $(CN)_2$ (∼2.5%)/Ar mixtures in the presence of O_2 (<0.5%) at total pressures of 80 kPa. [CN] monitored by absorption spectroscopy at 388.2 nm. BULLOCK and COOPER 1972 (12)	Rate constants determined for reactions of each vibrational level of CN up to v=4. Authors claim excellent reproducibility of their data and believe the apparent negative activation energy shown to be correct. However they later admit that O^1D atoms may be produced in the system, and these could affect the results. Used by (23).
4.7×10^{12}	298	Flash photolysis study. No details given, but the method probably similar to that in (20). SCHACKE and WOLFRUM 1972 (18).	Optical pumping used to produce vibrationally excited CN up to v=6. Steady decrease in k_1 from v=0 to 6.
6.3×10^{12}	298	Flash photolysis/flow system. $(CN)_2/O_2$ mixtures flowed through photolysis cell. No details of pressures given. [CN] monitored by kinetic absorption spectroscopy at 421.6 nm. SCHACKE, SCHMATJKO and WOLFRUM 1973 (20)	Results confirm earlier work (18) in that k_1 decreases as the vibrational level increases.

$CN + O_2 \rightarrow CNO + O$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
6.0×10^{12} 5.4×10^{12} 7.2×10^{12} 7.5×10^{12} 9.4×10^{12}	298 330 347 360 391	Flash photolysis/flow system. $(CN)_2$ (∿30 Pa)/ O_2 mixtures flowed through photolysis cell at a total pressure such that $[O_2] > [CN]$. [CN] monitored by absorption spectroscopy at 388.3 nm, [CNO] at 398 nm. ALBERS, HOYERMANN, SCHACKE, SCHMATJKO, WAGNER and WOLFRUM 1975 (22)	Results from [CN] and [CNO] measurements in good agreement. Authors derive expression $k_1 = 3.2 \times 10^{13} \exp(-500/T)\ cm^3\ mol^{-1}\ s^{-1}$ over the temperature range 275-398 K. $CN + O_2 \rightarrow CNO + O$ 1
$6.0 \times 10^{13} \exp(-840/T)$	Flame Temperatures	Flame study. $H_2/N_2/O_2$ (4.5:8:1) flames, total pressure not given. $(CN)_2$ (<1%) added to the pre-flame mixture. Reaction followed mass-spectrometrically. MULVIHILL and PHILLIPS 1975 (23)	Expression is computer fit to data. Initially authors obtained $k_1/k_3 = 0.15$ at ∿1500 K. In view of the discrepancy between this and the result of (6), this ratio was rejected, and k_1 assessed to agree with the value of (12) at 375 K, also with their own findings that $k_1 >> k_4$. $CN + NO \rightarrow CO + N_2$ 3 $CN + H_2 \rightarrow HCN + H$ 4

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	500	Review of gas phase chemistry of re-entry. HEICKLEN 1967 (4)	Quotes (2), and uses k_1 from it to determine k_2 and k_3 from the ratios of (3). $O + CN \rightarrow CO + N$ 2
		Review of the reactions of atoms and small radicals. CLYNE 1968 (7)	Quotes (6).
		Review of oxidation of inorganic non-metallic compounds. HEICKLEN and COHEN 1972 (14)	Quotes (1,2,6).
		Review of reactions involving halogen, nitrogen and sulphur compounds. WHITE 1972 (19)	Quotes (2).

$CN + O_2 \rightarrow CNO + O$

REVIEW ARTICLES - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		Selected value for use in methane / air combustion. ENGLEMAN 1976 (24)	Considers only the direct path reaction 1' and derives $k_{1'} = 6.9x10^{11}\ cm^3\ mol^{-1}\ s^{-1}$, with $E_{1'}=0$, from data of (2).

Discussion

Cyanogen is readily dissociated in flames, and the reaction between cyano radicals and oxygen is an important first step in the consumption of these radicals. Despite the importance of reaction 1 in flames, there has been only one indirect study of it at flame temperatures [22], the difficulty in cyanogen systems being the number of complicating side reactions that can occur. Flash photolysis has proved the most successful tool in studying reaction 1 at lower temperatures, where the initial rate of CN disappearance can be monitored without complications.

$$CN + O_2 \rightarrow CNO + O \qquad (1)$$

There is no corresponding halogen reaction with which to compare 1. In the cases of chlorine and bromine, the reverse reaction predominates, while here CNO reacts rapidly with the oxygen atom, splitting the carbon-nitrogen bond.

$$O + CNO \rightarrow CO + NO$$

The discharge flow studies [3,6] have the disadvantage of complicating side reactions, allowing only the direct determination of rate constant ratios. In the later investigation [6], Boden and Thrush obtain a value of k_1 by using their own value of k_6 determined earlier. The agreement with other values of k_1 is poor, although the estimation of $E_1 \sim 0 \pm 1500$ J mol^{-1} (350 cal mol^{-1}) is reasonable. Difficulties may have arisen from the addition of O_2 so late in the reaction when the competing reaction 2 has been in progress for some time, and we also note the disagreement in the rate constant ratios determined in [3 and 6].

$$O + CN \rightarrow N + CO \qquad (2)$$

$$O + (CN)_2 \rightarrow CN + CNO \qquad (6)$$

We prefer the flash photolysis studies [1,2,18,20,22] which show good agreement over the narrow temperature range considered. Overall evidence seems to indicate a slight positive activation energy, within the limits set by Boden and Thrush [6]. Bullock and Cooper [12] report a negative activation energy from pulse radiolysis of $(CN)_2/O_2$ mixtures, but nevertheless their results agree well with the other low temperature work. They suspected production of $O(^1D)$ in the system, making allowances for reaction 6′, but not 2′

$$O(^1D) + CN \rightarrow N + CO \qquad (2')$$

$$O(^1D) + (CN)_2 \rightarrow CN + CNO \qquad (6')$$

The expression of Mulvihill and Phillips [23] is not a direct experimental determination, formulated only to agree with theory and correlate with the low temperature results. We suspect the activation energy $E_1 = 7$ kJ mol^{-1} (1.7 kcal mol^{-1}) may be too high.

On the basis of the low temperature flash photolysis work, and the general conclusion that the activation energy is very small, we recommend the expression

$$k_1 = 2.4 \times 10^{13} \exp(-450/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 290–400 K, with error limits of ±30%. We cannot recommend a value of k_1 at flame temperatures.

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F9 $CN + NO \rightarrow CO + N_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (KJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-635.955	-24.137	110.154
300	-635.951	-24.146	109.466
500	-636.114	-24.548	65.171
1000	-636.863	-25.564	31.930
1500	-637.575	-26.142	20.836
2000	-638.382	-26.598	15.283
2500	-639.734	-27.200	11.946
3000	-641.918	-27.991	9.714
3500	-644.901	-28.911	8.114
4000	-648.486	-29.865	6.908
4500	-652.432	-30.790	5.965
5000	-656.541	-31.677	5.205

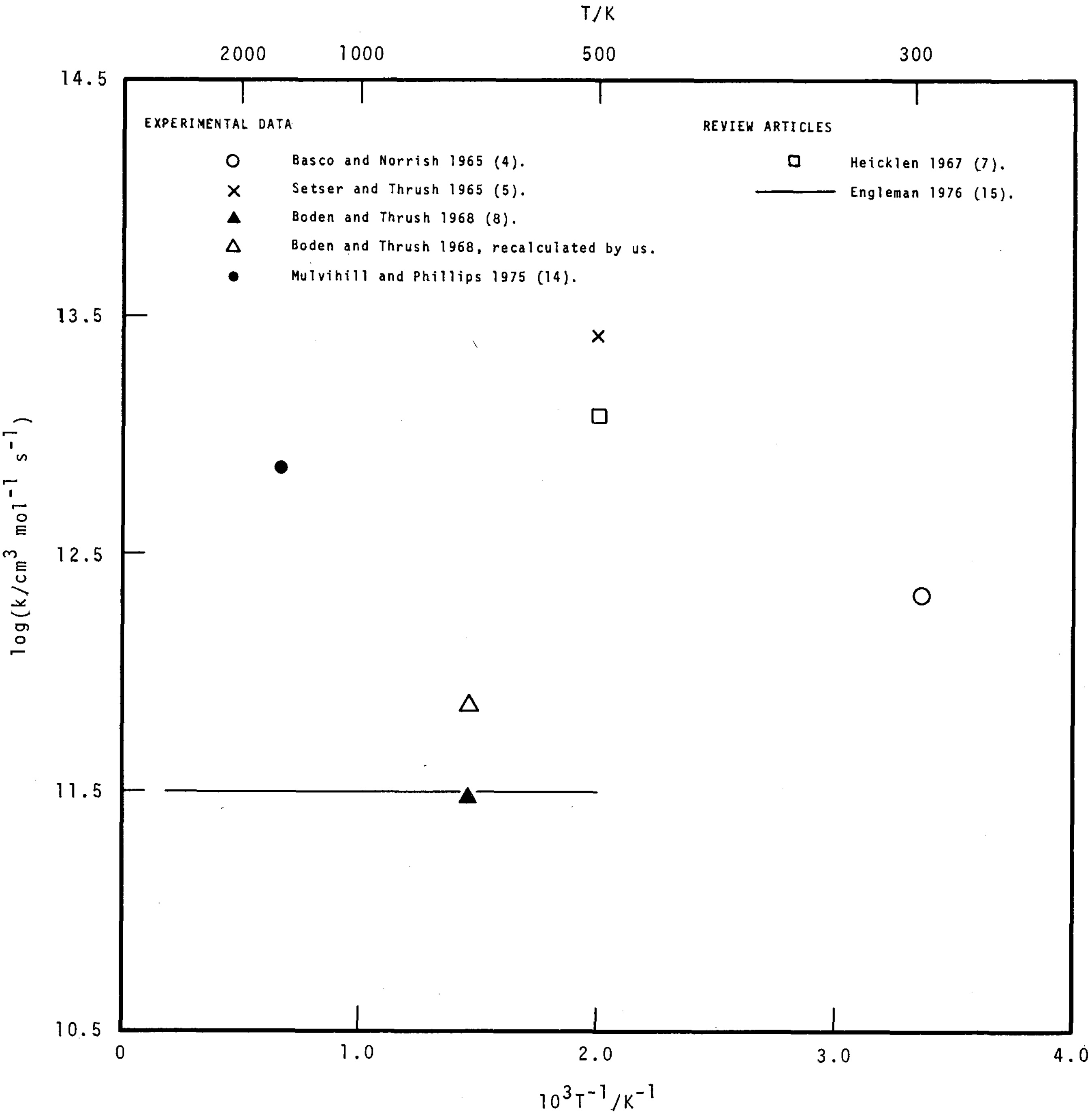
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
2.1×10^{12}	298	Flash photolysis study. $(CN)_2$ (2.5-4%) or BrCN (3%)/N_2 mixtures at total pressures of 33.3-75.0 kPa in the presence of NO (<5%). Photolysis of NO prevented by NO filter. [CN] followed by absorption spectroscopy at 359-421.6 nm and NO at 227-237 nm. BASCO and NORRISH 1965 (4)	Both CN and NO observed in several vibrational states after the flash. Addition of NO rapidly removed the CN spectrum, giving another unidentified spectrum, which the authors took to be NOCN, by analogy with similar halogen reactions, giving NOCl and NOBr in the same region. $NO + CN (+M) \rightarrow NOCN(+M)$ 1' Repeated flashing of the mixture produced vibrationally excited NO, again analogous to NOCl and NOBr. Following the decay of [CN] in excess NO gave the rate constant quoted or the third order form $k_{1'} = 1.3 \times 10^{17}$ cm^6 mol^{-2} s^{-1}. Quoted by (8,10,11).

$CN + NO \rightarrow CO + N_2$



$CN + NO \rightarrow CO + N_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	493-503	Discharge flow system. 100% N_2 at 133-667 Pa pressure, NO added in excess downstream, $(CN)_2$ added further downstream. O_2 added near the observation point at 0.67-4.00 Pa pressure. [CN] monitored by emission spectroscopy at 388.3 nm. SETSER and THRUSH 1965 (5)	Ratio k_1/k_2 given as 2.7 at 500 K by monitoring the quenching of CN $A^2\Pi$ and $B^2\Sigma^+$, assuming that NO removes ground state CN. By monitoring the decay of [CN] in the presence and absence of O_2, the effect of reaction 2 on k_1+k_3 could be observed, and hence k_1/k_2 determined from the authors own value of k_3/k_2. $CN + NO \rightarrow CO + N_2$ 1 $CN + O_2 \rightarrow CNO + O$ 2 $O + CN \rightarrow CO + N$ 3 Used by (7). Using our value for k_2 (this Volume, section F8), we obtain $k_1=2.6x10^{13}$ cm^3 mol^{-1} s^{-1} at 500 K. Authors deduced an activation energy $E_1 \sim 4$kJ mol^{-1} (1 kcal mol^{-1}) by comparison with E_2.
$3.0x10^{11}$	687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added in excess downstream. $(CN)_2$ added to the reaction cell. O_2 added later to the reaction cell at 0.33-2.50 Pa pressure. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (8)	Ratio k_1/k_2 calculated from absorption measurements as 0.06. Authors used their own value of k_2 to give k_1. Using our value of k_2 (this Vol., section F8) we obtain $k_1=7.5x10^{11}$ cm^3 mol^{-1} s^{-1} at 687 K. Reaction 1' considered to be very unlikely to occur at this temperature. Emission results showed NO 20 times more efficient than O_2 at quenching [CN*], and thus they assumed that NO was not removing ground state CN here, but some other energy carrier. Quoted by (9, 11,12,13,14,15).
$7.3x10^{12}$	1500	Flame study. $H_2/N_2/O_2$ (4.5: 8:1) flames, total pressure not given. $(CN)_2$ and NO (<1%) added to the preflame mixture. Reaction followed mass spectrometrically. MULVIHILL and PHILLIPS 1975 (14)	Initially authors monitored disappearance of NO on addition of $(CN)_2$ to the flame, and obtained k_1/k_2=6.5 at $\sim$700 K. As this disagreed with the results of (8), these results were rejected on the grounds that NO was being removed by NH radicals. $CN + NO \rightarrow CO + N_2$ 1 $CN + O_2 \rightarrow CNO + O$ 2 At 1500 K, [CN] is kept constant by the equilibrium in reaction 4. Any decay in [HCN] on addition of NO is attributed to removal of CN by reaction 1.

$CN + NO \rightarrow CO + N_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		MULVIHILL and PHILLIPS 1975 (14) continued	$CN + H_2 \rightleftharpoons H + HCN$ 4 By this method, the value of k_1 given was obtained. Combining this with the result from (8), the authors obtained $k_1=1.1\text{x}10^{14}$ $\exp(-4040/T)$ $cm^3\ mol^{-1}\ s^{-1}$.

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.2\text{x}10^{13}$	500	Review of gas phase chemistry of re-entry. HEICKLEN 1967 (7)	Value of k_1 determined from k_1/k_2 ratio from (5) and k_2 from (3). Quoted by (15). Accepts possibility of NOCN formation at 298 K.
		Review of reactions of atoms and small free radicals. CLYNE 1968 (9)	Quotes (8). No comittal as to nature of products.
$3.1\text{x}10^{11}$	All	Selected value for use in methane/air combustion. ENGLEMAN 1976 (15)	Value based on that of (8). Activation energy assumed to be zero. Author notes lack of good experimental data and suggests caution in use of this k_1.

Discussion

Nitric oxide is a major product of cyanogen combustion systems, and its reaction with CN radicals is thus of importance under these conditions. Although the reaction is fast, it is most probably slower than reactions 2 and 3 at 1000 K. As these reactions are in competition with reaction 1 in combustion systems this makes the study of reaction 1 difficult.

$$CN + NO \rightarrow CO + N_2 \qquad (1)$$

$$CN + O_2 \rightarrow CNO + O \qquad (2)$$

$$O + CN \rightarrow N + CO \qquad (3)$$

Even the reaction mechanism is uncertain, there being no direct evidence for reaction 1, which is favoured on the grounds of its very high exothermicity [2,8], even though it is a four centre reaction. However, Basco and Norrish [4] prefer the combination reaction 1′ by analogy with the NO-halogen reactions.

$$CN + NO\ (+M) \rightarrow NOCN\ (+M) \qquad (1')$$

Their room temperature flash photolysis study is the only direct investigation of reaction 1. They pass no opinion as to whether the combination is second or third order, quoting both rate constants. They do report an unidentified spectrum in the region of the nitrosyl halides, and also production of vibrationally excited NO on photolysis of the mixture believed to contain NOCN, behaviour typical of nitrosyl halides. However, we find no evidence from any other source for the existence of NOCN as a stable product in this reaction, although Galvin and Pritchard [1] claim to have mass-spectrometric evidence of it from the photolysis of ICN in the presence of NO.

The three higher temperature studies [5,8,14] all follow reaction 1 indirectly, and are all at different temperatures. There is no clear trend as to activation energy, and we can recommend none as having higher accuracy than any other. The discrepancy between Thrush's two results [5,8] can be explained by the two methods of absorption and emission spectroscopy used. This discrepancy would appear to indicate that NO, unlike O and O_2, does not react readily with CN radicals, but with another energy carrier, preventing their excitation.

We believe that further direct studies of reaction 1 are needed, in the absence of O_2 and H_2, and hence make no recommendation for k_1.

Rate of the Reverse Reaction

There are no experimental data on the rate of the reverse reaction −1.

$$CO + N_2 \rightarrow CN + NO \qquad (-1)$$

McKenzie [6] derives an expression $k_{-1} = 10^3 T^2 \exp(-92\,010/T)$ cm^3 mol^{-1} s^{-1} from transition state theory, for use in entry to the Martian atmosphere. However, using JANAF data for K_1, this gives $k_1 \sim 10^{-6}$ cm^3 mol^{-1} s^{-1} at 500 K, which is far too low, indicating that the expression for k_{-1} is considerably in error.

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Note Added in Proof

Recent experiments by Lam et al. (J. Chem. Phys. **69**, 2877 (1978)) suggest the occurrence of both channels, 1 and 1′, for CN removal by NO.

$$CN + NO \rightarrow CO + N_2 \qquad (1)$$

$$CN + NO\ (+M) \rightarrow NOCN\ (+M) \qquad (1')$$

In their work CN was produced by flash photolysis of C_2N_2 (0.2 torr, 27 Pa) in mixtures with NO (1% or 2%)/Ar. A flowing system was used total pressures covering the range 5–25 torr (0.7–3.3 kPa). [CN] was monitored by laser resonance fluorescence at several wavelengths in the 386 nm region.

The apparent second order rate constant varied with pressure as expected if both 1 and 1′ are operative. At 300 K values of $k_1 = (7.2 \pm 0.4) \times 10^{10}$ cm^3 mol^{-1} s^{-1} and $k_{1'}(M = Ar) = (2.8 \pm 0.5) \times 10^{17}$ cm^6 mol^{-2} s^{-1} were obtained which we recommend for this temperature with error limits of ±50%.

F10 $CN + NH_3 \rightarrow HCN + NH_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	- 86.441	1.092	15.203
300	- 86.433	1.125	15.110
500	- 85.358	3.849	9.119
1000	- 83.345	6.740	4.706
1500	- 82.186	7.703	3.265
2000	- 81.684	7.991	2.551
2500	- 82.107	7.820	2.124
3000	- 84.011	7.130	1.835
3500	- 87.337	6.113	1.623
4000	- 91.914	4.891	1.457
4500	- 97.613	3.552	1.320
5000	-104.299	2.130	1.202

RECOMMENDED RATE CONSTANT

$k = 1.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}

$= 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

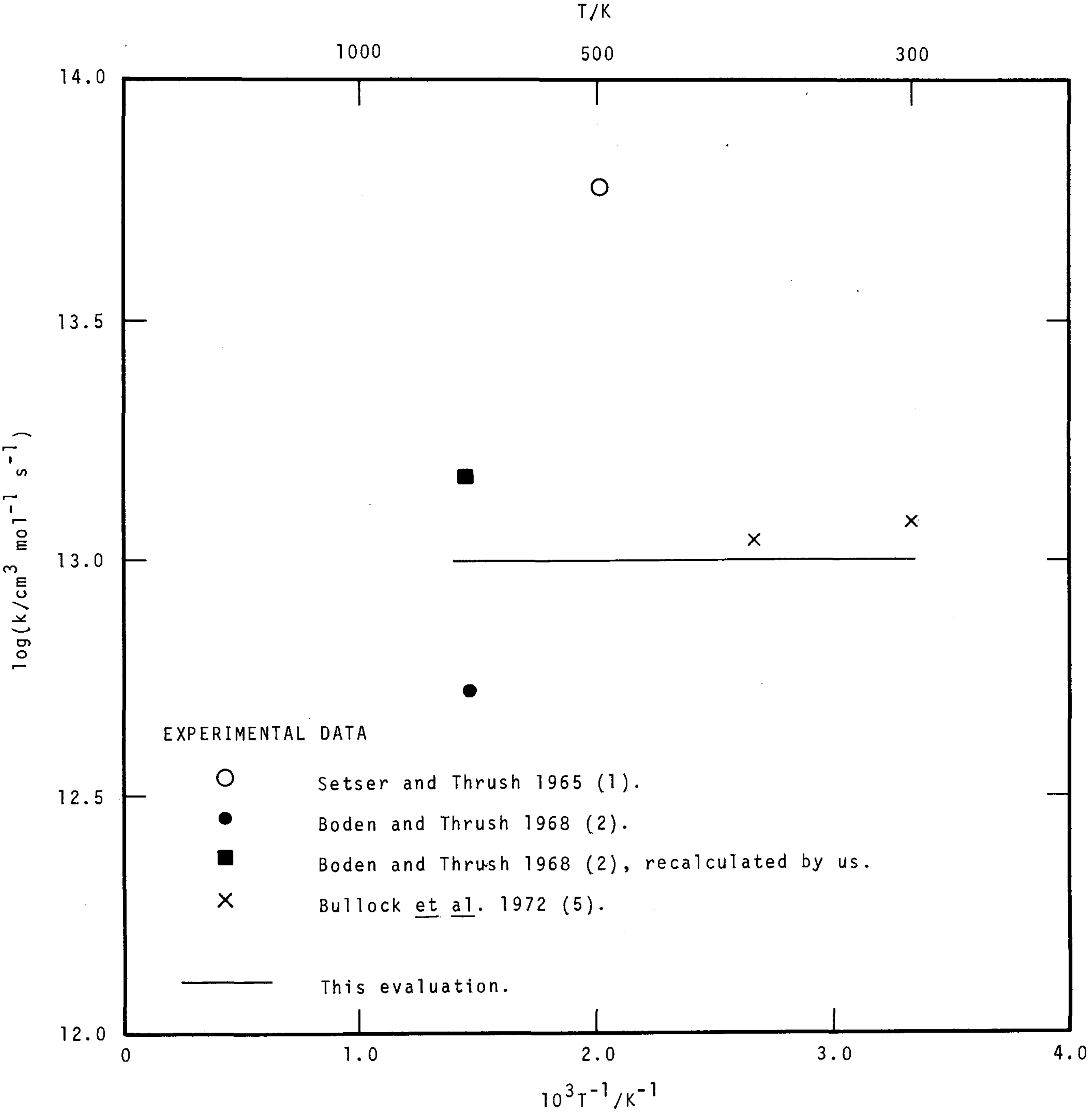
Temperature Range: 300-700 K.

Suggested Error Limits for Rate Constant: a factor of three.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	493-503	Discharge flow system. 100% N_2 at 133-667 Pa pressure, NO added downstream, $(CN)_2$ further downstream. NH_3 added near the observation point. [CN] monitored by emission spectroscopy at 388.3 nm. SETSER and THRUSH 1965 (1)	Ratio k_1/k_2 given as 6.2 at 500 K by monitoring the quenching of CN $A^2\Pi$ and $B^2\Sigma^+$. $CN + O_2 \rightarrow CNO + O$ 2 $CN + NH_3 \rightarrow HCN + NH_2$ 1 k_2/k_3 determined earlier by adding O_2 in place of NH_3 and observing its effect on [CN] decay. $O + CN \rightarrow N + CO$ 3 Mechanism does not take into account removal by NH_3 of any other precursor of excited CN. Using our value of k_2 (This Vol.,

$CN + NH_3 \rightarrow HCN + NH_2$



$CN + NH_3 \rightarrow HCN + NH_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		*SETSER and THRUSH 1965 (1) continued.	section F8) we obtain $k_1=6.1\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ at 500 K. Quoted by (4).
5.3×10^{12}	687	Discharge capacity flow system. 100% N_2 at 200-667 Pa pressure, NO added downstream, $(CN)_2$ added to the reaction cell. NH_3 added later to the reaction cell at <1 Pa pressure. [CN] monitored by emission and absorption spectroscopy at 388.3 nm. BODEN and THRUSH 1968 (2)	Ratio k_1/k_2 calculated as in (1) from absorption results, and given as 1.2 after allowing for the effect of reaction 4. $O + (CN)_2 \rightarrow CN + CNO$ 4 Considerable discrepancy between emission and absorption results. Authors used their own value of k_2 to obtain k_1. Using our value of k_2 (This Vol., section F8) we obtain $k_1=1.5\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ at 687 K. Quoted by (3,4,5,6).
1.2×10^{13} 1.1×10^{13}	300 375	Pulse radiolysis of $(CN)_2$ ($\sim$2%)/Ar mixtures at a total pressure of 95.1 kPa, in the presence of NH_3 (40-400 Pa). [CN] monitored by absorption spectroscopy at 388.3 nm, [NH_2] at 597.6 nm. BULLOCK, COOPER, GORDON and MULAC 1972 (5)	Result at 300 K is averaged from [CN] and [NH_2] data, but agreement between two sets is within 10%. Authors conclude that there is a small negative activation energy $E_1=-2.1$ kJ mol^{-1} (-0.5 kcal mol^{-1}), which they claim gives reasonable agreement with the result of (2) at 687 K.

REVIEW ARTICLE

		Review of reactions of atoms and small free radicals. CLYNE 1968 (3)	Quotes (2).

Discussion

Ammonia, like oxygen and nitric oxide, is a good scavenger for CN radicals. Evidence seems to suggest that reaction 1 is fast at room temperature, probably faster than reaction 2 or 5, and on a par with reaction 3.

$$CN + NH_3 \rightarrow HCN + NH_2 \quad (1)$$

$$CN + O_2 \rightarrow CNO + O \quad (2)$$

$$O + CN \rightarrow N + CO \quad (3)$$

$$CN + NO \rightarrow CO + N_2 \quad (5)$$

The only direct study of reaction 1 [5] suggests a slight negative activation energy, the authors citing the low value obtained by Boden and Thrush [2] at 687 K as further evidence for their claim. However, their system has produced unusually low activation energies for reactions 2 and 6; this could be a fault inherent in their method. Using our value of k_1 recalculated from Thrush's result we obtain a slight positive activation energy.

$$CN + CH_4 \rightarrow HCN + CH_3 \quad (6)$$

Ignoring the value obtained from Setser and Thrush [1] because of the effect of excited species, we are left with three values of k_1 approximately equal [2,5]. We thus consider the activation energy E_1 to be ~ 0 and recommend the value

$$k_1 = 1.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 300–700 K, with error limits of a factor of three.

References

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Miscellaneous Reactions Involving CN Radicals

F11 CN + CN → C_2 + N_2

Information on the mutual reaction between CN radicals comes from two shock tube studies of CN radicals and C_2.

$$CN + CN \rightarrow C_2 + N_2; \quad (1)$$

$$\Delta H^\circ_{298} = -32.545 \text{ kJ mol}^{-1} \ (-7.779 \text{ kcal mol}^{-1})$$

Fairbairn [1] measured the rate of decay of [CN] following the shock tube decomposition of $(CN)_2$ (0.1–5%)/Ar mixtures over the temperature range 3400–4800 K. Total pressures varied between 0.24–0.44 atm (24.3–44.6 kPa). [CN] was monitored by absorption spectroscopy behind incident shocks at 388.3 nm, and in some experiments, $[C_2]$ at 516.5 nm. The author assumed that reaction 1 was the only reaction removing CN, and from his results we derive the expression $k_1 = 2.5 \times 10^{17} \exp(-48\,000/T)$ cm^3 mol^{-1} s^{-1}. He admits that other side reactions such as reaction 2 could remove CN, but was unable to state their importance.

$$C + CN \rightarrow N + C_2 \quad (2)$$

More recent data on other CN reactions suggest they could indeed be important in this temperature range.

Patterson and Greene [2] followed CN and C_2 emission following the pyrolysis of BrCN (1–5%)/Ar mixtures at 0.07–4.00 kPa pressure behind incident shocks. [CN] was followed at 421.6 nm, and $[C_2]$ at 516.5 nm. The data from $[C_2]$ formation gave the expression $k_1 = 1.6 \times 10^{15} \exp(-21\,700/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 3800–7000 K. The data from [CN] decay were generally in good agreement, except for lean mixtures at higher temperatures, when the rate of disappearance increased markedly. This was assumed to be due to direct dissociation via reaction 3.

$$CN + M \rightarrow C + N + M \quad (3)$$

The agreement between the two expressions is best at around 4500 K, where we recommend a value of $k_1 = 1 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, but the difference in activation energies prevents any evaluation of temperature dependence.

References

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F12 CN + N → C + N_2

As with CN decomposition and recombination, the mechanism of the reaction between nitrogen atoms and the cyano radical is not well understood and has given grounds for controversy. The question is whether N_2 molecules are formed directly as in reaction 1, or by a two step process via reactions 2 and 3.

$$CN + N \rightarrow C + N_2; \quad (1)$$

$$\Delta H^\circ_{298} = -192.61 \text{ kJ mol}^{-1} \ (-46.035 \text{ kcal mol}^{-1})$$

$$N + CN + M \rightarrow CN_2 + M \quad (2)$$

$$N + CN_2 \rightarrow CN + N_2 \quad (3)$$

Safrany and Jaster [3] put forward a chain mechanism involving reaction 1 that accounted for N_2 formation without depleting [CN] in a $(CN)_2$/active nitrogen system.

$$CN + N \rightarrow C + N_2 \quad (1)$$

$$C + (CN)_2 \rightarrow C_2N + CN$$

$$N + C_2N \rightarrow CN + CN$$

However, this mechanism is criticised by Berger and Kistiakowsky [6] who claim it does not account for isotopic scrambling observed by them in a similar system. They used a flow system, producing excited $N_2A\,^3\Sigma$ from a discharge through pure N_2 at 400 Pa. A mixture of $^{12,12}(CN)_2$, $^{13,13}(CN)_2$ and $^{12,13}(CN)_2$ was added downstream at 307 mPa. CN radicals were produced following de-excitation of the excited N_2 by the $(CN)_2$. The reaction was followed mass spectrometrically. Assuming reaction 1 to be the rate determining step gives $k_1=6\times10^{12}$ cm^3 mol^{-1} s^{-1} at 298 K.

The only other determination of k_1 comes from Slack and Fishburne [5], who re-evaluated data from [2 and 4] on CN pyrolysis over the temperature range 2500–15000 K. They were able to use literature values for all of the rate constants in their mechanism except k_1 and k_4, both of which were set at 4×10^{13} cm^3 mol^{-1} s^{-1} and varied until the best computer fit was obtained.

$$C + CN \rightarrow N + C_2 \quad (4)$$

In this way they obtained the best fit with $k_1=2\times10^{14}$ cm^3 mol^{-1} s^{-1} with little or no temperature dependence. Recently, this value has been revised by Slack [7,8], giving $k_1=4.4\times10^{14}\exp(-4600/T)$ cm^3 mol^{-1} s^{-1}, the activation energy being determined by the semi-empirical method of Hirschfelder [1]. However, in his own experimental investigation of CN pyrolysis, Slack obtained $k_1=1.25\times10^{13}\exp(23\,000/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 5000–8000 K, assuming $k_1>>k_4$, and taking $[N]=k_5[CN][M]t/2$ at time t.

$$CN + M \rightarrow C + N + M \quad (5)$$

The agreement between the various estimates of k_1 is very poor. It is clear that the secondary reactions in CN decomposition are not yet well understood, and consequently we make no recommendation for k_1.

References

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F13 $CN + N + M \rightarrow CN_2 + M$

The catalytic recombination of nitrogen atoms by reactions 1 and 2 was put forward by Jennings and Linnett [1], and the mechanism has been used by several authors [3,4,6,7] until the possible effect of reaction 3 was recently proposed [5].

$$CN + N + M \rightarrow CN_2 + M; \quad (1)$$

$$\Delta H^\circ_{298}=-477.67 \text{ kJ mol}^{-1} \ (-114.17 \text{ kcal mol}^{-1})$$

$$N + CN_2 \rightarrow CN + N_2 \quad (2)$$

$$N + CN \rightarrow C + N_2 \quad (3)$$

Here CN_2 is taken to be the symmetrical NCN radical.

Campbell and Thrush [3] found $k_1=5.6\times10^{15}$ cm^6 mol^{-2} s^{-1} at 293 K. They were studying the recombination of N atoms following a discharge through N_2 in a flow tube. If the N_2 contained traces of CH_4, CN could be observed right along the flow tube, and the N atom recombination rate was enhanced. [CN] was determined by titration with NH_3, [N] was determined by titration with NO. Computer analysis showed that the acceleration of the N atom recombination was first order in [N], [CN] and total pressure, leading the authors to believe reaction 1 to be rate determining. However, Thrush [6] has since criticised the ammonia titration method, believing that most NH_3 would react with excited N_2 molecules present rather than the CN radicals.

Arrington et al. [6] also believed reaction 1 to be the key reaction in the catalytic recombination of N atoms in the cyanogen-active nitrogen system. They used a flow system, with a discharge through N_2 at 0.13–1.46 kPa pressure. C_2H_2 was added downstream so that $[C_2H_2]\leqslant0.5[N]$, and the reaction followed mass spectrometrically. In some experiments, the C_2H_2 was replaced by $(CN)_2$ itself at the same concentration. Assuming $k_1<k_2$, and taking k_4 from [2], they obtained $k_1\geqslant1\times10^{18}$ cm^6 mol^{-2} s^{-1} at 303 K, from the $(CN)_2$ results, and $k_1\leqslant7\times10^{18}$ cm^6 mol^{-2} s^{-1} from the C_2H_2 results. Due to complicating secondary reactions the latter value is only approximate, although we believe it to be nearer to the truth than the lower bound, as the value of k_4 chosen from [2] is somewhat high.

$$CN + CN + M \rightarrow (CN)_2 + M \quad (4)$$

Provencher and McKenney [7] obtained an order of magnitude estimate for $k_1\sim10^{16}$ cm^6 mol^{-2} s^{-1} at 298 K, using a similar cyanogen-active nitrogen system over a pressure range of 0.2–1.33 kPa, monitoring [CN] by emission spectroscopy at 388.3 nm. Until the reaction mechanism is clarified, we can make no recommendation for k_1.

References

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F14 $CN + C \rightarrow N + C_2$

Like reaction 2, reaction 1 is an important secondary reaction in CN decomposition. There have been no direct determinations of k_1, the situation being complicated by a lack of knowledge of the part played by these secondary reactions in CN decomposition.

$$CN + C \rightarrow N + C_2; \qquad (1)$$

$$\Delta H^\circ_{298} = 160.26 \text{ kJ mol}^{-1} \text{ (38.303 kcal mol}^{-1}\text{)}$$

$$CN + N \rightarrow C + N_2 \qquad (2)$$

In their re-evaluation of the data on CN decomposition from earlier shock tube studies [2,3], Slack and Fishburne [4] set $k_1 = 4 \times 10^{13}$ cm^3 mol^{-1} s^{-1} and temperature independent, and then made a computer fit to the data, varying k_1 and k_2 until a fit was obtained. In this way they obtained $k_1 = 2 \times 10^{13}$ cm^3 mol^{-1} s^{-1} over the temperature range 2500–15000 K.

Subsequently this value has been revised by Slack [5,6], giving $k_1 = 3 \times 10^{14} \exp(-18\,000/T)$ cm^3 mol^{-1} s^{-1}, with activation energy determined by the semi-empirical method of Hirschfelder [1]. However, in his own experimental investigation of CN pyrolysis, Slack obtained $k_1 = 8.0 \times 10^8 \exp(57\,500/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 5500–6700 K, suppressing the faster reaction 2 by adding 4% N_2 to the initial mixture, and setting $[C] = k_3[CN][M]t/2$ at time t.

$$CN + M \rightarrow C + N + M \qquad (3)$$

The large negative activation energy is similar to that obtained by him for reaction 2, and in total disagreement with the computer fit to earlier data. In view of this, we make no recommendation for k_1.

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F15 $CN + CO_2 \rightarrow CO + CNO$

The removal of CN radicals from hydrocarbon flames normally occurs by reaction 2, but this route is not open in fuel-rich flames. Here, most CN is converted to HCN via reaction 3, but the nature of the equilibrium in this reaction still leaves some free CN in the flame.

$$CN + O_2 \rightarrow CNO + O \qquad (2)$$

$$CN + H_2 \rightleftharpoons HCN + H \qquad (3)$$

Haynes et al. [1] made a study of fuel-rich hydrocarbon/air flames with small quantities of added pyridine, all CN-containing species being determined in alkaline solution with a cyanide specific ion electrode. Decay of trace amounts of [CN] not consumed in reaction 3 was attributed to reaction 1.

$$CN + CO_2 \rightarrow CO + CNO; \qquad (1)$$

$$\Delta H^\circ_{298} = 7.268 \text{ kJ mol}^{-1} \text{ (1.737 kcal mol}^{-1}\text{)}$$

A further investigation was made in an H_2 (21%)/CO flame with trace amounts of pyridine added. Under these conditions authors assumed only reaction 1 could remove the CN, and obtained $k_1 = 3.7 \times 10^{12}$ cm^3 mol^{-1} s^{-1} over the temperature range 1800–2400 K. Morley [2], in mass-spectrometric studies of hydrocarbon/O_2/Ar flames to which trace amounts of NO, NH_3,CH_3CN or pyridine were added, believed CN removal was due to reaction 4, but gave no value for k_4.

$$CN + OH \rightarrow CNO + H \qquad (4)$$

If reaction 1 has little or no activation energy, as suspected by Haynes *et al.*, *it* should be possible to ascertain its importance by room temperature studies under more controllable conditions. At this stage we can make no recommendation for k_1.

References

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F16 $NOCN + M \rightarrow NO + CN + M$

The thermal decomposition of nitrosyl cyanide has been studied by Dorko et al.[3], with a similar system to that used by them in NOCl and NF_3 dissociation studies [1,2]

$$NOCN + M \rightarrow NO + CN + M; \qquad (1)$$

Thermodynamic data unavailable for NOCN

They shocked NOCN (0.4%)/Ar mixtures at total pressures of 0.98–2.12 atm, monitoring [NOCN] by i.r. emission spectroscopy at 4.59 μm behind reflected shocks. Using a simple Lindemann mechanism, they obtained $k_1^\circ = 5.6 \times 10^{13} \exp(-14\,500/T)$ cm^3 mol^{-1} s^{-1} over the temperature range 1400–1700 K. They claim that the activation energy is in good agreement with the central C–N bond energy, and believed the reaction was occurring near its low pressure limit.

References

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Miscellaneous Reactions Involving HCN

F17 HCN + M → H + CN + M

Hydrogen cyanide is stable to very high temperatures, its dissociation becoming measurable only at about 2000 K, and only important in HCN-containing systems above about 3000 K.

$$\mathrm{HCN + M \rightarrow H + CN + M}; \qquad (1)$$

$$\Delta H^\circ_{298} = 517.99 \text{ kJ mol}^{-1} \text{ (123.80 kcal mol}^{-1}\text{)}$$

Because of the high temperatures required to dissociate HCN, there are few data available, only two investigations having been reported [1,2]. Lachmann et al. [1] added CH_4(10–15%)/Ar mixtures to a nitrogen plasma stream, so that $[CH_4]:[N_2] \leqslant 3:100$, and followed the ensuing reactions mass spectrometrically. Thus they were unable to elucidate any mechanism for the process, and were only able to report an overall rate constant for HCN removal, $k_{ov} = 2.0 \times 10^{12}$ $\exp(-17\,000/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$ over the temperature range 3500–4500 K.

Roth and Just [2] studied the decomposition in a shock tube, using HCN ($<$0.05%)/Ar mixtures at ~200 kPa total pressure, and monitoring [H] by u.v. absorption spectroscopy at 121.5 nm behind reflected shocks. No subsequent reaction of H was observed and they obtained $k_1 = 5.7 \times 10^{16}$ $\exp(-59\,000/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$ over the temperature range 2200–2700 K.

The two expressions give widely differing results, but only the later work studied the elementary decomposition. In the absence of confirmation of these results, we make no recommendation for k_1.

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Note Added in Proof

Tabayashi et al. (Bull. Chem. Soc. Japan **50**, 1754 (1977)) have studied the thermal decomposition of HCN in a shock tube using HCN(0.2,0.5 and 1.0 mole %)/Ar mixtures at total pressures 0.35 and 1.16 atm (36 and 117 kPa) and temperatures 2600–3500 K. The [CN] was monitored behind the incident shock wave by u.v. absorption at 388.2 nm. Absorption coefficients for CN were obtained by relating the steady absorption observed late in the reaction to the value of [CN] calculated assuming equilibrium. An absorption coefficient (base e) of $(1.90 \pm 0.12) \times 10^7$ $\mathrm{cm^2\ mol^{-1}}$, independent of temperature, was found.

The initial rate of increase of [CN] was used to obtain the value of $k_1(\mathrm{M = Ar}) = (1.26 \pm 0.28) \times 10^{16}$ $\exp(-(50\,300 \pm 700)/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$. This expression is approximately a factor of 6 greater than that of Roth and Just [2] in the overlapping temperature region. More work is required before a recommendation can be made.

F18 H + (CN)$_2$ → HCN + CN

Of the two major reactions in $H_2/(CN)_2$ flames, reaction 1 is recognised today to be less important than reaction 2.

$$\mathrm{H + (CN)_2 \rightarrow HCN + CN}; \qquad (1)$$

$$\Delta H^\circ_{298} = 44.045 \text{ kJ mol}^{-1} \text{ (10.527 kcal mol}^{-1}\text{)}$$

The reaction has been considered in $H_2/(CN)_2$ systems by [1,5,6]. Robertson and Pease [1] concluded that $E_1 > E_2$ because of the splitting of the C–C bond. Phillips et al. [5,6] were unable to obtain any information from their flame studies due to the effect of side reactions of other CN containing species.

$$\mathrm{CN + H_2 \rightarrow HCN + H} \qquad (2)$$

Direct studies of reaction 1 have met with slightly more success. Haggart and Winkler [2] established the chain mechanism of reactions 1 and 2 in a discharge flow system, but only ascertained the nature of the products after they had been frozen down at 77 K. Safrany and Jaster [3] followed several reactions in the $H_2/(CN)_2$ system using a Wood-Bonhoeffer flow system, producing H atoms by a discharge through H_2 at 26.7 Pa pressure, and adding $(CN)_2$ downstream. The reaction was followed mass spectrometrically, but no attempt was made to determine rate constants. Dunn et al. [5] used an orthodox flow system, producing H atoms by a discharge through H_2(2.1–29.5%)/Ar mixtures at total pressures of 90.2–313 Pa. $(CN)_2$ was added downstream at 0.47–3.15 Pa pressure, and the reaction followed mass-spectrometrically. After correcting for H atom recombination, they obtained $k_1 = 5.2 \times 10^8$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$ at 300 K. Later, Mulvihill and Phillips [6] arbitrarily set $A_1 = 4.0 \times 10^{13}$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$, and chose E_1 to give an expression agreeing with the earlier low temperature result, giving $k_1 = 4.0 \times 10^{13}$ $\exp(-3400/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$. In view of the lack of accuracy of their other computations in this paper, we place no reliance on this expression.

The only other contribution comes from Albers [4] who claimed that at $T < 500$ K, H atoms react with $(CN)_2$ thus:

$$\mathrm{H + (CN)_2 + M \rightarrow H(CN)_2 + M} \qquad (1')$$

$$\mathrm{H + H(CN)_2 \rightarrow 2HCN} \qquad (3)$$

with $k_3 = 10^{11}$ $\exp(-1100/T)$ $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$. In the absence of further details we can only regard this as confirming that reaction 1 is slow at low temperature, and we make no recommendation for k_1.

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Note Added in Proof

The proposal [4] that the reaction of H with C_2N_2 occurs via (1′) and (3) has prompted Phillips (Int. J. Chem. Kin. **10**, 899 (1978)) *to reinvestigate the reaction using a discharge* flow system at pressures of ≅1 mm Hg (133 Pa) and temperatures 282–338 K. The rate of disappearance of C_2N_2 was followed mass spectrometrically for various values of $[H_2]/[H]$.

The results were interpreted in terms of a modified form of the Albers mechanism (4),(5),(6),(3).

$$H + C_2N_2 \rightleftharpoons HC_2N_2^* \qquad (4)$$

$$H + HC_2N_2^* \rightarrow 2HCN \qquad (5)$$

$$H_2 + HC_2N_2^* \rightarrow H_2 + HC_2N_2 \qquad (6)$$

$$H + HC_2N_2 \rightarrow 2HCN \qquad (3)$$

A value of $k_4=(9.0\pm1.2)\times10^8$ cm^3 mol^{-1} s^{-1} could be derived for the range 282–319 K. This is approximately a factor of 3 lower than the rate constant quoted by Albers et al. which they identified with k_3. Further work on this system is required.

F19 CN + H$_2$O → HCN + OH

Reaction 1 has been largely ignored in $(CN)_2$ flame studies, where removal of the CN radical by H_2, O_2, CO_2 or OH has been preferred [2,3,4].

$$CN + H_2O \rightarrow HCN + OH; \qquad (1)$$

$$\Delta H^\circ_{298} = -18.451 \text{ kJ mol}^{-1} \ (-4.410 \text{ kcal mol}^{-1})$$

Paul and Dalby [1] considered reaction 1 at room temperature, flash photolysing $(CN)_2$ in the presence of H_2O, and monitoring [CN] decay at 416 nm. They obtained $k_1 = 3\times10^{11}$ cm^3 mol^{-1} s^{-1} at 301 K, no further details being given.

References

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G1 $BrCN + M \rightarrow Br + CN + M$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	360.81	129.18	-56.465	-60.853
300	360.81	129.20	-56.074	-60.465
500	360.87	129.44	-30.939	-35.552
1000	359.52	127.64	-12.112	-17.026
1500	357.85	126.28	- 5.865	-10.955
2000	356.36	125.42	- 2.755	- 7.970
2500	355.34	124.96	- 0.897	- 6.209
3000	354.91	124.81	0.339	- 5.052
3500	354.97	124.82	1.222	- 4.236
4000	355.31	124.91	1.884	- 3.632
4500	355.70	125.00	2.401	- 3.166
5000	355.94	125.05	2.814	- 2.799

SI Units: $\log(K_p/Pa) = \log(K_p/atm) + 5.006$

$\log(K_p/mol\ m^{-3}) = \log(K_p/mol\ cm^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$k = 7.2 \times 10^{14} \exp(-36\ 800/T)\ cm^3\ mol^{-1}\ s^{-1}$ (M=Ar)

$= 1.2 \times 10^{-9} \exp(-36\ 800/T)\ cm^3\ molecule^{-1}\ s^{-1}$ (M=Ar)

Temperature Range 2000-4000 K.

Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.

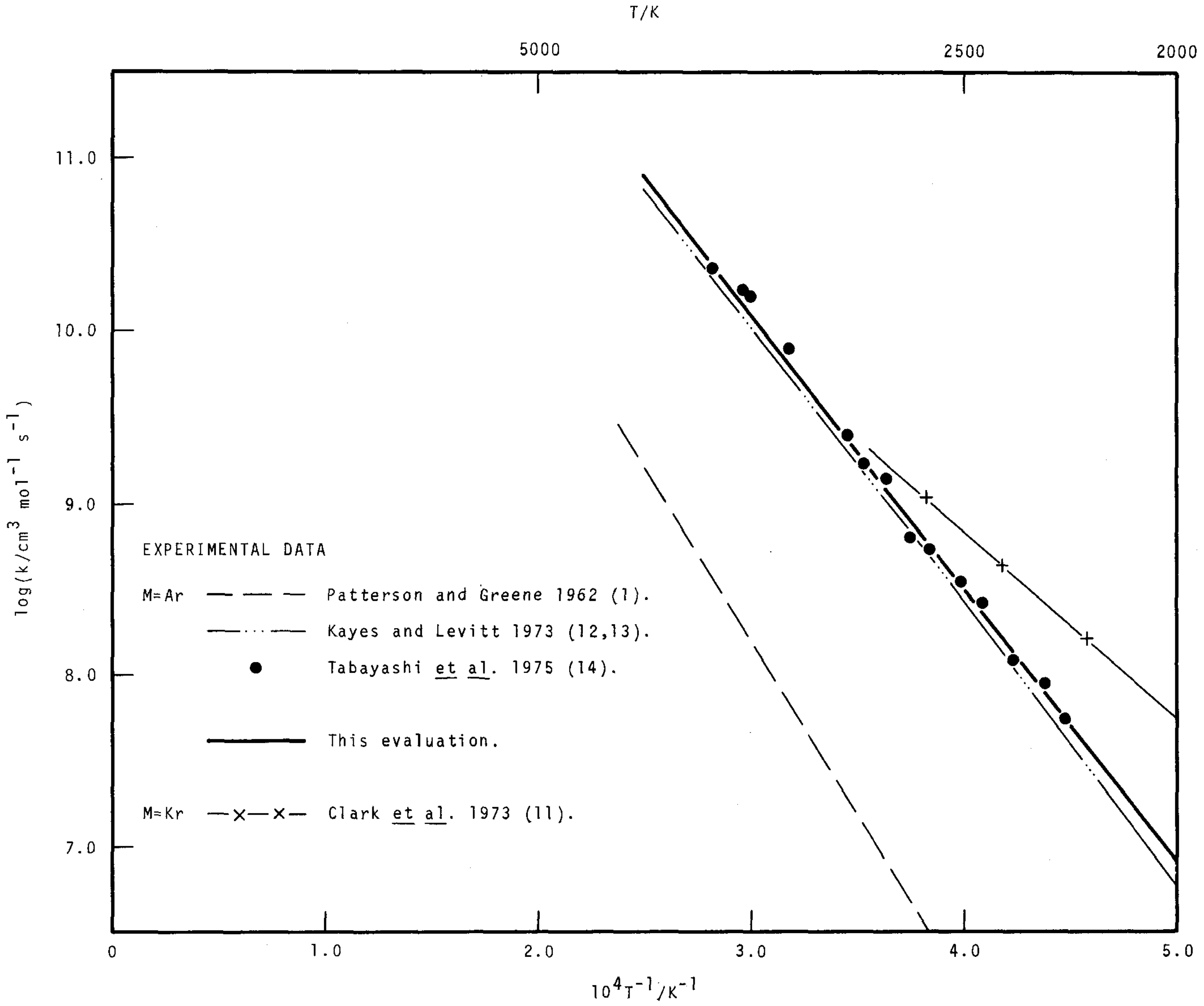
Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1}) = 14.86 \pm 0.20$

$\log(A/cm^3\ molecule^{-1}\ s^{-1}) = -8.92 \pm 0.20$

$E/J\ mol^{-1} = 306\ 000 \pm 21\ 000$

$E/cal\ mol^{-1} = 73\ 000 \pm 5\ 000$

$BrCN + M \rightarrow Br + CN + M$



$BrCN + M \rightarrow Br + CN + M$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
2nd ORDER RATE CONSTANT k_1^o			
$2.0\times10^{12}T^{0.5}\exp(-45\ 500/T)$ M=Ar	2600-4200	Shock tube study. BrCN (1-5%)/Ar mixtures at total pressures of 0.07-4.00 kPa. Incident shocks. [CN] monitored by emission spectroscopy at 421.6 nm. PATTERSON and GREENE 1962 (1)	Apparent rate constant for production of excited CN $B^2\Sigma^+$ determined. From this, assuming instant electronic relaxation, the expression for k_1, taking electronic excitation energy as 310 kJ mol^{-1} (74 kcal mol^{-1}). Further experiments above 4200 K unsuccessful as [CN] profiles too steep to be measured accurately. $BrCN + M \rightarrow Br + CN + M$ 1 Quoted by (3,6,7,8,11,12,13,14). Used by (10).
$1.5\times10^{13}\exp(-25\ 000/T)$ M=Kr	2000-2800	Shock tube study. BrCN (0.2-2%)/Ne and BrCN (1%) /Kr mixtures at total pressures ∿40 kPa. Reflected shocks. Reaction followed mass spectrometrically. CLARK, DOVE and FINKELMAN 1973 (11)	From the concentrations of the products, Br_2, $(CN)_2$ and BrCN, authors concluded that reactions 2 and 3 must be removing BrCN as well as the initiation reaction 1, and that the kinetics are more complex than reaction 1 suggests. $Br + BrCN \rightarrow CN + Br_2$ 2 $CN + BrCN \rightarrow Br + (CN)_2$ 3 The expression for k_1 is an assumed one, retaining the observed activation energy, but dividing each observed rate constant by between 2 and 3. The rate constants observed for decomposition in Ne are higher, but no attempt was made to fit an Arrhenius expression to them. Quoted by (14).
$5.0\times10^{20}T^{-1.5}\exp(-41\ 500/T)$ M=Ar	2000-4000	Shock tube study. BrCN (0.5-10%)/Ar mixtures at total pressures of 0.4-2.67 kPa. Incident shocks. [CN] monitored by emission spectroscopy at 421.5 nm, $[C_2]$ at 513.5 nm. KAYES and LEVITT 1973 (12, 13)	The apparent rate constant was found to vary considerably with [BrCN], giving an apparent activation energy of 117 kJ mol^{-1} (28.0 kcal mol^{-1}) at 0.5% BrCN, and 344 kJ mol^{-1} (82.2 kcal mol^{-1}) at 10% BrCN. A reaction scheme including reactions 2,3,4 and 5 was thus proposed, after SCHOFIELD *et al.* (4). $Br_2 + M \rightarrow Br + Br + M$ 4 $(CN)_2 + M \rightarrow CN + CN + M$ 5

$BrCN + M \rightarrow Br + CN + M$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		KAYES and LEVITT 1973 (12, 13) continued.	Taking k_4 from (5) and k_5 from (2), a computer fit was made for those mixtures containg >5% BrCN, giving the expression quoted. The scheme failed to explain the low activation energy obtained with lean mixtures, which the authors believed to be due to formation of vibrationally excited $(CN)_2$, which is readily deactivated by BrCN, but otherwise decomposes to give more CN radicals. Quoted by (14).
$5.5x10^{7}$ M=Ar	2235	Shock tube study. BrCN (0.2-1%)/Ar mixtures at 1.00-4.43 kPa pressure. Incident shocks. [CN] monitored by absorption spectroscopy at 421.6 nm. TABAYASHI, KAJIMOTO and FUENO 1975 (14)	Rate constants taken from the initial appearance of CN, thus all subsequent reactions were ignored. $BrCN + M \rightarrow Br + CN + M$ 1 Authors derive expression $k_1=1.6x10^{15}\exp(-38\ 600/T)\ cm^3\ mol^{-1}\ s^{-1}$, and rearranged it to a Fowler-Guggenheim expression to give $k_1=1.2x10^{12}\ (41\ 100/T)^{1.5}\exp(-41\ 100/T)\ cm^3\ mol^{-1}\ s^{-1}$.
$8.9x10^{7}$	2279		
$1.2x10^{8}$	2363		
$2.6x10^{8}$	2442		
$3.5x10^{8}$	2504		
$5.4x10^{8}$	2604		
$6.1x10^{8}$	2668		
$1.4x10^{9}$	2749		
$1.7x10^{9}$	2826		
$2.5x10^{9}$	2893		
$8.0x10^{9}$	3143		
$1.6x10^{10}$	3334		
$1.7x10^{10}$	3364		
$2.2x10^{10}$	3553		

REVIEW ARTICLE

Method and Reference	Comments
Review of unimolecular reactions in thermal systems. TROE and WAGNER 1967 (7)	Quotes (1), giving their expression in Arrhenius form as $k_1=2.0x10^{14}\exp(-47\ 000/T)\ cm^3\ mol^{-1}\ s^{-1}$.

Discussion

The dissociation kinetics of cyanogen bromide have proved more complex than those of either Br_2 or $(CN)_2$. The two free radicals produced both react rapidly with the parent species, consequently there has only been one direct measurement of the rate constant k_1 [14], all other expressions being indirect estimates. The general position seems to be that both rate and thermodynamic data fall intermediate between those for Br_2 and $(CN)_2$ decomposition, being nearer the latter.

$$\mathrm{BrCN} + \mathrm{M} \rightarrow \mathrm{Br} + \mathrm{CN} + \mathrm{M} \qquad (1)$$

All four experimental investigations have been shock tube studies under low pressure second order conditions. The two most recent [12,14] show very good agreement despite adopting different views as to the mechanism and adopting different methods of calculating k_1. Initial work by Levitt and Parsons [9] had found the dissociation kinetics to be complex. Subsequently Kayes and Levitt [12,13] found the apparent activation energy obtained to be dependent on [BrCN]. Only for rich mixtures ($\geqslant 5\%$ BrCN) was this observed activation energy $\approx$D(BrCN); for lean mixtures it was very much less. They attributed this to the production of vibrationally excited $(CN)_2$, formed in reaction 3, but rapidly deactivated by BrCN.

$$\mathrm{CN} + \mathrm{BrCN} \rightarrow \mathrm{Br} + (\mathrm{CN})_2^v \qquad (3)$$

Thus they used only their results from the experiments on rich mixtures and obtained values of k_1, k_2 and k_3 by a computer fit to the data.

$$\mathrm{Br} + \mathrm{BrCN} \rightarrow \mathrm{CN} + \mathrm{Br}_2 \qquad (2)$$

Clark et al. [11] used a similar reaction scheme, but used weak BrCN/Ne and Kr mixtures, ignoring the possibility of production of excited $(CN)_2$, except to attribute to it the lower activation energy found with Ne as diluent compared with the Kr results. However, the value of E_1 for M=Kr is also low, and we suspect this may also be due to $(CN)_2^v$. The considerable error apparent in the work of Patterson and Greene [1] can be ascribed simply to a failure to consider any other reactions following the simple dissociation.

Tabayashi et al. [14] were the only authors to couple absorption spectroscopy to their shock tube, and to obtain direct measurements of k_1 by considering only the initial decomposition, thus avoiding the controversy over the subsequent reaction mechanism. That their agreement with the results of Kayes and Levitt is so good would seem to add weight to the arguments of the latter regarding the mechanism, and we accordingly recommend:

$$k_1(\mathrm{M}=\mathrm{Ar}) = 7.2\times10^{14} \exp(-36\,800/T) \ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

based on their two expressions over the temperature range 2000–4000 K, with error limits of ±50%.

References

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[2] Tsang, W., Bauer, S. H., and Cowperthwaite, M., J. Chem. Phys. **36**, 1768 (1962).
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G2 $Br + BrCN \rightarrow CN + Br_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	168.00	24.753	-28.140
300	167.99	24.732	-27.958
500	167.07	22.439	-16.281
1000	163.44	17.506	- 7.622
1500	158.86	13.811	- 4.811
2000	153.91	10.966	- 3.447
2500	149.31	8.908	- 2.665
3000	145.43	7.489	- 2.141
3500	142.32	6.527	- 1.784
4000	139.78	5.845	- 1.520
4500	137.58	5.326	- 1.319
5000	135.51	4.891	- 1.160

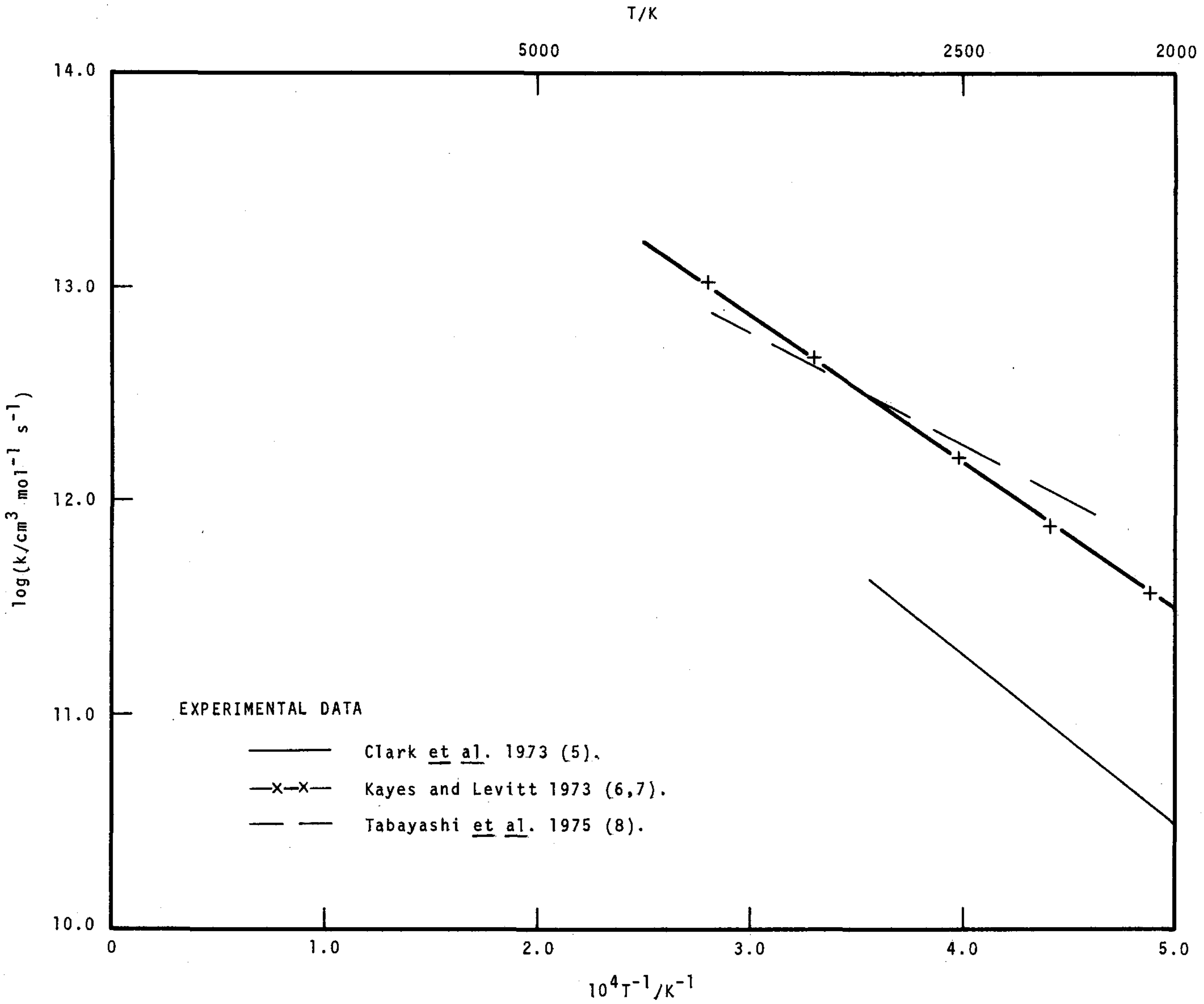
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
3.1×10^{14} exp(-18 500/T)	2000-2800	Shock tube study. BrCN (0.2-2%)/Ne and BrCN (1%) /Kr mixtures at total pressures ∿40 kPa. Reflected shocks. Reaction followed mass spectrometrically. CLARK, DOVE and FINKELMAN 1973 (5)	Major products found to be Br_2, $(CN)_2$ and BrCN. Authors assumed reaction 1 and 2 must occur rapidly after the initial dissociation. $Br + BrCN \rightarrow CN + Br_2$ 1 $CN + BrCN \rightarrow Br + (CN)_2$ 2 $BrCN + M \rightarrow Br + CN + M$ 3 The expression quoted comes from a computer fit to the data. No further details given.
$1\times10^{13}T^{0.5}$ exp(-14 600/T)	2000-4000	Shock tube study. BrCN (0.5-10%)/Ar mixtures at total pressures of 0.4-2.67 kPa. Incident shocks. [CN] monitored by emission spectroscopy at 421.5 nm, [C_2] at 513.5 nm. KAYES and LEVITT 1973 (6,7)	Two separate reaction schemes proposed, one for rich (≥5% BrCN) and the other for lean mixtures. Only in the former case where vibrationally excited $(CN)_2$ was rapidly deactivated was it possible to obtain rate constants. Initial value of

$Br + BrCN \rightarrow CN + Br_2$



$Br + BrCN \rightarrow CN + Br_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		KAYES and LEVITT 1973 (6,7) continued.	$k_1=1x10^{12}T^{0.5}$ exp(-14 600/T) was chosen by comparison with other CN reactions (1,2,3,4), and a computer fit to the data obtained. Quoted by (8).
$2.0x10^{14}$ exp(-11 600/T)	2200-3600	Shock tube study. BrCN (0.2-1%)/Ar mixtures at 1.00-4.43 kPa pressure. Incident shocks. [CN] monitored by absorption spectroscopy at 421.6 nm. TABAYASHI, KAJIMOTO and FUENO 1975 (8)	Computer fit to data, k_3 having been determined from data on the initial rate of appearance of CN. Unlike the previous authors, TABAYASHI et al. also considered reaction 4 in their scheme. $BrCN + BrCN \rightarrow Br_2 + (CN)_2$ 4

Discussion

It is generally accepted [5,7] that in the thermal dissociation of cyanogen bromide, the Br atoms and CN radicals produced immediately attack the parent molecule, thus complicating the kinetics of the dissociation. The endothermic reaction 1 proceeds quite rapidly at shock tube temperatures, although the thermodynamics favour the reverse reaction.

$$Br + BrCN \rightarrow CN + Br_2 \qquad (1)$$

In this respect it follows the pattern of inter-halogen reactions, e.g., $Cl + Br_2$ is favoured over $Br + BrCl$.

There are no direct determinations of the rate of reaction 1. All three of the available expressions for k_1 come from computer fits to shock tube data obtained in the pyrolysis of BrCN. As with the initial BrCN decomposition, there is good agreement between the work of Kayes and Levitt [6,7] and Tabayashi et al. [8], but discrepancy between these two and that of Clark et al. [5]. This is hard to explain; Tabayashi et al. and Clark et al. work with lean mixtures whereas Kayes and Levitt use richer mixtures because they consider excited $(CN)_2$ to be a problem, and there are differences in the third body (Ne, Kr or Ar) used in these studies, but none of these seems sufficient to explain the differences in the results found.

The activation energy obtained by Tabayashi et al. seems unacceptably low, and in view of the differences between the remaining data we make no recommendation.

References

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[5] Clark, T. C., Dove, J. E., and Finkelman, M., Proc. 9th Int. Shock Tube Symp. 196 (1973).

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[8] Tabayashi, K., Kajimoto, O., and Fueno, T., J. Phys. Chem. **79**, 204 (1975).

G3 $CN + BrCN \rightarrow Br + (CN)_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K
298	-200.39	-34.418	33.315
300	-200.39	-34.409	33.098
500	-199.80	-32.957	19.154
1000	-197.17	-29.380	8.767
1500	-193.90	-26.744	5.358
2000	-190.68	-24.886	3.683
2500	-188.23	-23.790	2.694
3000	-186.97	-23.326	2.039
3500	-186.91	-23.313	1.576
4000	-187.88	-23.581	1.225
4500	-189.64	-24.008	0.953
5000	-191.98	-24.518	0.731

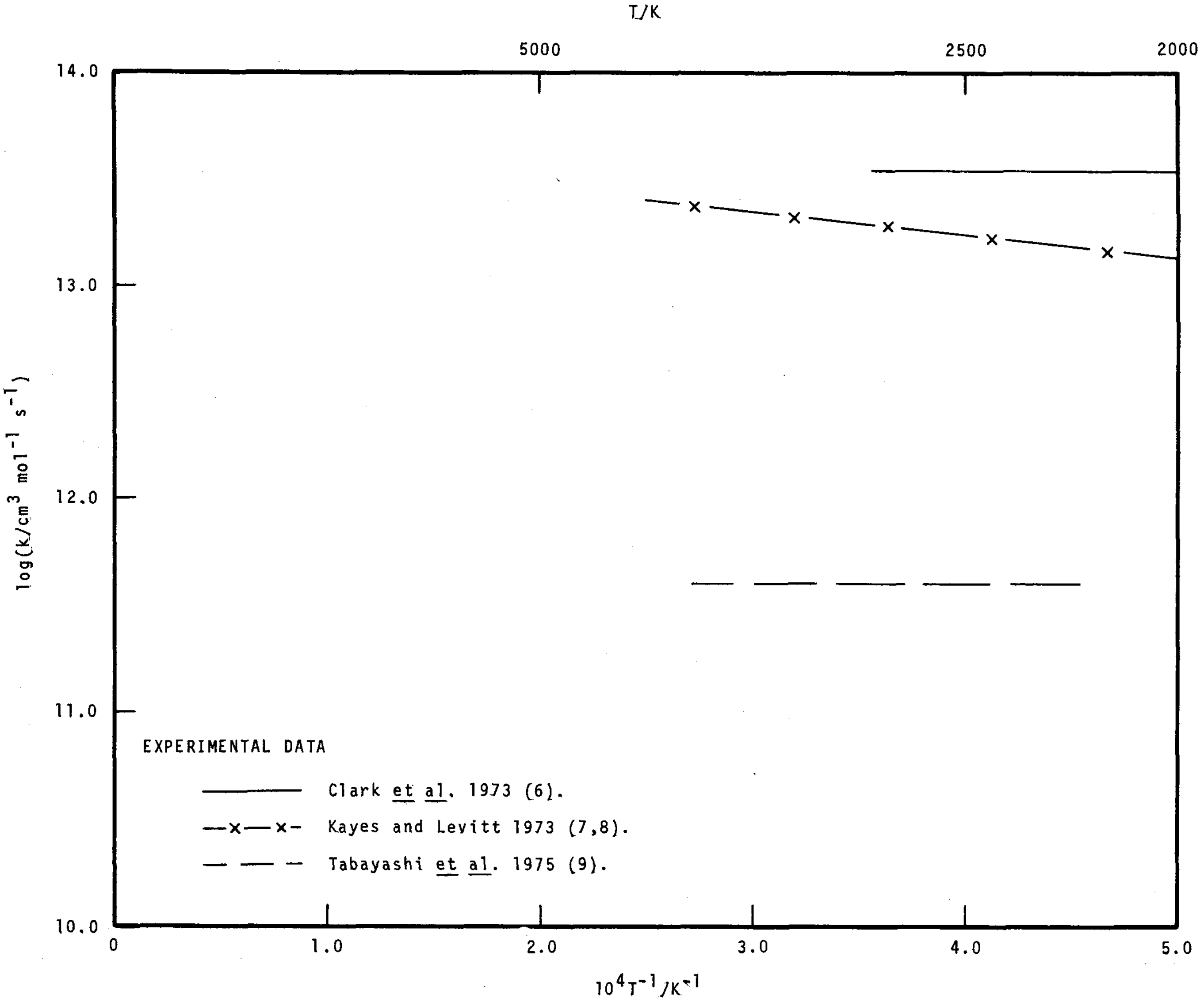
RECOMMENDED RATE CONSTANT

No recommendation, see Discussion.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
3.5×10^{13}	2000-2800	Shock tube study. BrCN (0.2-2%)/Ne and BrCN (∿1%) /Kr mixtures at total pressures ∿40 kPa. Reflected shocks. Reaction followed mass spectrometrically. CLARK, DOVE and FINKELMAN 1973 (6)	Major products found to be Br_2, $(CN)_2$ and BrCN. Authors assumed reactions 1 and 2 must occur rapidly after the initial dissociation, and took E_1=0 on account of the exothermicity of the reaction. $CN + BrCN \rightarrow Br + (CN)_2$ 1 $Br + BrCN \rightarrow CN + Br_2$ 2 $BrCN + M \rightarrow Br + CN + M$ 3 The expression quoted comes from a computer fit to the data. No further details given.
$5.0 \times 10^{11} T^{0.5} \exp(-1000/T)$	2000-4000	Shock tube study. BrCN (0.5 -10%)/Ar mixtures at total pressures of 0.4-2.67 kPa. Incident shocks. [CN] monitored by emission spectroscopy at 421.5 nm, [C_2] at 513.5 nm. KAYES and LEVITT 1973 (7,8)	Authors believed vibrationally excited $(CN)_2$ was formed in reaction 1. For rich (⩾5% BrCN) mixtures, this was rapidly deactivated, but complicated the kinetics in lean mixtures. An initial value for k_1 was chosen, by comparison with similar CN

$CN + BrCN \rightarrow Br + (CN)_2$



$CN + BrCN \rightarrow Br + (CN)_2$

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		KAYES and LEVITT 1973 (7,8) continued.	reactions in the literature, (1, 2,3,4) to have the same A factor, but slightly lower activation energy than the expression quoted, which was then obtained by a computer fit to the experimential data. Quoted by (9).
4.0×10^{11}	2200-3600	Shock tube study. BrCN (0.2 -1%)/Ar mixtures at 1.00-4.43 kPa pressures. Incident shocks. [CN] monitored by absorption spectroscopy at 421.6 nm. TABAYASHI, KAJIMOTO and FUENO 1975 (9)	Computer fit to data, k_3 having been determined from data on the initial stages of the reaction. Unlike previous studies, authors also considered reaction 4 in their schemes. $BrCN + BrCN \rightarrow Br_2 + (CN)_2$ 4

Discussion

Following the initial decomposition of cyanogen bromide, the parent molecule is attacked by both Br atoms and CN radicals. Reaction 1 is exothermic, and assumed to have little or no activation energy. As would be expected from analogous inter-halogen reactions, reaction 1 is fast, with the equilibrium always in favour of the forward reaction.

$$CN + BrCN \rightarrow Br + (CN)_2 \qquad (1)$$

There are no direct determinations of the rate of reaction 1. The two temperature-independent values and the one expression for k_1 come from computer fits to shock tube data obtained in the pyrolysis of BrCN. In contrast to the data on reactions 2 and 3, the agreement this time is between the value of Clark et al. [6] and the expression of Kayes and Levitt [7,8], both very much higher than the value of Tabayashi et al. [9]. As has been explained when considering reaction 2 (section G2), the reasons for the discrepancies are not clear and it is not possible to make a recommendation for k_1. At room temperature, the expression of [7] would agree well with the value of [9], but this value is well below the expected rate for an inter-halogen reaction such as reaction 5 [5], with which reaction 1 would be expected to show similarities. On the other hand, the apparently more reasonable value of Clark et al. [6] must be suspect on account of likely errors in other rate constants in this system.

$$Br + BrCN \rightarrow CN + Br_2 \qquad (2)$$

$$BrCN + M \rightarrow Br + CN + M \qquad (3)$$

$$Cl + BrCl \rightarrow Br + Cl_2 \qquad (5)$$

References

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Miscellaneous Reaction Involving ClCN

G4 ClCN + M → Cl + CN + M

The thermal decomposition of cyanogen chloride has not received the same attention as that of BrCN, but, as might be expected, the features are similar, the kinetics being complicated by a series of fast secondary reactions similar to those for BrCN.

$$ClCN + M \rightarrow Cl + CN + M; \qquad (1)$$

$$\Delta H^\circ_{298} = 418.48 \text{ kJ mol}^{-1} \text{ (100.02 kcal mol}^{-1}\text{)}$$

The only experimental study of the decomposition comes from Schofield et al. [1], who shocked ClCN (0.5–5.0%)/Ar mixtures at total pressures of 1.00–7.00 kPa, monitoring [CN] by absorption spectroscopy at 388.3 nm behind incident shocks. From the initial conditions, where only reactions 1 and 2 were considered important, the authors obtained $k_1/k_2 = 3.1 \times 10^3 \exp(-43\,000/T)$ over the temperature range 2000–2800 K.

$$CN + ClCN \rightarrow Cl + (CN)_2 \qquad (2)$$

Assuming $E_2 = 25$ kJ mol^{-1} (6 kcal mol^{-1}), approximate values were obtained for k_1, k_2 and k_3, and taking order of magnitude approximations for k_4, k_5 and k_6, a computer fit to the data was made.

$$(CN)_2 + M \rightarrow CN + CN + M \qquad (3)$$

$$Cl + ClCN \rightarrow CN + Cl_2 \qquad (4)$$

$$Cl_2 + M \rightarrow Cl + Cl + M \qquad (5)$$

$$ClCN + ClCN \rightarrow Cl_2 + (CN)_2 \qquad (6)$$

This gave $k_1 = 3.4 \times 10^{16} \exp(-46\,000/T)$ cm^3 mol^{-1} s^{-1}, almost identical to our expression for k_3, (section F1) but with much higher A factor and activation energy than k_5 (section B1).

Reference

[1] Schofield, D., Tsang, W., and Bauer, S. H., J. Chem. Phys. **42**, 2132 (1965).

H1 H + HALOMETHANES

THERMODYNAMIC DATA

Thermodynamic data for halogen-substituted methyl radicals are not available.

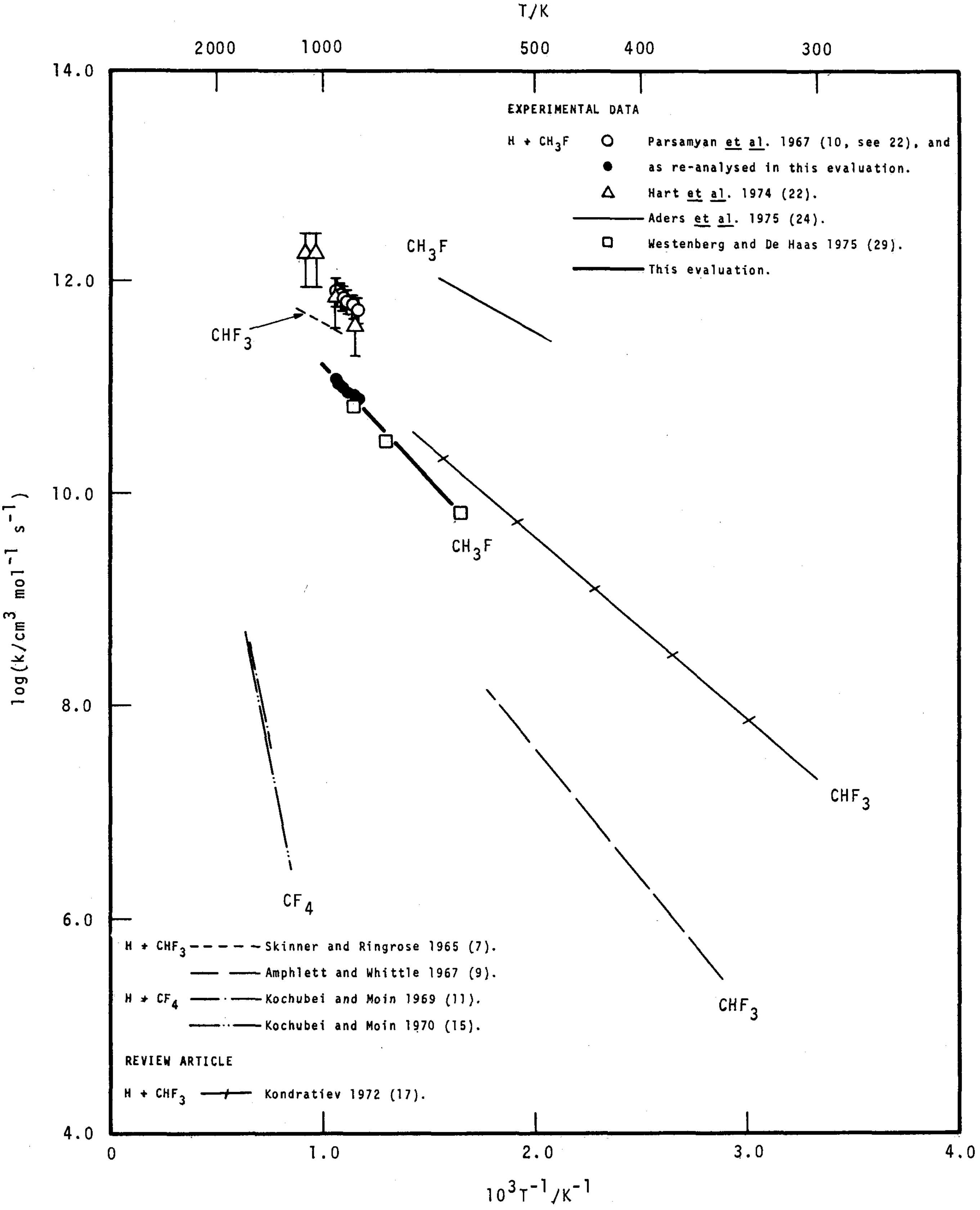
RECOMMENDED RATE CONSTANTS

$H + CH_3F$: $k = 2.30 \times 10^{13} \exp(-4950/T)$ cm^3 mol^{-1} s^{-1}
$= 3.82 \times 10^{-11} \exp(-4950/T)$ cm^3 molecule^{-1} s^{-1}
Temperature Range: 600-1000 K.
Suggested Error Limits for Calculated Rate Constant:
a factor of 5 over the quoted temperature range.

$H + CH_3Br$: $k = 5.10 \times 10^{13} \exp(-2940/T)$ cm^3 mol^{-1} s^{-1}
$= 8.47 \times 10^{-11} \exp(-2940/T)$ cm^3 molecule^{-1} s^{-1}
Temperature Range: 298-2000 K.
Suggested Error Limits for Calculated Rate Constant:
a factor of 3 over the quoted temperature range.
Note: this expression is only tentative.

$H + CF_3Br$: $k = 1.47 \times 10^{14} \exp(-4700/T)$ cm^3 mol^{-1} s^{-1}
$= 2.44 \times 10^{-10} \exp(-4700/T)$ cm^3 molecule^{-1} s^{-1}
Temperature Range: 700-1700 K.
Suggested Error Limits for Calculated Rate Constant:
a factor of 2 over the quoted temperature range.

H + FLUOROMETHANES



H + HALOMETHANES

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$H + CH_3F \rightarrow CH_3 + HF$	
	858-933	Static system. H_2(80%) /O_2 mixtures with added CH_3F (1%-3.17%). Total pressures ∿5-8 mm Hg (0.67-1.07 kPa). Reaction followed manometrically. PARSAMYAN, AZATYAN and NALBANDYAN 1967 (10)	From variation of first ignition limit with $[CH_3F]$, authors obtained ratio $k_1k_4/k_2(k_3+k_4)$ $H + CH_3F \rightarrow CH_3 + HF$ 1 $H + O_2 \rightarrow OH + O$ 2 $CH_3 + O_2 \rightarrow HCHO + OH$ 3 $\rightarrow$ termination 4 Using $k_2=1.02\times10^{14}\exp(-8250/T)$ cm^3 mol^{-1} s^{-1} (3) authors gave various values for ratio $k_1k_4/(k_3+k_4)$, from 858-933 K, as shown below. HART *et al*. (22) derived the following values of k_1 from these results: T/K $\frac{k_1k_4}{k_3+k_4}$/cm^{3}mol^{-1}s^{-1} k_1/cm^{3}mol^{-1}s^{-1} 858 2.86×10^{10} $(5.58\pm1.67)\times10^{11}$ 873 3.16×10^{10} $(6.16\pm1.85)\times10^{11}$ 888 3.31×10^{10} $(6.45\pm1.94)\times10^{11}$ 903 3.64×10^{10} $(7.10\pm2.13)\times10^{11}$ 918 3.88×10^{10} $(7.59\pm2.28)\times10^{11}$ 933 4.23×10^{10} $(8.27\pm2.48)\times10^{11}$ No details as to what values had been used for k_3 or k_4 were given. Correcting the above ratios $k_1k_4/(k_3+k_4)$ with our own recommendation for k_2 (Volume 1,p.9) and using WALKER's recommended values for k_3 and k_4 (35), we derive the values of k_1 below: T/K k_1/cm^{3}mol^{-1}s^{-1} 858 7.81×10^{10} 873 8.60×10^{10} 888 8.98×10^{10} 903 9.83×10^{10} 918 1.05×10^{11} 933 1.14×10^{11}
$(4.1\pm2.1)\times10^{11}$	870	Flame study. H_2(90%) /O_2 (10%) mixtures burnt at 0.1 atm (10.1 kPa). CH_3F injected into flame as ∿1% of total. Reaction zone sampled and analysed by mass spectrometry. HART, GRUNFELDER and FRISTROM 1974 (22)	By measuring $[CH_3F]$ at various values of distance between CH_3F injection point and (upstream) sampling point, authors obtained k_1 directly. Dominant reaction assumed to be reaction 1. $H + CH_3F \rightarrow CH_3 + HF$ 1 Rate constants k_5 determined in same work $H + CH_3Br \rightarrow CH_3 + HBr$ 5 used to generate ratios k_1/k_5. Using expression for k_5 derived from authors' own data and those of DAVIES *et al*. (14) authors quote $k_1=(6.3\pm4.6)\times10^{13}\exp\{-(4120\pm690)/T\}$ cm^3 mol^{-1} s^{-1} (300-1088 K).
$(7.2\pm3.6)\times10^{11}$	942		
$(1.9\pm1.0)\times10^{12}$	1029		
$(1.9\pm1.0)\times10^{12}$	1088		

H + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(6.3\pm0.4)\mathrm{x}10^{13}\ \exp\{-(2620\pm150)/T\}$	482-646	Discharge flow system. H_2/He mixtures passed through discharge. CH_3F added downstream, giving $1\mathrm{x}10^{-9} < [CH_3F] < 1.39\mathrm{x}10^{-8}$ mol cm^{-3}, with $[CH_3F]/[H]$ varied from 5 to 10. Total pressures 1.6-18 mm Hg (0.21-2.4 kPa). [H] followed by esr spectrometry, and products measured by mass spectrometry. ADERS, PANGRITZ and WAGNER 1975 (24)	First order rate constant obtained from [H] decay. Stoichiometry $\Delta[H]/\Delta[CH_3F]$ found to be 1.3-1.4, which authors believed due to contribution from reaction 6, $H + CH_3F \rightarrow CH_3 + HF$ 1 $\rightarrow CH_4 + F$ 6 owing to principal products being HF, CH_4, and C_2H_6. Absence of detectable amounts of H_2 indicated reaction 7 to be negligible. $H + CH_3F \rightarrow CH_2F + H_2$ 7
$(6.7\pm0.4)\mathrm{x}10^{9}$ $(3.2\pm0.3)\mathrm{x}10^{10}$ $(6.9\pm0.7)\mathrm{x}10^{10}$	605 768 871	Discharge flow system. H_2(<2%)/He mixtures passed through discharge. CH_3F added downstream through moveable inlet. $[H]/[CH_3F]$ ratios 100-250. [H] monitored by esr spectrometry, and $[CH_3F]$ decay by mass spectrometry. WESTENBERG and DE HAAS 1975 (29)	Pseudo first order decay of $[CH_3F]$ used to derive k_1. Authors considered activation energy of reaction 6 to be high, as for reaction with CH_4 $H + CH_4 \rightarrow CH_3 + H_2$ and reaction 7 being endothermic, led them to ignore reactions 6 and 7 $H + CH_3F \rightarrow CH_4 + F$ 6 $\rightarrow XH_2F + H_2$ 7 These data expressed as $k_1=1.8\mathrm{x}10^{13}\ \exp(-4730/T)\ cm^3\ mol^{-1}\ s^{-1}$.
		$H + CHF_3 \rightarrow CF_3 + H_2$	
$5.0\mathrm{x}10^{12}\ \exp(-2520/T)$	938-1141	Shock tube study. H_2(8%)/O_2(2%)/Ar mixtures plus added CF_3Br (0.8%). Total pressures behind incident shocks ∿5 atm (506.5 kPa). $[CF_3Br]$ followed by ir absorption, and emission monitored in range 330-550 nm. SKINNER and RINGROSE 1965 (7)	Induction times before onset of emission modelled by H_2/O_2 system plus reactions $H + CF_3Br \rightarrow CF_3 + HBr$ 22 $H + CF_3 + M \rightarrow CHF_3 + M$ $CF_3 + H_2 \rightarrow H + CHF_3$ -8 $H + HBr \rightarrow Br + H_2$ Best agreement obtained using $k_{-8}=7.75\mathrm{x}10^{11}\ \exp(-12\ 650/T)\ cm^3\ mol^{-1}\ s^{-1}$, from which expression for k_8 obtained, using K_8. $H + CHF_3 \rightarrow CF_3 + H_2$ 8

H+ HALOMETHANES

REVIEW ARTICLE

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
1.05×10^{13} exp(-3940/T)	300-700	Review. Based on author's own recommended value of k_{-8} and equilibrium constant. KONDRATIEV 1972 (17)	Author also lists expression for k_8 $H + CHF_3 \rightleftharpoons CF_3 + H_2$ 8,-8 as least squares fit to data of (7 and 9), namely $k_8=3.39\times10^{14}$ exp{-(7260±350)/T} cm^3 mol^{-1} s^{-1} (336-1300 K).

$H + CF_4 \rightarrow CF_3 + HF$

EXPERIMENTAL DATA

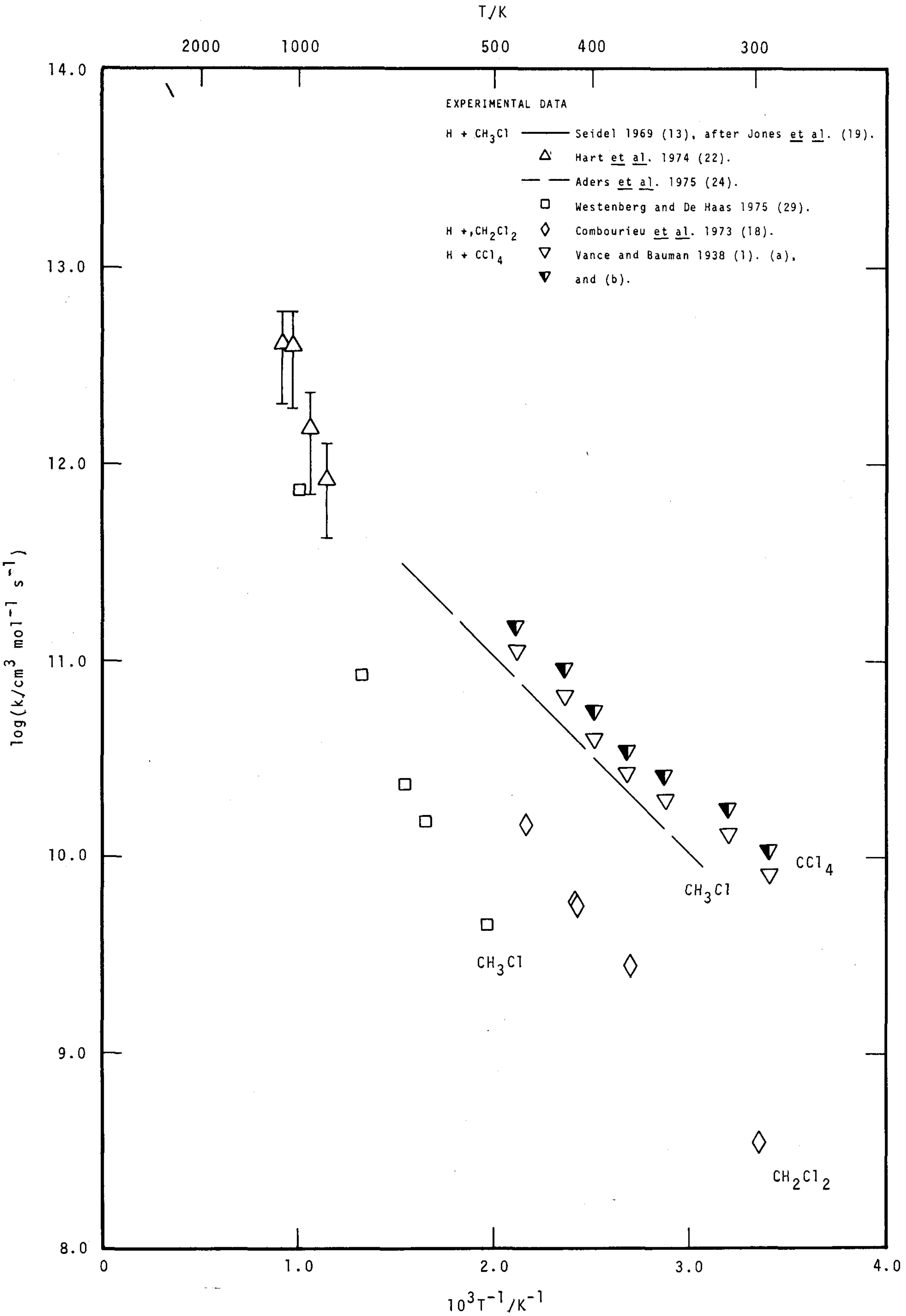
Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
7.1×10^{14} exp(-21 990/T)	1323-1523	Flow system. CF_4(24.2%)/H_2(40%)/N_2 mixtures passed at 1 atm (101.3 kPa) through furnace. Reaction products analysed gravimetrically and by ir spectrometry. KOCHUBEI and MOIN 1969 (11)	H_2 percentage varied (no details available) and degree of CF_4 conversion found ½ order in $[H_2]$, and reaction products gave $[HF]/[CH_4]=4$. Overall rate constant for CF_4/H_2 reaction given as 1.4×10^{15} exp(-48 210/T) $cm^{3/2}$ $mol^{-1/2}$ s^{-1}. Authors explained their results in terms of mechanism $H_2 + M \rightleftharpoons H + H + M$ 9 $H + CF_4 \rightarrow CF_3 + HF$ 10 $CF_3 + H_2 \rightarrow H + CHF_3$ -8 $CHF_3 \rightarrow CF_2 + HF$ $CF_2 + H_2 \rightarrow CHF + HF$ $CHF + H_2 \rightarrow CH_2 + HF$ $CH_2 + H_2 \rightarrow CH_4$ and considered reaction 10 to be rate controlling step in CF_4 removal. Substituting for $[H_2]$ the equilibrium value $[H]^2/K_9$ in overall rate expression, authors derived k_{10} as shown.
	1173-1573	Flow system. CF_4(31.7-54.6%)/H_2(18.2-24.4%)/O_2(2.5-4.25%)/CO(5.72-19.5%)/N_2(8.55-40.13%) mixtures passed at 1 atm (10.1 kPa) through furnace. Reaction products analysed gravimetrically. KOCHUBEI and MOIN 1970 (15)	Assuming removal of CF_4 and CO_2 to be solely via reactions 10 and 11 respectively, $H + CF_4 \rightarrow CF_3 + HF$ 10 $H + CO_2 \rightarrow CO + OH$ 11 authors obtained ratio $k_{10}/k_{11}=10.9$ exp(-10 270/T), at low degrees of conversion. Authors used k_{11} from (12) to derive $k_{10}=1.09\times10^{15}$ exp(-22 440/T) cm^3 mol^{-1} s^{-1}. Using our recommended expression for k_{11} (Volume 3, p. 251) we derive $k_{10}=1.64\times10^{15}$ exp(-23 570/T) cm^3 mol^{-1} s^{-1} for this work.

H + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$H + CH_3Cl \rightarrow CH_3 + HCl$	
	2821-3023	Flow system. H_2 thermally dissociated in oven and passed into reaction vessel to react with CH_3Cl stream. [HCl] determined by thermal conductivity, and [H] by measuring [H_2] collected in trap. SEIDEL 1969 (13)	From rate of HCl production, author derived activation energy E_{12}=33.9 kJ mol^{-1} (8.09 kcal mol^{-1}). JONES et al. (19) derived the expression k_{12}=3.09x10^{14} exp(-4030/T) cm^3 mol^{-1} s^{-1} from this value and author's quoted steric factor. This expression shown on Arrhenius plot. $H + CH_3Cl \rightarrow CH_3 + HCl$ 12
(8.4±4.2)x10^{11} (1.5±0.8)x10^{12} (3.9±2.0)x10^{12} (4.0±2.0)x10^{12}	870 942 1029 1088	Flame study. H_2(90%)/ O_2(10%) mixtures burnt at 0.1 atm (10.1 kPa). CH_3Cl injected into flame at ∿1% of total. Reaction zone sampled and analysed by mass spectrometry. HART, GRUNFELDER and FRISTROM 1974 (22)	Method as for CH_3F (see above). From rate constants k_5 derived in same work $H + CH_3Cl \rightarrow CH_3 + HCl$ 12 $H + CH_3Br \rightarrow CH_3 + HBr$ 5 authors generated ratios k_{12}/k_5. Using expression for k_5 derived from authors' own data and those of DAVIES et al. (14) authors derived k_{12}=(9.5±5.2)x10^{13} exp{-(3840±490)/T} cm^3 mol^{-1} s^{-1} (300-1088 K).
(1.1±0.3)x10^{13} exp{-(2320± 150)/T}	326-652	Discharge flow system. H_2/He mixtures passed through discharge. CH_3Cl added downstream, giving 1x10^{-9}≤[CH_3Cl]< 1.39x10^{-8} mol cm^{-3}. [CH_3Cl]/[H] ratio varied from 4-18. Total pressures 1.6-18 mm Hg (0.21-2.4 kPa). [H] followed by esr spectrometry, and products measured by mass spectrometry. ADERS, PANGRITZ and WAGNER 1975 (24)	Method as for CH_3F (see above). Stoichiometry Δ[H]/Δ[CH_3Cl] found to vary from 1.6 to 1.3 over [CH_3Cl]/[H] ratio range. Principal products CH_4, C_2H_6 and HCl, and absence of detectable H_2, indicated reaction 13 as negligible $H + CH_3Cl \rightarrow CH_2Cl + H_2$ 13 and variation in CH_4 and C_2H_6 yields with pressure showed competition between reactions 12 and 14 $H + CH_3Cl \rightarrow CH_3 + HCl$ 12 $\rightarrow CH_4 + Cl$ 14 Expression for k_{12} derived from overall rate constant, corrected for stoichiometry at [CH_3Cl]/[H] = 8, and over pressure range 3-11 mm Hg (0.4-1.5 kPa).
(4.4±0.1)x10^9 1.5x10^{10} (2.3±0.1)x10^{10} (8.4±0.2)x10^{10} (7.4±0.2)x10^{11}	510 605 647 755 998	Discharge flow system. H_2(<2%)/He mixtures passed through discharge. CH_3Cl added downstream through moveable inlet. [H]/[CH_3Cl] ratios 100-250. [H] monitored by esr spectrometry, and [CH_3Cl] decay by mass	Method as for CH_3F (see above). Authors expressed these data by k_{12}=3.7x10^{13} exp (-4680/T) cm^3 mol^{-1} s^{-1}.

H + CHLOROMETHANES



H + HALOMETHANES

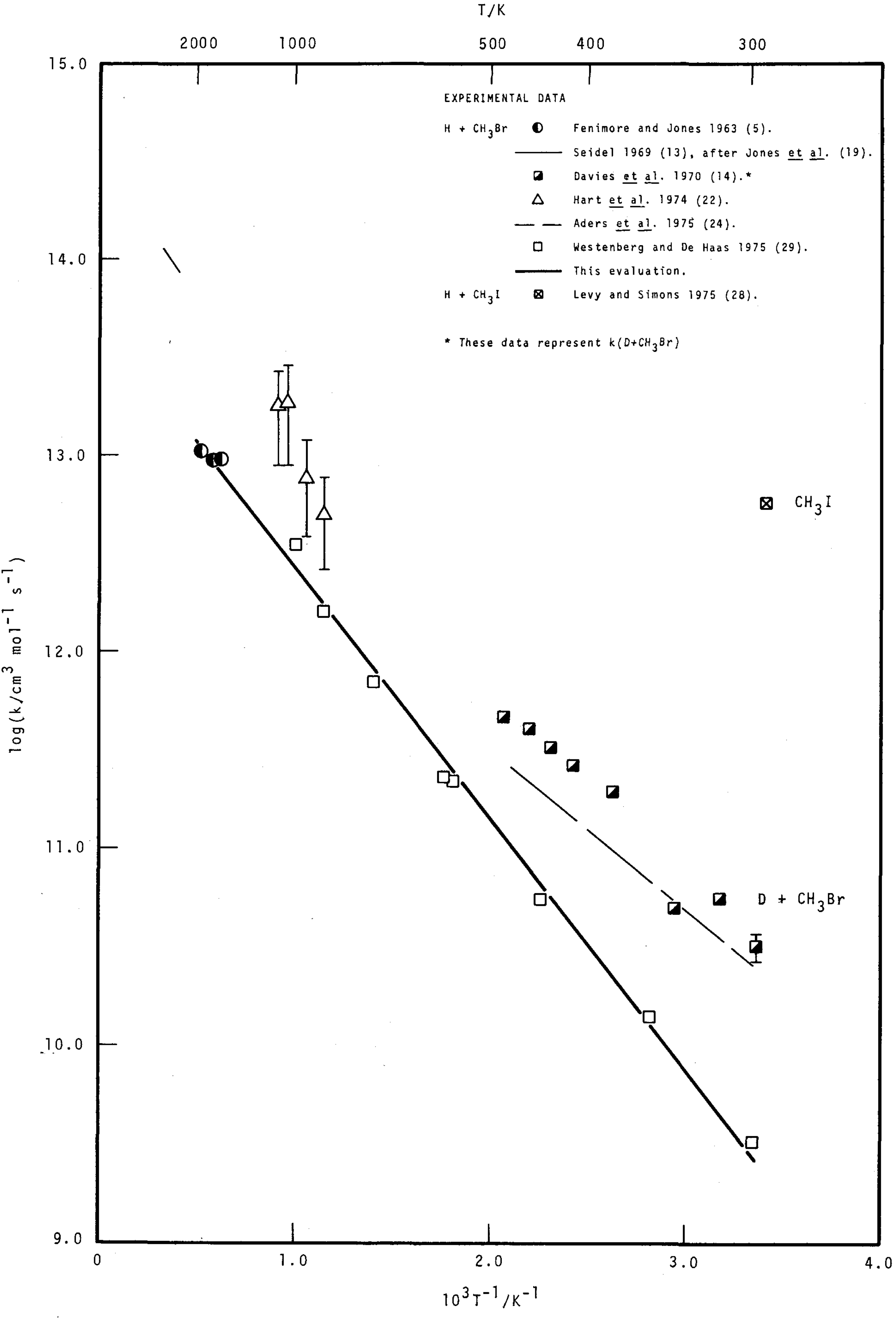
EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		spectrometry. WESTENBERG and DE HAAS 1975 (29)	
		$H + CH_2Cl_2 \rightarrow CH_2Cl + HCl$	
3.61×10^{8}	298	Discharge flow system. H_2/He mixtures passed through discharge. CH_2Cl_2 added downstream through moveable inlet, such that $0.39 < [H]/[CH_2Cl_2] < 12.1$. Total pressures ∿1 mm Hg (133.3 Pa). Mass spectrometry used to follow [H], [CH_2Cl_2], [HCl] and [CH_4]. COMBOURIEU, LE BRAS and PATY 1973 (18)	[H] calibrated by titration vs. NO_2. Stoichiometry $\Delta[H]/\Delta[CH_2Cl_2]$ found to vary from 4 to 30 over range of $[H]/[CH_2Cl_2]$ values. Authors explained findings by mechanism $H + CH_2Cl_2 \rightarrow CH_2Cl + HCl$ 15 $H + HCl \rightarrow Cl + H_2$ 16 $Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$ $Cl + Cl + wall \rightarrow Cl_2$ $H + Cl_2 \rightarrow Cl + HCl$ Values of k_{15} determined with excess H atoms, from pseudo first order CH_2Cl_2 decay. These data expressed as $k_{15}=1.08\times10^{13}\exp(-3070/T)$ cm^3 mol^{-1} s^{-1}. Quoted by (23 and 29) and results reproduced in (34).
2.87×10^{9}	370		
5.72×10^{9}	411		
5.87×10^{9}	414		
1.49×10^{10}	462		
		$H + CCl_4 \rightarrow CCl_3 + HCl$	
(a) 8×10^{9}	294	Discharge flow system. H_2 passed through discharge and CCl_4 added downstream, with $5.7\times10^{-10} \leqslant [CCl_4] \leqslant 2.4\times10^{-8}$ mol cm^{-3}. Total pressures 0.77-0.99 mm Hg (102.6-132 Pa), and $0.174 < [CCl_4]/[H] < 11.64$. [H] determined by thermal conductivity, and [HCl] by freezing out and titrating with $Ba(OH)_2$. VANCE and BAUMAN 1938 (1)	Authors analysed their results according to production of HCl from spherical flames, characterising reaction vessel as (a) cylinder, (b) sphere. Two sets of rate constants were thereby obtained, as shown. Values of k_{17} found to increase with low [CCl_4], $H + CCl_4 \rightarrow CCl_3 + HCl$ 17 *indicating secondary reactions such as* $H + CCl_3 \rightarrow CCl_2 + HCl$ and values of k_{17} are those at high [CCl_4]. Authors expressed all data as $k_{17}=2.17\times10^{11}T^{\frac{1}{2}}\exp(-1740/T)$ cm^3 mol^{-1} s^{-1}, whereas JONES et al. (19) quote these data in form $k_{17}=5.89\times10^{12}\exp(-1960/T)$ cm^3 mol^{-1} s^{-1}. Original expression quoted by (23).
1.3×10^{10}	323		
2.0×10^{10}	348		
2.7×10^{10}	373		
4.0×10^{10}	398		
6.6×10^{10}	423		
1.15×10^{11}	473		
(b) 1.1×10^{10}	294		
1.8×10^{10}	323		
2.6×10^{10}	348		
3.5×10^{10}	373		
5.6×10^{10}	398		
9.1×10^{10}	423		
1.51×10^{11}	473		

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	800-1000	Flame study. CCl_4 added to H_2(18.8%)/O_2 (4.6%)/N_2 flame. [H] determined by chemiluminescence produced by addition of Na salts. DIXON-LEWIS and WILLIAMS 1955 (2)	Few details available. Authors quote E_{17}=16.3 kJ mol^{-1} (3.9 kcal mol^{-1}). $H + CCl_4 \rightarrow CCl_3 + HCl$ 17
	2137-2468	Flow system. H_2 thermally dissociated in oven and passed into reaction vessel to react with CCl_4 stream. [HCl] determined by thermal conductivity, and [H] by measuring [H_2] as collected in trap. SEIDEL, MARTIN and MIETZNER 1965 (6)	Authors derived activation energy E_{17}= 20.3 kJ mol^{-1} (4.86 kcal mol^{-1}) from rate of HCl production.
		$H + CH_3Br \rightarrow CH_3 + HBr$	
	1600-1900	Flame study. H_2(21.2%)/N_2O(25.4%)/NO(20.3%)/CH_3Br(5.1%)/Ar(28%), H_2(18.9%)/O_2(13.8%)/NO(27.2%)/CH_3Br(3.2%)/Ar(27%), and H_2(28.8%)/O_2(12.8%)/NO(25.6%)/CH_3Br(0.5%)/Ar(32.2%) mixtures burnt at 100 and 70 mm Hg (13.3 and 9.3 kPa). Flames sampled and analysed by mass spectrometry. FENIMORE and JONES 1963 (5)	From relative rates of CH_3Br and N_2O removal, authors obtained ratio k_5/k_{18} $H + CH_3Br \rightarrow CH_3 + HBr$ 5 $H + N_2O \rightarrow N_2 + OH$ 18 Authors used k_{18}/k_2 from (4), and k_2=4x10^{14} exp(-9060/T) cm^3 mol^{-1} s^{-1} $H + O_2 \rightarrow OH + O$ 2 to derive k_5=1.2x10^{13} cm^3 mol^{-1} s^{-1} (1600 and 1700 K), and 1.4x10^{13} cm^3 mol^{-1} s^{-1} (1900 K). Using our expression for k_2 (Volume 1, p.9) we derive k_5=9.63x10^{12} cm^3 mol^{-1} s^{-1} (1600 K), 9.42x10^{12} cm^3 mol^{-1} s^{-1} (1700 K), and 1.06x10^{13} cm^3 mol^{-1} s^{-1} (1900 K). These data reproduced by WILSON (8). WESTENBERG and DE HAAS (29) used authors' k_5/k_{18} at 1900 K, and k_{18} of (25) to derive k_5=5.5x10^{12} cm^3 mol^{-1} s^{-1}.

H + CH_3Br, CH_3I


T/K
2000
1000
500
400
300
15.0
14.0
13.0
12.0
11.0
10.0
9.0
log(k/cm³ mol⁻¹ s⁻¹)
0
1.0
2.0
3.0
4.0
10³T⁻¹/K⁻¹
EXPERIMENTAL DATA
H + CH₃Br ◐ Fenimore and Jones 1963 (5).
—— Seidel 1969 (13), after Jones et al. (19).
◩ Davies et al. 1970 (14).*
△ Hart et al. 1974 (22).
— — Aders et al. 1975 (24).
□ Westenberg and De Haas 1975 (29).
—— This evaluation.
H + CH₃I ⊠ Levy and Simons 1975 (28).
* These data represent k(D+CH₃Br)
CH₃I
D + CH₃Br

H + HALOMETHANES

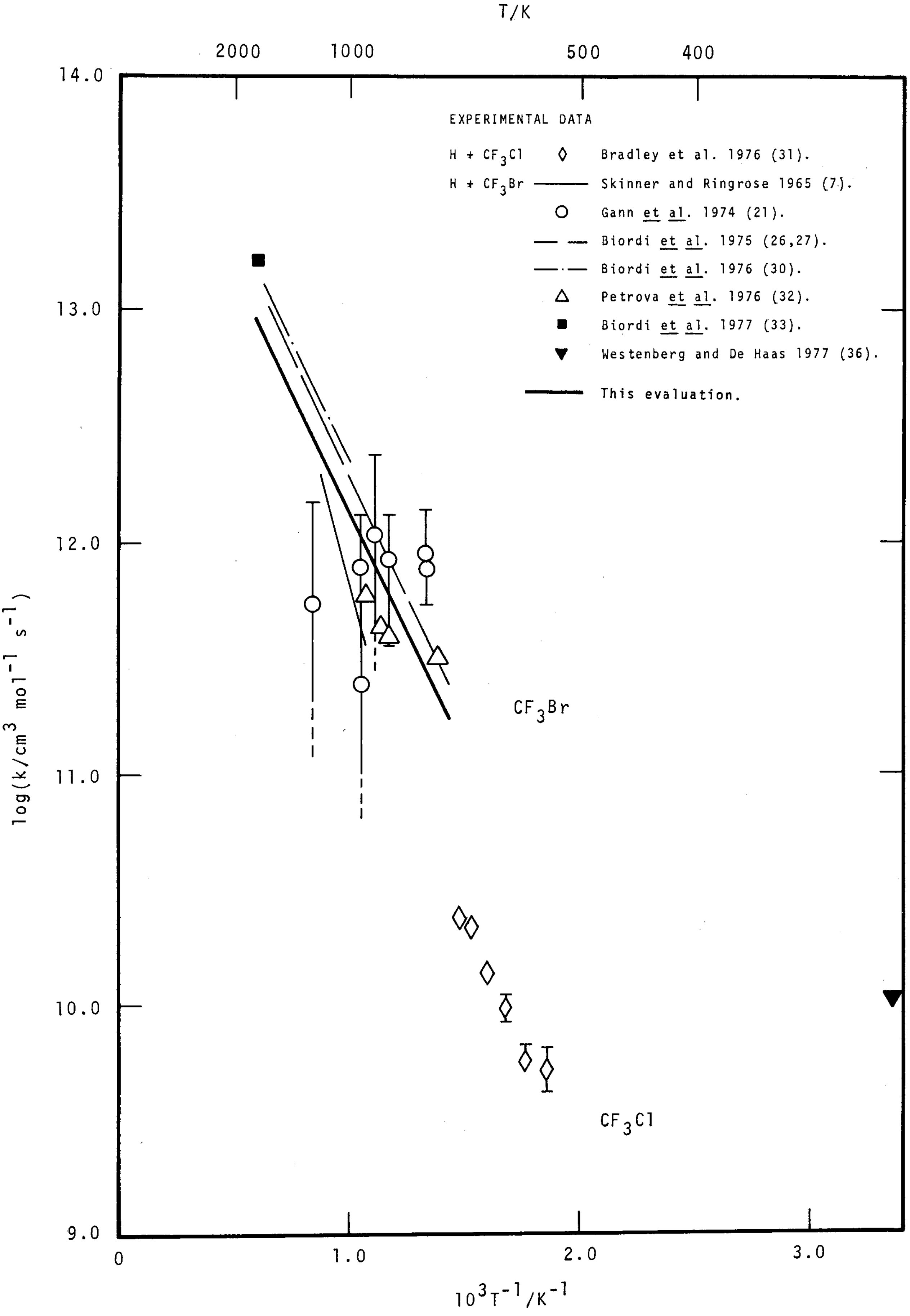
EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
	2472-3021	Flow system. H_2 thermally dissociated in oven and passed into reaction vessel to react with CH_3Br stream. [HBr] determined by thermal conductivity, and [H] by measuring [H_2] collected in trap. SEIDEL 1969 (13)	Author derived activation energy E_5=28.9 kJ mol^{-1} (6.9 kcal mol^{-1}) from rate of HBr production. JONES *et al.*(19) derived the expression $k_5=3.55\times10^{14}$ exp(-3470/T) cm^3 mol^{-1} s^{-1} from E_5 and author's quoted steric factor. This expression shown on Arrhenius plot.
	297-480	Discharge flow system. D_2(≤5%)/Ar mixtures passed through discharge. CH_3Br added downstream via moveable inlet. Total pressures 1.02-7.01 mm Hg (136-934.4 Pa). [D] monitored by esr spectrometry. DAVIES, THRUSH and TUCK 1970 (14)	Stoichiometry determined for each run, by plotting Δ[D]/[CH_3Br] vs. [CH_3Br], and found to vary from 10 (1.02 mm Hg; 136 Pa) to 3.6 (5.16 mm Hg; 687.8 Pa). From pseudo first order decay of [D], authors obtained k_{5D}, after allowing for stoichiometry. $D + CH_3Br \rightarrow CH_3 + DBr$ 5D Authors quote $k_{5D}=(3.2\pm0.52)\times10^{10}$ cm^3 mol^{-1} s^{-1} at 297 K, and following values obtained from graph: T/K $k_{5D}/cm^3 mol^{-1} s^{-1}$ 315 5.65×10^{10} 339 5.02×10^{10} 380 1.96×10^{11} 413 2.63×10^{11} 431 3.31×10^{11} 453 4.16×10^{11} 480 4.74×10^{11} These results expressed as $k_{5D}=(5.41\pm0.18)\times10^{13}$ exp{-(2150±130)/T} cm^3 mol^{-1} s^{-1}. These data multiplied by 2 by HART *et al.* (22) and WESTENBERG and DE HAAS (29) to give k_5.
$(5.2\pm2.6)\times10^{12}$ $(7.9\pm4.0)\times10^{12}$ $(1.9\pm1.0)\times10^{13}$ $(1.8\pm0.9)\times10^{13}$	870 942 1029 1088	Flame study. H_2(90%)/O_2(10%) mixtures burnt at 0.1 atm (10.1 kPa). CH_3Br injected into flame as ∿1% of total. Reaction zone sampled and analysed by mass spectrometry. HART, GRUNFELDER and FRISTROM 1974 (22)	Method as for CH_3F (see above). Weighted least squares fit to these data and those of DAVIES *et al.*(14), multiplied by √2 to correct for D isotope effect, expressed as $k_5=(1.1\pm0.3)\times10^{14}$ exp{-(2330±100)/T} cm^3 mol^{-1} s^{-1} (297-1090 K). $H + CH_3Br \rightarrow CH_3 + HBr$ 5
$(1.3\pm0.3)\times10^{13}$ exp{-(1860±130)/T}	298-474	Discharge flow system. H_2/He mixtures passed through discharge. CH_3Br added downstream, giving 1×10^{-9}≤[CH_3Br]≤	Method as for CH_3F (see above). Stoichiometry found to vary from 1.5 to 8 over range 10≥[CH_3Br]/[H]≥ 3. No pressure dependence found for 2.5-12 mm Hg (0.33-1.6 kPa). Authors identified

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		$1.39x10^{-8}$ mol cm^{-3}, with $[CH_3Br]/[H]$ varied over range 4-30. Total pressures 1.6-18 mm Hg (0.21-2.4 kPa). [H] followed by esr spectrometry, and products measured by mass spectrometry. ADERS, PANGRITZ and WAGNER 1975 (24)	CH_4, C_2H_6, HBr, Br_2, H_2 and Br atoms among products, and concluded reaction mechanism to be $H + CH_3Br \rightarrow CH_3 + HBr$ 5 $H + HBr \rightarrow Br + H_2$ 19 $Br + Br + wall \rightarrow Br_2$
$(3.3\pm0.3)x10^9$ $1.4x10^{10}$ $5.5x10^{10}$ $2.2x10^{11}$ $(2.3\pm0.1)x10^{11}$ $(7.0\pm0.2)x10^{11}$ $1.6x10^{12}$ $(3.6\pm0.3)x10^{12}$	298 355 442 550 568 712 870 996	Discharge flow system. H_2(<2%)/He mixtures passed through discharge. CH_3Br added downstream through moveable inlet. [H]/$[CH_3Br]$ ratios 100-250. [H] monitored by esr spectrometry, and $[CH_3Cl]$ decay by mass spectrometry. WESTENBERG and DE HAAS 1975 (29)	Method as for CH_3F (see above). These data expressed as $k_5=2.8x10^{13}\ exp(-2670/T)\ cm^3\ mol^{-1}\ s^{-1}$.
		$H + CH_3I \rightarrow CH_3 + HI$	
$(5.86\pm0.29)x10^{12}$	293±2	Flash photolysis study. CH_3I (∿6 Pa)/Ar (∿6 kPa) mixtures photolysed at λ>170 nm. HI monitored by transient absorption spectrometry, spectra being analysed by microdensitometry. LEVY and SIMONS 1975 (28)	Authors assumed sole removal of H atoms, following primary photolysis $CH_3I + h\nu \rightarrow CH_2I + H$ to be reaction 20 $H + CH_3I \rightarrow CH_3 + HI$ 20 Assuming 1:1 correspondence between HI formed and H removed, authors obtained value of k_{20} presented here.
		$H + CF_3Cl \rightarrow CF_3 + HCl$	
$(5.11\pm1.0\ )x10^9$ $(5.71\pm1.0\ )x10^9$ $(9.85\pm1.2\ )x10^9$ $(1.38\pm0.04)x10^{10}$ $(2.12\pm0.1\ )x10^{10}$ $(2.33\pm0.2\ )x10^{10}$	538 567 595 625 653 676	Discharge flow system. H_2/Ar mixtures passed through discharge. CF_3Cl added downstream via moveable inlet, such that $[CF_3Cl]/[H]$ varied over range 110-458. Total pressures ∿2 mm Hg (266.6 Pa).	From pseudo first order decay of H atoms, authors obtained overall rate constant k'. These displayed rapid increase with decreasing $[CF_3Cl]/[H]$, with limiting values being reached at high $[CF_3Cl]/[H]$ ratios. Values of k' showed no variation with added H_2. Authors explained results in terms of mechanism

H + CF_3Cl, CF_3Br



H + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		[H] monitored by esr spectrometry. BRADLEY, WHYTOCK and ZALESKI 1976 (31)	$H + CF_3Cl \rightarrow CF_3 + HCl$ 21 $H + HCl \rightleftharpoons Cl + H_2$ 16,-16 reaction -16 being unimportant. Limiting stoichiometry at $[CF_3Cl]/[H] > 100$ led authors to identify k' under these conditions with k_{21}. We have averaged authors tabulated values, which they fitted by expression $k_{21}=1.70\times10^{13} \exp\{-(4430\pm230)/T\}$ cm^3 mol^{-1} s^{-1}.
		$H + CF_3Br \rightarrow CF_3 + HBr$	
$4.36\times10^{15} \exp(-8780/T)$	938-1141	Shock tube study. Method as for CHF_3 (see above). SKINNER and RINGROSE 1965 (7)	Induction times modelled by adding reactions $H + CF_3Br \rightarrow CF_3 + HBr$ 22 $H + CF_3 + M \rightarrow CHF_3 + M$ $CF_3 + H_2 \rightarrow H + CHF_3$ -8 $H + HBr \rightarrow Br + H_2$ 19 to H_2/O_2 mechanism. Calculated induction times highly sensitive to k_{22}.
$(7.83\pm2.4)\times10^{11}$ $(9.03\pm4.8)\times10^{11}$ $(8.43\pm4.8)\times10^{11}$ $(1.08^{+1.33}_{-1.08})\times10^{12}$ $(2.4^{+7.2}_{-2.4})\times10^{11}$ $(7.83\pm5.4)\times10^{11}$ $(5.42^{+9.6}_{-5.4})\times10^{11}$	751 751 854 903 953 953 1195	Discharge flow system. O_2 or O_2(3%)/He mixtures passed through discharge, without being dried (c.f (20)), leaving (50±5) ppm H_2O impurity in O_2. CF_3Br added downstream through moveable inlet, giving $[CF_3Br]/[O]$ ratios in range 0.13-1.0. Total pressures ∿1-10 mm Hg (0.13-1.3 kPa). [O] determined by titration with NO_2, and $[CF_3Br]$ decay followed by gas chromatography. GANN, FRANKIEWICZ and WILLIAMS 1974 (21)	Authors investigated effects of H_2O impurity in O_2 upon rate of CF_3Br removal, principally by reaction 23 $O + CF_3Br \rightarrow CF_3 + BrO$ 23 Elimination of contribution of reaction 23 (using data for k_{23} found in their previous study (20)) gave values for $k_{22}[X]$, where X is either H or OH or both. Authors assumed H_2O completely dissociated, and calculated $0.9 > [OH]/[H] > 0.01$. Average value for [X] taken as 30 ppm, considered an upper limit. Authors remarked that resulting lower limits to k_{22} were consistent with data for k_{22} of BIORDI <u>et al</u>. (27). $H + CF_3Br \rightarrow CF_3 + HBr$ 22
$2.2\times10^{14} \exp(-4760/T)$	700-1550	Flame study. CH_4(10.3 %)/O_2(21.6%)/Ar mixtures with added (0.3 %)CF_3Br. Total pressures 32 mm Hg (4.3 kPa). Absorption spectrometry 306-312 nm used to monitor [OH], and mass spectrometry to follow [H],	Rate constants k_{22} determined from CF_3Br removal rates, after allowing for thermal decomposition, assuming (a) $k_{22} \gg k_{24}$, and (b) $k_{22}=k_{24}$ $H + CF_3Br \rightarrow CF_3 + HBr$ 22 $OH + CF_3Br \rightarrow CF_3 + BrOH$ 24 At low temperatures little difference in values of k_{22} determined according to (a) and (b).

H + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		[CF_3Br], [HF], [HBr] and other transients. BIORDI, LAZZARA and PAPP 1975 (26 and 27)	
$2.3x10^{14}$ exp(-4630/T)	1000-1600	Flame study. Method as for (26). BIORDI, LAZZARA and PAPP 1976 (30)	Method as for (26), but with species mole fraction profiles smoothed both by pencil follower technique and by polynomial curve fitting.
	723-933	Static system. H_2(66.7 %)/O_2 mixtures with added CF_3Br ((a) <1%, (b) ≤0.1%). Total pressures 5-40 mm Hg (0.67-5.3 kPa). Reaction followed manometrically. PETROVA, AZATYAN, BARATOV, MAKEEV and KONDENKO 1976 (32)	(a) From variation of first ignition limit on addition of CF_3Br, authors obtained ratio k_{22}/k_2 $H + CF_3Br \rightarrow CF_3 + HBr$ 22 $H + O_2 \rightarrow OH + O$ 2 Authors quoted $k_{22}=3.1x10^{11}$ (853 K), $3.5x10^{11}$ (883 K), and $4.7x10^{11}$ cm^3 mol^{-1} s^{-1} (933 K). Using our recommended expression for k_2 (Volume 1, p.9) we derive $k_{22}=3.88x10^{11}$, $4.40x10^{11}$, and $5.95x10^{11}$ cm^3 mol^{-1} s^{-1}. (b) Variation of second ignition limit with [CF_3Br] gave ratios k_{22}/k_{25} and k_2/k_{25} $H + O_2 + M \rightarrow HO_2 + M$ 25 Elimination of k_{25} gave $k_{22}=2.6x10^{11}$ cm^3 mol^{-1} s^{-1} at 723 K. Again using our recommendation for k_2 we derive $k_{22}=3.19$ $x10^{11}$ cm^3 mol^{-1} s^{-1} (723 K). Authors considered value (b) less accurate than data from (a).
$1.6x10^{13}$	1666	Flame study. CH_4(10.1 %)/O_2(21.2%)/Ar flames with added CF_3Br (1.1 %). Total pressures 32 mm Hg (4.3 kPa). Sampling and analysis as for (26 and 30). BIORDI, LAZZARA and PAPP 1977 (33)	Under conditions of maximum CF_3Br decay rate, authors found that this decay could be equally well explained by thermal decomposition or by removal by reaction 22 $H + CF_3Br \rightarrow CF_3 + HBr$ 22 Assuming reaction 22 to be solely responsible, authors obtained value for k_{22} presented here.
$(1.03\pm0.02)x10^{10}$	298±1	Flash photolysis study. NH_3(<1%)/Ar/CF_3Br mixtures at total pressures 10.9-40 mm Hg (1.5-5.3 kPa). $1x10^{-9} \leq [CF_3Br] \leq 1.7x10^{-8}$ mol cm^{-3}. [H] monitored by Lyman-α resonance fluorescence. WESTENBERG and DE HAAS 1977 (36)	Pseudo first order decay of [H] used to determine k_{22}. Results independent of flash energy over range used, indicating secondary reactions not important.

Discussion

Although there have been a considerable number of studies of the rate of reaction of H atoms with various halogenated methanes, there are only a few reactions for which there are sufficient data for us to make any recommendation. For the most part, the measurements that have been made are scattered over a wide variety of halomethanes.

H + Fluoromethanes

The only fluorinated methane species which has been studied in this context by more than one group of investigators is CH_3F

$$H + CH_3F \rightarrow CH_3 + HF \qquad (1)$$

Discharge flow systems have been used by Aders et al. [24] and Westenberg and De Haas [29], and their values for k_1 at ~600 K differ by more than 2 orders of magnitude. We consider the data of [29] to be more reliable, as their pseudo first order decay study of $[CH_3F]$ was conducted under an excess of H atoms of between 100 and 250, whereas the low excess of CH_3F (between 5 and 8) used by [24] cannot be considered sufficient to establish with certainty pseudo first order conditions for H atom removal. Furthermore, the determination by [24] of the stoichiometry of reaction 1 was made at a ratio $[CH_3F]/[H]$ of 10, i.e., under different conditions than for the measurement of $-d[H]/dt$. Hart et al. [22] have derived values of k_1 from the ratios $k_1k_4/(k_3+k_4)$ of Parsamyan et al. [10]

$$CH_3 + O_2 \rightarrow HCHO + OH \qquad (3)$$

$$\rightarrow \text{termination} \qquad (4)$$

which agree with their own (flame study) data. However, our re-analysis of these results gives values of k_1 in good agreement with Westenberg and De Haas' [29]. On the basis of this good agreement we tentatively recommend the expression

$$k_1 = 2.30 \times 10^{13} \exp(-4950/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the temperature range 600–1000 K. Uncertainty limits of a factor of 5 should be allowed for.

For reaction 8 Amphlett and Whittle [9] derived the expression $k_8 = 3.2 \times 10^{12} \exp(-5640/T)$ cm^3 mol^{-1} s^{-1}

$$H + CHF_3 \rightarrow CF_3 + H_2 \qquad (8)$$

from the reverse rate constant k_{-8}, which gives considerably lower values of k_{-8} than the expression derived by Skinner and Ringrose [7]. Although the data of Kochubei and Moin [11,15] for reaction 10

$$H + CF_4 \rightarrow CF_3 + HF \qquad (10)$$

have not been verified (and therefore we make no recommendation for k_{10}) we believe they are of the correct order of magnitude. Consequently, if there is any systematic variation of Arrhenius parameters with the degree of CH_4 fluorination (as seems to be indicated by the available data [10,11,15,22,29]), (see fig. 1) then the recommended expression of Kondratiev [17] for k_8 is probably at least an order of magnitude too high.

H + Chloromethanes

As for CH_3F, there is a considerable discrepancy between the discharge flow data for reaction 12 of [24 and 29].

$$H + CH_3Cl \rightarrow CH_3 + HCl \qquad (12)$$

For the same reasons outlined in the previous case, we consider Westenberg and De Haas' data [29] to be more reliable, but there is again poor agreement between these results and the flame data of Hart et al. [22]. An extrapolation of the latter could be argued to match the flow system results of Seidel [13], as expressed by Jones et al. [19], but we give little weight to these data.

Consequently, in view of the lack of agreement between the data for k_{12}, and only one set each of actual values for k_{15} and k_{17}

$$H + CH_2Cl_2 \rightarrow CH_2Cl + HCl \qquad (15)$$

$$H + CCl_4 \rightarrow CCl_3 + HCl \qquad (17)$$

we make no recommendations for k_{12}, k_{15} or k_{17}.

H + $CH_3Br \rightarrow CH_3$ + HBr

There have been five investigations of reaction 5

$$H + CH_3Br \rightarrow CH_3 + HBr \qquad (5)$$

using flames [5,22], thermal flow systems [13] and discharge flow systems [24,29], and one of the isotopic reaction 5D

$$D + CH_3Br \rightarrow CH_3 + DBr \qquad (5D)$$

using a discharge flow system [14].

The disagreement between the discharge flow data of Aders et al. [24] and Westenberg and De Haas [29] is not as great for reaction 5 as it is for reactions 1 and 12. The flame data of Fenimore and Jones [5] are in reasonable agreement with the results of [29], despite the slight upward curvature in k_5 at high temperatures observed by the latter. Because of the poor agreement of the data of [13 and 22] with the other results, we have not considered them further and tentatively recommend the expression

$$k_5 = 5.10 \times 10^{13} \exp(-2940/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

based on the data of [5,24 and 29], with error limits of a factor 3 over the temperature range 298–2000 K.

The data for k_{5D} of Davies et al. [14] lie considerably above those for k_5, and if conversion factors for the isotope effect of ~1.4 are used [16,22,29] then these results are pushed even higher. The expression for k_5 derived from these (converted) data and their own by [22] therefore gives gross overestimates at low temperatures (300–500 K).

$H + CH_3I \rightarrow CH_3 + HI$

There has been only one study of reaction 20,

$$H + CH_3I \rightarrow CH_3 + HI \qquad (20)$$

namely the flash photolysis investigation by Levy and Simons [28], giving only a value of k_{20} at room temperature. No recommendation for k_{20} is made.

$H + CF_3Cl \rightarrow CF_3 + HCl$

Bradley et al. [31] used a discharge flow system in the only study of reaction 21

$$H + CF_3Cl \rightarrow CF_3 + HCl \qquad (21)$$

As their results are the only values of k_{21} available, no recommendation is made.

$H + CF_3Br \rightarrow CF_3 + HBr$

Biordi et al. have made several studies of reaction 22

$$H + CF_3Br \rightarrow CF_3 + HBr \qquad (22)$$

using flame systems [26,27,30,33], and their data display a temperature dependence similar to that of the data of Petrova et al. [32], obtained in a static H_2/O_2 inhibition study. These two sets of data are separated by a factor of ~2.

Of the remaining data, the discharge flow results of Gann et al. [21] are widely scattered and subject to large uncertainty. The H_2/O_2 induction time measurements of Skinner and Ringrose [7] are very sensitive to k_{22} and hence should lead to very precise values, but their results do not agree well with the other data. The only low (room) temperature result [36] is greater than extrapolations of the high temperature data by more than two orders of magnitude.

On the basis of the results of [27,29,32 and 33] we recommend the expression

$$k_{22} = 1.47 \times 10^{14} \exp(-4700/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

within the temperature range 700–1700 K, with uncertainty limits of a factor of 2.

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H2 O + HALOMETHANES

THERMODYNAMIC DATA

Thermodynamic data are unavailable for halogen-substituted methyl radicals.

RECOMMENDED RATE CONSTANTS

$O + CH_3Cl$: $k = 1.05 \times 10^{13} \exp(-3450/T)$ cm^3 mol^{-1} s^{-1}

$= 1.74 \times 10^{-11} \exp(-3450/T)$ cm^3 molecule^{-1} s^{-1}

Temperature Range: 300-1000 K

Suggested Error Limits for Calculated Rate Constant: a factor of 2 at 300 K, falling to ±50% at 1000 K.

$O + CH_3Br$: $k = 1.33 \times 10^{13} \exp(-3700/T)$ cm^3 mol^{-1} s^{-1}

$= 2.21 \times 10^{-11} \exp(-3700/T)$ cm^3 molecule^{-1} s^{-1}

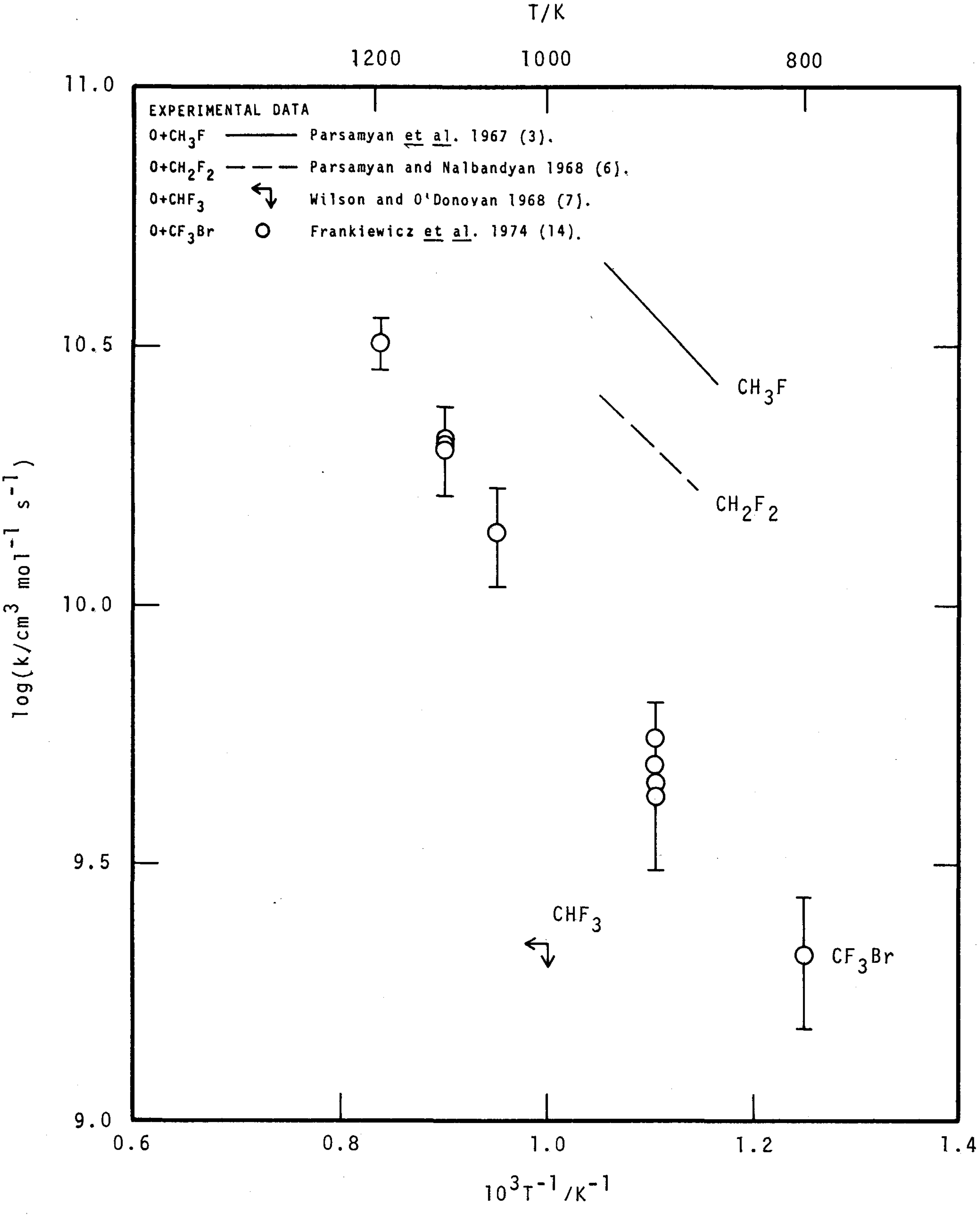
Temperature Range: 350-1000 K

Suggested Error Limits for Calculated Rate Constant: a factor of 2 over the whole temperature range.

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$O + CH_3F \rightarrow CH_2F + OH$	
$7.83 \times 10^{12} \exp\{-(4880 \pm 400)/T\}$	858-948	Static system. CH_3F (1-3.17% and 1.5-4%) added to H_2(80%)/O_2 (20%) and CO (67%)/O_2(33%) mixtures, respectively. Total pressures <17 mm Hg (2.3 kPa). Reaction monitored manometrically. PARSAMYAN, AZATYAN and NALBANDYAN 1967 (3)	From decrease in lower ignition limit of CO/O_2 mixtures upon addition of CH_3F, authors obtained k_1. $O + CH_3F \rightarrow CH_2F + OH$ 1
		$O + CH_2F_2 \rightarrow CHF_2 + OH$	
$2.65 \times 10^{12} \exp(-4430/T)$	873-953	Static system. H_2(80%)/O_2 (20%) and CO (67%)/O_2 (33%) mixtures with added CH_2F_2 (0.99-3% and 1-4% respectively). Total pressures <12 mm Hg (1.6 kPa). Reaction followed manometrically.	Lowering of first ignition limit of CO/O_2 mixtures gave k_2 as shown. This expression may be relative to k_3 $O + CH_2F_2 \rightarrow CHF_2 + OH$ 2 $H + O_2 \rightarrow O + OH$ 3

O + FLUOROMETHANES, CF_3Br

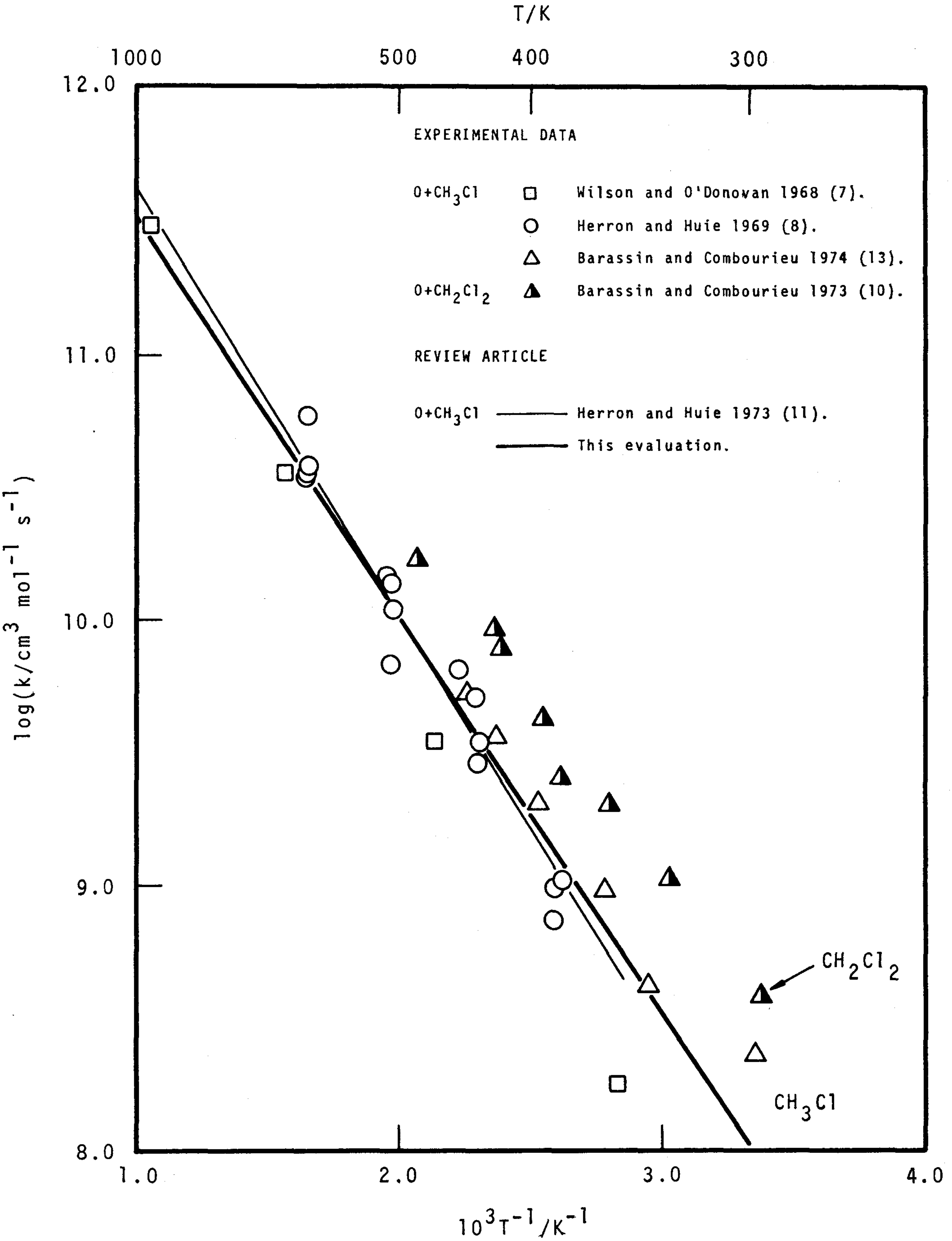


O + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		PARSAMYAN and NALBANDYAN 1968 (6)	
		$O + CHF_3 \rightarrow CF_3 + OH$	
	<1000	Discharge flow system. Method and conditions as for CH_3Cl, below. WILSON and O'DONOVAN 1968 (7)	No reaction observable, even at 1000 K. k_4 given as <0.01 k_5 $O + CHF_3 \rightarrow CF_3 + OH$ 4 $O + CH_4 \rightarrow CH_3 + OH$ 5 Using HERRON and HUIE's recommendation for k_5 (11) we derive $k_4 <$ $2.22 \times 10^9\ cm^3\ mol^{-1}\ s^{-1}$.
		$O + CH_3Cl \rightarrow CH_2Cl + OH$	
	353-949	Discharge flow system. O atoms produced by titration of N atoms with NO. CH_3Cl added downstream, giving total pressures $\sim$1 mm Hg (133.3 Pa). $[CH_3Cl]$ monitored by mass spectrometry. WILSON and O'DONOVAN 1968 (7)	Rate constant ratio k_6/k_5 calculated from relative removal of CH_3Cl and (in separate experiments (4)) CH_4. $O + CH_3Cl \rightarrow CH_2Cl + OH$ 6 $O + CH_4 \rightarrow CH_3 + OH$ 5 Values of k_6/k_5 tabulated as follows: T/K $k_6k_5^{-1}$ $k_6/cm^3mol^{-1}s^{-1}$ 353 $\sim$3.4 $\sim 1.8 \times 10^8$ 468 2.83±0.07 $(3.56 \pm 0.09) \times 10^9$ 638 2.16±0.04 $(3.63 \pm 0.07) \times 10^{10}$ 949 1.76±0.05 $(3.06 \pm 0.09) \times 10^{11}$ and expressed as $k_6/k_5 = 1.1 \exp(438/T)$. Using k_5 of (4), k_6 quoted as $1.8 \times 10^{13} \exp(-3990/T)$ $cm^3\ mol^{-1}\ s^{-1}$. We have used the recommended expression for k_5 of HERRON and HUIE (11) to derive the values of k_6 shown above. Quoted by (12). Used by (11).
1.08×10^9	381	Discharge flow system. O_2 (1-5%)/Ar mixtures passed through discharge. CH_3Cl added downstream through moveable inlet, so that $[O]/[CH_3Cl] \simeq 100$. Total pressures 281-318 Pa, and $4.07 \times 10^{-10} \leq [O] \leq 1.23 \times 10^{-9}$ $mol\ cm^{-3}$. Mass spectrometry used to monitor $[CH_3Cl]$ and $[O]$, latter calibrated by titration with NO_2. HERRON and HUIE 1969 (8)	Reaction mechanism assumed to be $O + CH_3Cl \rightarrow CH_2Cl + OH$ 6 $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$ 7 $O + OH \rightarrow H + O_2$ 8 Steady state analysis, using estimated values for k_6, k_7 and k_8, gave $[OH] \simeq 10^{-5}\ [O]$, therefore reaction 7 disregarded. Values of k_6 derived from integrated form of rate equation for $[CH_3Cl]$, i.e. pseudo first order assumption. Invariance of k_6 with $[CH_3Cl]/[O]$ indicated unimportance of other secondary reactions. These data expressed
7.40×10^8	385		
9.80×10^8	385		
2.93×10^9	434		
3.48×10^9	434		
5.22×10^9	437		
6.70×10^9	448		
1.12×10^{10}	505		
1.38×10^{10}	506		
6.88×10^9	508		
1.48×10^{10}	513		
3.88×10^{10}	603		
6.15×10^{10}	603		
3.48×10^{10}	607		
3.51×10^{10}	607		

O + CHLOROMETHANES



O + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		HERRON and HUIE 1969 (8) continued.	as $\log(k_6/cm^3\ mol^{-1}\ s^{-1}) = (13.4 \pm 0.2) - (3880 \pm 220)/2.303\ T$. Used by (11).
2.30×10^8 4.30×10^8 9.90×10^8 2.09×10^9 3.77×10^9 5.41×10^9	298 339 359 395 421 443	Discharge flow system. O_2 ($\sim 5\%$)/He mixture passed through discharge. CH_3Cl added downstream, such that $8.78 \times 10^{-9} \leqslant [O] \leqslant 1.31 \times 10^{-8}$ mol cm^{-3}, and $1.63 \times 10^{-10} \leqslant [CH_3Cl] \leqslant 2.43 \times 10^{-10}$ mol cm^{-3}. Total pressures 2.5-3 mm Hg (333.3-400 Pa). Reaction followed by mass spectrometry. BARASSIN and COMBOURIEU 1974 (13)	Pseudo first order decay of CH_3Cl used to determine k_6. Stoichiometry determined as (1.5±0.5). These data expressed by $k_6 = 1.3 \times 10^{13} \exp(-3470/T)\ cm^3\ mol^{-1}\ s^{-1}$. This expression also reported by (18).
	511-1000	Discharge flow system. CH_3Cl and CH_3Br added simultaneously to O/He mixtures via sliding inlet. $[O]/[CH_3Cl + CH_3Br] > 50$. [O] measured by esr spectrometry, calibrated by NO_2 titration, and $[CH_3Cl]$ and $[CH_3Br]$ followed mass spectrometrically. WESTENBERG and DE HAAS 1975 (17)	Values of ratio k_9/k_6 obtained by monitoring relative pseudo first order decays of both $[CH_3Br]$ and $[CH_3Cl]$. $O + CH_3Cl \rightarrow CH_2Cl + OH$ 6 $O + CH_3Br \rightarrow CH_2Br + OH$ 9 These data have been used solely in the derivation of k_9 (see below).

REVIEW ARTICLE

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.7 \times 10^{13} \exp(-3690/T)$	350-1000	Review. Recommended expression derived from data of (7 and 8). HERRON and HUIE 1973 (11)	

EXPERIMENTAL DATA

$O + CH_2Cl_2 \rightarrow CHCl_2 + OH$

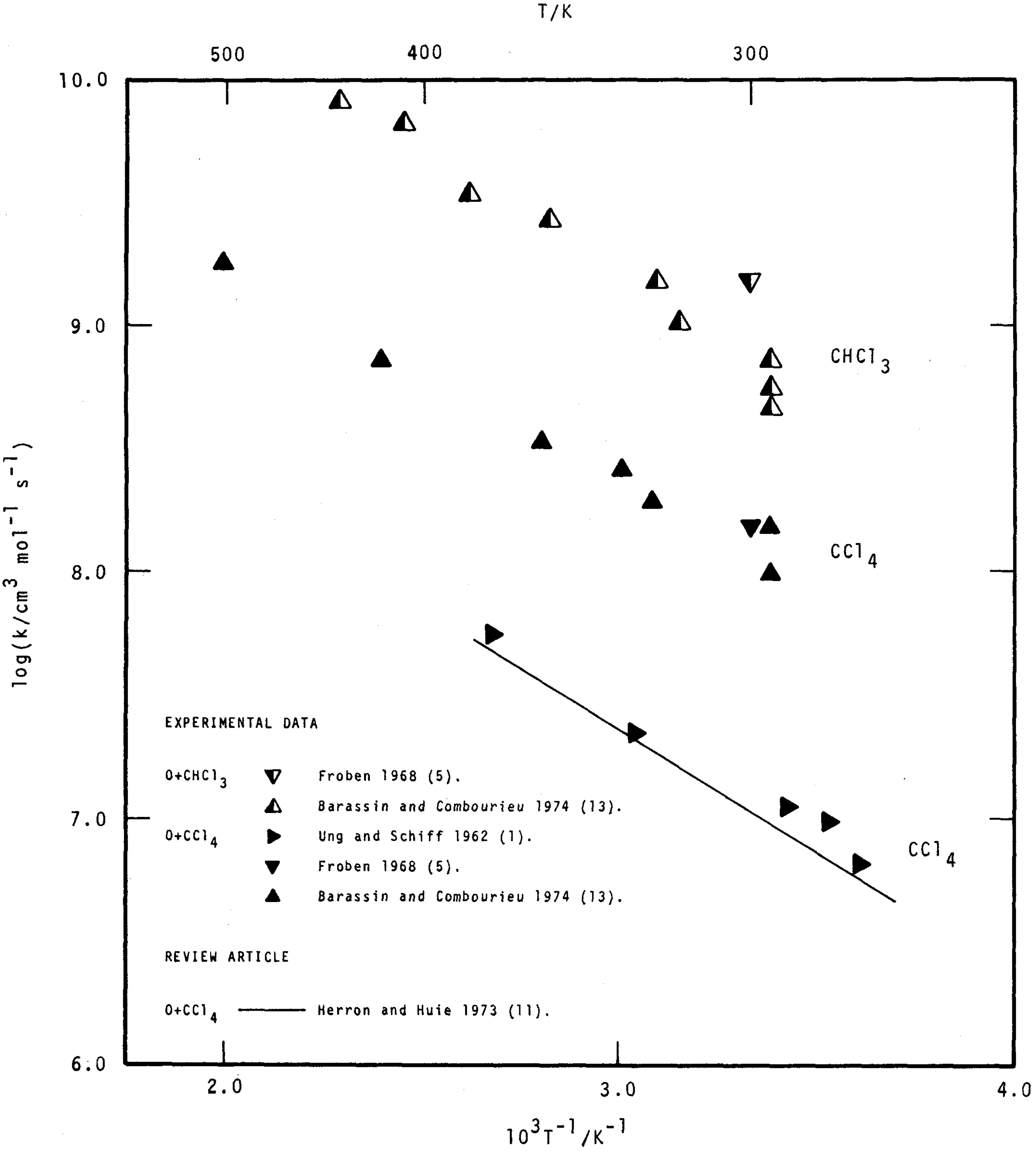
Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
3.90×10^8 1.09×10^9 2.04×10^9 2.63×10^9 4.35×10^9 7.97×10^9 9.40×10^9 1.70×10^{10}	295 330 357 383 393 418 423 483	Discharge flow system. Method as for CH_3Cl, above. Total pressure ~ 2.6 mm Hg (346.6 Pa), with $2.7 \times 10^{-9} \leqslant [O] \leqslant 6.4 \times 10^{-9}$ mol cm^{-3}, and $4.0 \times 10^{-11} \leqslant [CH_2Cl_2] \leqslant 9.2 \times 10^{-11}$ mol cm^{-3}. [O] calibrated by titration	Stoichiometry determined as (1.2 ±0.2) for 293-423 K. k_{10} from pseudo first order CH_2Cl_2 decay. These data expressed by $k_{10} = 5.9 \times 10^{12} \exp(-2870/T)\ cm^3\ mol^{-1}\ s^{-1}$. $O + CH_2Cl_2 \rightarrow CHCl_2 + OH$ 10 This expression also quoted by (18).

O + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		with NO_2. BARASSIN and COMBOURIEU 1973 (10).	
		$O + CHCl_3 \rightarrow CCl_3 + OH$	
1.5×10^9	300	Discharge flow system. O atoms produced by N+NO reaction or by passing O_2 through discharge. $CHCl_3$ added downstream. Total pressures 0.2-5 mm Hg (26.7-666.5 Pa). Esr spectrometry used to follow [O]. FROBEN 1968 (5)	From pseudo first order decay of [O], value of k_{11} determined. $O + CHCl_3 \rightarrow CCl_3 + OH$ 11 Stoichiometry of 3 obtained by comparing consumption of O atoms with that upon substitution of equal pressure of CH_4, together with stoichiometry of 4 for reaction 5 (2,4) $O + CH_4 \rightarrow CH_3 + OH$ 5 Author also considered alternative reaction $O + CHCl_3 \rightarrow CHCl_2 + ClO$ Quoted by (12).
4.70×10^8 5.60×10^8 7.30×10^8 1.00×10^9 1.48×10^9 2.72×10^9 3.36×10^9 6.69×10^9 8.17×10^9	295 295 295 318 337 355 382 409 433	Discharge flow system. Method as for CH_3Cl, above. Total pressures 2.45-2.95 mm Hg (326.6-393.2 Pa), and [O] 7.14×10^{-9}-1.07×10^{-8} mol cm^{-3}, $[CHCl_3]$ 1.1×10^{-10}-1.9×10^{-10} mol cm^{-3}. BARASSIN and COMBOURIEU 1974 (13)	Pseudo first order $CHCl_3$ decay used to determine k_{11}. Authors measured stoichiometry $[O]/\Delta[CHCl_3]$ as (1.2±0.5). These data given as $k_{11} = 2.9 \times 10^{12} \exp(-2520/T)$ $cm^3\ mol^{-1}\ s^{-1}$, as quoted also by (18).
		$O + CCl_4 \rightarrow CCl_3 + ClO$	
$(6.62 \pm 0.2\ ) \times 10^6$ $(9.88 \pm 0.2\ ) \times 10^6$ $(1.13 \pm 0.03) \times 10^7$ $(2.23 \pm 0.05) \times 10^7$ $(5.68 \pm 0.2\ ) \times 10^7$	277 283 292 329 373	Discharge flow system. O atoms produced by passing O_2 through discharge, or titrating N atoms with NO. CCl_4 added downstream, giving $[CCl_4]$ 3.8×10^{-7} to 4.9×10^{-6} mol cm^{-3} at total pressures 2-4.2 mm Hg (266.6-559.9 Pa). O atom concentrations 4.2×10^{-10}-2.7×10^{-9} mol cm^{-3}. [O] determined by monitoring $O+NO_2$ chemiluminescence, and $[CCl_4]$ by gas chromatography. UNG and SCHIFF 1962 (1)	k_{12} derived from removal of CCl_4. No dependence found of k_{12} upon pressure. These values expressed by $k_{12} = (1.99 \pm 0.9) \times 10^{10} \exp\{-(2270 \pm 150)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. $O + CCl_4 \rightarrow CCl_3 + ClO$ 12 This expression does not in fact match the data - an error has been made in converting from cm^3-mol-s units (as shown correctly in authors' graphical presentation) to cm^3-molecule-s units. A_{12} should be 2.5×10^{10} $cm^3\ mol^{-1}\ s^{-1}$.

O + CHLOROMETHANES



O + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.5x10^8$	300	Discharge flow system. Method and conditions as for $CHCl_3$, above. FROBEN 1968 (5)	By comparing consumption of O atoms by CCl_4 and equal pressure of CH_4, and knowing stoichiometry of reaction 5 $O + CH_4 \rightarrow CH_3 + OH$ 5 (2,4) authors obtained stoichiometry of 2. Hence corrected value of k_{12}, determined from pseudo first order decay of [O]. $O + CCl_4 \rightarrow CCl_3 + ClO$ 12
$9.60x10^7$	296	Discharge flow system. Method as for CH_3Cl, above. Total pressures 2.65-3.25 mm Hg (353.3-433.2 Pa), [O] $7.82x10^{-9}$-$1.09x10^{-8}$ mol cm^{-3}, and [CCl_4] $3.14x10^{-10}$-$1.68x10^{-9}$ mol cm^{-3}. BARASSIN and COMBOURIEU 1974 (13)	k_{12} derived as for CH_3Cl. Authors express these data as $k_{12}=1.6x10^{11}\ exp(-2160/T)\ cm^3\ mol^{-1}\ s^{-1}$.
$1.53x10^8$	296		
$1.95x10^8$	325		
$2.60x10^8$	330		
$3.34x10^8$	358		
$7.13x10^8$	418		
$1.79x10^9$	502		

REVIEW ARTICLE

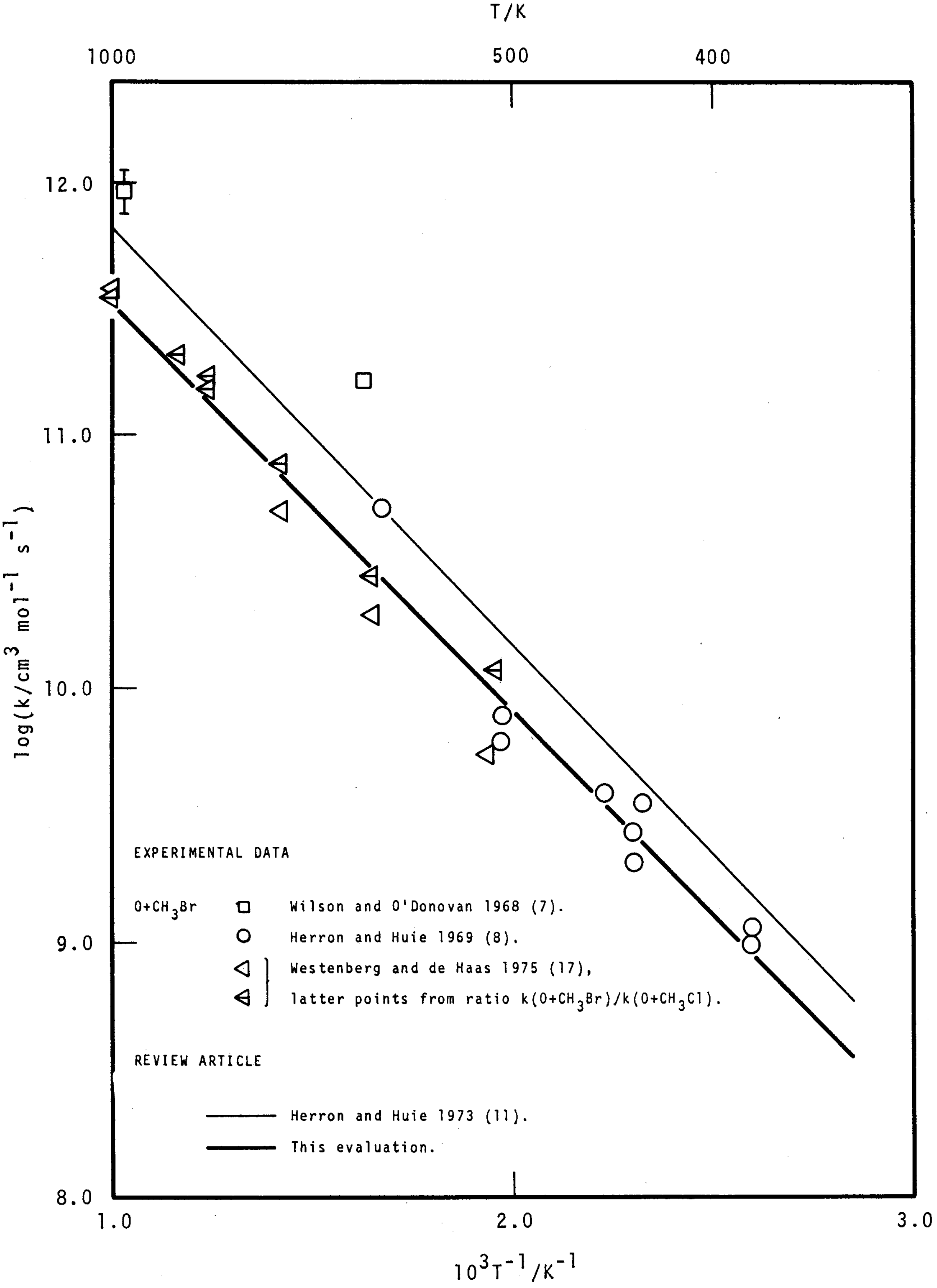
Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2.0x10^{10}\ exp(-2260/T)$	270-380	Review. Expression is that of UNG and SCHIFF (1). HERRON and HUIE 1973 (11)	Uncritically uses the incorrect expression of (1).

EXPERIMENTAL DATA

$O + CH_3Br \rightarrow CH_2Br + OH$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	613 and 966	Discharge flow system. Method and conditions as for CH_3Cl, above. WILSON and O'DONOVAN 1968 (7)	Rate constant ratio k_{13}/k_5 derived as in reaction with CH_3Cl. $O + CH_3Br \rightarrow CH_2Br + OH$ 13 $O + CH_4 \rightarrow CH_3 + OH$ 5 Authors also note possibility of reaction 13' $O + CH_3Br \rightarrow CH_3 + BrO$ 13' From values of k_{13}/k_5, (13±2) and (5±1) at 613 and 966 K respectively, authors quote $(k_{13}+k_{13}') \approx 2x10^{13}\ exp(-3020/T)\ cm^3\ mol^{-1}\ s^{-1}$, using k_5 of (4). Quoted by (9) and used by (16). Using HERRON and HUIE's recommendation for k_5 (11) we derive $k_{13}=(1.63\pm0.3)x10^{11}$ (613 K) and $(9.45\pm1.9)x10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ (966 K).

O + BROMOMETHANE



O + HALOMETHANES

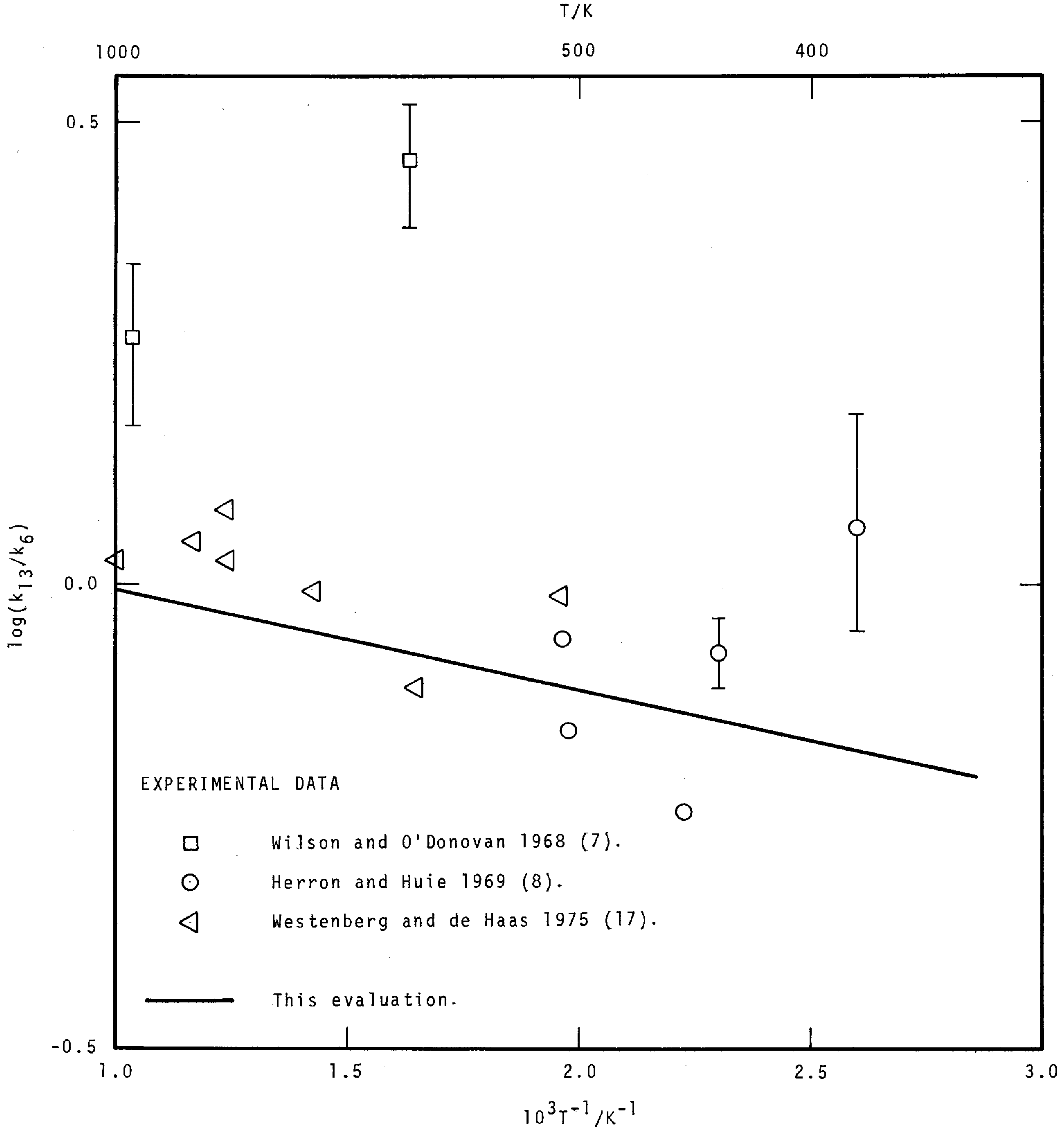
EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
9.60×10^{8}	385	Discharge flow system. Method as for CH_3Cl, above. Total pressures 281-318 Pa, and $3.95\times10^{-10} \leq [O] \leq 1.15\times10^{-9}$ mol cm^{-3}. O atoms in ∿100-fold excess over CH_3Br. HERRON and HUIE 1969 (8)	Values of k_{13} obtained as for CH_3Cl. These data considered less reliable than those for CH_3Cl, so only approximate expression quoted: $k_{13} \approx 10^{13} \exp(-3500/T)$ cm^3 mol^{-1} s^{-1}.
1.13×10^{9}	385		
3.47×10^{9}	429		
2.01×10^{9}	433		
2.70×10^{9}	434		
3.82×10^{9}	448		
7.81×10^{9}	505		
6.03×10^{9}	508		
5.10×10^{10}	595		
$(5.4 \pm0.3)\times10^{9}$	517	Discharge flow system. CH_3Br added to excess O atoms ($[O]/[CH_3Br] > 50$) via moveable inlet. [O] monitored by esr spectrometry, calibrated by titration with NO_2, and $[CH_3Br]$ by mass spectrometry. WESTENBERG and DE HAAS 1974 (17)	Pseudo first order decay of $[CH_3Br]$ used to determine k_{13}. Arrhenius form quoted as $3.5\times10^{13} \exp(-4560/T)$ cm^3 mol^{-1} s^{-1}. Values of k_{13}/k_6 obtained by simultaneous addition of CH_3Br and CH_3Cl $O + CH_3Br \rightarrow CH_2Br + OH$ 13 $O + CH_3Cl \rightarrow CH_2Cl + OH$ 6 quoted as follows: T/K $k_{13}k_6^{-1}$ $k_{13}/cm^3mol^{-1}s^{-1}$ 511 0.97 1.19×10^{10} 607 0.77 2.75×10^{10} 703 0.98 7.61×10^{10} 807 1.06 1.51×10^{11} 807 1.20 1.70×10^{11} 856 1.11 2.07×10^{11} 1000 1.06 3.53×10^{11} Authors quote average value $k_{13}/k_6 = (1.02\pm0.12)$ over whole temperature range, i.e. equal within experimental error. We have used our recommended expression for k_6 to derive k_{13} values above.
$(1.9 \pm0.2)\times10^{10}$	602		
$(5.0 \pm0.1)\times10^{10}$	703		
$(1.10\pm0.04)\times10^{11}$	811		
$(3.7 \pm0.1)\times10^{11}$	1000		

REVIEW ARTICLE

$3.0\times10^{13} \exp(-3800/T)$	350-1000	Review. Recommended expression derived from data of (7 and 8). HERRON and HUIE 1973 (11)	

$O + CH_3Br/O + CH_3Cl$



O + HALOMETHANES

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$O + CF_3Br \rightarrow CF_3 + BrO$	
$(2.11\pm0.6)\times10^9$	800	Discharge flow system. 100% O_2 or O_2 (3%)/He mixtures passed through discharge, and CF_3Br added downstream via moveable inlet. Total pressures 1.32-10 mm Hg (176 Pa-1.3 kPa), $2.0\times10^{-10} < [O] < 1.2\times10^{-9}$ mol cm^{-3}, and $1.0\times10^{-10} < [CF_3Br] < 2.8\times10^{-10}$ mol cm^{-3}. $O+NO_2$ chemiluminescence used to calibrate [O], and $[CH_3Br]$ monitored by gas chromatographic sampling. FRANKIEWICZ, WILLIAMS and GANN 1974 (14)	Values of k_{14} obtained from decay of CF_3Br in reaction vessel. Arrhenius expression given as $k_{14} = (9.03\pm3.0)\times10^{12}\exp\{-(6790\pm500)/T\}$ cm^3 mol^{-1} s^{-1}. $O + CF_3Br \rightarrow CF_3 + BrO$ 14 Computer simulation using various kinetic models showed that reactions such as $Br + CF_3Br \rightarrow CF_3 + Br_2$ $F + CF_3Br \rightarrow CF_3 + BrF$ could be disregarded and that reaction 14 could account for almost entire CF_3Br removal. Effects of artificially added H_2O impurity on k_{14} measured in (15). Expression used by (16).
$(4.28\pm1.2)\times10^9$	905		
$(4.58\pm0.9)\times10^9$	905		
$(4.94\pm0.9)\times10^9$	905		
$(5.54\pm0.9)\times10^9$	905		
$(1.39\pm0.3)\times10^{10}$	1050		
$(1.99\pm0.4)\times10^{10}$	1110		
$(2.05\pm0.3)\times10^{10}$	1110		
$(2.11\pm0.3)\times10^{10}$	1110		
$(3.19\pm0.4)\times10^{10}$	1195		

Discussion

Reactions of oxygen atoms with halogenated methanes have been studied for only a few species, mostly chloromethanes, and all but two of these studies used the discharge flow technique. For all but the totally halogenated species the reaction has been assumed to be one of H atom abstraction, on the basis of thermodynamic considerations.

O + Fluoromethanes

Only one investigation has been made of the reaction of O atoms with each of the fluorinated methanes CH_3F, CH_2F_2 and CHF_3, and also of trifluorobromomethane CF_3Br.

$$O + CH_3F \rightarrow CH_2F + OH \qquad (1)$$

$$O + CH_2F_2 \rightarrow CHF_2 + OH \qquad (2)$$

$$O + CHF_3 \rightarrow CF_3 + OH \qquad (4)$$

$$O + CF_3Br \rightarrow CF_3 + BrO \qquad (14)$$

Parsamyan et al. have measured k_1 [3] and k_2 [6] using the inhibition of CO/O_2 combustion. Wilson and O'Donovan [7], using discharge flow-mass spectrometric techniques, could not observe any reaction with CHF_3 even at 1000 K, and so only an upper limit to k_4 was quoted. Frankiewicz et al. [14] used gas chromatography to follow CF_3Br and obtained k_{14} over the temperature range 800–1200 K.

As there are no confirmatory data for any of these reactions, we make no recommendation for k_1, k_2, k_4 or k_{14}.

O + Chloromethanes

Mass spectrometry and pseudo first order kinetic analysis of the substrate removal have been used in all but one of the investigations of reactions with chloromethanes.

Reaction 6 has been studied most widely [7,8,13,17].

$$O + CH_3Cl \rightarrow CH_2Cl + OH \qquad (6)$$

Wilson and O'Donovan [7] measured k_6 relative to k_5

$$O + CH_4 \rightarrow CH_3 + OH \qquad (5)$$

and Westenberg and de Haas [17] used k_9 as a reference.

$$O + CH_3Br \rightarrow CH_2Br + OH \qquad (9)$$

Because there are more absolute data for k_6 than for k_9 we have chosen to reverse this preference and derive values of k_9 from the quoted values of k_9/k_6 and our recommended expression

$$k_6 = 1.05\times10^{13} \exp(-3450/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

based on the data of [7,8 and 13]. These data agree to within a factor of 3 at low temperatures (350–400 K) and within ~50% at ~600 K. We recommend this expression be used with uncertainty limits of a factor 2 at 300 K, falling to ±50% at 1000 K.

Reactions 10, 11 and 12 have all been studied by Barassin and Combourieu [10,13]

$$O + CH_2Cl_2 \rightarrow CHCl_2 + OH \qquad (10)$$

$$O + CHCl_3 \rightarrow CCl_3 + OH \qquad (11)$$

$$O + CCl_4 \rightarrow CCl_3 + ClO \qquad (12)$$

following the various chloromethanes by mass spectrometry under conditions of excess [O]. Froben [5] employed the inverse conditions, using e.s.r. spectrometry to monitor O atoms in excess $CHCl_3$ and CCl_4. The stoichiometries of reactions 11 and 12 were based on an assumption of 4 for that of reaction 5 [2,4]

$$O + CH_4 \rightarrow CH_3 + OH \qquad (5)$$

Froben's resulting value for k_{12} is in good agreement with those of [13] whereas his k_{11} value is higher by a factor of ~2. Froben's experimental data for k_{11} are therefore suspect. The early study of reaction 12 by Ung and Schiff, using gas chromatography [1], enabled k_{12} to be derived from the decay of CCl_4. However the conditions used were those of CCl_4 excess, and so an overestimation of the value of [O] has led to greatly depressed values of k_{12}. Furthermore there is a discrepancy between the quoted Arrhenius expression and the original data.

We make no recommendations for k_{10}, k_{11} or k_{12}.

O + Bromomethane

There is more scatter between the data of [7 and 8] for k_{13} than there is for k_6

$$O + CH_3Br \rightarrow CH_2Br + OH \qquad (13)$$

$$O + CH_3Cl \rightarrow CH_2Cl + OH \qquad (6)$$

and the absolute data of Westenberg and de Haas [17] have not improved matters. There is almost an order of magnitude difference between the values of k_{13} of [7 and 17] at ~600 K. This is emphasized further by Wilson and O'Donovan's very high values for the ratio k_{13}/k_6 [7], as shown in figure 5. Their values of k_{13} must therefore be considered suspect. On the basis of the data of [8 and 17] we recommend the expression

$$k_{13} = 1.33\times10^{13} \exp(-3700/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

within error limits of a factor 2 over the temperature range 350-1000 K.

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H3 OH + HALOMETHANES

THERMODYNAMIC DATA

Thermodynamic data for halogen-substituted methyl and ethyl radicals are not available.

RECOMMENDED RATE CONSTANTS

OH + CH_3Br: k = 4.42 x 10^{11} exp(-873/T) cm^3 mol^{-1} s^{-1}
= 7.34 x 10^{-13}exp(-873/T) cm^3 $molecule^{-1}$ s^{-1}
Temperature Range: 240-360 K
Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.
Note: this is an interim expression.

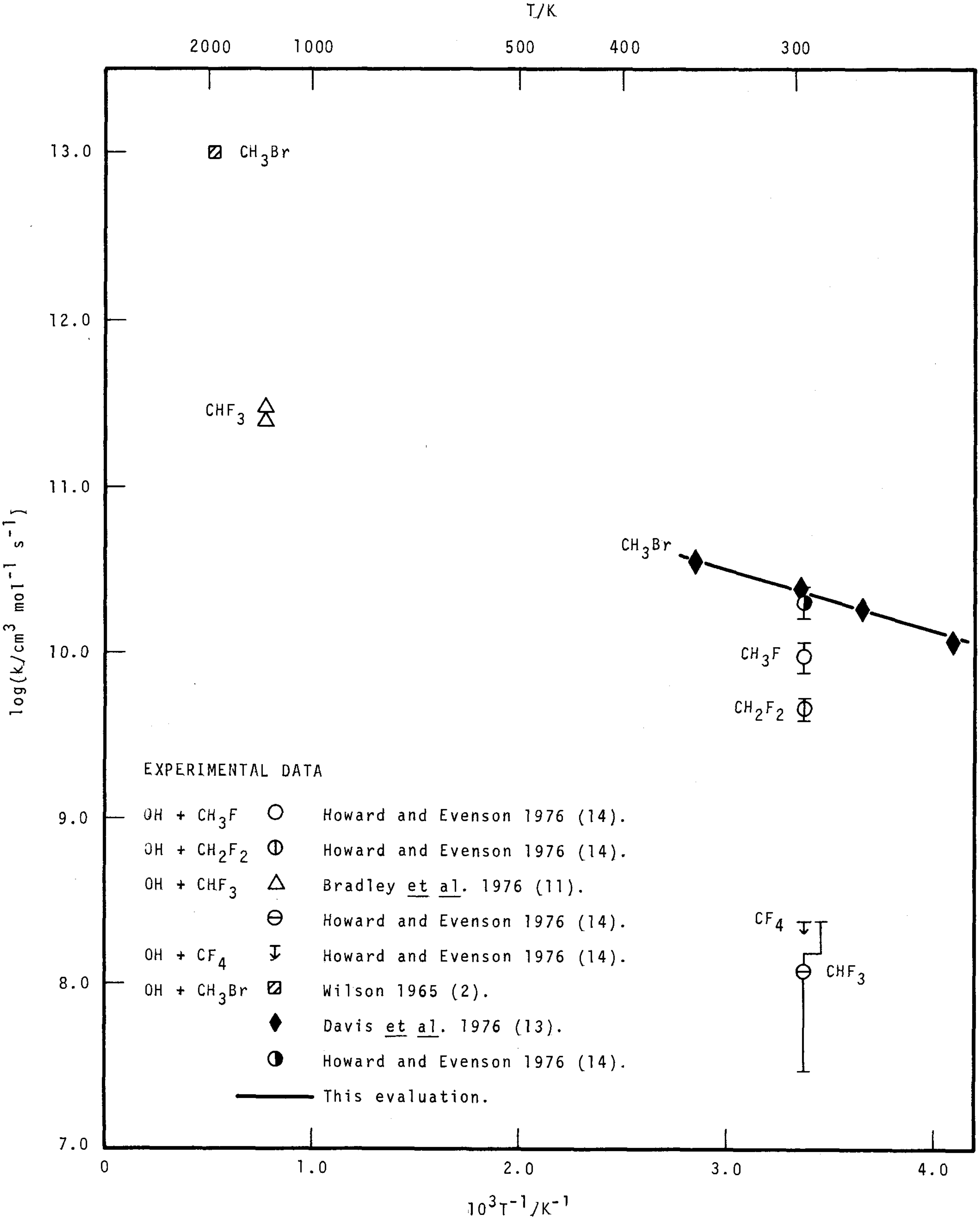
OH + CH_3Cl: k = 1.61 x 10^{12} exp(-1220/T) cm^3 mol^{-1} s^{-1}
= 2.67 x 10^{-12}exp(-1220/T) cm^3 $molecule^{-1}$ s^{-1}
Temperature Range: 250-450 K
Suggested Error Limits for Calculated Rate Constant: ±20% over the quoted temperature range.

OH + CH_2Cl_2: k = 2.89 x 10^{12} exp(-1090/T) cm^3 mol^{-1} s^{-1}
= 4.80 x 10^{-12}exp(-1090/T) cm^3 $molecule^{-1}$ s^{-1}
Temperature Range: 240-400 K
Suggested Error Limits for Calculated Rate Constant: ±50% over the quoted temperature range.

OH + $CHCl_3$: k = 2.82 x 10^{12} exp(-1130/T) cm^3 mol^{-1} s^{-1}
= 4.68 x 10^{-12}exp(-1130/T) cm^3 $molecule^{-1}$ s^{-1}
Temperature Range: 240-380 K
Suggested Error Limits for Calculated Rate Constant: a factor of 2 over this temperature range.
Note: this expression is that of DAVIS _et al._ (13) and is considered only an interim value.

OH + CH_2FCl: k = 1.81 x 10^{12} exp(-1280/T) cm^3 mol^{-1} s^{-1}
= 3.01 x 10^{-12}exp(-1280/T) cm^3 $molecule^{-1}$ s^{-1}
Temperature Range: 240-380 K
Suggested Error Limits for Calculated Rate Constant: ±50% over this temperature range.
Note: this is an interim expression.

OH + FLUOROMETHANES, CH_3Br



OH + HALOMETHANES

RECOMMENDED RATE CONSTANTS - CONTINUED

$OH + CHFCl_2$: $k = 8.57 \times 10^{11} \exp(-1160/T)$ $cm^3\ mol^{-1}\ s^{-1}$

$= 1.42 \times 10^{-12} \exp(-1160/T)$ $cm^3\ molecule^{-1}\ s^{-1}$

Temperature Range: 240-450 K

Suggested Error Limits for Calculated Rate Constant: ±15% over quoted temperature range.

$OH + CHF_2Cl$: $k = 7.67 \times 10^{11} \exp(-1670/T)$ $cm^3\ mol^{-1}\ s^{-1}$

$= 1.27 \times 10^{-12} \exp(-1670/T)$ $cm^3\ molecule^{-1}\ s^{-1}$

Temperature Range: 250-450 K

Suggested Error Limits for Calculated Rate Constant: ±25% over this temperature range.

$OH + CH_3CCl_3$: $k = 2.11 \times 10^{12} \exp(-1560/T)$ $cm^3\ mol^{-1}\ s^{-1}$

$= 3.50 \times 10^{-12} \exp(-1560/T)$ $cm^3\ molecule^{-1}\ s^{-1}$

Temperature Range: 260-400 K

Suggested Error Limits for Calculated Rate Constant: ±30% over the quoted temperature range.

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		$OH + CH_3F \rightarrow CH_2F + H_2O$	
$(9.64 \pm 2.1) \times 10^9$	296±2	Discharge flow system. H_2/He mixtures passed through discharge, and NO_2 in excess added before addition of CH_3F via moveable inlet. Typical [OH] values given as 1.7×10^{-15}-1.7×10^{-13} mol cm^{-3}, and $5 \times 10^{-11} \leqslant [CH_3F] \leqslant 1.2 \times 10^{-8}$ mol cm^{-3}. Total pressures 107-1300 Pa. Laser magnetic resonance used to follow decay of [OH]. HOWARD and EVENSON 1976 (14)	Value of k_1 determined from pseudo first order decay of OH, with small correction for OH removal at wall. Authors attempted to correlate k_1 with D(C-H), and gave estimated expression $k_1 = 1.57 \times 10^{12} \exp(-1510/T)$ $cm^3\ mol^{-1}\ s^{-1}$. Preliminary value of $k_1 = 9.03 \times 10^9$ $cm^3\ mol^{-1}\ s^{-1}$ (296 K) reported to HAMPSON and GARVIN (8) by HOWARD, and used by (10). $OH + CH_3F \rightarrow CH_2F + H_2O$ 1

OH + HALOMETHANES

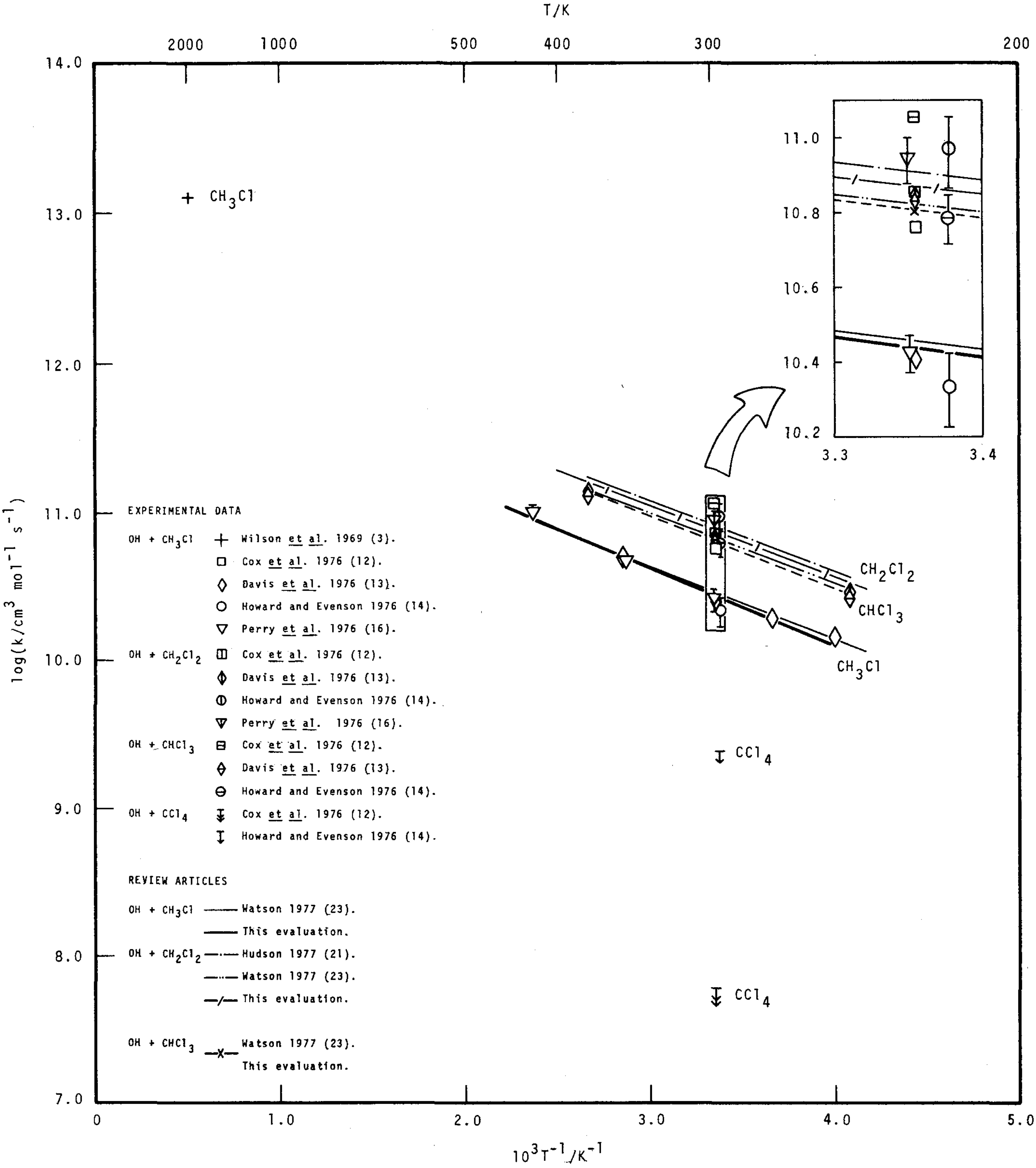
EXPERIMENTAL DATA - CONTINUED

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$	
$(4.70\pm0.7)\times10^9$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	Value of k_2 determined as for k_1, above. Correlation of k_2 with D(C-H). Estimated expression $k_2=1.27\times10^{12}\exp(-1660/T)$ cm^3 mol^{-1} s^{-1}. $OH + CH_2F_2 \rightarrow CHF_2 + H_2O$ 2 k_2 at 296 K reported by (8) and used by (10).
		$OH + CHF_3 \rightarrow CF_3 + H_2O$	
(a) 2.55×10^{11} (b) 3.12×10^{11}	1300 1300	Shock tube study. H_2O_2/CF_3H (1.27×10^{-8}-3.88×10^{-8} mol cm^{-3})/Ar($\sim10^{-6}$ mol cm^{-3}) mixtures behind incident shocks. [OH] monitored by uv absorption at 309.2 nm. BRADLEY, CAPEY, FAIR and PRITCHARD 1976 (11)	Computer simulation of [OH] profiles reproduced overall features of these profiles, with highest sensitivity to rate constants of simplest reaction mechanism $H_2O_2 + M \rightarrow OH + OH + M$ $OH + H_2O_2 \rightarrow HO_2 + H_2O$ $OH + CHF_3 \rightarrow CF_3 + H_2O$ 3 $OH + OH \rightarrow H_2O + O$ Analogous experiments performed with CH_4. Curve fitting made on basis of (a) match to both $[OH]_{max}$ and time taken to reach $\frac{1}{2}[OH]_{max}$, and (b) match to $[OH]_{max}$ only. Using technique (a), experiments with CH_4 gave $k_4=1.34\times10^{12}$ cm^3 mol^{-1} s^{-1}. Results for CHF_3 expressed as $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 ratio $k_3/k_4=0.19$. Technique (b) gave $k_4=1.64\times10^{12}$ cm^3 mol^{-1} s^{-1}, but no data for k_3 reported. Assuming the value of k_3/k_4 to hold for both methods (a) and (b), we have obtained the values of k_3 presented here. Both values of k_4 quoted as "preliminary".
$(1.20^{+1.20}_{-0.90})\times10^8$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	Pseudo first order decay of [OH] used to determine k_3, as for k_1, above. $OH + CHF_3 \rightarrow CF_3 + H_2O$ 3 Correlation of k_3 with D(C-H). Estimated expression $k_3=9.03\times10^{11}\exp(-2640/T)$ cm^3 mol^{-1} s^{-1}. Preliminary value $k_3=1.75\times10^9$ cm^3 mol^{-1} s^{-1} communicated to (8) by HOWARD, and used by (10).

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		$OH + CF_4 \rightarrow CF_3 + HOF$	
$<2.4x10^8$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	Authors found no consistent indication of reaction OH with CF_4. Upper limit presented here is largest value obtained from series of pseudo first order [OH] plots. $OH + CF_4 \rightarrow CF_3 + HOF$ 6
		$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	
$1.3x10^{13}$	1850-2100	Flame study. CH_4/O_2 flame with added CH_3Cl. Flame sampled and analysed by mass spectrometry. No details available. WILSON, O'DONOVAN and FRISTROM 1969	These authors present this value of k_7 $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$ 7 details for which "to be published". WILSON (4) gives no further elaboration of this comment in his review. Details probably as for reaction with CH_3Br (see below).
	298	Photolysis flow system. $N_2(66\%)/O_2$ mixtures at 1 atm (101.3 kPa), with added HNO_2 (12.5 ppm), NO_2(0.6 ppm), and NO(0.8 ppm), photolysed at 360 nm. CH_3Cl added, with $[CH_3Cl]/[HNO_2+NO_2+NO] \leqslant 300$. $[NO_x]$ $(=[HNO_2+NO_2+NO])$ determined by chemiluminescence NO_x analyser. COX, DERWENT, EGGLETON and LOVELOCK 1976 (12)	NO formation rate reduced by addition of CH_3Cl. Value of $[CH_3Cl]/[NO_x]$ required to reduce d[NO]/dt to zero taken as measure of k_7. Comparison with equivalent value of $[CH_4]/[NO_x]$ gave ratio k_7/k_4. $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 Using $k_4=4.22x10^9\ cm^3\ mol^{-1}\ s^{-1}$, authors quote $k_7=5.12x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$. Principal error in these measurements believed to be uncertainty in number of NO molecules oxidised following each OH reaction step. Using our recommended expression for k_4 (Volume 5, to be published) we derive $k_7=5.77x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ at 298 K.
$(1.43±0.08)x10^{10}$ $(1.96±0.04)x10^{10}$ $(2.58±0.1\ )x10^{10}$ $(4.99±0.2\ )x10^{10}$	250 273 298 350	Flash photolysis study. H_2O (200 and 400 μm Hg; 26.7-53.3 Pa)/CH_3Cl(0-250 μm Hg; 33.3 Pa)/He (20-200 mm Hg; 2.7-26.7 kPa) mixtures. [OH] monitored by resonance fluorescence at 307 nm. DAVIS, MACHADO, CONAWAY, OH and WATSON 1976 (13)	Pseudo first order decay of [OH] used to determine k_7 $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$ 7 Variation of flash energy or pressure found to give insignificant variation of k_7. Weighted least squares analysis gave $k_7=(1.11±0.1)x10^{12}\ exp\{-(1100±35)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. These data reported as $k_7=(1.02±0.1)x10^{12}$

OH + CHLOROMETHANES



OH + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		DAVIS, MACHADO, CONAWAY, OH and WATSON 1976 (13) continued.	exp(-1070/T) by (8), and used by (19,10 and 17). WATSON (23) reports value of $k_7=(2.71\pm0.5)\times10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ at 298 K measured by DAVIS, HOGAN and OH (7).
$(2.17\pm0.5)\times10^{10}$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	k_7 derived from pseudo first order decay of [OH]. Authors attempted correlation of k_7 with D(C-H). Estimated expression $k_7=1.57\times10^{12}\ \exp(-1270/T)\ cm^3\ mol^{-1}\ s^{-1}$.
$(2.65\pm0.3)\times10^{10}$ $(4.88\pm0.5)\times10^{10}$ $(1.01\pm0.1)\times10^{11}$	298.4 349.3 422.6	Flash photolysis flow study. H_2O(0.01-0.03 mm Hg; 1.3-4 Pa)/CH_3Cl/Ar (2.5-50 mm Hg; 3.3-6.7 kPa) mixtures. Resonance fluorescence of OH at 306.4 nm used to follow reaction. PERRY, ATKINSON and PITTS 1976 (16)	Large excess of CH_3Cl over OH enabled pseudo first order kinetics of OH to be used. [OH] decay curves built up from repeated flashes. Least squares fit to these data given as $k_7=2.47\times10^{12}\ \exp\{-(1360\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$. $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$ 7

REVIEW ARTICLE

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.31\pm0.3)\times10^{12}\exp\{-(1140\pm67)/T\}$	240-422	Review. Preferred expression obtained from least squares fit to data of (13 and 16). WATSON 1977 (23)	Preferred value at 298 K of $k_7=(2.53\pm0.2)\times10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ derived as mean of data of (13, 14 and 16). Expression used by (21 and 22).

$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Photolysis flow system. Method as for CH_3Cl, above, with added $[CH_2Cl_2]/[NO_x]$ ratio ⩽200. COX, DERWENT, EGGLETON and LOVELOCK 1976 (12)	Value of k_8/k_4 determined from reduction of NO formation rate, as for reaction 7. $OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$ 8 $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 Authors used $k_4=4.22\times10^9\ cm^3\ mol^{-1}\ s^{-1}$ to derive $k_8=6.26\times10^{10}\ cm^3\ mol^{-1}\ s^{-1}$. We have used our recommended expression for k_4 (Volume 5, to be published) to derive $k_8=7.06\times10^{10}\ cm^3\ mol^{-1}\ s^{-1}$.

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(2.86\pm0.3)\times10^{10}$ $(6.99\pm0.3)\times10^{10}$ $(1.34\pm0.3)\times10^{11}$	245 298 375	Flash photolysis study. H_2O (50-400 μm Hg: 6.7-53.3 Pa) /CH_2Cl_2(5-120 μm Hg: 0.7-16 Pa)/He(20-200 mm Hg; 2.7-26.7 kPa) mixtures. [OH] resonance fluorescence at 307 nm used to follow reaction. DAVIS, MACHADO, CONAWAY, OH and WATSON 1976 (13)	k_8 derived as for k_7, above. Weighted least squares fit to these results given as $k_8=(2.57\pm0.4)\times10^{12}\exp\{-(1090\pm80)/T\}$ cm^3 mol^{-1} s^{-1}. WATSON (23) reports value for k_8 of DAVIS, HOGAN and OH (7) at 298 K, of $(9.03\pm2.4)\times10^{10}$ cm^3 mol^{-1} s^{-1}.
$(9.33\pm2.05)\times10^{10}$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	Pseudo first order decay of [OH] used to determine k_8. $OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$ 8 D(C-H) correlated with this value of k_8, and authors gave estimated expression $k_8=1.27\times10^{12}\exp(-770/T)$ cm^3 mol^{-1} s^{-1}.
$(8.73\pm1.2)\times10^{10}$	298.5	Flash photolysis flow study. Method as for CH_3Cl, above. PERRY, ATKINSON and PITTS 1976 (16)	[OH] pseudo first order decay used to determine k_8, as for k_7, above.

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$3.13\times10^{12}\exp(-1090/T)$	245-375	Review. Evaluated expression based on all available data. HUDSON 1977 (21)	Expression for use in stratospheric modelling of ClO_x chemistry.
$(2.57\pm0.4)\times10^{12}\exp\{-(1090\pm80)/T\}$	245-375	Review. Preferred expression is that of DAVIS *et al.* (13). WATSON 1977 (23)	Preferred value at 298 K given as simple mean of values of (7, 13,14 and 16), i.e. $(8.43\pm1.2)\times10^{10}$ cm^3 mol^{-1} s^{-1}

$OH + CHCl_3 \rightarrow CCl_3 + H_2O$

EXPERIMENTAL DATA

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
	298	Photolysis flow system. Method as for CH_3Cl, above, with added $[CHCl_3]/[NO_x]$ ratios ≤300. COX, DERWENT, EGGLETON and LOVELOCK 1976 (12)	Reduction of NO formation rate upon addition of $CHCl_3$ or CH_4 gave ratio k_9/k_4, as for reaction 7. $OH + CHCl_3 \rightarrow CCl_3 + H_2O$ 9 $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 Authors used $k_4=4.22\times10^9$ cm^3 mol^{-1} s^{-1} to derive $k_9=1.01\times10^{11}$ cm^3 mol^{-1} s^{-1}. Using our recommended expression for k_4 (Volume

OH + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
		COX, DERWENT, EGGLETON and LOVELOCK 1976 (12) continued.	5, to be published) we derive $k_9=1.14x10^{11}\ cm^3\ mol^{-1}\ s^{-1}$.
$(2.64\pm0.2)x10^{10}$ $(6.87\pm0.4)x10^{10}$ $(1.31\pm0.8)x10^{11}$	245 298 375	Flash photolysis study. H_2O (50 and 200 μm Hg; 6.7-26.7 Pa)/$CHCl_3$(10-200 μm Hg; 1.3 -26.7 Pa)/He(40-200 mm Hg; 5.3-26.7 kPa) mixtures. Reaction followed by monitoring OH resonance fluorescence at 307 nm. DAVIS, MACHADO, CONAWAY, OH and WATSON 1976 (13)	k_9 derived as for k_7, above. Weighted least squares fit to these data given as $k_9=(2.82\pm0.4)$ $x10^{12}\ exp\{-(1130\pm110)/T\}\ cm^3$ $mol^{-1}\ s^{-1}$. This expression preferred by WATSON (23), and used by (21 and 22).
$(6.08\pm0.9)x10^{10}$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	k_3 determined as for k_7, above. $OH + CHCl_3 \rightarrow CCl_3 + H_2O$ 9 Correlation between this value and D(C-H). Estimated $k_9=9.03x$ $10^{11}\ exp(-800/T)\ cm^3\ mol^{-1}\ s^{-1}$. YUNG *et al*. (9) used value at 296 K, together with estimated E_9 to derive $k_9=6.02x10^{11}\ exp(-630/T)\ cm^3\ mol^{-1}\ s^{-1}$.

REVIEW ARTICLE

$(6.38\pm0.9)x10^{10}$	298	Review. Preferred value is mean of those of (13 and 14). WATSON 1977 (23)	Preferred expression is that of DAVIES *et al*. (13).

$OH + CCl_4 \rightarrow CCl_3 + HOCl$

EXPERIMENTAL DATA

	298	Photolysis flow system. Method as for CH_3Cl, above, with $[CCl_4]/[NO_x]$ ratios ≤400. COX, DERWENT, EGGLETON and LOVELOCK 1976 (12)	Reduction of NO formation rate compared for both CCl_4 and CH_4. Virtual ineffectiveness of CCl_4 in reducing d[NO]/dt gave $k_{10}<6x$ $10^7\ cm^3\ mol^{-1}\ s^{-1}$, using $k_4=4.22x$ $10^9\ cm^3\ mol^{-1}\ s^{-1}$. Using our recommended expression for k_4 (Volume 5, to be published) only slightly increases this upper limit to $6.8x10^7\ cm^3\ mol^{-1}\ s^{-1}$. $OH + CCl_4 \rightarrow CCl_3 + HOCl$ 10 $OH + CH_4 \rightarrow CH_3 + H_2O$ 4

OH + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

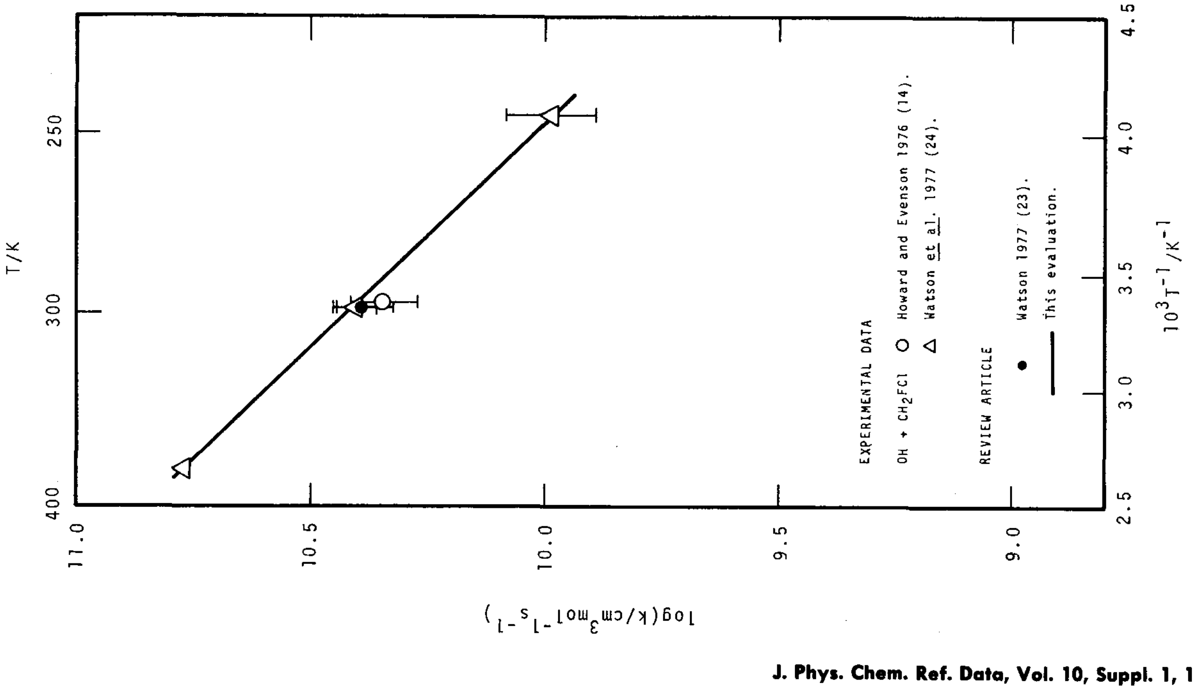
Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$<2.41\times10^9$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	k_{10} derived from pseudo first order decay of [OH]. $OH + CCl_4 \rightarrow CCl_3 + HOCl$ 10
$OH + CH_3Br \rightarrow CH_2Br + H_2O$			
	1800-2000	Flame study. CH_4(8.66%)/O_2(89.63%) flame with added (1.71%) CH_3Br. Total pressure 0.05 atm (5.06 kPa). Flame sampled and analysed by mass spectrometry. WILSON 1965 (2)	Value of [OH] determined from net rate of CH_4 disappearance, assuming reaction 4 to be principal removal reaction and $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 using k_4 of FRISTROM (1). From this value of [OH] k_{11} derived from rate of CH_3Br removal $OH + CH_3Br \rightarrow CH_2Br + H_2O$ 11 Author obtained $k_{11} \approx 1.5\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ over temperature range 1800-2000 K. Using our recommended expression for k_4 (Volume 5, to be published) we derive $9.20\times10^{12} \leqslant k_{11} \leqslant 1.11\times10^{13}$ $cm^3\ mol^{-1}\ s^{-1}$ over this range. In later quotation of this work WILSON <u>et al</u>. (3) give temperature range as 1775-1825 K. Used by (5).
$(1.21\pm0.07)\times10^{10}$ $(1.90\pm0.09)\times10^{10}$ $(2.49\pm0.3\ )\times10^{10}$ $(3.66\pm0.2\ )\times10^{10}$	244 273 298 350	Flash photolysis study. H_2O(50-400 μm Hg; 6.7-53.3 Pa)/CH_3Br(25-250 μm Hg; 3.3-33.3 Pa)/He(20-200 mm Hg; 2.7-26.7 kPa) mixtures. [OH] followed by resonance fluorescence at 307 nm. DAVIS, MACHADO, CONAWAY, OH and WATSON 1976 (13)	Values of k_{11} derived from pseudo first order decay of [OH]. No significant deviation found in k_{11} with flash energy or pressure. Weighted least squares analysis gave $k_{11}=(4.78\pm0.5)\times10^{11}\exp\{-(890\pm60)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$. Used by (21,22). These data reported as $k_{11}=(5.0\pm0.5)\times10^{11}\exp(-916/T)$ $cm^3\ mol^{-1}\ s^{-1}$ by (8), and used by (10 and 17).
$(2.11\pm0.5)\times10^{10}$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	Pseudo first order decay of [OH] used to determine k_{11} $OH + CH_3Br \rightarrow CH_2Br + H_2O$ 11 Estimated expression $k_{11}=1.57\times10^{12}\exp(-1270/T)$ $cm^3\ mol^{-1}\ s^{-1}$ derived. Authors also correlated k_{11} with D(C-H).

OH + HALOMETHANES

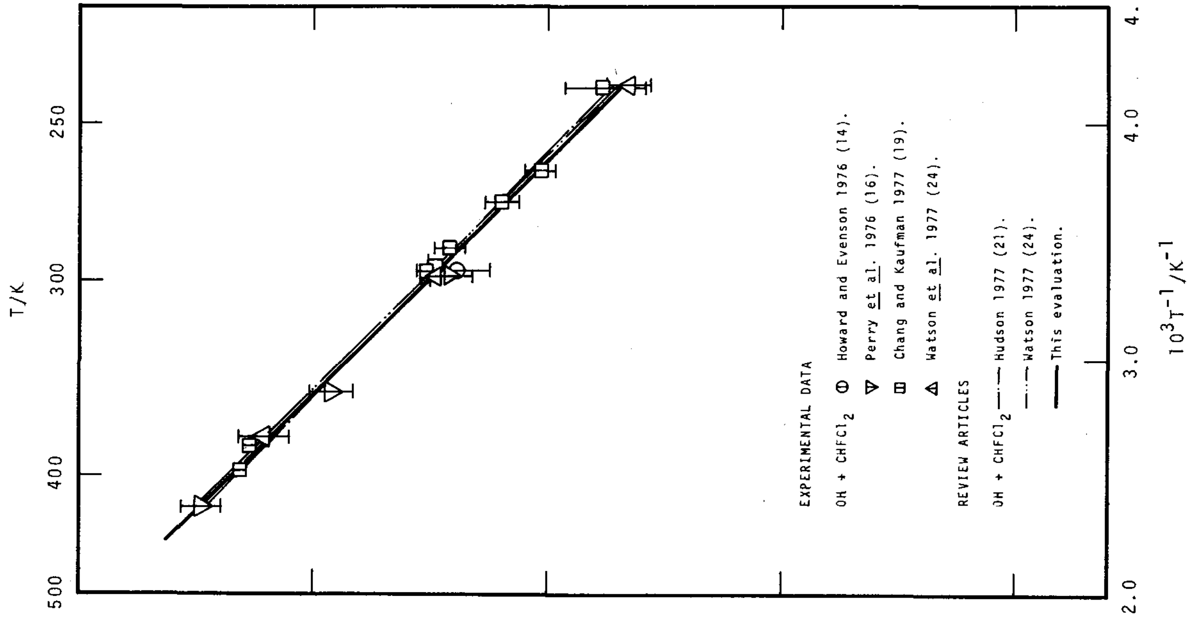
EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$OH + CH_2FCl \rightarrow CHFCl + H_2O$			
$(2.23\pm0.4)x10^{10}$	296±2	Discharge flow system. Method as for CH_3F, above. HOWARD and EVENSON 1976 (14)	k_{12} derived as for k_1, above. Correlation of this value with D(C-H). Estimated $k_{12}=1.27x10^{12}$ $exp(-1200/T)\ cm^3\ mol^{-1}\ s^{-1}$. $OH + CH_2FCl \rightarrow CHFCl + H_2O$ 12
$(9.94\pm0.2)x10^9$ $(2.54\pm0.3)x10^{10}$ $(5.90\pm0.2)x10^{10}$	245 298 375	Flash photolysis study. H_2O(50-400 μm Hg; 6.7-53.3 Pa)/CH_2FCl(0-250 μm Hg; 33.3 Pa)/He(40-200 mm Hg; 5.3-26.7 kPa) mixtures, giving [OH]≈$5x10^{-13}$ mol cm^{-3}. CH_2FCl in excess of OH by $1.5x10^3$-$1.5x10^5$. OH resonance fluorescence monitored at 307 nm. WATSON, MACHADO, CONAWAY, WAGNER and DAVIS 1977 (24)	Pseudo first order decay of [OH] used to determine k_{12}. These values expressed in Arrhenius form as $k_{12}=(1.71\pm0.2)x10^{12}$ exp{-(1260±50)/T} $cm^3\ mol^{-1}\ s^{-1}$. This expression preferred by HUDSON (21) and WATSON (23).
REVIEW ARTICLE			
$(2.47\pm0.4)x10^{10}$	298	Review. Value is mean of room temperature values of (14 and 24). WATSON 1977 (23)	Preferred expression is that of WATSON *et al*. (24). For use in modelling stratospheric ClO_x kinetics.
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$			
EXPERIMENTAL DATA			
$(1.57\pm0.2)x10^{10}$	296±2	Discharge flow system. H_2/He mixture passed through discharge, and NO_2 added in excess before $CHFCl_2$ addition via moveable inlet. Typical [OH] values quoted as $1.7x10^{-15}$-$1.7x10^{-13}$ mol cm^{-3}, with $5x10^{-11}\leqslant[CHFCl_2]\leqslant1.2x10^{-8}$ mol cm^{-3}. Total pressures 107-1300 Pa. Laser magnetic resonance used to follow decay of [OH]. HOWARD and EVENSON 1976 (14)	Value of k_{13} determined from pseudo first order decay of OH, with small correction for OH removal at wall. $OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$ 13 Authors correlated k_{13} with D(C-H), and gave estimated expression $k_{13}=9.03x10^{11}$ exp(-1200/T) $cm^3\ mol^{-1}\ s^{-1}$.

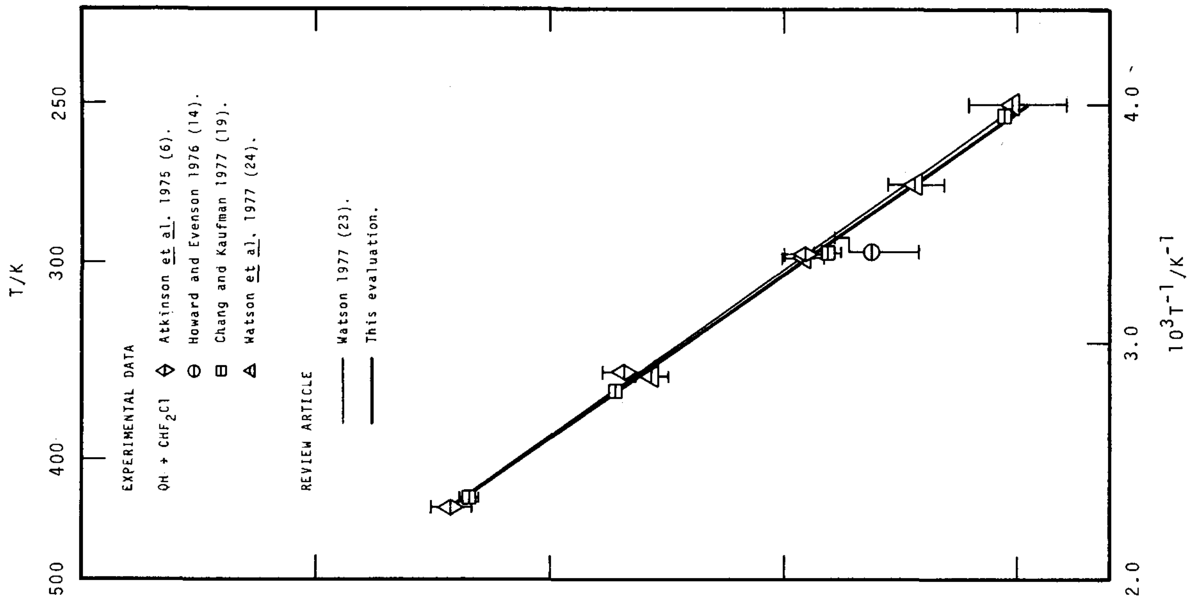
$OH + CH_2FCl \rightarrow CHFCl + H_2O$



$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$



$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$



OH + HALOMETHANES

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(1.63\pm0.2)x10^{10}$ $(2.89\pm0.3)x10^{10}$ $(5.48\pm0.5)x10^{10}$	298.4 349.5 421.7	Flash photolysis flow study. H_2O(0.01-0.03 mm Hg; 1.3-4 Pa)/$CHFCl_2$/Ar(25-50 mm Hg; 3.3-6.7 kPa) mixtures. Resonance fluorescence at 306.4 nm used to monitor [OH]. PERRY, ATKINSON and PITTS 1976 (16)	Large excess ($\sim10^4$-fold) of $CHFCl_2$ over OH enabled pseudo first order OH kinetics to be assumed. Repeated flashes, with flow system removing reaction products and renewing reaction mixture, used to build up [OH] decay curves. Authors give expression $k_{13}=1.05x10^{12}\ exp\{-(1250\pm150)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ as least squares fit to these data.
$(7.71\pm1.5\ )x10^9$ $(1.04\pm0.08)x10^{10}$ $(1.63\pm0.1\ )x10^{10}$ $(1.83\pm0.07)x10^{10}$ $(4.32\pm0.1\ )x10^{10}$ $(4.53\pm0.2\ )x10^{10}$	241 250 288 296 380 396	Discharge flow system. H_2/He mixture passed through discharge, and NO_2 added downstream giving $1.7x10^{-14} < [OH] < 8.3x10^{-13}\ mol\ cm^{-1}$. Excess $CHFCl_2$ added further downstream through moveable inlet. Total pressures $\sim$2-6 mm Hg (266.6-800 Pa). [OH] monitored by resonance fluorescence at 309 nm. CHANG and KAUFMAN 1977 (19)	Pseudo first order decay of [OH] used to derive k_{13} $OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$ 13 Major impurity CHF_2Cl (0.63%) had no affect on results as k_{14} is almost an order of magnitude slower than k_{13} $OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$ 14 Arrhenius expression for these data given as $k_{13}=(6.99\pm1.02)x10^{11}\ exp\{-(1073\pm40)/T\}\ cm^3\ mol^{-1}\ s^{-1}$.
$(6.75\pm0.7)x10^9$ $(1.26\pm0.1)x10^{10}$ $(1.73\pm0.2)x10^{10}$ $(4.02\pm0.5)x10^{10}$	245 273 298 375	Flash photolysis study. H_2O (50-400 μm Hg; 6.7-53.3 Pa) /$CHFCl_2$(0-400 μm Hg; 53.3 Pa)/He(40-200 mm Hg; 5.3-26.7 kPa) mixtures, giving $[OH]\approx5x10^{-13}\ mol\ cm^{-3}$, and $[CHFCl_2]/[OH]\approx1.5x10^3$ to $1.5x10^5$. Resonance fluorescence at 307 nm used to follow [OH]. WATSON, MACHADO, CONAWAY, WAGNER and DAVIS 1977 (24)	Pseudo first order kinetics of OH used to determine k_{13}. Authors give Arrhenius expression $k_{13}=(1.13\pm0.1)x10^{12}\ exp\{-(1250\pm30)/T\}\ cm^3\ mol^{-1}\ s^{-1}$ for these data.

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$7.83x10^{11}\ exp(-1130/T)$	241-422	Review. This expression derived from "all available data". HUDSON 1977 (21)	For use in modelling stratospheric chemistry.
$(9.58\pm1.2)x10^{11}\ exp\{-(1200\pm70)/T\}$	245-423	Review. Expression based on least squares fit to data of (16 and 24). WATSON 1977 (23)	Preferred value of k_{13} at 298 K given as $(1.69\pm0.2)x10^{10}\ cm^3\ mol^{-1}\ s^{-1}$, as average of data of (14,16 and 24).

OH + HALOMETHANES

EXPERIMENTAL DATA

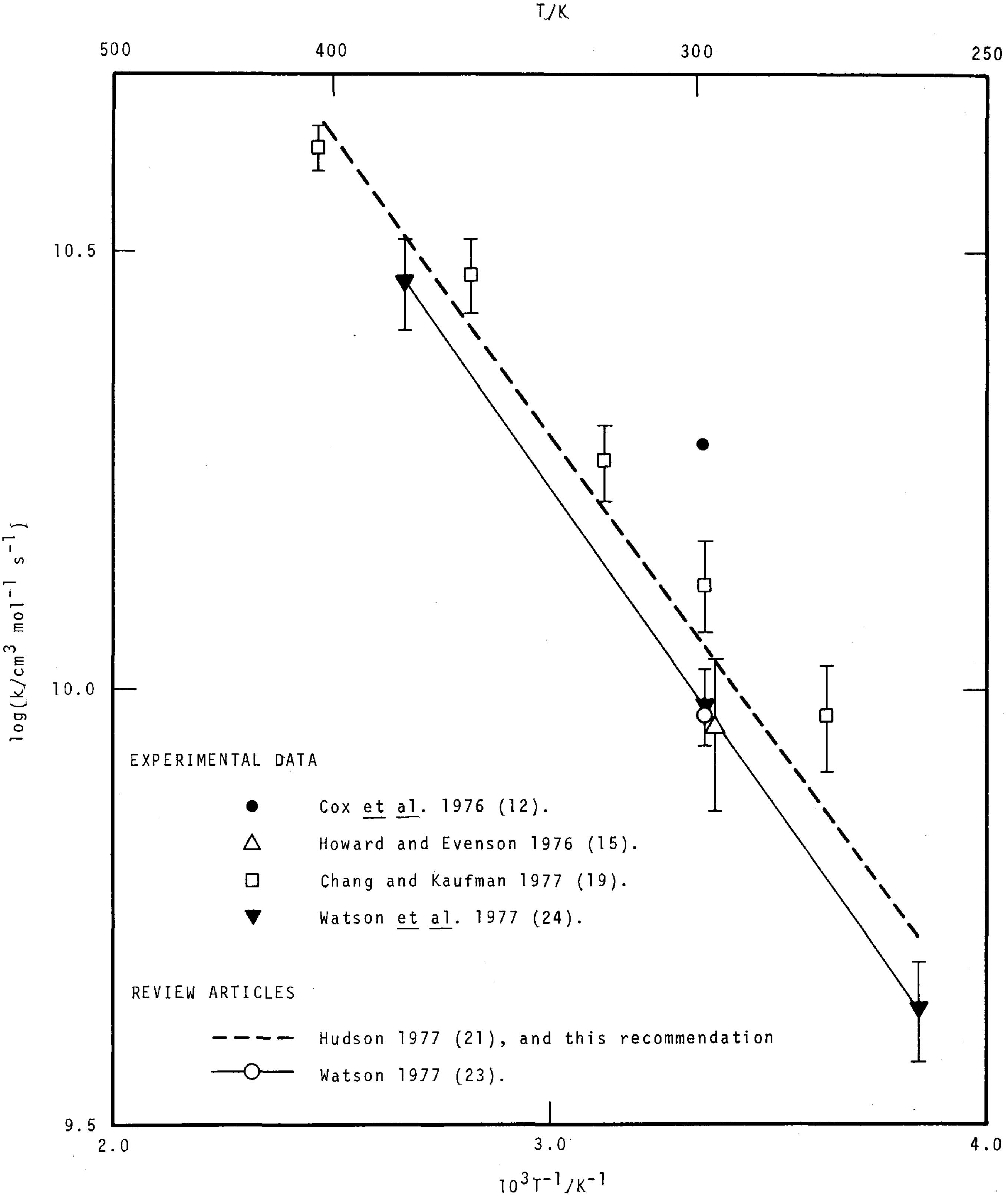
Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
		$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	
$(2.86\pm0.3)x10^9$ $(6.93\pm0.7)x10^9$ $(1.63\pm0.2)x10^{10}$	296.9 348.0 433.7	Flash photolysis flow system. H_2O(0.01-0.03 mm Hg; 1.3-4 Pa)/CHF_2Cl/Ar (15-25 mm Hg; 2.0-3.3 kPa) mixtures. Resonance fluorescence of OH followed at 306.4 nm. ATKINSON, HANSEN and PITTS 1975 (6)	Initial [CHF_2Cl] limited by its quenching effect on OH($^2\Sigma^+$). [OH] decay profiles built up by repetitive flashing, and k_{14} determined from pseudo first order [OH] decay. Arrhenius fit given for these data as $k_{14}=7.29x10^{11}$ exp{-(1640±150)/T} cm^3 mol^{-1} s^{-1}. Used by (9 and 10). $OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$ 14
$(2.05\pm0.4)x10^9$	296±2	Discharge flow system. Method as for $CHFCl_2$, above. HOWARD and EVENSON 1976 (14)	Pseudo first order [OH] decay used to determine k_{14}. Correlation of this value with D(C-H). Estimated $k_{14}=9.03x10^{11}$ exp(-1800/T) cm^3 mol^{-1} s^{-1}.
$(1.07\pm0.01)x10^9$ $(2.56\pm0.02)x10^9$ $(7.23\pm0.02)x10^9$ $(1.50\pm0.06)x10^{10}$	253 296 358 427	Discharge flow system. Method as for $CHFCl_2$, above. CHANG and KAUFMAN 1977 (19)	k_{14} derived from pseudo first order OH decay, as for k_{13}, above. $OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$ 14 Authors give expression for these data as $k_{14}=(7.23\pm1.0)x10^{11}$ exp{-(1660±40)/T} cm^3 mol^{-1} s^{-1}.
$(1.02\pm0.2)x10^9$ $(1.67\pm0.2)x10^9$ $(2.89\pm0.3)x10^9$ $(6.08\pm0.5)x10^9$	250 273 298 350	Flash photolysis study. H_2O(50-400 μm Hg; 6.7-53.3 Pa)/CHF_2Cl(0-1300 μm Hg; 173.3 Pa)/He (40-200 mm Hg; 5.3-26.7 kPa) mixtures. [OH]≃$5x10^{-13}$ mol·cm^{-3}, and $1.5x10^3$<[CHF_2Cl]/[OH]<$1.5x10^5$. OH resonance fluorescence monitored at 307 nm. WATSON, MACHADO, CONAWAY, WAGNER and DAVIS 1977 (24)	Method as for k_{12}, above. Authors fitted Arrhenius expression $k_{14}=(5.57\pm0.6)x10^{11}$ exp{-(1580±70)/T} cm^3 mol^{-1} s^{-1} to these data.
		REVIEW ARTICLE	
$(7.29\pm1.0)x10^{11}$ exp{-(1650±80)/T}	250-434	Review. Expression derived from least squares fit to data of (6 and 24). WATSON 1977 (23)	Preferred value of k_{14} at 298 given as mean of data of (6,14 and 24): $k_{14}=(2.59\pm0.5)x10^9$ cm^3 mol^{-1} s^{-1}. Expression used by (22), and also adopted by HUDSON (21) but with E_{14}/R quoted as 1660 K, after inclusion of data of (19).

OH + METHYL CHLOROFORM

EXPERIMENTAL DATA

Rate Constant k (cm^3 mol^{-1} s^{-1})	Temperature (K)	Method and Reference	Comments
$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$			
	298	Flow photolysis system. CH_3CCl_3 added to synthetic air containing HONO (12.5 ppm), NO (0.8 ppm) and NO_2 (0.6 ppm), at 1 atm (101.3 kPa). $[CH_3CCl_3]/[NO_x]$ ratios increased from ∿20 to 300 (where NO_x=NO+NO_2+HONO). Mixtures irradiated at 360 nm and NO formation rate monitored using chemiluminescent analyser. COX, DERWENT, EGGLETON and LOVELOCK 1976 (12)	Increasing addition of CH_3CCl_3 led to decrease in NO formation rate. Value of $[CH_3CCl_3]/[NO_x]$ at $d[NO]/dt=0$ taken as measure of rate of reaction 15 $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$ 15 Comparison with value of $[CH_4]/[NO_x]$ at $d[NO]/dt=0$ gave ratio k_{15}/k_4 $OH + CH_4 \rightarrow CH_3 + H_2O$ 4 as 4.0. Using $k_4=4.22\times10^9$ cm^3 mol^{-1} s^{-1}, authors quote $k_{15}=1.69\times10^{10}$ cm^3 mol^{-1} s^{-1}. We have used our recommended expression for k_4 (Volume 5, to be published) to derive $k_{15}=1.90\times10^{10}$ cm^3 mol^{-1} s^{-1}.
$(9.03\pm1.8)\times10^9$	296	Discharge flow system. H atoms from discharge added to NO_2, giving $1.66\times10^{-15} \leqslant [OH] \leqslant 1.66\times10^{-13}$ mol cm^{-3}. CH_3CCl_3 (1.33×10^{-11}-9.96×10^{-9} mol cm^{-3})/He (4.3×10^{-8}-4.3×10^{-7} mol cm^{-3}) mixtures added downstream through moveable inlet. [OH] monitored by laser magnetic resonance spectrometry. HOWARD and EVENSON 1976 (15)	Purity of CH_3CCl_3 found to be important. Repeated purification led to reduction of value of k_{15} determined from pseudo first order decay of [OH]. Value quoted here could not be reduced by further purification.
$(9.33\pm1.3)\times10^9$ $(1.32\pm0.2)\times10^{10}$ $(1.83\pm0.2)\times10^{10}$ $(2.98\pm0.3)\times10^{10}$ $(4.14\pm0.2)\times10^{10}$	275 298 320 355 405	Discharge flow system. H atoms from discharge added to NO_2, giving $1.66\times10^{-14} \leqslant [OH] \leqslant 8.3\times10^{-13}$ mol cm^{-3}. Total pressures (in He diluent) 2.2-5.7 mm Hg (293.3-760 Pa). CH_3CCl_3 added downstream through moveable inlet, giving $1.78\times10^{-10} \leqslant [CH_3CCl_3] \leqslant 5.8\times10^{-9}$ mol cm^{-3}. Resonance fluorescence at 309 mm used to monitor [OH]. CHANG and KAUFMAN 1977 (19)	CH_3CCl_3 purified by fractional distillation. k_{14} derived from pseudo first order [OH] decay. These data expressed in Arrhenius form as $k_{15}=(1.17\pm0.1)\times10^{12}\exp\{-(1331\pm57)/T\}$ cm^3 mol^{-1} s^{-1}. Authors comment on difference between their data and those of (15 and 24). $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$ 15

$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$



OH + METHYL CHLOROFORM

EXPERIMENTAL DATA - CONTINUED

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$(4.29\pm0.6)\times10^9$ $(9.58\pm1.0)\times10^9$ $(2.92\pm0.4)\times10^{10}$	260 298 375	Flash photolysis study. H_2O (50-400 µm Hg; 6.7-53.3 Pa)/CH_3CCl_3 (25-1000 µm Hg; 3.3-133.3 Pa)/He (40 mm Hg; 5.3 kPa) mixtures, giving [OH] typically 5.0×10^{-13} mol cm^{-3}, and $1.5\times10^3 \leq [CH_3CCl_3]/[OH] \leq 1.5\times10^5$. Resonance fluorescence used to monitor [OH]. WATSON, MACHADO, CONAWAY, WAGNER and DAVIS 1977 (24)	Variation in flash energies (45-245 J), and in number of flashes per sample, showed no significant effects of OH removal by radical-radical processes, e.g. $OH + OH \rightarrow H_2O + O$ $OH + OH + M \rightarrow H_2O_2 + M$ $H + OH + M \rightarrow H_2O + M$ Values of k_{15} determined from pseudo first order decay of [OH]. These values expressed in Arrhenius form as $k_{15}=(2.24\pm0.2)\times10^{12}\exp\{-(1627\pm50)/T\}$ $cm^3\ mol^{-1}\ s^{-1}$.

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Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2.11\times10^{12}\exp(-1562/T)$	260-405	Evaluation. Expression based on "all available data". HUDSON 1977 (21)	
$(2.24\pm0.2)\times10^{12}\exp\{-(1627\pm50)/T\}$ 9.33×10^9	260-375 298	Evaluation. Preferred expression is that of (24). Excellent agreement between room temperature data of (15 and 24) gives preferred value at 298 K. WATSON 1977 (23)	Used by (22).

Discussion

OH + Fluoromethanes, Methyl Bromide

Apart from the room temperature discharge flow measurements of k_1, k_2 and k_3 by Howard and Evenson [14]

$$OH + CH_3F \rightarrow CH_2F + H_2O \quad (1)$$

$$OH + CH_2F_2 \rightarrow CHF_2 + H_2O \quad (2)$$

$$OH + CHF_3 \rightarrow CF_3 + H_2O \quad (3)$$

the only other measurements of the rate of reaction of OH with fluoromethanes have been those of Bradley et al. [11] at 1300 K, using a shock tube to determine k_3. In view of the lack of data, we make no recommendations for k_1, k_2 or k_3. (Note that in all cases the reaction has been considered to be one of H abstraction, rather than of halogen.) We are also unable to make a recommendation for the halogen abstraction rate constant, k_6.

$$OH + CF_4 \rightarrow CF_3 + HOF \quad (6)$$

For the reaction of OH with methyl bromide,

$$OH + CH_3Br \rightarrow CH_2Br + H_2O \quad (11)$$

the flash photolysis results of Davis et al. [13] over the temperature range 244–350 K agree well with the discharge flow measurement at room temperature by Howard and Evenson [14]. The value at 1800–2000 K by Wilson [2] from a flame study is a factor of ~30 greater than that given by extrapolating the data of Davis et al. [13]. As an interim recommendation we give the expression

$$k_{11} = 4.42\times10^{11} \exp(-873/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 240–360 K, with error limits of ±50%.

OH + Chloromethanes

The reactions of OH with CH_3Cl, CH_2Cl_2 and $CHCl_3$ have been studied by a variety of methods, over a temperature range of ~250–400 K.

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O \quad (7)$$

$$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O \quad (8)$$

$$OH + CHCl_3 \rightarrow CCl_3 + H_2O \quad (9)$$

The room temperature data for k_7 of [13,14 and 16], obtained by flash photolysis, discharge flow, and flash photolysis flow methods, respectively, are in good agreement. Watson [23] took his recommended value at 298 K as the mean of these results. The photolysis flow result of Cox et al. [12], omitted by Watson, lies more than a factor of 2 above these values. Cox et al. admit that there is an uncertainty over the removal of NO following each initial OH/CH_3Cl reaction. We therefore place little weight on this result [12].

Although Perry et al. [16] give a higher activation energy than Davis et al. [13], the actual values of k_7 at 298 and 350 K agree very well. The result from a flame study by Wilson et al. [3] lies almost an order of magnitude above the extrapolated data of [13 and 16]. Without evidence of strong non-Arrhenius behaviour in the region 400–1800 K, we give no further consideration to this value. On the basis of the data of [13,14 and 16] we recommend the expression

$$k_7 = 1.61\times10^{12} \exp(-1220/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 250–450 K, within uncertainty limits of ±20% over this range.

The value of Cox et al. [12] for k_8 at 298 K is in good agreement with that of Davis et al. [13], in contrast with the former's measurement of k_7 and k_9. And yet there seems to be no obvious reason why the removal of NO by RO_2 radicals produced by the sequence

$$OH + RH \rightarrow R + H_2O$$

$$R + O_2 \rightarrow RO_2$$

should be any less effective for $RH{=}CH_2Cl_2$ than for $RH{=}CH_3Cl$ or $CHCl_3$. The other room temperature values of k_8 [14,16] are less than 50% above those of [12 and 13], and so, accepting the temperature dependence of k_8 by Davis et al. [13], we recommend the expression

$$k_8 = 2.89\times10^{12} \exp(-1090/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for temperatures 240–400 K, within uncertainty limits of ±50%.

The measurement by Cox et al. [12] for k_9 at 298 K is higher by nearly a factor of 2 than those of [13 and 14]. Because of the doubts about Cox et al.'s method, already mentioned, we prefer the others' results and recommend as an interim value the expression of Davis et al. [13] for k_9, i.e.,

$$k_9 = 2.82\times10^{12} \exp(-1130/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Lack of data prevents us making any recommendation for k_{10}.

$$OH + CCl_4 \rightarrow CCl_3 + HOCl \quad (10)$$

OH + Chlorofluoromethanes

There are considerable data on the rate of OH radical removal by the chlorofluoromethanes CH_2FCl (Fluorocarbon FC-31), $CHFCl_2$ (FC-21), and CHF_2Cl (FC-22).

The system with the fewest data, $OH+CH_2FCl$, has been studied by discharge flow [14] and flash photolysis [24] methods. Values of k_{12} at room temperature

$$OH + CH_2FCl \rightarrow CHFCl + H_2O \quad (12)$$

are within 15% of each other. Watson [23] took his preferred value of k_{12} as the arithmetic mean of the two results. As the measurement of k_{12} by Watson et al. [24] was by the same method as for k_{11}, we again make an interim recommendation, i.e.,

$$k_{12} = 1.81\times10^{12} \exp(-1280/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the temperature range 240–380 K. The uncertainty in k_{12} is ±50% over this range.

The discharge flow [14,19] and flash photolysis [16,24] data for k_{13} are in good agreement

$$\text{OH} + \text{CHFCl}_2 \rightarrow \text{CFCl}_2 + \text{H}_2\text{O} \qquad (13)$$

At room temperature, there is less than 10% difference from the average value. For k_{13} we recommend the expression

$$k_{13} = 8.57\times10^{11} \exp(-1160/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for temperatures 240–450 K, with uncertainty limits in k_{13} of ±15% over the whole range.

There are slightly fewer data for reaction 14

$$\text{OH} + \text{CHF}_2\text{Cl} \rightarrow \text{CF}_2\text{Cl} + \text{H}_2\text{O} \qquad (14)$$

but again the agreement between the flash photolysis data [6,24] and discharge flow results [14,19] is good. There is no systematic variation between the data of [6 and 24], obtained at pressures of up to 3.3 kPa and 26.7 kPa, respectively, nor between the data of [14 and 19], at pressures of $\leqslant$1.3 kPa and $\leqslant$800 Pa, respectively. We therefore recommend the expression

$$k_{14} = 7.67\times10^{11} \exp(-1670/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the temperature range 250–450 K. Uncertainty limits in k_{14} are ±25% over this range.

The rates of reaction of OH with the fully halogenated chlorofluoromethanes FC-11, FC-12 and FC-13

$$\text{OH} + \text{CFCl}_3 \rightarrow \text{products} \qquad (16)$$

$$\text{OH} + \text{CF}_2\text{Cl}_2 \rightarrow \text{products} \qquad (17)$$

$$\text{OH} + \text{CF}_3\text{Cl} \rightarrow \text{products} \qquad (18)$$

are very much smaller than with any of the other halogenated methane species. Only upper limits for k_{16}, k_{17} and k_{18} have been measured, using flash photolysis [6], photolysis flow [12], and discharge flow [14,19] systems. At room temperature the upper limits for k_{16} were determined at 6.02×10^6 [12], 3.01×10^8 [14], and 6.02×10^8 cm^3 mol^{-1} s^{-1} [6]; for k_{17}, 6.02×10^7 [12], 2.4×10^8 [14], and 6.02×10^8 cm^3 mol^{-1} s^{-1} [6]; and for k_{18}, 4.22×10^8 cm^3 mol^{-1} s^{-1} [14]. Upper limits to these rate constants at higher temperatures were found to be not much greater: at 423.8 K Atkinson et al. [6] obtained $k_{16}\leqslant6.02\times10^8$ cm^3 mol^{-1} s^{-1}, and Chang and Kaufman [18] measured $k_{16}\leqslant3.01\times10^8$ cm^3 mol^{-1} s^{-1} at 480 K. Atkinson et al. [6] found the same limit for k_{17} at 423.8 K, and Chang and Kaufman's limit for k_{17} at 480 K was 6.02×10^8 cm^3 mol^{-1} s^{-1} [18].

OH + Methyl Chloroform

Methyl chloroform (1,1,1-trichloroethane) has been found [20] to be the most prevalent of the halogenated C$_2$ species and therefore its removal by OH is an important step in the chemistry of the stratosphere

$$\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow \text{CH}_2\text{CCl}_3 + \text{H}_2\text{O} \qquad (15)$$

The best agreement is between the discharge flow data of Howard and Evenson [15] and the flash photolysis results of Watson et al. [24] at ~298 K. The discharge flow data of Chang and Kaufman [19] are up to 60% higher than those of [24] but there is reasonable agreement over the temperature dependence. The room temperature value of Cox et al. [12] is (as for the previously discussed chloromethanes) at odds with the other data, being almost a factor of 2 too high. A least squares fit to all the results but that of [12] gives $k_{15} = 2.06\times10^{12} \exp(-1555/T)$ cm^3 mol^{-1} s^{-1}, but this is almost identical to the expression of Hudson [21] and so we recommend the latter

$$k_{15} = 2.11\times10^{12} \exp(-1560/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for 260–400 K. Error limits of ±30% should be allowed over this range.

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Note Added in Proof

Additional measurements of the rates of the reaction of OH with chlorinated compounds have been made by Butler, Solomon and Snelson [J. Air Pollution Control Assn. **28**, 1131 (1978)]. In a competitive reaction system OH radicals produced by the static photolysis of H_2O_2, reacted with CO in the presence and absence of the chlorinated hydrocarbon. The rate constants were deduced from the initial rates of CO_2 production. The CO_2 was monitored chromatographically. Details of mixture composition are not given, except that the pressure was made up to 400 mm Hg (53 kPa) with an N_2/O_2 mixture. Values of k_7, k_8 and k_{15} were obtained relative to k_{19}, and also depended on k_{20}.

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O \qquad (7)$$

$$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O \qquad (8)$$

$$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O \qquad (15)$$

$$OH + CO \rightarrow CO_2 + H \qquad (19)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (20)$$

The authors used our recommended value for k_{20} (Vol. 1, p. 193), and a value for k_{19} based on their own data [Chem. Phys. Letts. **54**, 19 (1978)]. k_{19} is now known to be pressure dependent and the authors work suggested that under the conditions of the above experiments it had achieved a limiting high pressure value, but this pressure dependence cannot be regarded as having been fully established. The rate constants thus obtained at 303 K were as follows:

k_7	$(1.9 \pm 0.5) \times 10^{10}$ cm^3 mol^{-1} s^{-1}
k_8	$(1.6 \pm 0.6) \times 10^{10}$ cm^3 mol^{-1} s^{-1}
k_{15}	$\leqslant 3.4 \times 10^{10}$ cm^3 mol^{-1} s^{-1}

The low vapour pressure of CH_3CCl_3 permitted determination of only an upper limit for k_{15}, given above, and a most probable value, $k_{15} = 1.3 \times 10^{10}$ cm^3 mol^{-1} s^{-1}. The latter is in good agreement with our recommendation.

The authors reject their own value of k_8 which is a factor of five below our recommendation at this temperature, postulating that their low value may have been due to secondary regeneration of OH in presence of oxygen.

$$CHCl_2 + O_2 \rightarrow CHCl_2O_2$$

$$CHCl_2O_2 \rightarrow COCl_2 + OH$$

The value of k_7 is rather lower than previously measured values but we make no change to our recommendation at this stage.

Further studies of the reactions of OH with chlorofluoromethanes have been made by Handwerk and Zellner [Ber. Bunsenges. Phys. Chem. **82**, 1161 (1978)]. The systems studied were

$$OH + CH_2FCl \rightarrow CHFCl + H_2O \qquad (12)$$

and

$$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O \qquad (14)$$

U.v. resonance absorption was used to follow the decay of OH generated by the flash photolysis of H_2O in presence of an excess of the chlorofluoromethane. The following mixture compositions were used.

CH_2FCl work	- H_2O(0.2–1.0 mm Hg; 30–130 Pa)/CH_2FCl(3–6 mm Hg; 400–800 Pa)/He, at total pressures of 12–18 mm Hg (1.6–2.4 kPa).
CHF_2Cl work	- H_2O(0.2–1.0 mm Hg; 30–130 Pa)/CHF_2(10–27 mm Hg; 1.3–3.6 kPa).

In preliminary experiments at flash energies up to 420 J, k_{14} was observed to be flash energy dependent. Thus for all rate constant determinations flash energies were made sufficiently low (50 J) that the rate constants did not differ significantly from their extrapolated zero flash energy values. Under these conditions the initial ratio, [chlorofluoromethane]/[OH] was 10^4–10^5. It was also demonstrated that under these conditions absorption by the chlorofluoromethanes did not affect the measured rate constants.

Values of k/cm^3 mol^{-1} s^{-1} were obtained as follows:

k_{12}	k_{14}	T/K
	1.2×10^9	263
1.7×10^{10}	1.6×10^9	273
	3.1×10^9	283
2.1×10^{10}	2.8×10^9	293
6.6×10^{10}	1.1×10^{10}	373

These were expressed by the authors as $k_{12} = (1.9 \pm 0.5) \times 10^{12} \exp[-(1320 \pm 100)/T]$ and $k_{14} = (1.3 \pm 0.4) \times 10^{12} \exp[-(1780 \pm 150)/T]$.

These new data tend to confirm our recommendations for k_{12} and k_{14}.

SUMMARY TABLE

EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

HOMOGENEOUS GAS PHASE REACTIONS OF HALOGEN- AND CYANIDE-CONTAINING SPECIES

	Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
Br ATOM REACTIONS						
1	$Br + Br + M \rightarrow Br_2 + M$	$1.48 \times 10^{14} \exp(856/T)$ (M=Ar)	290 - 2000	± 0.18	C 2	d,g
2	$Br + BrCN \rightarrow CN + Br_2$	No recommendation	-	-	G 2	
3	$Br + BrCl \rightarrow Cl + Br_2$	2.0×10^{9}	298	± 1.0	E13	a
4	$Br + CH_4 \rightarrow HBr + CH_3$	$4.7 \times 10^{13} \exp(-9180/T)$	200 - 600	± 0.3	C 8	
5	$Br + ClO_2 \rightarrow BrO + ClO$	No recommendation	-	-	E24	
6	$Br + F_2 \rightarrow BrF + F$	No recommendation	-	-	E21	
7	$Br + H + M \rightarrow HBr + M$	$1.92 \times 10^{21}\ T^{-1.865}$ (M=Ar)	1500 - 4000	± 0.5	C 3	a
8	$Br + HBr \rightarrow H + Br_2$	$2.72 \times 10^{14} \exp(-22\ 340/T)$	500 - 1700	± 0.3	C 7	a
9	$Br + H_2 \rightarrow HBr + H$	$1.70 \times 10^{14} \exp(-9640/T)$	500 - 1700	± 0.18	C 4	
10	$Br + H_2O \rightarrow OH + HBr$	1.1×10^{-25}	295	± 0.5	C10	a
11	$Br + IBr \rightarrow I + Br_2$	No recommendation	-	-	E23	
12	$Br + ICl \rightarrow I + BrCl$	No recommendation	-	-	E22	
13	$Br + NF_2 + M \rightarrow NF_2Br + M$	No recommendation	-	-	E26	
14	$Br + NOCl \rightarrow NO + BrCl$	No recommendation	-	-	E25	
15	$Br + N_2O \rightarrow N_2 + BrO$	No recommendation	-	-	C19	
16	$Br + OH \rightarrow O + HBr$	$2.75 \times 10^{12} \exp(-8715/T)$	265 - 430	± 0.3	C 9	a
17	$Br + O_3 \rightarrow BrO + O_2$	$5.40 \times 10^{12} \exp(-640/T)$	200 - 360	± 0.18	C14	

BrCN MOLECULE REACTIONS (see also reaction 2)						
18	$BrCN + CN \rightarrow Br + (CN)_2$	No recommendation	-	-	G 3	
19	$BrCN + M \rightarrow Br + CN + M$	$7.2 \times 10^{14} \exp(-36\,800/T)$ (M=Ar)	2000 - 4000	± 0.2	G 1	
BrCl MOLECULE REACTIONS (see also reaction 3)						
20	$BrCl + Cl \rightarrow Br + Cl_2$	No recommendation	-	-	E17	
21	$BrCl + O \rightarrow Cl + BrO$	No recommendation	-	-	E27	
BrO RADICAL REACTIONS						
22	$BrO + BrO \rightarrow$ products	No recommendation	-	-	C13	
23	$BrO + ClO \rightarrow BrCl + O_2$	No recommendation	-	-	E28	
24	$BrO + NO \rightarrow Br + NO_2$	No recommendation	-	-	C17	
25	$BrO + O \rightarrow Br + O_2$	No recommendation	-	-	C15	
Br_2 MOLECULE REACTIONS						
26	$Br_2 + Cl \rightarrow Br + BrCl$	1.0×10^{14}	298	± 1.0	E13	
27	$Br_2 + F \rightarrow Br + BrF$	1.3×10^{14}	298 - 300	± 0.5	E 5	
28	$Br_2 + H \rightarrow HBr + Br$	$2.28 \times 10^{11} T \exp(-220/T)$	500 - 1700	± 0.3	C 6	h
29	$Br_2 + M \rightarrow Br + Br + M$	$2.35 \times 10^{14} \exp(-21\,630/T)$ (M=Ar)	1300 - 2500	± 0.5	C 1	b,g
30	$Br_2 + N \rightarrow NBr + Br$	No recommendation	-	-	C16	
31	$Br_2 + NO + NO \rightarrow 2NOBr$	$4.75 \times 10^{10} \exp(-630/T)$	270 - 330	± 0.12	C22	g
32	$Br_2 + O \rightarrow BrO + Br$	8.38×10^{12}	303 ± 3	± 0.06	C12	
33	$Br_2 + S \rightarrow SBr + Br$	No recommendation	-	-	C23	
C ATOM REACTION						
34	$C + CN \rightarrow N + C_2$	No recommendation	-	-	F14	
CF_4 MOLECULE REACTION (see also reactions 165 and 246)						
35	$CF_4 + M \rightarrow CF_3 + F + M$	No recommendation	-	-	A35	
CH_3 RADICAL REACTIONS						
36	$CH_3 + Cl_2 \rightarrow Cl + CH_3Cl$	2.16×10^{11}	300 ± 3	± 0.07	B61	
37	$CH_3 + HBr \rightarrow Br + CH_4$	$5.37 \times 10^{12} \exp(-810/T)$	300 - 500	± 0.3	C 8	i

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

	Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
CH_3 RADICAL REACTIONS continued						
38	$CH_3 + HCl \rightarrow Cl + CH_4$	$2.34 \times 10^{11} \exp(-1160/T)$	300 - 500	± 0.4	B 7	i
39	$CH_3 + HF \rightarrow F + CH_4$	4.1×10^{-11}	300	± 0.1	A 6	a
40	$CH_3 + HI \rightarrow I + CH_4$	$4.17 \times 10^{12} \exp(-650/T)$	350 - 600	± 0.2	D 9	i
41	$CH_3 + I_2 \rightarrow CH_3I + I$	No recommendation	-	-	D10	
CH_4 MOLECULE REACTIONS (see also reaction 4)						
42	$CH_4 + CN \rightarrow HCN + CH_3$	No recommendation	-	-	F 6	
43	$CH_4 + Cl \rightarrow HCl + CH_3$	$1.10 \times 10^{7}\ T^{1.97} \exp(-750/T)$	200 - 500	± 0.13	B 7	
44	$CH_4 + F \rightarrow HF + CH_3$	4.0×10^{13}	300 ± 3	± 0.08	A 6	
45	$CH_4 + I \rightarrow HI + CH_3$	No recommendation	-	-	D 9	
CN RADICAL REACTIONS (see also reactions 18,34 and 42)						
46	$CN + CN \rightarrow C_2 + N_2$	1.0×10^{13}	4500	± 0.2	F11	g,j
47	$CN + CN + M \rightarrow (CN)_2 + M$	$3.8 \times 10^{14} \exp(15\,000/T)$ (M=Ar)	2000 - 4000	± 0.3	F 1	a,g
48	$CN + CO_2 \rightarrow CO + CNO$	No recommendation	-	-	F15	
49	$CN + (CN)_2 \rightarrow$ products	3.2×10^{9}	300	± 0.5	F 2	j
50	$CN + H_2 \rightarrow HCN + H$	$6.8 \times 10^{13} \exp(-2700/T)$	300 - 1000	± 0.2	F 5	e
50'	$CN + H_2O \rightarrow HCN + OH$	No recommendation	-	-	F19	
51	$CN + M \rightarrow C + N + M$	$2.0 \times 10^{14} \exp(-75\,000/T)$ (M=Ar)	5000 - 12 000	± 0.2	F 4	c
52	$CN + N \rightarrow C + N_2$	No recommendation	-	-	F12	
53	$CN + N + M \rightarrow CN_2 + M$	No recommendation	-	-	F13	
54	$CN + NH_3 \rightarrow HCN + NH_2$	1.0×10^{13}	300 - 700	± 0.5	F10	j
55	$CN + NO \rightarrow CO + N_2$	No recommendation	-	-	F 9	f
56	$CN + O \rightarrow CO + N$	1.0×10^{13}	298	± 0.2	F 7	
57	$CN + O_2 \rightarrow CNO + O$	$2.4 \times 10^{13} \exp(-450/T)$	290 - 400	± 0.12	F 8	

CO MOLECULE REACTIONS						
58	$CO + F + M \rightarrow COF + M$	2.0×10^{16} (M=He)	295	± 0.3	A32	j
59	$CO + FO \rightarrow CO_2 + F$	No recommendation	-	-	A34	
60	$CO + F_2 \rightarrow COF + F$	No recommendation	-	-	A33	
60'	$CO + N_2 \rightarrow CN + NO$	No recommendation	-	-	F9	
COCl RADICAL REACTIONS						
61	$COCl + Cl \rightarrow CO + Cl_2$	$1.3 \times 10^{15} \exp(-1670/T)$	300 - 600	-	B60	k
62	$COCl + NOCl \rightarrow$ products	No recommendation	-	-	B46	
63	$COCl + NO_2 \rightarrow NO + Cl + CO_2$	No recommendation	-	-	B59	
COF_2 MOLECULE REACTION						
64	$COF_2 + M \rightarrow F + COF + M$	No recommendation	-	-	A31	
$(CN)_2$ MOLECULE REACTIONS (see also reaction 49)						
64'	$(CN)_2 + H \rightarrow HCN + CN$	No recommendation		-	F18	
65	$(CN)_2 + M \rightarrow CN + CN + M$	$3.2 \times 10^{16} \exp(-47\ 500/T)$ (M=Ar)	2000 - 4000	± 0.3	F 1	g
66	$(CN)_2 + O \rightarrow CN + CNO$	$2.5 \times 10^{13} \exp(-5500/T)$	500 - 700	± 0.3	F 3	
Cl ATOM REACTIONS (see also reactions 20,26,43 and 61)						
67	$Cl + CD_4 \rightarrow DCl + CD_3$	$1.49 \times 10^{7}\ T^{1.97} \exp(-1580/T)$	300 - 500	± 0.25	B 7	
68	$Cl + Cl + M \rightarrow Cl_2 + M$	$2.23 \times 10^{14} \exp(906/T)$ (M=Ar)	195 - 520	± 0.15	B 2	b,d,g
69	$Cl + ClO \rightarrow O + Cl_2$	$1.05 \times 10^{12} \exp(-4590/T)$	174 - 602	± 0.18	B12	a
70	$Cl + ClONO_2 \rightarrow$ products	No recommendation	-	-	B50	
71	$Cl + ClOO \rightarrow$ products	No recommendation	-	-	B18	
72	$Cl + ClO_2 \rightarrow ClO + ClO$	3.6×10^{13}	298	± 0.18	B11	
73	$Cl + Cl_2O \rightarrow ClO + Cl_2$	No recommendation	-	-	B20	
74	$Cl + F_2 \rightarrow ClF + F$	No recommendation	-	-	E16	
75	$Cl + H + M \rightarrow HCl + M$	$2.6 \times 10^{13} \exp(9940/T)$ (M=Ar)	2900 - 7000	± 0.2	B 3	a
76	$Cl + HBr \rightarrow HCl + Br$	4.7×10^{12}	295	± 0.07	E14	
76'	$Cl + HCl \rightarrow H + Cl_2$	$1.0 \times 10^{14} \exp(-23\ 885/T)$	250 - 730	± 0.18	B6	a
77	$Cl + HI \rightarrow HCl + I$	No recommendation	-	-	E15	
78	$Cl + HNO_3 \rightarrow$ products	No recommendation	-	-	B58	
79	$Cl + HO_2 \rightarrow HCl + O_2$	1.66×10^{13}	300 ± 5	>± 0.5	B24	
80	$Cl + H_2 \rightarrow H + HCl$	$1.45 \times 10^{13} \exp(-2200/T)$	200 - 650	± 0.2	B 4	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

	Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
	<u>Cl ATOM REACTIONS</u> continued					
81	$Cl + H_2O \rightarrow OH + HCl$	$1.68 \times 10^{13} \exp(-8670/T)$	210 - 500	± 0.1	B 9	a, c, e
82	$Cl + H_2O_2 \rightarrow HCl + HO_2$	No recommendation	-	-	B16	
83	$Cl + I + M \rightarrow ICl + M$	No recommendation	-	-	E19	
84	$Cl + ICl \rightarrow I + Cl_2$	No recommendation	-	-	E18	
85	$Cl + NCl_2 \rightarrow NCl + Cl_2$	No recommendation	-	-	B30	
86	$Cl + NF_2 + M \rightarrow NF_2Cl + M$	No recommendation	-	-	E20	
87	$Cl + NO + M \rightarrow NOCl + M$	$5.3 \times 10^{15} \exp(520/T)$ $(M=Cl_2)$	200 - 670	± 0.25	B35	b
88	$Cl + NOCl \rightarrow NO + Cl_2$	No recommendation	-	-	B38	
89	$Cl + N_2O \rightarrow N_2 + ClO$	No recommendation	-	-	B56	
90	$Cl + N_3Cl \rightarrow N_3 + Cl_2$	No recommendation	-	-	B32	
91	$Cl + OH \rightarrow O + HCl$	$5.9 \times 10^{12} \exp(-2860/T)$	290 - 720	± 0.3	B 8	a
92	$Cl + O_2 \rightarrow O + ClO$	$8.76 \times 10^{14} \exp(-27\ 700/T)$	200 - 500	± 0.18	B13	a
93	$Cl + O_2 + M \rightarrow ClOO + M$	No recommendation	-	-	B17	
94	$Cl + O_3 \rightarrow ClO + O_2$	$1.48 \times 10^{13} \exp(-210/T)$	200 - 400	± 0.15	B10	
	<u>ClCN MOLECULE REACTION</u>					
95	$ClCN + M \rightarrow Cl + CN + M$	No recommendation	-	-	G 4	
	<u>ClF MOLECULE REACTION</u>					
96	$ClF + M \rightarrow F + Cl + M$	No recommendation	-	-	E 7	
	<u>ClF_3 MOLECULE REACTIONS</u>					
97	$ClF_3 + H \rightarrow$ products	No recommendation	-	-	E12	
98	$ClF_3 + M \rightarrow ClF_2 + F + M$	No recommendation	-	-	E11	
99	$ClF_3 + NF_2 \rightarrow$ products	No recommendation	-	-	E31	

ClO RADICAL REACTIONS (see also reactions 23 and 69)

100	$ClO + ClO \rightarrow$ products	$5.75 \times 10^{11} \exp(-1295/T)$	295 - 600	± 0.18	B15	g
101	$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	No recommendation	-	-	B21	
102	$ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl$	No recommendation	-	-	B22	
103	$ClO + NO \rightarrow Cl + NO_2$	1.0×10^{13}	298	± 0.3	B33	f
104	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$1.68 \times 10^{15} \exp(1070/T)$ $(M=N_2)$	240 - 500	± 0.08	B48	d
105	$ClO + O \rightarrow Cl + O_2$	$5.70 \times 10^{13} \exp(-183/T)$	200 - 500	± 0.18	B13	
106	$ClO + O_2 \rightarrow O + ClO_2$	3.5×10^{-34}	298	± 0.25	B14	a
107	$ClO + O_3 \rightarrow$ products	No recommendation	-	-	B23	

$ClONO_2$ MOLECULE REACTIONS (see also reaction 70)

108	$ClONO_2 + O \rightarrow$ products	$1.83 \times 10^{12} \exp(-810/T)$	213 - 295	± 0.18	B49	
109	$ClONO_2 + OH \rightarrow$ products	No recommendation	-	-	B51	

ClO_2 MOLECULE REACTIONS (see also reactions 5 and 72)

110	$ClO_2 + F_2 \rightarrow F + FClO_2$	No recommendation	-	-	E 9	
111	$ClO_2 + H \rightarrow ClO + OH$	3.4×10^{13}	298	± 0.15	B26	
112	$ClO_2 + NO \rightarrow NO_2 + ClO$	No recommendation	-	-	B54	
113	$ClO_2 + NO_2 \rightarrow NO_3 + ClO$	No recommendation	-	-	B55	
114	$ClO_2 + O \rightarrow ClO + O_2$	3.3×10^{11}	298	± 0.25	B14	

Cl_2 MOLECULE REACTIONS (see also reaction 36)

115	$Cl_2 + F \rightarrow ClF + Cl$	No recommendation	-	-	E 1	
116	$Cl_2 + H \rightarrow Cl + HCl$	$8.6 \times 10^{13} \exp(-590/T)$	250 - 730	± 0.18	B 6	
117	$Cl_2 + M \rightarrow Cl + Cl + M$	$2.32 \times 10^{13} \exp(-23\,630/T)$ $(M=Ar)$	1550 - 2800	± 0.18	B 1	b,g
118	$Cl_2 + N \rightarrow NCl + Cl$	No recommendation	-	-	B28	
119	$Cl_2 + NCl \rightarrow NCl_2 + Cl$	No recommendation	-	-	B29	
120	$Cl_2 + NO + NO \rightarrow 2NOCl$	$4.1 \times 10^{10} \exp(-2500/T)$	250 - 500	± 0.11	B37	g
121	$Cl_2 + O \rightarrow Cl + ClO$	$2.51 \times 10^{12} \exp(-1368/T)$	174 - 602	± 0.18	B12	
122	$Cl_2 + S \rightarrow SCl + Cl$	No recommendation	-	-	B62	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
Cl_2O MOLECULE REACTIONS (see also reactions 73,101 and 102)					
123 $Cl_2O + H \rightarrow$ products	No recommendation	-	-	B27	
124 $Cl_2O + N \rightarrow NCl + ClO$	No recommendation	-	-	B52	
125 $Cl_2O + NO_2 \rightarrow NO_2Cl + ClO$	No recommendation	-	-	B53	
126 $Cl_2O + O \rightarrow ClO + ClO$	No recommendation	-	-	B19	
DI MOLECULE REACTION					
127 $DI + DI \rightarrow D_2 + I_2$	$4.73 \times 10^{13} \exp(-22\,690/T)$	660 - 780	± 0.08	D 7	g
F ATOM REACTIONS (see also reactions 27,44,58 and 115)					
128 $F + F + M \rightarrow F_2 + M$	$3.25 \times 10^{8}\ T \exp(3190/T)$ (M=Ar)	1400 - 2600	± 0.11	A 2	a,g
129 $F + F_2O \rightarrow FO + F_2$	No recommendation	-	-	A13	
130 $F + H + M \rightarrow HF + M$	$7.5 \times 10^{12} \exp(17\,680/T)$ (M=Ar)	3500 - 6000	± 0.3	A 3	a
131 $F + HBr \rightarrow HF + Br$	3.3×10^{13}	300	± 0.2	E 3	j
132 $F + HCl \rightarrow HF + Cl$	7.0×10^{12}	298 - 300	± 0.08	E 2	
133 $F + HF \rightarrow H + F_2$	$1.33 \times 10^{13} \exp(-50\,680/T)$	298 - 500	± 0.23	A 5	a
134 $F + HI \rightarrow HF + I$	4.1×10^{13}	300 ± 3	± 0.15	E 4	j
135 $F + H_2 \rightarrow HF + H$	1.5×10^{13}	300 ± 3	± 0.11	A 4	f
136 $F + ICl \rightarrow$ products	No recommendation	-	-	E 8	
137 $F + I_2 \rightarrow I + IF$	No recommendation	-	-	E 6	
138 $F + NF_2 + M \rightarrow NF_3 + M$	$1.9 \times 10^{14} \exp(4500/T)$ (M=Ar)	1000 - 2000	± 0.3	A16	a
138'F $+ NF_3 \rightarrow NF_2 + F_2$	No recommendation	-	-	A18	
139 $F + NO + M \rightarrow NOF + M$	3.0×10^{16} (M=He)	250 - 300	± 0.2	A22	b
140 $F + NOCl \rightarrow$ products	No recommendation	-	-	E10	
141 $F + NO_2 + M \rightarrow NO_2F + M$	No recommendation	-	-	A25	
142 $F + O_2 + M \rightarrow FO_2 + M$	2.07×10^{15} (M=He)	291 - 300	± 0.1	A 9	
143 $F + O_3 \rightarrow FO + O_2$	No recommendation	-	-	A 8	

FO RADICAL REACTION (see also reaction 59)										
144	FO	+ FO	→ F	+ F	+ O_2	No recommendation	-	-	A10	
F_2 MOLECULE REACTIONS (see also reactions 6,60,74 and 110)										
145	F_2	+ H	→ HF	+ F		8.8 x 10^{13} exp(-1210/T)	290 - 570	± 0.23	A 5	
146	F_2	+ M	→ F	+ F	+ M	2.12 x 10^{13} exp(-16 970/T)(M=Ar)	1400 - 2600	± 0.11	A 1	d,e,g
147	F_2	+ NF_2	→ NF_3	+ F		No recommendation	-	-	A18	
148	F_2	+ NO	→ NOF	+ F		4.2 x 10^{11} exp(-1150/T)	250 - 375	± 0.5	A23	
149	F_2	+ NO_2	→ NO_2F	+ F		No recommendation	-	-	A26	
150	F_2	+ NO_3F	→ NO_2F	+ F	+ FO	No recommendation	-	-	A30	
151	F_2	+ O	→ F	+ FO		No recommendation	-	-	A11	
152	F_2	+ OH	→ HF	+ F	+ O	No recommendation	-	-	A12	
153	F_2	+ S	→ SF	+ F		No recommendation	-	-	A44	
F_2O MOLECULE REACTION (see also reaction 129)										
154	F_2O	+ M	→ F	+ FO	+ M	1.8 x 10^{15} exp(-17 500/T)(M=Ar)	800 - 1300	± 0.5	A 7	b,d
155	F_2O	+ NF_2	→ NF_3	+ FO		No recommendation	-	-	A28	
156	F_2O	+ NO_2	→ NO_2F	+ FO		No recommendation	-	-	A27	
F_2O_2 MOLECULE REACTION										
157	F_2O_2	+ M	→ F	+ FO_2	+ M	No recommendation	-	-	A14	
F_2SO_2 MOLECULE REACTION										
158	F_2SO_2	+ M	→ SO_2F	+ F	+ M	No recommendation	-	-	A42	
F_2SO_3 MOLECULE REACTION										
159	F_2SO_3	+ M	→ F	+ FSO_3	+ M	1.0 x 10^{15} exp(-16 500/T)	360 - 390	± 0.2	A41	b,j,1
$F_2S_2O_6$ MOLECULE REACTIONS										
160	$F_2S_2O_6$	+ M	→ FSO_3	+ FSO_3	+ M	3.5 x 10^{15} exp(-12 000/T)	260 - 290	± 0.2	A40	j,1
161	$F_2S_2O_6$	+ NO	→ FSO_3	+ FSO_3NO		No recommendation	-	-	A43	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
H ATOM REACTIONS (see also reactions 7,28,75,97,111,116,123,130 and 145)					
162 H + CCl_4 → CCl_3 + HCl	No recommendation	-	-	H 1	
163 H + CF_3Br → CF_3 + HBr	1.47 x 10^{14} exp(-4700/T)	700 - 1700	± 0.3	H 1	
164 H + CF_3Cl → CF_3 + HCl	No recommendation	-	-	H 1	
165 H + CF_4 → CF_3 + HF	No recommendation	-	-	H 1	
166 H + CHF_3 → CF_3 + H_2	No recommendation	-	-	H 1	
167 H + CH_2Cl_2 → CH_2Cl + HCl	No recommendation	-	-	H 1	
168 H + CH_3Br → CH_3 + HBr	5.10 x 10^{13} exp(-2940/T)	298 - 2000	± 0.5	H 1	
169 H + CH_3Cl → CH_3 + HCl	No recommendation	-	-	H 1	
170 H + CH_3F → CH_3 + HF	2.30 x 10^{13} exp(-4950/T)	600 - 1000	± 0.7	H 1	
171 H + CH_3I → CH_3 + HI	No recommendation	-	-	H 1	
172 H + HBr → H_2 + Br	6.25 x 10^{13} exp(-1210/T)	500 - 1700	± 0.18	C 5	a
173 H + HCN → CN + H_2	3.8 x 10^{14} exp(-12 400/T)	300 - 1000	± 0.5	F 5	a
174 H + HCl → Cl + H_2	7.97 x 10^{12} exp(-1710/T)	200 - 650	± 0.2	B 5	a
175 H + HF → F + H_2	No recommendation	-	-	A 4	
176 H + HI → H_2 + I	4.74 x 10^{13} exp(-330/T)	600 - 1000	± 0.08	D 4	a
177 H + I_2 → HI + I	4.31 x 10^{14} exp(-217/T)	600 - 800	± 0.2	D 5	
178 H + NF_3 → NF_2 + HF	No recommendation	-	-	A21	
179 H + NOCl → NO + HCl	1.0 x 10^{13}	300	± 0.3	B39	
HBr MOLECULE REACTIONS (see also reactions 8,37,76,131 and 172)					
180 HBr + M → H + Br + M	8.5 x 10^{21} T^{-2} exp(-44 280/T)(M=Ar)	1450 - 4000	± 0.5	C 3	d
181 HBr + N → NH + Br	No recommendation	-	-	C21	
182 HBr + NO_2 → HNO_2 + Br	No recommendation	-	-	C20	

183	$HBr + O \rightarrow Br + OH$	$2.4 \times 10^{12} \exp(-1360/T)$	265 - 430	± 0.3	C 9	c,e
184	$HBr + OH \rightarrow Br + H_2O$	2.9×10^{12}	295	± 0.5	C10	j
185	$HBr + O_2 \rightarrow Br + HO_2$	No recommendation	-	-	C11	
<u>HCN MOLECULE REACTION</u> (see also reaction 173)						
186	$HCN + M \rightarrow H + CN + M$	No recommendation	-	-	F17	
<u>HCl MOLECULE REACTIONS</u> (see also reactions 38,132 and 174)						
187	$HCl + M \rightarrow H + Cl + M$	$4.4 \times 10^{13} \exp(-41\,140/T)$ (M=Ar)	2900 - 7000	± 0.2	B 3	b
188	$HCl + NO_2 \rightarrow HNO_2 + Cl$	No recommendation	-	-	B57	
189	$HCl + O \rightarrow Cl + OH$	$6.87 \times 10^{12} \exp(-3370/T)$	290 - 720	± 0.3	B 8	e
190	$HCl + OH \rightarrow Cl + H_2O$	$2.25 \times 10^{12} \exp(-514/T)$	210 - 500	± 0.1	B 9	c,e
191	$HCl + O_2 \rightarrow HO_2 + Cl$	No recommendation	-	-	B25	
<u>HF MOLECULE REACTION</u> (see also reactions 39,133 and 175)						
192	$HF + M \rightarrow H + F + M$	$3.12 \times 10^{13} \exp(-49\,980/T)$ (M=Ar)	3500 - 6500	± 0.3	A 3	b
<u>HI MOLECULE REACTIONS</u> (see also reactions 40,77,134 and 176)						
193	$HI + HI \rightarrow H_2 + I_2$	$2.55 \times 10^{13} \exp(-22\,020/T)$	400 - 800	± 0.12	D 7	a,g
194	$HI + HNO \rightarrow H_2 + NOI$	No recommendation	-	-	D23	
195	$HI + I \rightarrow H + I_2$	2.63×10^{6}	1000	± 0.2	D 5	a
196	$HI + NO \rightarrow HNO + I$	No recommendation	-	-	D22	
197	$HI + OH \rightarrow I + H_2O$	6.9×10^{12}	298	± 0.25	D 8	j
198	$HI + O_2 \rightarrow I + HO_2$	No recommendation	-	-	D13	
<u>HNO MOLECULE REACTION</u> (see also reaction 194)						
199	$HNO + I_2 \rightarrow HI + NOI$	No recommendation	-	-	D24	
<u>HNO_3 MOLECULE REACTION</u> (see reaction 78)						
<u>HO_2 RADICAL REACTION</u> (see reaction 79)						
<u>H_2 MOLECULE REACTIONS</u> (see also reactions 9,50,80 and 135)						
200	$H_2 + I \rightarrow HI + H$	$1.69 \times 10^{14} \exp(-16\,930/T)$	600 - 1000	± 0.08	D 3	
201	$H_2 + I + I \rightarrow HI + HI$	see reaction 202	-	-	D 6	g
202	$H_2 + I_2 \rightarrow HI + HI$	$1.94 \times 10^{14} \exp(-20\,620/T)$	400 - 800	± 0.12	D 6	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
H_2O MOLECULE REACTIONS (see reactions 10 and 81)					
H_2O_2 MOLECULE REACTION (see reaction 82)					
I ATOM REACTIONS (see also reactions 45,83,195,200 and 201)					
203 I + I + M → I_2 + M	2.36×10^{14} exp(754/T) (M=Ar)	290 - 1250	± 0.1	D 2	b,d,g,h
204 I + NO + M → NOI + M	No recommendation	-	-	D15	f
205 I + NOI → NO + I_2	No recommendation	-	-	D17	
206 I + NO_2 + M → NO_2I + M	No recommendation	-	-	D18	
207 I + NO_2I → NO_2 + I_2	No recommendation	-	-	D19	
208 I + N_2O → N_2 + IO	No recommendation	-	-	D21	
209 I + O_3 → IO + O_2	No recommendation	-	-	D11	
IBr MOLECULE REACTION (see also reaction 11)					
210 IBr + N → products	No recommendation	-	-	E30	
ICl MOLECULE REACTION (see also reactions 12,84 and 136)					
211 ICl + N → products	No recommendation	-	-	E29	
IO RADICAL REACTION					
212 IO + IO → IOO + I	No recommendation	-	-	D12	
I_2 MOLECULE REACTIONS (see also reaction 41,137,177,199 and 202)					
213 I_2 + M → I + I + M	8.25×10^{13} exp(-15 250/T) (M=Ar,N_2)	800 - 2000	± 0.08	D 1	b,g
214 I_2 + N → NI + I	No recommendation	-	-	D14	
N ATOM REACTION (see also reactions 30,52,53,118,124,181,210,211 and 214)					
215 N + NOCl → NO + NCl	No recommendation	-	-	B40	
NCl RADICAL REACTION (see reaction 119)					

NCl_2 RADICAL REACTION (see also reaction 85)						
216	$NCl_2 + NCl_2 \rightarrow$ products	No recommendation	-	-	B31	
NF RADICAL REACTION						
217	$NF + NF \rightarrow N_2 + F_2$	No recommendation	-	-	A19	g
NF_2 RADICAL REACTIONS (see also reactions 13,86,99,138,147 and 155)						
218	$NF_2 + M \rightarrow NF + F + M$	$7.6 \times 10^{14} \exp(-25\,700/T)$ (M=Ar)	1500 - 2500	± 0.5	A17	b
219	$NF_2 + NF_2 \rightarrow NF_3 + NF$	No recommendation	-	-	A20	g
220	$NF_2 + NF_2 + M \rightarrow N_2F_4 + M$	4.7×10^{15} (M=Ar)	293	± 0.2	A15	b,g
NF_3 MOLECULE REACTION (see also reaction 178)						
221	$NF_3 + M \rightarrow NF_2 + F + M$	$4.1 \times 10^{16} \exp(-24\,160/T)$ (M=Ar)	1100 - 1800	± 0.3	A16	
NH_3 MOLECULE REACTION (see reaction 54)						
NO MOLECULE REACTION (see also reactions 24,31,55,87,103,112,120,139,148,161,196 and 204)						
222	$NO + NO_2Cl \rightarrow NOCl + NO_2$	No recommendation	-	-	B43	
NOBr MOLECULE REACTIONS						
223	$NOBr + M \rightarrow NO + Br + M$	No recommendation	-	-	C18	
224	$NOBr + NOBr \rightarrow NO + NO + Br_2$	$1.2 \times 10^{12} \exp(-5990/T)$	270 - 330	± 0.12	C22	a,g
NOCN MOLECULE REACTION						
225	$NOCN + M \rightarrow NO + CN + M$	No recommendation	-	-	F16	
NOCl MOLECULE REACTIONS (see also reactions 14,62,88,140,179 and 215)						
225'	$NOCl + M \rightarrow NO + Cl + M$	$1.3 \times 10^{15} \exp(-16\,100/T)$ (M=Ar)	800 - 1500	± 0.3	B34	b,d
226	$NOCl + NO_2 \rightarrow NO_2Cl + NO$	No recommendation	-	-	B42	
226'	$NOCl + NOCl \rightarrow NO + NO + Cl_2$	$1.0 \times 10^{12} \exp(-11\,400/T)$	250 - 500	± 0.18	B36	a,g
227	$NOCl + NO_2Cl \rightarrow NO + NO_2 + Cl_2$	No recommendation	-	-	B45	
228	$NOCl + NO_3 \rightarrow NO_2Cl + NO_2$	No recommendation	-	-	B44	
229	$NOCl + O \rightarrow NO + ClO$	2.5×10^{10}	298	± 0.2	B41	j
NOI MOLECULE REACTION (see also reaction 205)						
230	$NOI + NOI \rightarrow NO + NO + I_2$	$5.0 \times 10^{13} \exp(-2600/T)$	320 - 450	± 0.24	D16	g,j
NO_2 MOLECULE REACTION (see also reactions 63,104,113,125,141,149,156,182,206 and 226)						
231	$NO_2 + NO_3F \rightarrow NO_2F + NO_3$	No recommendation	-	-	A29	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

Reaction	Rate Constant k (cm-mol-s units)	Temperature Range (K)	Error in log k	Section	Notes
NO_2Cl MOLECULE REACTION (see also reactions 222 and 227)					
232 $NO_2Cl + M \rightarrow NO_2 + Cl + M$	$5.5 \times 10^{14} \exp(-12\,700/T)$ (M=Ar)	450 - 1000	± 0.25	B47	b,d
NO_2I MOLECULE REACTION (see also reaction 207)					
233 $NO_2I + NO_2I \rightarrow NO_2 + NO_2 + I_2$	No recommendation	-	-	D20	g
NO_3 RADICAL REACTION (see reaction 228)					
NO_3F MOLECULE REACTION (see also reactions 150 and 231)					
234 $NO_3F + M \rightarrow NO_3 + F + M$	$1.6 \times 10^{15} \exp(-16\,000/T)$	350 - 390	± 0.11	A24	b,l
N_2F_4 MOLECULE REACTION					
235 $N_2F_4 + M \rightarrow NF_2 + NF_2 + M$	$1.39 \times 10^{15} \exp(-9990/T)$	300 - 500	± 0.28	A15	b,g,j,l
N_2O MOLECULE REACTIONS (see reactions 15,89 and 208)					
N_3Cl MOLECULE REACTION (see reaction 90)					
O ATOM REACTIONS (see also reactions 21,25,32,56,66,105,108,114,121,126,151,183,189 and 229)					
236 $O + CCl_4 \rightarrow CCl_3 + ClO$	No recommendation	-	-	H 2	
237 $O + CF_3Br \rightarrow CF_3 + BrO$	No recommendation	-	-	H 2	
238 $O + CHCl_3 \rightarrow CCl_3 + OH$	No recommendation	-	-	H 2	
239 $O + CHF_3 \rightarrow CF_3 + OH$	No recommendation	-	-	H 2	
240 $O + CH_2Cl_2 \rightarrow CHCl_2 + OH$	No recommendation	-	-	H 2	
241 $O + CH_2F_2 \rightarrow CHF_2 + OH$	No recommendation	-	-	H 2	
242 $O + CH_3Br \rightarrow CH_2Br + OH$	$1.33 \times 10^{13} \exp(-3700/T)$	350 - 1000	± 0.3	H 2	j
243 $O + CH_3Cl \rightarrow CH_2Cl + OH$	$1.05 \times 10^{13} \exp(-3450/T)$	300 - 1000	± 0.3	H 2	c
244 $O + CH_3F \rightarrow CH_2F + OH$	No recommendation	-	-	H 2	

OH RADICAL REACTIONS (see also reactions 16,91,109,152,184,190 and 197)								
245	OH	+ CCl_4	→ CCl_3 + HOCl	No recommendation	-	-	H 3	
246	OH	+ CF_4	→ CF_3 + HOF	No recommendation	-	-	H 3	
247	OH	+ $CHCl_3$	→ CCl_3 + H_2O	$2.82 \times 10^{12} \exp(-1130/T)$	240 - 380	± 0.3	H 3	
248	OH	+ $CHFCl_2$	→ $CFCl_2$ + H_2O	$8.57 \times 10^{11} \exp(-1160/T)$	240 - 450	± 0.1	H 3	
249	OH	+ CHF_2Cl	→ CF_2Cl + H_2O	$7.67 \times 10^{11} \exp(-1670/T)$	250 - 450	± 0.1	H 3	
250	OH	+ CHF_3	→ CF_3 + H_2O	No recommendation	-	-	H 3	
251	OH	+ CH_2Cl_2	→ $CHCl_2$ + H_2O	$2.89 \times 10^{12} \exp(-1090/T)$	240 - 400	± 0.2	H 3	
252	OH	+ CH_2FCl	→ $CHFCl$ + H_2O	$1.81 \times 10^{12} \exp(-1280/T)$	240 - 380	± 0.18	H 3	j
253	OH	+ CH_2F_2	→ CHF_2 + H_2O	No recommendation	-	-	H 3	
254	OH	+ CH_3Br	→ CH_2Br + H_2O	$4.42 \times 10^{11} \exp(-873/T)$	240 - 360	± 0.18	H 3	
255	OH	+ CH_3CCl_3	→ CH_2CCl_3 + H_2O	$2.11 \times 10^{12} \exp(-1560/T)$	260 - 400	± 0.1	H 3	
256	OH	+ CH_3Cl	→ CH_2Cl + H_2O	$1.61 \times 10^{12} \exp(-1220/T)$	250 - 450	± 0.1	H 3	
257	OH	+ CH_3F	→ CH_2F + H_2O	No recommendation	-	-	H 3	
O_2 MOLECULE REACTIONS (see reactions 57,92,93,106,142,185,191 and 198)								
O_3 MOLECULE REACTIONS (see reactions 17,94,107,143 and 209)								
S ATOM REACTIONS (see reactions 33, 122 and 153)								
SF_3 RADICAL REACTION								
258	SF_3	+ M	→ SF_2 + F + M	No recommendation	-	-	A38	
SF_4 MOLECULE REACTION								
259	SF_4	+ M	→ SF_3 + F + M	No recommendation	-	-	A37	
SF_5 RADICAL REACTION								
260	SF_5	+ SF_5	→ SF_6 + SF_4	No recommendation	-	-	A39	
SF_6 MOLECULE REACTION								
261	SF_6	+ M	→ SF_5 + F + M	No recommendation	-	-	A36	

SUMMARY TABLE (continued). EVALUATED KINETIC DATA FOR HIGH TEMPERATURE REACTIONS, VOLUME IV

a. Rate constant k_f calculated using $k_f = k_r K_c$

b. Relative efficiencies of other collision partners (M) are discussed in the main text.

c. Error in log k is greater at the lower end of the temperature range.

d. Expressions for rate constant using different collision partners given in the main text.

e. Error in log k is greater at the higher end of the temperature range.

f. See note added in proof to the main text.

g. The rate constant k of the elementary reaction aA + bB + ... → mM + nN + ... is defined by the relat

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \dots = k[A]^a[B]^b \dots = \frac{1}{m}\frac{d[M]}{dt} = \frac{1}{n}\frac{d[N]}{dt} = \dots$$

h. An alternative expression is given in the main text.

i. This recommendation is that of KERR and PARSONAGE (1976).

j. Expression is based on two sets of data only.

k. This expression is probably an upper limit.

l. This expression is for the high pressure first order rate constant.

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CH_3F	+ O		→ CH_2F	+ OH		H 2
CH_3F	+ OH		→ CH_2F	+ H_2O		H 3
CH_3I	+ H		→ CH_3	+ HI		H 1
CH_4	+ Br		→ HBr	+ CH_3		C 8
CH_4	+ CN		→ HCN	+ CH_3		F 6
CH_4	+ Cl		→ HCl	+ CH_3		B 7
CH_4	+ F		→ HF	+ CH_3		A 6
CH_4	+ I		→ HI	+ CH_3		D 9
CN	+ BrCN		→ Br	+ $(CN)_2$		G 3
CN	+ C		→ N	+ C_2		F14
CN	+ CD_4		→ DCN	+ CD_3		F 6
CN	+ CH_4		→ HCN	+ CH_3		F 6
CN	+ CN		→ C_2	+ N_2		F11
CN	+ CN	+ M	→ $(CN)_2$	+ M		F 1
CN	+ CO_2		→ CO	+ CNO		F15
CN	+ $(CN)_2$		→ products			F 2
CN	+ H_2		→ HCN	+ H		F 5
CN	+ M		→ C	+ N	+ M	F 4
CN	+ N		→ C	+ N_2		F12
CN	+ N	+ M	→ CN_2	+ M		F13
CN	+ NH_3		→ HCN	+ NH_2		F10
CN	+ NO		→ CO	+ N_2		F 9
CN	+ O		→ CO	+ N		F 7
CN	+ O_2		→ CNO	+ O		F 8
CO	+ F	+ M	→ COF	+ M		A32
CO	+ FO		→ CO_2	+ F		A34
CO	+ F_2		→ COF	+ F		A33
CO	+ N_2		→ CN	+ NO		F 9
COCl	+ Cl		→ CO	+ Cl_2		B60
COCl	+ NOCl		→ products			B46
COCl	+ NO_2		→ NO	+ Cl	+ CO_2	B59
COF_2	+ M		→ F	+ COF	+ M	A31
CO_2	+ CN		→ CO	+ CNO		F15
$(CN)_2$	+ CN		→ products			F 2
$(CN)_2$	+ M		→ CN	+ CN	+ M	F 1
$(CN)_2$	+ O		→ CN	+ CNO		F 3
Cl	+ BrCl		→ Br	+ Cl_2		E17
Cl	+ Br_2		→ Br	+ BrCl		E13
Cl	+ CD_4		→ DCl	+ CD_3		B 7
Cl	+ CH_2D_2		→ DCl	+ CH_2D		B 7
Cl	+ CH_2D_2		→ HCl	+ CHD_2		B 7
Cl	+ CH_4		→ HCl	+ CH_3		B 7
Cl	+ COCl		→ CO	+ Cl_2		B60
Cl	+ Cl	+ M	→ Cl_2	+ M		B 2
Cl	+ ClO		→ O	+ Cl_2		B12
Cl	+ $ClONO_2$		→ products			B50
Cl	+ ClOO		→ products			B18
Cl	+ ClO_2		→ ClO	+ ClO		B11
Cl	+ Cl_2O		→ ClO	+ Cl_2		B20
Cl	+ DT		→ D	+ TCl		B 4
Cl	+ DT		→ T	+ DCl		B 4
Cl	+ D_2		→ D	+ DCl		B 4
Cl	+ F_2		→ ClF	+ F		E16
Cl	+ H	+ M	→ HCl	+ M		B 3
Cl	+ HBr		→ HCl	+ Br		E14
Cl	+ HCl		→ H	+ Cl_2		B 6
Cl	+ HD		→ D	+ HCl		B 4
Cl	+ HD		→ H	+ DCl		B 4
Cl	+ HI		→ HCl	+ I		E15
Cl	+ HNO_3		→ products			B58
Cl	+ HO_2		→ HCl	+ O_2		B24
Cl	+ HT		→ H	+ TCl		B 4
Cl	+ HT		→ T	+ HCl		B 4
Cl	+ H_2		→ H	+ HCl		B 4
Cl	+ H_2O		→ OH	+ HCl		B 9
Cl	+ H_2O_2		→ HCl	+ HO_2		B16
Cl	+ I	+ M	→ ICl	+ M		E19
Cl	+ ICl		→ I	+ Cl_2		E18
Cl	+ NCl_2		→ NCl	+ Cl_2		B30
Cl	+ NF_2	+ M	→ NF_2Cl	+ M		E20
Cl	+ NO	+ M	→ NOCl	+ M		B35
Cl	+ NOCl		→ NO	+ Cl_2		B38
Cl	+ NO_2	+ M	→ NO_2Cl	+ M		B47
Cl	+ N_2O		→ N_2	+ ClO		B56
Cl	+ N_3Cl		→ N_3	+ Cl_2		B32
Cl	+ OH		→ O	+ HCl		B 8
Cl	+ O_2		→ O	+ ClO		B13
Cl	+ O_2	+ M	→ ClOO	+ M		B17
Cl	+ O_3		→ ClO	+ O_2		B10
Cl	+ T_2		→ T	+ TCl		B 4

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NCl_2	+ NCl_2		→ products			B31
NF	+ NF		→ N_2	+ F	+ F	A19
NF_2	+ Br	+ M	→ NF_2Br	+ M		E26
NF_2	+ Cl	+ M	→ NF_2Cl	+ M		E20
NF_2	+ ClF_3		→ NF_3	+ ClF_2		E31
NF_2	+ F	+ M	→ NF_3	+ M		A16
NF_2	+ F_2		→ NF_3	+ F		A18
NF_2	+ F_2O		→ NF_3	+ FO		A28
NF_2	+ M		→ NF	+ F	+ M	A17
NF_2	+ NF_2		→ NF_3	+ NF		A20
NF_2	+ NF_2	+ M	→ N_2F_4	+ M		A15
NF_3	+ F		→ NF_2	+ F_2		A18
NF_3	+ H		→ NF_2	+ HF		A21
NF_3	+ M		→ NF_2	+ F	+ M	A16
NH_3	+ CN		→ HCN	+ NH_2		F10
NO	+ BrO		→ Br	+ NO_2		C17
NO	+ CN		→ CO	+ N_2		F 9
NO	+ Cl	+ M	→ NOCl	+ M		B35
NO	+ ClO		→ Cl	+ NO_2		B33
NO	+ ClO_2		→ NO_2	+ ClO		B54
NO	+ Cl_2		→ NOCl	+ Cl		B38
NO	+ F	+ M	→ NOF	+ M		A22
NO	+ F_2		→ NOF	+ F		A23
NO	+ $F_2S_2O_6$		→ FSO_3	+ FSO_3NO		A43
NO	+ HI		→ HNO	+ I		D22
NO	+ I	+ M	→ NOI	+ M		D15
NO	+ NO	+ Br_2	→ 2NOBr			C22
NO	+ NO	+ Cl_2	→ 2NOCl			B37
NO	+ NO_2Cl		→ NOCl	+ NO_2		B43
NOBr	+ M		→ NO	+ Br	+ M	C18
NOBr	+ NOBr		→ NO	+ NO	+ Br_2	C22
NOCN	+ M		→ NO	+ CN	+ M	F16
NOCl	+ Br		→ NO	+ BrCl		E25
NOCl	+ COCl		→ products			B46
NOCl	+ Cl		→ NO	+ Cl_2		B38
NOCl	+ F		→ products			E10
NOCl	+ H		→ NO	+ HCl		B39
NOCl	+ M		→ NO	+ Cl	+ M	B34
NOCl	+ N		→ NO	+ NCl		B40
NOCl	+ NOCl		→ NO	+ NO	+ Cl_2	B36

NOCl	+ NO_2		→ NO_2Cl	+ NO		B42
NOCl	+ NO_2Cl		→ NO	+ NO_2	+ Cl_2	B45
NOCl	+ NO_3		→ NO_2Cl	+ NO_2		B44
NOCl	+ O		→ NO	+ ClO		B41
NOI	+ I		→ NO	+ I_2		D17
NOI	+ NOI		→ NO	+ NO	+ I_2	D16
NO_2	+ COCl		→ NO	+ Cl	+ CO_2	B59
NO_2	+ Cl	+ M	→ NO_2Cl	+ M		B47
NO_2	+ ClO	+ M	→ $ClONO_2$	+ M		B48
NO_2	+ ClO_2		→ NO_3	+ ClO		B55
NO_2	+ Cl_2O		→ NO_2Cl	+ ClO		B53
NO_2	+ F	+ M	→ NO_2F	+ M		A25
NO_2	+ F_2		→ NO_2F	+ F		A26
NO_2	+ F_2O		→ NO_2F	+ FO		A27
NO_2	+ HBr		→ HNO_2	+ Br		C20
NO_2	+ HCl		→ HNO_2	+ Cl		B57
NO_2	+ I	+ M	→ NO_2I	+ M		D18
NO_2	+ NOCl		→ NO_2Cl	+ NO		B42
NO_2	+ NO_3F		→ NO_2F	+ NO_3		A29
NO_2Cl	+ M		→ NO_2	+ Cl	+ M	B47
NO_2Cl	+ NO		→ NOCl	+ NO_2		B43
NO_2Cl	+ NOCl		→ NO	+ NO_2	+ Cl_2	B45
NO_2I	+ I		→ NO_2	+ I_2		D19
NO_2I	+ NO_2I		→ $2NO_2$	+ I_2		D20
NO_3	+ NOCl		→ NO_2Cl	+ NO_2		B44
NO_3F	+ F_2		→ NO_2F	+ F	+ FO	A30
NO_3F	+ M		→ NO_3	+ F	+ M	A24
NO_3F	+ NO_2		→ NO_2F	+ NO_3		A29
N_2	+ CO		→ CN	+ NO		F 9
N_2F_4	+ M		→ NF_2	+ NF_2	+ M	A15
N_2O	+ Br		→ N_2	+ BrO		C19
N_2O	+ Cl		→ N_2	+ ClO		B56
N_2O	+ I		→ N_2	+ IO		D21
N_3Cl	+ Cl		→ N_3	+ Cl_2		B32
O	+ BrCl		→ Cl	+ BrO		E27
O	+ BrO		→ Br	+ O_2		C15
O	+ Br_2		→ BrO	+ Br		C12
O	+ CCl_4		→ CCl_3	+ ClO		H 2
O	+ CF_3Br		→ CF_3	+ BrO		H 2
O	+ $CHCl_3$		→ CCl_3	+ OH		H 2

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O	+ CHF_3		→ CF_3	+ OH		H 2
O	+ CH_2Cl_2		→ $CHCl_2$	+ OH		H 2
O	+ CH_2F_2		→ CHF_2	+ OH		H 2
O	+ CH_3Br		→ CH_2Br	+ OH		H 2
O	+ CH_3Cl		→ CH_2Cl	+ OH		H 2
O	+ CH_3F		→ CH_2F	+ OH		H 2
O	+ CN		→ CO	+ N		F 7
O	+ $(CN)_2$		→ CN	+ CNO		F 3
O	+ ClO		→ Cl	+ O_2		B13
O	+ $ClONO_2$		→ products			B49
O	+ ClO_2		→ ClO	+ O_2		B14
O	+ Cl_2		→ Cl	+ ClO		B12
O	+ Cl_2O		→ ClO	+ ClO		B19
O	+ DBr		→ Br	+ OD		C 9
O	+ DCl		→ Cl	+ OD		B 8
O	+ F_2		→ F	+ FO		A11
O	+ HBr		→ Br	+ OH		C 9
O	+ HCl		→ Cl	+ OH		B 8
O	+ NOCl		→ NO	+ ClO		B41
OH	+ Br		→ O	+ HBr		C 9
OH	+ CCl_4		→ CCl_3	+ HOCl		H 3
OH	+ CF_4		→ CF_3	+ HOF		H 3
OH	+ $CHCl_3$		→ CCl_3	+ H_2O		H 3
OH	+ $CHFCl_2$		→ $CFCl_2$	+ H_2O		H 3
OH	+ CHF_2Cl		→ CF_2Cl	+ H_2O		H 3
OH	+ CHF_3		→ CF_3	+ H_2O		H 3
OH	+ CH_2Cl_2		→ $CHCl_2$	+ H_2O		H 3
OH	+ CH_2FCl		→ CHFCl	+ H_2O		H 3
OH	+ CH_2F_2		→ CHF_2	+ H_2O		H 3
OH	+ CH_3Br		→ CH_2Br	+ H_2O		H 3
OH	+ CH_3CCl_3		→ CH_2CCl_3	+ H_2O		H 3
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