Chemical Kinetics Data Survey VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)

David Garvin, R. F. Hampson, Editors

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

January 1974

Supersedes NBSIR 73-203 (May 1973)

Prepared for
natic Impact Assessment Program
artment of Transportation
hington, D. C. 20590

NBSIR 73-430

CHEMICAL KINETICS DATA SURVEY
VII. TABLES OF RATE AND PHOTOCHEMICAL DATA FOR MODELLING OF THE STRATOSPHERE (REVISED)

David Garvin, R. F. Hampson, Editors

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

January 1974

Supersedes NBSIR 73-203 (May 1973)

Prepared for
Climatic Impact Assessment Program,
Department of Transportation
Washington, D. C. 20590

U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Table of Contents

Chemical Kinetics Data Survey

VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)

Abstract

Chemical kinetic and photochemical data for gas phase reactions pertinent to the chemistry of the stratosphere are presented in four tables. These tables give recommended values and also cite recent experimental work. They give data in the following subject areas: chemical reactions and photochemistry of neutral species, energy transfer reactions, high temperature air reactions, and ion-molecule reactions.

Key words: atmospheric chemistry, chemical kinetics, data evaluation, energy transfer, gas phase, high temperature air chemistry, ion-molecule reactions, optical absorption cross sections, photochemistry, quantum yield, rate constants.

1. Introduction

This report consists of a set of tables of rate constants and photochemical data. These are preliminary tables designed for use in modelling of the stratosphere. They are being distributed now for interim use and for criticism by kineticists.

The tables are an extract from the chapter "Chemistry of the Stratosphere" by H. S. Johnston, P. J. Crutzen, R. J. Cvetanovic, M. L. Corrin, D. D. Davis, E. E. Ferguson, D. Garvin, R. F. Hampson, R. D. Hudson, L. J. Kieffer, H. I. Schiff and R. L. Taylor, in "The Natural Stratosphere" E. Reiter, editor, Climatic Impact Assessment Program Monograph No. 1. The present tables are essentially those in the version of this monograph which will be distributed in the Summer of 1974.

The first version of the table of data on the chemical reactions and photochemistry of neutral species was prepared by the Chemistry Panel on the Natural Stratosphere in December, 1972 at the Fort Lauderdale, Florida meeting and received limited distribution in the first preliminary draft of CIAP Monograph No. 1. A revised and expanded version was distributed in NBSIR 73-203 in May, 1973. This version incorporates changes and additions suggested at the meeting of the Chemistry Panel in Boulder, Colorado in October, 1973. From time to time, interim versions of this table have been distributed on a limited basis. Since October, 1973 the date of preparation has been given in the upper left hand corner of each page. The version of CIAP Monograph 1, to be distributed in 1974 has tables dated 12/3/73. This version distributed here dated January 4, 1974 supersedes all earlier versions. It is virtually the same as that dated 12/3/73.

The tables include contributions of rate evaluations by other scientists. These contributors represented in the present edition are D. L. Baulch, D. D. Drysdale and D. G. Horne, University of Leeds; J. Heicklen, Pennsylvania State University; A. C. Lloyd, University of California, Riverside; T. G. Slanger, Stanford Research Institute; J. Troe and K. Glanzer, Ecole Polytechnique Federale de Lausanne; K. H. Welge, York University; and W. H. Breckenridge, University of Utah.

The tables are in several parts:

(1) Chemical reactions and photochemistry of neutral species (by the entire Chemistry Panel).
(2) Vibrational energy transfer processes (R. Taylor).
(3) High temperature air reactions (R. Taylor).
(4) Ion-molecule reactions (E. E. Ferguson).

Bibliographies are included. These are also taken from the chapter. Occasionally the tables include comments that refer the reader to the text. This auxilliary information has not been included in this report.

It is the goal of the authors of these tables to provide recommended values for as many chemical processes pertinent to the stratosphere as possible. Where practical the basis of the recommendation has been made evident by citing recent experimental work.

But this is a preliminary selection. There may be pertinent work that has been omitted, incorrect citations of numbers, inadequate interpretation and even faulty recommendations. The reader will provide a valuable service by pointing these out to us and by suggesting better recommendations. Comments by readers have been helpful in improving these tables, and we would like to express our appreciation for them.

Correspondence about these tables should be sent either to David Garvin, B-152 Chemistry Building, National Bureau of Standards, Washington, D. C. 20234 or to H. S. Johnston, Department of Chemistry, University of California, Berkeley, California 94720.

2. Related Material

These tables rely heavily upon other modern data evaluation work. Some pertinent sources are summarized here.

Contributors to this data survey were mentioned in the introduction. Their evaluations are given in more detail in NBS Report 73-206 (May 1973).

Evaluations by a team of chemists at NBS have been published in J. Phys. Chem. Ref. Data 2, 267 (1973). Earlier versions of these evaluations had been distributed as NBS Report 10692 (January 1972) and NBS Report 10828 (April 1972). Additional evaluations have been published in NBSIR 73-207 (August 1973).

Evaluations by a group at the University of Leeds under the direction of D. L. Baulch have been published in "Evaluated Kinetic Data for High Temperature Reactions, volume 1, Homogeneous gas phase reactions of the H_2-O_2 system" D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, (Butterworths, London, 1972) and volume 2, "Homogeneous gas phase reactions of the H_2-N_2-O_2 system" D. L. Baulch, D. D. Drysdale and D. G. Horne, (Butterworths, London, 1973). Earlier evaluations by the same group have appeared in five reports from the Department of Physical Chemistry, University of Leeds, entitled "High Temperature Reaction Rate Data".

Data on reactions occurring in photochemical smog have been evaluated in "The Mechanism of Photochemical Smog Formation" by K. L. Demerjian, J. A. Kerr and J. G. Calvert (to appear in Advances in Environmental Science and Technology, J. N. Pitts, Jr. and R. L Metcalf, editors, Wiley-Interscience, volume 4, 1974).

3. Needed Work

Although recommendations have been made for rate constants, absorption coefficients and quantum yields of many of the reactions thought to be important in the polluted stratosphere, much remains to be done. We will welcome suggestions of the best values to be used for any of the reactions denoted as not evaluated in the chemical reaction matrix immediately before Table I. These will be incorporated in the later versions of the tables. We will also welcome comments and corrections of any of the recommendations.

4. Tables from "The Natural Stratosphere" Climatic Impact Assessment Program Monograph No. 1, E. Reiter, editor

4.1 Chemical Reactions and Photochemistry of Neutral Species (Chemical Panel)

4.1.1 Introduction

These tables provide current (January, 1974) information on reaction rate constants, quantum yields and absorption cross sections. For many reactions, best estimates or recommended values are given. The reactions included in the tables are summarized on a "reaction grid" in section 4.1.4, Arrangement of the Tables. That grid also shows processes for which data (or data evaluations) are needed.

Most of the more important stratospheric reactions are in the tables. A number of the less important ones and some related systems are included, often simply for comparison.

The data have been selected by members of the Chemistry Panel and by other kineticists who have volunteered to review reactions of interest to them. Several principles have been used in the selection and presentation of data.

(a) Where there is a recent published evaluation of the data and there are no newer data, the evaluation is adopted. The original data covered by the evaluation are not listed separately.

(b) Where there is an evaluation but there are new data, both are listed and a preferred value is indicated (marked by an asterisk).

(c) Where desirable, the available recent data sets are listed, and a selection is made or a preferred value is synthesized from them.

These selections are necessarily tentative because there is much current research on these atmospheric reactions. Indeed, we have often been influenced in making our selections by preliminary results that have been made available to us. As new data are published they will be incorporated in the tables. The persons making new selections or syntheses are usually identified by initials. These are either authors of the chapter or contributors identified below.

The Panel expresses its appreciation to scientists who have provided reports on their current work and who have suggested improvements. We are particularly indebted to those who have contributed evaluations of data: D. L. Baulch, D. D. Drysdale and D. G. Horne, University of Leeds; J. Heicklen, Pennsylvania State University; A. C. Lloyd, University of California, Riverside; T. G. Slanger, Stanford Research Institute; J. Troe and K. Glanzer, Ecole Polytechnique Federale de Lausanne; K. H. Welge, York University; and W. H. Breckenridge, University of Utah.

Earlier versions of these tables have appeared in the first draft of this Monograph (November 1972) and as NBSIR 73-203 (May 1973). Probably there will be future versions. The latest one should be used. Each is identified by a date on each page of the tables.

4.1.2 Conventions Concerning Rate Constants

A. General Convention. Almost all of the reactions in the tables are elementary processes. For them the rate expression is derivable from a statement of the reaction, e.g.

$$A + 2B \rightarrow AB_2$$

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

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

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

B. Dissociation and Combination Reactions. Some reactions of these types are not of integral kinetic order over the stratospheric pressure and temperature range. That is, although they require an energy transfer agent, "M," they are in the "pressure fall-off region". For many such reactions we tabulate rate constants that include the effect of the energy transfer agent and give rates for various altitudes. The reactions are written to deemphasize "M," e.g.,

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

or

$$HNO_3 \xrightarrow{M} HO + NO_2$$

The rate expressions to be used do not have the concentration of M in them, e.g., Rate = $k[NO_2]$ $[NO_3]$ and $k[HNO_3]$ respectively The units given for the k's, s^{-1} for first order, and cm^{+3} $molecule^{-1}s^{-1}$ for second order, are consistent with this convention.

The altitude, temperature and number density regime used in these cases is

altitude/km	temp./K	log[M]/molecule cm^{-3}
15	220	18.60
20	217	18.27
25	222	17.93
30	227	17.58
35	235	17.26
40	250	16.92
45	260	16.60

Except for the temperature at 15 km this table follows the U.S. standard atmosphere, 1962. In tables to be prepared in the future we intend to allow for observed temperature and number density variations at each altitude.

C. Forward and Reverse Reactions. In some cases there are no data on a reaction of interest but there are data on the "reverse" reaction. Occasionally, for

$$A \rightarrow B \ (f)$$
$$B \rightarrow A \ (r)$$

an evaluation will use the data on the "reverse" reaction together with an equilibrium constant to obtain the other rate constant. Obviously this is an approximation but it often is a useful method of estimating non-measured physical properties.

The tables contain notations to warn the reader when this procedure has been used, such as "based on reverse reaction," or when both reactions f and r are listed together "$k_f = k_r K_{eq}$" or $k_r = k_f/K_{eq}$. These expressions, which are those used in the analyses, are based on equating the two rates at equilibrium:

$$R_f = R_r$$

$$k_f[A] = k_r[B]$$

$$K_{eq} = [B]/[A] = k_f/k_r.$$

4.1.3 Convention Concerning Optical Absorption Coefficients

These are reported in the tables as "absorption cross sections per molecule, base e" They are defined by the equations

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

$$\sigma = (1/([N]\ell))\ln(I_o/I)$$

where I_o and I are the intensities of incident and transmitted light, σ is the absorption cross section, cm^2 $molecule^{-1}$, [N] is the concentration of absorbers, molecules cm^{-3}, and ℓ is the path length, cm. Other definitions and units are frequently used. The terms "absorption coefficient" and "extinction coefficient" are common. It is always necessary to know what concentration units, path length units and type of logarithim (base e or base 10) are used in the definition. To convert "cross sections" to absorption coefficients in $(\text{atm at } 273\ K)^{-1}cm^{-1}$, base e, multiply by 2.69×10^{19}.

4.1.4 Arrangement of the Table

A. Reaction Grid. The contents of the data table and the location of a reaction in it are shown on the "reaction grid," that follows this discussion.

This grid shows the molecules of interest for stratospheric chemistry along the top and left edges. The symbol "K" in the intersection for two reactants means that data for the reaction are in the table Combination reactions, $A + B + M \rightarrow AB + M$ are above the main diagonal. Bimolecular reactions, typically $A + B \rightarrow C + D$, are below the diagonal.

B. Sequence of Reactions. The order in which reactions are listed follows the grid. All reactions of O atoms, the first species, shown in its row and column are listed first, then those of the second species, $O(^1D)$, with all species other than O atoms, and so on. Thus a particular reaction is placed with the reactant highest (or to the left) on the grid. Bimolecular and combination reactions appear together.

The algorithm used to assign reaction locations is to construct an ordered ascending sequence of number pairs (or triplets), one for each reaction according to the following rules:

(a) Assign numbers to each reactant in an equation. Use the numbers at the left side of the grid.

(b) Arrange this set of numbers in ascending order, e.g 1, 3 not 3, 1; 4, 10, 11 not 10, 11, 4

(c) Order the sets in ascending order, giving priority to the lower number in the corresponding position of two sets being compared, e.g. 1,4; 1,7; 4,10,10; 4,10,11; 18, 24 etc. This completes the assignment of reaction sequence.

If a reaction is not filed according to this scheme, a cross reference appears at the proper spot. Exceptions are made principally to put forward and reverse reactions together.

C. <u>Status of the Data</u>. The reaction grid also shows what data are available and what are needed. A "dash" (-) means that the reaction may be ignored for stratospheric chemistry. An "O" means that data are needed or existing data should be evaluated. Often this means the reaction is important, but at times it means that data are required so that the importance of the reaction can be assessed. A blank intersection merely means that no decision can be made at present. Finally, data are included in the table for some reactions that are unimportant. They are presented for comparison.

ChemicalReaction Matrix

K = Data in table, O = Data selection or new data needed,
- = Unimportant for stratospheric chemistry, E = Data elsewhere in the chapter, (Blank) = Role of process not assessed

Combination Reactions: A + B + M → AB + M

		ABS.σ	Q.Y.	E.TR.	DISS.	O	O(1D)	O(1S)	O2	O2(1Δ)	O2(1Σ)	O3	N	NO	NO2	NO3	N2	N2O	N2O5	NH	NH2	NH3	H	HO	HO2	H2	H2O	H2O2	HNO	HNO2	HNO3	SO	SO2	SO3	S2O	HS	H2S	HSO3	H2SO4	Cl	ClO	ClO2	ClO3	HCl	HOCl	HOClO	NOCl	NO2Cl	Cl2	CO	CO2	CHO	CH2O	CH3	CH3O	CH3O2	CH3OH	CH3OOH	CH3NO2	CH3NO3	CH4	C2H4	C2H6	C3H6	C3H8	C4H10
1	O	-	-	-	-	K			K			-	K	K	K	-	K	-	-			-	K	K	-		-	-			-		K	-					-													-	-	-	-	-										
2	O(1D)	-	-	K	-	-	-					-				-	K	-	-						-		-	-						-																																
3	O(1S)	-	-	K	-	K	-					-	-				-	-	-						-		-	-						-	-																						-										
4	O2	K	O	E	-		K	K	-	-	-	-		K	-	-	-	-	-			-	K	-	-		-	-		-	-		-	-	-				-	O										-			-	K	-	-										
5	O2(1Δ)				-		-		K	-		-		-	-	-	-	-	-			-		-	-		-	-			-			-					-											-			-		-	-										
6	O2(1Σ)				-		-		K	-	-	-		-	-	-	-	-	-			-		-	-		-	-			-			-					-											-			-		-	-										
7	O3	K	K	E	K	K	K	K	-	K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-				-											-		-	-	-	-	-										
8	N	-	-	-	-	-	-	-	K		-	K	K	-	-	-	-	-	-	-	-	-			-		-	-	-	-	-	-	-	-	-				-											-		-	-	-	-	-										
9	NO	K	O		K	K	K	K	K	K		K	K	K	-	-	-	-	-	-	-	-	K	K	O		-	-	-	-	-	-	-	-	-				-											-			-	K	K	K										
10	NO2	K	K	O	K	K	K	K	K			K	K	K	K	K	-	-	-	-	-	-		K	O		-	-	-	-	-	-	-	-	-				-											-			-	K	K	K										
11	NO3	K	K	O	K				K			-		K	K	K	-	-	-	-	-	-	-	O	-		-	-	-	-	-	-	-	-	-				-											-			-													
12	N2	-	-	E	K	K	K	K	K	K	K	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-				-											-		-	-	-	-	-										
13	N2O	E	O	-	K	K	K	K	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-				-											-		-	-	-	-	-										
14	N2O5	K	K	O	K	K			-	-	-				-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-				-											-				-												
15	NH				-		-		O								-	-		-		-					-	-	-	-	-								-											-		-	-	-	-	-										
16	NH2				-	K	-		O			O		K			-	-				-	K					-	-	-	-								-											-																
17	NH3			-	K	K	K	K	-			O		-	K		-	-			-	-	-	-				-	-	-	-								-											-		-	-	-	-	-										
18	H	-	-	-	-	-	-		K			K	-	-	K		-	K				K	K	K			-	-	-	-	-								-																											
19	HO	O	O	E	K	K			-			K	K	K	-		K	-			K	K	K	K	-		-	-	-	-	-		K						-											-																
20	HO2	O	O	O	K	K			-	-	-	K		K	K	-	-	-				-	K	K	-		-	-	-	-	-								-											-			-													
21	H2	-	-	-	K	K	K	-	K	-	-	-		K	-	-	-	-	-	-	K	-	-	K	K	-																																								
22	H2O	O	O	E	K	K	K	K	K	-	K	-	-	K	-	K	-	-	K	-	K	-	K	K	K	-	-	-	-	-									-											-		-	-	-	-	-										
23	H2O2	K	O	-	K	K	K		K	-	-	-		K	-		-	-				-	K	K	-	-	K	-	-	-	-								-											-	-	-	-	-	-	-										
24	HNO	O	O		K				K					-			-	-				-	K	K		-	-		K										-													-	-	-	-	-										
25	HNO2	E	O	O	-	K			-			-			-		-	-					K	K	-	-			-	-									-													-	-	-	-	-										
26	HNO3	K	K	O	K	K			-	-	-	-			-	-	-	-	-	-	-	O	K	K	-	-	-	-	-		-								-													-	-	-	-	-										
27	SO	O	O		-				K	K		K	-				-															K		-	-				-											-			-													
28	SO2	O	O	O	-				-	K	-	O	-				-	-						K	K	-							-																	-			-	K												
29	SO3	O	O	-	-	K			-	-	-	-	-				-							O		-	O						-																	-			-													
30	S2O				-							O	-				-	-								-									-															-			-													
31	HS				-												-																																																	
32	H2S				-												-	-																			-																													
33	HSO3																																																																	
34	H2SO4	O	O		-		O		-	-	-	-	-	-	-		-	-	O						-	-			-	-	-		-		-				-											-		-	-	-	-	-										
35	Cl				-							K					-	-							O	O		O																																						
36	ClO	O	O			K						O					-																							K																										
37	ClO2	O				K											-								O																																									
38	ClO3																-								O																																									
39	HCl	O			-												-						O	K																-																										
40	HOCl																-																																																	
41	HOClO																-																																																	
42	NOCl																-																																																	
43	NO2Cl																-																																-																	
44	Cl2	O	O		-					-							-																																	-																
45	CO			E	-		K		-	K		K	-	-	-	-	-	K	-	-	-	-		K	K	-	-	-	-	-	-	-	-	-	-				-											-		-	-		-	-										
46	CO2	-	-	E	-	-	K	K	-	-	-	-		-	-	-	-	-	-	-	-	-	-		-		-	-	-	-	-		-	-	-				-											-	-															
47	CHO				-	K	-		K				-				-	-				-	-			-	-			-	-								-											-	-															
48	CH2O	K	K		-	K			-	-	-	-		-			-	-				-	K	K	K	-	-	-	-	-	-																			-	-		-													
49	CH3				-	K	-		K				-		K		-	-				-				-	-				-																			-	-															
50	CH3O				-		-		K				-	K	K		-	-					-			-	-				-								-											K	-					-										
51	CH3O2				-				O				-	K	K	-	-	-				-	-		K	-	-			-	-	-	-	-	-				-											-	-					K										
52	CH3OH																																																																	
53	CH3OOH	O	O		-					-	-						-	-				-	-				-	-	-	-	-		-	-	-				-											-		-	-	-	-	-										
54	CH3NO2	O	K	O	-					-	-						-	-				-	-				-	-	-	-	-		-																	-		-	-	-	-	-										
55	CH3NO3	O	O	O	-					-	-	-					-	-				-	-				-	-	-	-	-		-																	-		-	-	-	-	-										
56	CH4	-	-	-	-	K	K	K	-	-	-	K		-	-	-	-	-	-	-	-	-	-	K	-		-	-	-	-	-		-	-	-				-	K										-		-	-	-	-	-										
57	C2H4				-	K						K												K	K																																									
58	C2H6				-	K	K																	K	K																																									
59	C3H6				-	K						K												K																																										
60	C3H8				-																				K																																									
61	C4H10				-																			K	K																																									

Bimolecular Reactions: A + B → C + D + ...

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Notes and Reliability of log k
— $O + O + M \rightarrow O_2 + M$			
*Johnston (1968) review	1000< T <8000	$3.80 \times 10^{-30}\ T^{-1} \exp(-170/T)$ $M = O_2$	± 0.3
Campbell, Gray (1973)	298	4.8×10^{-33} $M = N_2$	± 0.03
	196	10.1×10^{-33}	± 0.02
— $O + O(^1S) \rightarrow$		see $O(^1S) + O \rightarrow$	
— $O(^3P) + O_2 + M \rightarrow O_3 + M$ (f)			
— $O_3 + M \rightarrow O + O_2 + M$ (r)			
*This Survey (D.D.D. and D.G.)	200–346	$6.6 \times 10^{-35} \exp(510/T)$ $M = Ar$ Rel. M efficiencies: $Ar(1.0)\ N_2(1.6)\ O_2(1.7)\ H_2O(15)$	$\pm .07$
Johnston (1968) eval.	200–1000	$4.6 \times 10^{-35} \exp(1050/T)$ $M = O_3$	± 0.1
		$k_r = 1.65 \times 10^{-9} \exp(-11400/T) cm^3 molecule^{-1} s^{-1}$	± 0.1
		Rel. M efficiencies: $O_3(1.0)$, $Ar(0.25)$, $O_2(0.44)$, $N_2(0.39)$	
Huie, Herron, Davis (1972)	200–346	$6.6 \times 10^{-35} \exp(510/T)$ $M = Ar$ Rel. M efficiencies: $Ar(1.0)$, $He(0.9)$, $N_2(1.7)$	
Mulcahy, Williams (1968)	213–386	$4.7 \times 10^{-35} \exp(840/T)$ $M = Ar$ Rel. M efficiencies: $Ar(1.0)\ He(0.8)\ CO_2(3.4)\ O_2(1.1)$	
Meaburn, et al (1968)	300	1.0×10^{-33} $M = CO_2$ Rel. M efficiencies: $CO_2(1.0)$, $CO(0.44)$, $N_2O(0.88)$	

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
Stuhl, Niki (1971)	300	5.4×10^{-34} $cm^6 molecule^{-2} s^{-1}$ M = N_2	
		Rel. M efficiencies:	
		$N_2(1.0)$ $O_2(1.18)$, CO(1.24)	
Donovan, Husain, Kirsch (1970)	300	5.0×10^{-34} $cm^6 molecule^{-2} s^{-1}$ M = Ar	
		Rel. M efficiencies:	
		Ar(1.0), Kr(0.98), He(0.92)	
Hippler, Troe (1971)	300	8×10^{-34} M = N_2	
Slanger, Black (1970)	300	4.4×10^{-34} M = Ar, Rel. eff. Ar(1.0), $N_2(1.6)$	
Francis (1969)	300	1.24×10^{-34} M = O_2	
Sauer (1967)	300	2.28×10^{-34} M = Ar	
— $O + O_2 + M \rightarrow O_3^* + M$			
Bevan, Johnson (1973)	300	$5.4 \times 10^{-34} cm^6 molecule^{-2} s^{-1}$ M = O_2	(a)
		Rel. efficiencies: $O_2(1.0)$, Ar(0.50), $N_2O(2.4)$, $CO_2(2.5)$, $SF_6(5.7)$	
		(a) Vibrationally excited O_3 followed as fn. of time using absn. $250 < \lambda < 330$nm.	
— $O(^3P) + O_3 \rightarrow O_2 + O_2$			
Hampson (1973) eval.	220-1000	1.9×10^{-11} exp (-2300/T)	
*This Survey			
(D.D.D., H.I.S, and H.J.)	220-1000	1.9×10^{-11} exp (-2300/T)	±0.1 (a)
McCrumb, Kaufman (1972)	269-409	1.1×10^{-11} exp (-2155/T)	
Lundell, Ketcheson, Schiff (1969)	300	1.5×10^{-14}	
Husain, Kirsch, Donovan (1972)	300	1.3×10^{-14}	
Davis, Wong, Lephardt (1973)	220-353	2.0×10^{-11} exp (-2280/T)	

(a) The preferred value of this survey is based on the high temperature data included in Hampson (1973) and the low temperature data of McCrumb and Kaufman and of Davis, et al.

Reactions of O with O_2 and O_3

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— O + N + M -> NO + M			
*Baulch, et al (1973) review	200-400	$1.8 \times 10^{-31} (T)^{-0.5} cm^6 molecule^{-2} s^{-1}$, $M = N_2$	±0.2
— O + NO -> N + O_2 (f)			
— O_2 + N -> NO + O (r)			
*Baulch, et al (1973) review	1000-3000	$k_f = 2.5 \times 10^{-15} T \exp(-19500/T)$	±0.12 at 1000K (a)
	300-3000	$k_r = 1.1 \times 10^{-14} T \exp(-3150/T)$	±0.12 300<T<1500K
		(a) $k_f = k_r K_{eq}$. Error in log k increases to ±0.3 at 3000K	
— O + NO -> NO_2 + hv			
Becker, et al (1973)	300	4.2×10^{-18}	
— O + NO + M -> NO_2 + M (f)			
— NO_2 + M -> NO + O + M (r)			
*Baulch, et al (1973) review	200-500	$3.0 \times 10^{-33} \exp(940/T)\ cm^6 molecule^{-2} s^{-1}$, $M = O_2$	±0.08
		Rel. M efficiencies: O_2(1.0), Ar(1.0), N_2(1.4)	
	1400-2400	$k_r = 1.8 \times 10^{-8} \exp(-33000/T) cm^3 molecule^{-1} s^{-1}$ M = Ar	±0.1
Hampson, et al (1973a) review	200-500	accepts above recommendation	
Slanger, Wood, Black (1973)	296	6.0×10^{-32} M = Ar	(a)
	241	13.0×10^{-32} M = Ar	(a)
		(a) slightly higher but supports recommendation.	
- O + NO + M -> NO_2 + M + hv			
Becker, et al (1973)	300	$7 \times 10^{-32}\ cm^6 molecule^{-2} s^{-1}$	

Reactions of O with N to NO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O(^3P) + NO_2 \rightarrow NO + O_2$ (f)			
— $O_2 + NO \rightarrow NO_2 + O$ (r)			
*This survey (D.D.D.)	230-550	9.1×10^{-12}	± 0.06
Baulch, et al (1973)	300-550	$k_f = 1.7 \times 10^{-11} \exp(-300/T)$	
		$k_r = k_f/K_{eq} = 2.8 \times 10^{-12} \exp(-23400/T)$	± 0.1
Davis, Herron and Huie (1972)	230-339	9.1×10^{-12}	
Clyne, Cruse (1971)	300	8.3×10^{-12}	
Harker, Johnston (1972)	300	9.2×10^{-12}	(a)
Clyne, Cruse (1972)	298	6.1×10^{-12}	
Slanger, et al (1973)	300	9.3×10^{-12}	(b)
	240	10.5×10^{-12}	
Hampson, et al (1973a) review	220-500	9.1×10^{-12}	± 0.08
Stuhl, Niki (1970)	300	4.4×10^{-12}	(b)
Bemand, Clyne, Watson (1973)	298-1055	$1.75 \times 10^{-10} \times (T)^{-0.52}$	
	298	$9.5 \pm 1.1 \times 10^{-12}$	
	(a) $k/k(O + NO + M)$ measured, where $k(ref) = 6.9 \times 10^{-32}$		
	(b) Similar techniques were used by Slanger and by Stuhl and Niki: Flash photolysis - chemiluminescence.		
— $O + NO_2 + M \rightarrow NO_3 + M$ (f)			
— $NO_3 + M \rightarrow NO_2 + O + M$ (r)			
*Hampson, et al (1973a) review	298	$1.0 \times 10^{-31} cm^6 molecule^{-2} s^{-1}$ $M = N_2$	± 0.2
Baulch, et al (1973) review	295	$k_f = 6.3 \times 10^{-32}$ $M = N_2$	± 0.4
		$k_r \sim 8 \times 10^{-42} cm^3 molecule^{-1} s^{-1}$, $M = N_2$	(a)
		(a) No reliable data. Value based on k_f	

Reactions of O with NO_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O + N_2 \rightarrow N + NO$		See reverse reaction	
— $O + N_2 + M \rightarrow N_2O + M$			
Baulch, et al (1973) review	1300-2500	$3.9 \times 10^{-35} \exp(-10400/T)\ cm^6 molecule^{-2} s^{-1}$ M = Ar	± 0.2 (a)
	900-2100	$5.5 \times 10^{-15} \exp(-11330/T)\ cm^3 molecule^{-1} s^{-1}$	± 0.2 (a,b)
		(a) $k_f = k_r K_{eq}$	
		(b) 2d order high pressure limit	
— $N_2O + M \rightarrow N_2 + O + M$			
Baulch, et al (1973) review	1300-2500	$8.3 \times 10^{-10} \exp(-29000/T)$ M = Ar	± 0.2
	900-2100	$1.3 \times 10^{+11} \exp(-30000/T) s^{-1}$	± 0.2 (a)
		(a) first order high pressure limit	
— $O + N_2O \rightarrow N_2 + O_2$ (1)			
— $O + N_2O \rightarrow NO + NO$ (2)			
— $NO + NO \rightarrow N_2O + O$ (2r)			
Baulch, et al (1973) review	1200-2000	$k_1 = 1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$	± 0.4 (a)
		$k_2 = 1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$	± 0.3
	1200-2000	$k_{2r} = 2.2 \times 10^{-12} \exp(-32100/T)$	± 0.3 (b)
		(a) Based on $k_1/k_2 = 1$	
		(b) $d[NO]/dt = -2k_{2r}[NO]^2$	
— $O + N_2O_5 \rightarrow$ products			
Davis (1973)	300	$< 2 \times 10^{-13}$	preliminary
— $O + NH_2 \rightarrow HNO + H$ (a)			
$\rightarrow HO + NH$ (b)			
Gehring, et al (1973)	300	3.5×10^{-12} $(k_a + k_b)$	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/$cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O + NH_3 \rightarrow HO + NH_2$ (f)			
— $HO + NH_2 \rightarrow O + NH_3$ (r)			
Baulch, et al (1973) review	300-1000	$k_f = 2.5 \times 10^{-12} \exp(-3020/T)$	±0.2
	300-1000	$k_r = k_f/K_{eq} = 1 \times 10^{-13}$	±0.2 (a)
*Kurylo, et al (1969) (D.G.)	361-677	$k_f = 6.6 \times 10^{-12} \exp(-3300/T)$	±0.3
Albers, et al (1969)	300-1000	$k_f = 2 \times 10^{-12} \exp(-3000/T)$	
Kondratiev (1970) review	350-1000	$k_f = 1.8 \times 10^{-12} \exp(-2500/T)$	
		Data of Albers, et al provide an upper limit when extrapolated to 220K	
		(a) $HO + NH_2 \rightarrow NH + H_2O$ may be preferred channel.	
— $O + H + M \rightarrow HO + M$			
Scofield (1973) review	1000-3000	$\sim2 \times 10^{-32}$ $cm^6 molecule^{-2} s^{-1}$ M = Ar	±1 estimate
Baulch, et al (1972) review		No recommendation	
— $O + HO \rightarrow H + O_2$ (f)			
— $O_2 + H \rightarrow O + HO$ (r)			
Baulch, et al (1972) review	300	$k_f = 3.8 \pm 1.7 \times 10^{-11}$	±0.17
*Baulch, et al (1972) review	700-2500	$k_r = 3.7 \times 10^{-10} \exp(-8450/T)$	±0.1
*Wilson (1972) review	300-2000	$k_f = 4.2 \pm 1.7 \times 10^{-11}$,	±0.3
— $O + HO + M \rightarrow HO_2 + M$			
Baulch, et al (1972) review		no recommendation	
— $O + HO_2 \rightarrow HO + O_2$			
Lloyd (1973) review	~300	$8 \times 10^{-11} \exp(-500/T)$	estimate
— $O + H_2 \rightarrow HO + H$ (f)			
— $H + HO \rightarrow O + H_2$ (r)			
Baulch, et al (1972) review	400-2000	$k_f = 3.0 \times 10^{-14}(T)\exp(-4480/T)$	±0.1
		$k_r = k_f/K_{eq} = 1.4 \times 10^{-14}(T)\exp(-3500/T)$	±0.15

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O + H_2O \rightarrow HO + HO$		See reverse reaction	
— $O + H_2O \rightarrow H + HO_2$			
Baulch, et al (1972) review		no recommendation	
— $O(^3P) + H_2O_2 = HO_2 + OH$ (a)			
$= H_2O + O_2$ (b)			
*This Survey (D.D.D.)	283-373	$k(a+b) = 2.75 \times 10^{-12} \exp(-2125/T) cm^3 molecule^{-1} s^{-1}$	± 0.07 (a)
Foner, Hudson (1962)	300	$\lesssim 4 \times 10^{-15}$	
Davis (1973)	283-373	$k(a+b) = 2.75 \times 10^{-12} \exp(-2125/T)$	± 0.06
	(a) There is presently no basis for assigning relative k values to the two possible channels for this reaction.		
— $O + HNO_2 \rightarrow HO + NO_2$			
This survey (D.G.)		No data. Probably faster than $O + HNO_3$, since it is 94 kJ/mol more exothermic.	
Baulch, et al (1973) review		No recommendation	
— $O + HNO_3 \rightarrow HO + NO_3$			
*Hampson, et al (1973) review	300	$< 1.5 \times 10^{-14}$	
Morley, Smith (1972)	300	$<1.3 \times 10^{-14}$	
Wayne (1973)	300	$< 1 \times 10^{-16}$	
Baulch, et al (1973) review	300	$<10^{-14}$	approximate upper limit
— $O + SO_2 + M \rightarrow SO_3 + M$			
Schofield (1973) review	250-1000	$1 \times 10^{-33} \exp(+500/T) cm^6 molecule^{-2} s^{-1}$, $M = O_2$, N_2, Ar, He	± 0.3 at 300K ± 0.6 at other temp.
*Davis (1973) (D.D.D., D.G.)	220-353	$3.4 \times 10^{-32} \exp(-1130/T)$ $M = N_2$ $N_2(1.0)$, He(.45), Ar(.87), $SO_2(56)$	

Reactions of O with H_2O to SO_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O + SO_3 \rightarrow SO_2 + O_2$			
Schofield (1973) review	1480-1550	$5 \times 10^{-10} \exp(-6000/T)$	Uncertain
Jacob, Winkler (1972)	300-500	$3 \times 10^{-16} \exp(-500/T)$	
— $O + ClO \rightarrow Cl + O_2$			
Watson (1973) review	300	$5.3 \pm 0.8 \times 10^{-11}$	±0.1
— $O + OClO \rightarrow ClO + O_2$			
Watson (1973) review	300	5×10^{-13}	±0.2
— $O + CHO \rightarrow CO_2 + H$ (a) $\rightarrow CO + HO$ (b)			
*Washida, et al (1973)	297	$2.1 \pm 0.4 \times 10^{-10}$ $(k_a + k_b)$	
— $O + CH_2O \rightarrow CHO + OH$			
*Demerjian, et al (1972) review	300	1.6×10^{-13}	
Mack, Thrush (1973)	300	1.5×10^{-13}	±0.05
— $O + CH_3 \rightarrow CH_2O + H$ (a) $\rightarrow CHO + H_2$ (b)			
Washida, Bayes (1973)	300	$k_a = 1.23 \times 10^{-10}$	±0.1
Washida, et al (1973)	300	k_b negligible $k_b/k_a < 0.05$	
Morris, Niki (1972)	300	$k_a = 9 \times 10^{-11}$	
Peeters, Mahnen (1973)	1100-1900	$k_a = 2.2 \times 10^{-10} \exp(-1000/T)$	
— $O + CH_4 \rightarrow$ products			
*Herron, Huie (1972) review	350-1000	$3.5 \times 10^{-11} \exp(-4550/T)$	±0.11
— $O + C_2H_4 \rightarrow$ products			
*Herron, Huie (1972) evaluation	200-500	$5.5 \times 10^{-12} \exp(-565/T)$	±0.08

Reactions of O with SO_3 to C_2H_4

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O + C_2H_6$ -> products			
*Herron, Huie (1972) evaluation	300–650	4.1×10^{-11} exp (-3200/T)	±0.11
— $O + C_3H_6$ -> products			
*Herron, Huie (1972) evaluation	200–500	4.1×10^{-12} exp (-38/T)	±0.08
— $O(^1D_2) + O_2$ -> $O_2(^1\Sigma_g^+) + O(^3P)$	298	7.4×10^{-11} cm^3 $molecule^{-1} s^{-1}$	±0.1 a
— $O(^1D_2) + O_3$ -> $O_2(^3\Sigma_2^-) + O_2$ (?) (a)	"	5.3×10^{-10} $(k_a + k_b)$ $k_a/k_b \sim 1$	±0.3 a,c
-> $O_2 + 2O(^3P)$ (b)	"		
— $O(^1D_2) + NO$ -> $NO + O(^3P)$	"	1.7×10^{-10}	±0.3 a
— $O(^1D_2) + NO_2$ -> $NO + O_2$	"	2.8×10^{-10}	±0.1 a
— $O(^1D_2) + N_2$ -> $N_2 + O(^3P)$	"	5.4×10^{-11}	±0.15 a
— $O(^1D_2) + N_2 + M$ -> $N_2O + M$	"	2.8×10^{-36} $cm^6 molecule^{-2} s^{-1}$	b
— $O(^1D_2) + N_2O$ -> $N_2 + O_2$ (a)	"	1.1×10^{-10} $cm^3 molecule^{-1} s^{-1}$	±0.1 a
-> 2NO (b)	"	1.1×10^{-10}	±0.1 a
— $O(^1D_2) + NH_3$ -> $NH_2 + HO$	298	(Probably about 3×10^{-10} No measurements available)	a,d
— $O(^1D_2) + H_2$ -> $HO + H$	"	2.9×10^{-10}	±0.1 a
— $O(^1D_2) + H_2O$ -> 2HO	"	3.5×10^{-10}	±0.1 a
— $O(^1D_2) + H_2O_2$ -> $HO + HO_2$	"	$>3 \times 10^{-10}$	d
— $O(^1D_2) + CO$ -> $CO + O(^3P)$	"	7.7×10^{-11}	±0.1 a
— $O(^1D_2) + CO_2$ -> $CO_2 + O(^3P)$	"	1.8×10^{-10}	±0.1 a
— $O(^1D_2) + CH_4$ -> $CH_3 + HO$ (a)	"	4.0×10^{-10} $(k_a + k_b)$ $k_a/k_b = 10$	±0.1 a
-> $CH_2O + H_2$ (b)			
— $O(^1D_2) + C_2H_6$ -> $C_2H_5 + HO$ (a)	"	4.8×10^{-10} $(k_a + k_b)$	±0.1 a
-> $CH_3 + CH_2OH$ (b)		(notes are on next page)	

Reactions of O with C_2H_6 and C_3H_6 and of $O(^1D)$

a. *Evaluation for this survey (R.J.C.). See details in text "Reactions of O($^1D_2$) Atoms,"

b. Gaedtke, et al (1972)

c. Further determinations are desirable. See details of evaluation.

d. Estimated, Experimental determination is necessary.

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliability of log k	
— O(^{1}S) + O(^{3}P) -> ?	300	7.5×10^{-12}	±0.2	a
— O(^{1}S) + O_2 -> ?	200-377	$4.3 \times 10^{-12}\exp(-850/T)$	±0.15	a
— O(^{1}S) + O_3 -> ?	300	5.8×10^{-10}	±0.07	a
— O(^{1}S) + NO -> ?	200-291	$3.2 \times 10^{-11}(T)^{0.5}$	±0.05	a
— O(^{1}S) + NO_2 -> ?	300	5×10^{-10}	±0.2	a
— O(^{1}S) + N_2 -> ?	200-380	$< 5 \times 10^{-17}$		a
— O(^{1}S) + N_2O -> ?	300	1.4×10^{-11}	±0.1	a
— O(^{1}S) + NH_3 -> ?	300	5×10^{-10}	±0.2	a
— O(^{1}S) + H_2O -> ?	300	$> 10^{-10}$	±1	a
— O(^{1}S) + CO_2 -> ?	200-450	$3.1 \times 10^{-11}\exp(-1320/T)$	±0.15	a
— O(^{1}S) + CH_4 -> ?	300	2×10^{-14}	±0.4	a

a) Rate constants evaluated for this survey by T. G. Slanger and K. H. Welge

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$			
Hampson, et al (1973a) review		$\emptyset = 1$ $175 < \lambda < 200$ nm	
— $O_2 + h\nu \rightarrow O(^3P) + O(^1D)$			
Hampson, et al (1973a) review		$\emptyset = 1$ $133 < \lambda < 175$ nm	
— $O_2 + h\nu \rightarrow$ 2 oxygen atoms			
Hampson, et al (1973a) review		$\emptyset = 1$ $106 < \lambda < 200$ nm	
— $O_2 + h\nu$			
Hampson, et al (1973a) review		Recommended values of absorption cross section $135 < \lambda < 243$ nm	
— $O_2 + N \rightarrow NO + O$		see reverse reaction	
— $O_2 + NO + NO \rightarrow NO_2 + NO_2$			
*Baulch, et al (1973) review	273–660	$3.3 \times 10^{-39} \exp(530/T)$ $cm^6 molecule^{-2} s^{-1}$ $k_1[NO]^2 [O_2] = -(1/2)d[NO]/dt$	±0.2
Stedman, Niki (1973)	300	2.0×10^{-38} where $d[NO_2]/dt = 2k[NO]^2[O_2]$	±0.1
— $O_2 + NO + NO_2 \rightarrow NO_2 + NO_3$		see reverse reaction	
— $O_2 + NO \rightarrow NO_2 + O$		see reverse reaction	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_2 + NO + M \rightarrow NO_3 + M$			
Baulch, et al (1973) review		No recommendation	
— $O_2 + NO_2 \rightarrow NO + O_3$		see reverse reaction	
— $O_2 + NO_3 \rightarrow NO_2 + O_3$		see reverse reaction	
— $O_2 + N_2 \rightarrow N_2O + O$			
*Baulch, et al (1973) review	1200-2000	$1.0 \times 10^{-10} \exp(-55.2 \times 10^3/T)$	±0.4 (a)
		(a) $k_f = k_r K_{eq}$	
— $O_2 + H \rightarrow HO + O$		see reverse reaction	
— $O_2 + H + M \rightarrow HO_2 + M$			
*This Survey (D.D.D.)	203-404	$6.7 \times 10^{-33} \exp(290/T)\ cm^6 molecule^{-2} s^{-1}$	±.07 (a)
		M = Ar or He, $k(300) = 1.8 \times 10^{-32}$	
		Rel. M efficiencies: Ar(1.0), He(1.0), N_2(3.1), O_2(3.1), H_2O(25)	
	(a) This evaluation is base on the 300 K data reviewed by Baulch, et al. (1972) and the recent studies by Hikida, et al (1971), Kurylo (1972) and Wong and Davis (1972).		
Baulch, et al (1972) eval.	300-2000	$4.1 \times 10^{-33} \exp(500/T)$ M = Ar	±.2
		Rel. M efficiencies: Ar(1.0), He(1.0), N_2(1.3), O_2(1.3), H_2O(21)	
Bishop, Dorfman (1970)	300	2.35×10^{-32} M = Ar	
Hikida, Eyre, Dorfman (1971)	300	1.64×10^{-32} M = Ar	
Ahumada, Michael, Osborne (1972)	300	0.75×10^{-32} M = He	
		Rel. M efficiencies: He(1.0), Ar(0.8)	
Allen, Moortgat (1973)	115-300	$1.4(\pm0.14) \times 10^{-33} \exp(+700(\pm50)/T)$, M = Ar	
		Rel. M efficiencies at 297K: Ar(1.0), He(0.97), H_2(1.28).	
Kurylo (1972)	203-404	$6.7 \times 10^{-33} \exp(235/T)$	

(continued on next page)

Reactions of O_2 with NO to H

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
		Rel. M efficiencies:	
		Ar(1.0), He(1.0), N_2(3.4)	
Wong, Davis (1973)	220-360	6.8×10^{-33} exp(340/T)	
		Rel. M efficiencies:	
		Ar(1.0), He(0.93) N_2(2.8), H_2(3.0), CH_4(21.5)	
Westenberg, DeHaas (1972)	300	1.9×10^{-32} M = Ar or He	
— $O_2 + H_2 \rightarrow H + HO_2$		see reverse reaction	
— $O_2 + H_2 \rightarrow HO + HO$			
Baulch, et al (1972) review		no recommendation	
— $O_2 + H_2O \rightarrow HO_2 + HO$			
Baulch, et al (1972) review		no recommendation	
— $O_2 + H_2O_2 \rightarrow HO_2 + HO_2$			
Baulch, et al (1972) review		no recommendation	
— $O_2 + HNO \rightarrow NO + HO_2$			
Demerjian, et al (1972) review	300	$< 2.1 \times 10^{-20}$, E/R > 5000K	estimated
— $O_2 + SO \rightarrow SO_2 + O$			
*Breckenridge, Miller (1972) (WHB)	300	$< 8 \times 10^{-17}$	
*Schofield (1973) review (WHB)	400-2500	3.0×10^{-13} exp (-2800/T)	±0.3
— $O_2 + CHO \rightarrow CO + HO_2$			
Demerjian, et al (1972) review	300	1.7×10^{-13}	estimated
Peeters, Mahnen (1973)	1400-1800	5×10^{-11}	
*Washida, et al (1973)	297	$k/k(O + CHO) = 2.74 \pm 0.21 \times 10^{-2}$	
		yielding $k = 5.7 \pm 1.2 \times 10^{-12}$	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_2 + CH_3 \rightarrow CH_2O + HO$			
Basco, et al (1972)	295	3×10^{-16}	estimated (a)
		a. Based on negative result and sensitivity limit. Other measurements at higher T suggest an appreciable activation energy.	
— $O_2 + CH_3 + M \rightarrow CH_3O_2 + M$			
Basco, et al (1972) (D.G.)	295	2.6×10^{-31}, $cm^6 molecule^{-2} sec^{-1}$, $M = N_2$ (low pressure limit)	
— $O_2 + CH_3 (+M) \rightarrow CH_3O_2$			
Basco, et al (1972) (D.G.)	295	4.3×10^{-13}, $cm^3 molecule^{-1} s^{-1}$, $M = N_2$, (2d order high pressure limit.) $k = 1.7 \times 10^{-13}$, $M = N_2$, at 30 torr.	
— $O_2 + CH_3O \rightarrow . . .$		see $CH_3O + O_2$	
— $O_2(^1\Delta) + M \rightarrow O_2 + M$			
*Hampson (1973) review	285-322	$2.2 \times 10^{-18} (T/300)^{0.8}$, $M = O_2$	±0.1
	300	$<2 \times 10^{-20}$, $M = N_2$	
Collins, et al (1973)	300	1.4×10^{-19}, $M = N_2$	±0.06
*Breckenridge, Miller (1972) (WHB)	300	$< 2 \times 10^{-15}$ $M = SO_2$	(a)
Fisher, McCarty (1966) (WHB)	300	$< 3 \times 10^{-16}$ $M = CO$	(a)
		(a) total rate, quenching and reaction	
— $O_2(^1\Delta) + O_3 \rightarrow 2O_2 + O$			
Clark, Jones, Wayne (1970)	195-439	$6.6 \times 10^{-13} \exp(-1560/T)$	±0.24
Findlay, Snelling (1971)	283-321	$4.5 \times 10^{-11} \exp(-2830/T)$	±0.11
Becker, et al (1972)	296-360	$6.0 \times 10^{-11} \exp(-2850/T)$	±0.17
Collins, et al (1973)	300	4.4×10^{-15}	±0.11
Schofield (1972) review	283-321	$4.5 \times 10^{-11} \exp(-2830/T)$	±0.11

Reactions of O_2 with CH_3 and of $O_2(^1\Delta)$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_2(^1\Delta) + SO \rightarrow O_2 + SO(^1\Delta)$			
Breckenridge, Miller (1972) (WHB)	300	$3.5 \pm 0.36 \times 10^{-13}$	
— $O_2(^1\Sigma) + M \rightarrow O_2 + M$			
*Hampson (1973) review	300	1.5×10^{-16}, $M = O_2$	± 0.12
		2.0×10^{-15}, $M = N_2$	± 0.1
		4×10^{-12}, $M = H_2O$	± 0.18
— $O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$			
*Hampson, et al. (1973) review		$\phi = 1$, $450 < \lambda < 750$ nm - Chappuis bands	
		$\phi = 0$ $250 < \lambda < 350$ nm	
Johnston (1973)		$k = 3.39 \times 10^{-4} s^{-1}$ (Daylight)	
		($450 < \lambda < 750$nm - Chappuis bands)	
— $O_3 + h\nu \rightarrow O(^3P) + O_2(^1\Delta$ or $^1\Sigma)$			
*Hampson, et al. (1973) review		$\phi = 1$, $310 < \lambda < 350$ nm - Huggins bands	
		$\phi = 0$, $\lambda < 310$ nm	
— $O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$			
*Hampson, et al. (1973) review		$\phi = 1$, $250 < \lambda < 310$ nm - Hartley bands	
		$\phi = 0$, $\lambda > 310$ nm	
Lin, DeMore (1973)		Results consistent with above recommendation.	
— $O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Sigma_g^+)$			
*Hampson, et al. (1973) review		$\phi = 0$, $250 < \lambda < 350$ nm	
— $O_3 + M \rightarrow O + O_2 + M$		see reverse reaction	
— $O_3 + N \rightarrow NO + O_2$			
*Baulch, et al (1973) review	300	5.7×10^{-13}	± 0.2

Reactions of $O_2(^1\Delta)$ with SO to O_3 with N

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_3 + NO \rightarrow NO_2 + O_2$ (f)			
— $O_2 + NO_2 \rightarrow NO + O_3$ (r)			
*Hampson, et al (1973) review	198-330	$k_f = 9 \times 10^{-13} \exp(-1200/T)$ cm^3 $molecule^{-1} s^{-1}$	±0.11
Stedman, Niki (1973)	298	$k_f = 1.73 \pm 0.1 \times 10^{-14}$	±0.2
Baulch, et al (1973) review	200-350	$k_f = 1.5 \times 10^{-12} \exp(-1330/T)$	±0.2
	200-350	$k_r = k_f/K_{eq} = 2.8 \times 10^{-12} \exp(-25400/T)$	±0.2
Ghormley, et al (1973)	298	$k_f = 1.41 \times 10^{-14}$	±0.01 precision
Bemand, et al (1973)	300	$1.81 \pm 0.13 \times 10^{-14}$	
— $O_3(001) + NO \rightarrow NO_2 + O_2$			
Gordon, Lin (1973)	300	2.5×10^{-13}	(a)
Kurylo, et al (1973)	300	2.2×10^{-13}	(a)
		(a) Rate ~20 times faster than with $O_3(000)$. $O_3(010)$ may be reactive species	
— $O_3 + NO_2 \rightarrow NO_3 + O_2$ (f)			
— $O_2 + NO_3 \rightarrow O_3 + NO_2$ (r)			
*This survey (D.D.D.,D.G.)	220-340	$k_f = 1.1 \times 10^{-13} \exp(-2450/T)$	±0.1
Hampson, et al (1973) review	298	$k_f = 5 \times 10^{-17}$	±0.2
Johnston, Yost (1949)	286-302	$k_f = 9.8 \times 10^{-12} \exp(-3500/T)$	
Baulch, et al (1973) review	286-302	$k_f = 9.8 \times 10^{-12} \exp(-3500/T)$	±0.3
	300	$k_r = 7 \times 10^{-34}$ based on k_f	±0.3
Wu, Morris, and Niki (1973)	299	$k_f = 4.4 \times 10^{-17}$	±0.06 (a)
Ghormley, et al (1973)	298	$k_f = 3.2 \times 10^{-17}$	±0.07
Davis (1973)	260-343	$k_f = 1.0 \times 10^{-13} \exp(-2420/T)$	±0.2
Johnston (1973)	231-268	$k_f = 1.23 \times 10^{-13} \exp(-2470/T)$	
Stedman, Niki (1973)	298	$k_f = 6.5 \pm 0.8 \times 10^{-17}$	
		(note on next page)	

Reactions of O_3 with NO and NO_2

(a) Revision, based on later experiments of value reported by Stedman and Niki (1973)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1}s^{-1}$		Notes and Reliability of log k
— $O_3 + H \rightarrow HO + O_2$				
*Hampson, et al (1973) review	300	2.6×10^{-11} cm^3 $molecule^{-1}s^{-1}$		±0.1 ?
— $O_3 + HO \rightarrow HO_2 + O_2$				
DeMore (1973)	300	8×10^{-14}		
Anderson, Kaufman (1973)	220–450	1.3×10^{-12} exp(−956/T)		
*Hampson, et al (1973) review	220–450	1.6×10^{-12} exp(−1000/T)		±0.3
Davis (1973)	298	7.4×10^{-14}		±0.06
Kurylo (1973)	298	6.5×10^{-14}		±0.06
— $O_3 + HO(v_1 > 0) \rightarrow$ products				
Coltharp, Worley, Potter (1971)	300	v_1(HO)	$k/cm^3 molecule^{-1}s^{-1}$	
		2	$1.9 \pm1.1 \times 10^{-12}$	
		3	$2.4 \pm0.9 \times 10^{-12}$	
		4	$2.8 \pm0.8 \times 10^{-12}$	
		5	$3.4 \pm0.7 \times 10^{-12}$	
		6	$5.3 \pm0.6 \times 10^{-12}$	
		7	$6.5 \pm0.5 \times 10^{-12}$	
		8	$6.7 \pm0.5 \times 10^{-12}$	
		9	$7.7 \pm0.3 \times 10^{-12}$	
— $O_3 + HO_2 \rightarrow (HO + 2O_2)$				
DeMore (1973)	300	3×10^{-15}		
Anderson (1973)	220–450	$k/k(HO + O_3 \rightarrow HO_2 + O_2) \lesssim 0.1$		
*This Survey (D.G.)	225–298	1×10^{-13} exp(−1250/T)		±0.3 a

(continued on next page)

Reactions of O_3 with H to HO_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
Lloyd (1973) review	200-500	$1.7 \times 10^{-13} \exp(-1400/T)$	$>\pm 0.3$ a,b
Simonaitis, Heicklen (1973)	225-298	$k/(k_{ref})^{0.5} = 1.9 \times 10^{-8} \exp(-1000/T)$ $(cm^3 molecule^{-1} s^{-1})^{0.5}$ (a) Reference reaction: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$. Preferred value is based on meas. of Simonaitis and Heicklen and k_{ref} given in these tables. (b) Pre-exponential factor increased	± 0.15 a
— $O_3 + SO \rightarrow O_2 + SO_2$			
Schofield (1973) review	223-303	$2.5 \times 10^{-12} \exp(-1050/T)$	± 0.5
— $O_3 + Cl \rightarrow ClO + O_2$			
Watson (1973) review	300	$1.85 \pm 0.36 \times 10^{-11}$	± 0.1
— $O_3 + CO \rightarrow CO_2 + O_2$			
Arin, Warneck (1972)	296	$<4 \times 10^{-25}$	
— $O_3 + CH_4 \rightarrow$ products			
Dillemuth, et al (1960)	310-340	$2.7 \times 10^{-13} \exp(-7700/T)$	
— $O_3 + C_2H_4 \rightarrow$ products			
Demerjian, et al (1972) review	300	2.7×10^{-18}	
DeMore (1969)	178-233	$3.2 \times 10^{-15} \exp(-2400/T)$	
Stedman, et al (1973)	300	$1.55 \pm 0.15 \times 10^{-18}$	
*This survey (D.G., R.H.)	200-300	$6 \times 10^{-15} \exp(-2400/T)$ (a) The room temperature recommendation of Demerjian et al and the value of Stedman et al have been combined with DeMore's activation energy.	(a)

Reactions of O_3 with SO to C_2H_4

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $O_3 + C_3H_6 \rightarrow C_3H_6O_3$			
Demerjian et al (1972) review	300	1.0×10^{-17}	
DeMore (1969)	183, 193, 300	$1.65 \times 10^{-15} \exp(-1600/T)$	(b)
Stedman, et al (1973)	300	$1.25 \pm 0.1 \times 10^{-17}$	
*This survey (D.G.,R.H.)	200-300	$7 \times 10^{-15} \exp(-1900/T)$	(a)

(a) The room temperature value of Stedman et al has been combined with DeMore's low temperature data.

(b) Includes 300K point of Hanst et al (1958)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Notes and Reliability of log k
— $N + N + M \rightarrow N_2 + M$			
*Baulch, et al (1973) review	100–600	$8.3 \times 10^{-34}\exp(+500/T)\mathrm{cm}^6\mathrm{molecule}^{-2}\mathrm{s}^{-1}$, $(M = N_2)$	± 0.2(200–600) <0.2 ($T<200$K)
		where $-d[N]/dt = 2k[N]^2[M]$	
— $N + NO \rightarrow N_2 + O$ (f)			
— $O + N_2 \rightarrow N + NO$ (r)			
*Baulch, et al (1973) review	300–5000	$k_f = 2.7 \times 10^{-11}$	± 0.1 (a)
	2000–5000	$k_r = 1.3 \times 10^{-10} \exp(-38000/T)$	± 0.3
		(a) Uncertainty increases to ± 0.3 for $T > 2000$. k_f based on 300 K data and $k_r(T > 2000)$.	
— $N + NO_2 \rightarrow$ all channels			
*Baulch, et al (1973) review	300	1.85×10^{-11}	
		no reliable estimate can be made for the relative importance of the four product channels: $\rightarrow NO + NO$, $\rightarrow N_2O + O$, $\rightarrow N_2 + O_2$, $\rightarrow N_2 + O + O$	
— $N + HO \rightarrow NO + H$			
*Baulch, et al (1973) review	300	5.3×10^{-11}	± 0.3 (a)
		(a) Based on $k/k(O + HO \rightarrow O_2 + H) = 1.4$	
— $NO + h\nu$			
Hampson, et al (1973a) review		Recommended values of oscillator strengths from which absorption cross sections can be derived are given for β, γ, δ, and ε bands. Recommended values of absorption cross section $106 < \lambda < 135$ nm. No recommended quantum yield values.	

Reactions of $N + N$ to $NO + h\nu$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1}s^{-1}$	Notes and Reliability of log k
— $NO + M \rightarrow N + O + M$			
*Baulch, et al (1973) review	4200–6700	Insufficient data for a reliable recommendation. Use, with caution: $6.6 \times 10^{-4}T^{-1.5} \exp(-75.5 \times 10^3/T)$ cm^3 $molecule^{-1}s^{-1}$ $(M = Ar, O_2, N_2)$ $k(M = NO, N, O)/k(Ar) \sim 18$	
— $NO + NO \rightarrow N + NO_2$			
Baulch, et al (1973) review	Endothermic. Unimportant compared to $NO + NO \rightarrow N_2O + O$		
— $NO + NO \rightarrow N_2O + O$		see reverse reaction	
— $NO + NO + O_2 \rightarrow NO_2 + NO_2$		see $O_2 + NO + NO \rightarrow NO_2 + NO_2$	
— $NO + NO_2 + H_2O \rightarrow 2HNO_2$			
Hampson, et al (1973) review	300	$<1.1 \times 10^{-55}$ cm^9 $molecule^{-3}s^{-1}$ where k is defined as: $-d[NO_2]/t = k[NO][NO_2][H_2O]^2$ main reaction probably is heterogeneous	
— $NO + NO_3 \rightarrow 2NO_2$			
Baulch, et al (1973) review	300	$\sim 2 \times 10^{-11}$	±0.7 estimate
Johnston (1966) review	300	8.3×10^{-12}	
*Harker, Johnston (1972)	300	8.7×10^{-12}	
(D.G.,D.D.D.)			
	Temperature effect is probably zero or very small.		
— $NO + NH_2 \rightarrow N_2 + H_2O^*$			
Gehring, et al (1973)	300	8×10^{-12}	±0.1

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $NO + H + M \rightarrow HNO + M$			
Baulch, et al (1973) review	230–700	$1.5 \times 10^{-32} \exp(300/T)\ cm^6 molecule^{-2} s^{-1}$ $M = H_2$	±0.2
*This survey (DG)	220–400	$2.1 \times 10^{-32} \exp(300/T)$	±0.2
Atkinson, Cvetanovic (1973)	286–390	$2.5 \times 10^{-32} \exp(270/T)$ $M = H_2$	
Allen, Moortgat (1973)	180–300	$5.6(\pm 0.6) \times 10^{-33} \exp(+375(\pm 65)/T)$, $M = Ar$	
Thrush (1973) review	230–700	$2 \times 10^{-32} \exp(+300/T)$, $M = H_2$	
— $NO + HO \rightarrow NO_2 + H$			
Baulch, et al (1973) review	298–633	$5.2 \times 10^{-12} \exp(-15.1 \times 10^3/T)$ (a)	±0.2(298K)
	based on $k = 5.8 \times 10^{-10} \exp(-740/T)$ for reverse reaction	(a) corrected expression	increasing to ±0.3(633K)
— $NO + HO(+M) \rightarrow HNO_2(+M)$			
Hampson, et al (1973a) review		Elevation/km k(T,M)	
	220	15 2.4×10^{-12}	±0.5 Relative
	217	20 1.5×10^{-12}	values from one
	222	25 8.9×10^{-13}	elevation to
	227	30 4.8×10^{-13}	another ±10%
	235	35 2.6×10^{-13}	$M = N_2$
	250	40 1.1×10^{-13}	
	260	45 5.9×10^{-14}	
Baulch, et al (1973) review	273–395	$2.2 \times 10^{-32} \exp(+1110/T)\ cm^6 molecule^{-2} s^{-1}$ $M=He$	±0.2 at 300K inc. to ±0.3 at 395 K
	300	$2 \times 10^{-12}\ cm^3 molecule^{-1} s^{-1}$ (2d order high pressure limit)	±0.3

Reactions of NO with H and HO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1}s^{-1}$	Notes and Reliability of log k
— $NO + HO_2 \rightarrow NO_2 + OH$			
* This survey (D.D.D.)	300	2×10^{-13}	±0.5
Lloyd (1973) review	300	1.7×10^{-13}, $E/R < 2000$	±0.3
Payne, Stief, and Davis (1973)	300	3×10^{-13}	±0.5 (a)
Simonaitis and Heicklen (1973)	300	$> 1.5 \times 10^{-13}$	±0.5 (a)
Baulch, et al (1973) review	300	3×10^{-13}	±0.8
	(a) $k/k(2HO_2 \rightarrow H_2O_2)$ measured		
— $NO + H_2 \rightarrow HNO + H$			
Baulch, et al (1973) review	2000	5.3×10^{-18} cm^3 $molecule^{-1}s^{-1}$	±0.2 (a)
		(a) No data. Value based on reverse rate	
— $NO + H_2O \rightarrow HNO + HO$			
Baulch, et al (1973) review	2000	4×10^{-18}	±0.2 (a)
		(a) No data. Value based on reverse rate.	(Corrected)
— $NO + H_2O_2 \rightarrow HO + HNO_2$			
*Hampson, et al (1973) review	300	$< 5 \times 10^{-20}$	
	500	$\sim 2 \times 10^{-20}$	
Gray, et al (1972)	300	$< 5 \times 10^{-20}$	
— $NO + CH_3 (+M) \rightarrow CH_3NO (+M)$			
Glanzer, Troe (1973) review	295	1.7×10^{-11} $cm^3 molecule^{-1}s^{-1}$ at high pressure	±0.15
— $NO + CH_3O \rightarrow . . .$		see $CH_3O + NO \rightarrow . . .$	
— $NO + CH_3O_2 \rightarrow CH_3O_2NO$ (a) $\rightarrow CH_2O + HONO$ (b) $\rightarrow CH_3O + NO_2$ (c)			
Demerjian, et al (1972) review	300	$k_c = 3.3 \times 10^{-12} \exp(-500/T)$	estimate

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliability of log k
Heicklen (1973) review	298	$k_a/k = 0.6 \pm 0.1$	
		$k_b/k = 0.4 \pm 0.1$	
		$k_c/k < 0.02$	
		$(k = k_a + k_b + k_c)$	
— $NO_2 + h\nu \rightarrow NO + O$			
Hampson, et al (1973a) review		λ/nm Ø(O(^{3}P))	
		295-398 1.0	
		400 0.70	
		405 0.29	
		410 0.12	
		420 0.02	
		440 0.001	
		absorption cross section data	
		$108 < \lambda < 500$ nm	
— $NO_2 + M \rightarrow NO + O + M$		see reverse reaction	
— $NO_2 + NO_2 \rightarrow NO + NO_3$			
Baulch, et al (1973) review		No recommendation	
— $NO_2 + NO_2 \rightarrow NO + NO + O_2$			
Baulch, et al (1973) review	600-2000	$3.3 \times 10^{-12} \exp(-13540/T)$	± 0.15 (600-1000 K)
		$k_1[NO_2]^2 = -(1/2)d[NO_2]/dt$	increasing to 0.3 at 2000 K
— $NO_2 + NO_2 + M \rightarrow N_2O_4 + M$			
Baulch, et al (1973) review	250-350	$4.7 \times 10^{-35} \exp(-860/T)$ cm^{6}molecule^{-2}s^{-1} $M = N_2$	± 0.15 (a)
		(a) $k_f = k_r K_{eq}$	

Reactions of NO_2 with hv to NO_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$			Notes and Reliability of log k
— $N_2O_4 + M \rightarrow NO_2 + NO_2 + M$					
Baulch, et al (1973) review	250-350	$4.2 \times 10^{-7} \exp(-5550/T)$		$M = N_2$	± 0.15
Schofield (1973) review	250-350	$3.3 \times 10^{-7} \exp(-5540/T)$		$M = N_2$	± 0.15
— $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ (f)					
— $O_2 + NO + NO_2 \rightarrow NO_2 + NO_3$ (r)					
*Baulch, et al (1973) review	300-850	$k_f = 2.3 \times 10^{-13} \exp(-1000/T)$			± 0.4 (a)
	300-500	$k_r = k_f/K_{eq} = 8 \times 10^{-41} \exp(400/T) cm^6 molecule^{-2} s^{-1}$			± 0.4
Johnston (1966) review	300-1100	$k_f = 3.8 \times 10^{-13} \exp(-2200/T)$			
		(a) Based on $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ and $2NO_2 \rightarrow 2NO + O_2$			
— $NO_2 + NO_3 (+M) \rightarrow N_2O_5 (+M)$					
*This survey (HSJ)		Elevation/km	k (T,M) $cm^3 molecule^{-1} s^{-1}$	Log (M)	
	220	15	1.9×10^{-12}	18.60	
	217	20	1.1×10^{-12}	18.27	
	222	25	6.6×10^{-13}	17.93	
	227	30	4.5×10^{-13}	17.58	
	235	35	2.7×10^{-13}	17.26	
	250	40	1.5×10^{-13}	16.92	
	260	45	7.1×10^{-14}	16.60	
— $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (f)					
— $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ (r)					
Baulch, et al (1973) review	300	$k_f = 2.8 \times 10^{-30} cm^6 molecule^{-2} s^{-1}$			± 0.3 (a)
	300	$3.8 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ (2d order high pressure limit)			± 0.4 (a)

(continued on next page)

Reactions of $N_2O_4 + M$ to $NO_2 + NO_3$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Notes and Reliability of log k
	300-340	$k_r = 2.2 \times 10^{-5} \exp(-9700/T)$ $cm^3 molecule^{-1} s^{-1}$		±0.3 (a)
	273-300	$5.7 \times 10^{14} \exp(-10600/T)$ s^{-1}		±0.4 (a)
		(limiting first order expression)		
		(a) $k_f = K_{eq} k_r$. $M = N_2O_5 + NO$		
— $NO_2 + NH_3 \rightarrow NH_2 + HNO_2$				
Bedford, Thomas (1972)	615-660	$6.7 \times 10^{-12} \exp(-13900/T)$		
— $NO_2 + H \rightarrow HO + NO$				
*Hampson, et al (1973) review	300	4.8×10^{-11}		±0.1
Baulch, et al (1973) review	298-633	$5.8 \times 10^{-10} \exp(-740/T)$		±0.2 at 298K increasing to ±0.3 at 633K
— $NO_2 + HO (+M) \rightarrow HNO_3 (+M)$				
*Tsang (1972) review		Elevation/km	k(T,M)	
Summarized in Hampson (1973a)				
	220	15	3.2×10^{-12}	±0.3 Relative
	217	20	2.5×10^{-12}	values from one
	222	25	1.6×10^{-12}	elevation to
	227	30	8.5×10^{-13}	another ±5%
	235	35	5.5×10^{-13}	$M = N_2$
	250	40	2.7×10^{-13}	
	260	45	1.4×10^{-13}	
— $NO_2 + HO + M \rightarrow HNO_3 + M$ (f)				
— $HNO_3 + M \rightarrow HO + NO_2 + M$ (r)				
Baulch, et al (1973) review	273-400	$k_f = 3.6 \times 10^{-32} \exp(+1100/T) cm^6 molecule^{-2} s^{-1}$		±0.2
		$M = He$		

(continued on next page)

Reactions of NO_2 with NH_3 to HO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
	800-1200	$k_r = 2.7 \times 10^{-9} \exp(-15400/T) cm^3 molecule^{-1} s^{-1}$ M = Ar	±0.4
	300	$k_f = 8 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ (2d order high pressure limit)	±0.4
— $NO_2 + HO_2 \rightarrow HNO_2 + O_2$			
Simonaitis, Heicklen (1973)	298	$> 3 \times 10^{-13}$ $k/k(HO_2 + NO \rightarrow HO + NO_2) = 7 \pm 1$ (a) Interpretation of photolysis experiments, comparison with $2HO_2 \rightarrow H_2O_2 + O_2$	(a)
— $NO_2 + CH_3 \rightarrow CH_3O + NO$			
Glanzer, Troe (1973) review	300-1400	3.3×10^{-11} (a) Based on $k/k(CH_3 + NO) = 3.3$ at room temperature and on shock wave pyrolysis of CH_3NO_2	±0.25 (a)
— $NO_2 + CH_3 (+M) \rightarrow CH_3NO_2 (+M)$			
Glanzer, Troe (1973) review	295	$2.8 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ (a) Based on high pressure limit rate ratio $k/k(CH_3 + NO) = 1.7$	±0.1 (a)
— $NO_2 + CH_3 + M \rightarrow CH_3NO_2 + M$			
Glanzer, Troe (1973) review	900-1400	$6.9 \times 10^{-31} cm^6 molecule^{-2} s^{-1}$, M = Ar (a) $k_f = k_r K_{eq}$	(a)
— $NO_2 + CH_3O \rightarrow . . .$		see $CH_3O + NO_2 \rightarrow . . .$	

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $NO_2 + CH_3O_2 \rightarrow CH_3O_2NO_2$ (a)			
$\rightarrow CH_2O + HONO_2$ (b)			
$\rightarrow CH_3O + NO_3$ (c)			
*Heicklen (1973) review	298	$k_a/k = 0.75 \pm 0.05$	
		$k_b/k = 0.25 \pm 0.1$	
		$k_c/k < 0.1$	

Reactions of NO_2 with CH_3O_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $NO_3 + h\nu \rightarrow NO + O_2$			
*Johnston (1972) review		Very strong absorption spectrum 600-700nm. Pre-dissociated spectra. Alternative products ($NO_2 + O$) energetically impossible at wave lengths above 576 nm. Destruction of NO_3 observed; primary products not observed.	
Johnston (1973)		$2.64 \times 10^{-2} s^{-1}$ (450-578nm) Daylight $4.34 \times 10^{-2} s^{-1}$ (579-680nm) Daylight	
— $NO_3 + M \rightarrow NO_2 + O + M$		see reverse reaction	
— $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$			
*Johnston (1966) review	600-1100	$4.3 \times 10^{-12} \exp(-3850/T)$	±0.3 (a)
*Baulch, et al (1973) review	293-309	$5 \times 10^{-12} \exp(-3000/T)$ (a) $-d[NO_3]/dt = 2k[NO_3]^2$. Based on rate of O_3 decomp. in presence of N_2O_5	±0.5 (a)
— $NO_3 + H_2O \rightarrow HNO_3 + HO$			
Baulch, et al (1973) review	300	2.3×10^{-26} (a) $k_f = k_r K_{eq}$	±0.3 (a)
— $N_2 + M \rightarrow N + N + M$			
*Baulch, et al (1973) review	6000-15000	$6.1 \times 10^{-3} T^{-1.6} \exp(-113{,}200/T) cm^3 molecule^{-1} s^{-1}$ $M = N_2$	±0.5
— $N_2 + HO \rightarrow N_2O + H$			
*Baulch, et al (1973) review	700-2500	$5.4 \times 10^{-12} \exp(-40.4 \times 10^3/T)$ (a) $k_f = k_r K_{eq}$ (corrected expression)	±0.2 (a)

Reactions of $NO_3 + h\nu$ to $N_2 + HO$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}		Notes and Reliability of log k
— $N_2O + M \rightarrow N_2 + O + M$		.see reverse reaction		
— $N_2O + H \rightarrow N_2 + HO$				
Baulch, et al (1973) review	700-2500	$1.26 \times 10^{-10} \exp(-7600/T)$		± 0.2
Baldwin, et al (1973)	773	4.3×10^{-15}		± 0.15
— $N_2O + CO \rightarrow$ products				
Milks, Matula (1973)	1169-1655	$3.5 \times 10^{-13} \exp(-8650/T)$		
— $N_2O_5 + h\nu \rightarrow$ . . .				
*Jones, Wulf (1937)		λ/nm	Absn. cross sect./cm^{2}molecule^{-1}, base e	Scatter: 25%
		285	4.6×10^{-20}	Reliability
		290	3.8×10^{-20}	unknown
		300	2.3×10^{-20}	
		310	1.2×10^{-20}	
		320	0.69×10^{-20}	
		330	0.39×10^{-20}	
		340	0.24×10^{-20}	
		350	0.17×10^{-20}	
		360	0.095×10^{-20}	
Holmes, Daniels (1934)		265	$18. \times 10^{-20}$	
		280	8.3×10^{-20}	
		>302	Zero	
Murphy (1969)		$0.5 \times \phi(-N_2O_5) = \phi(O) = 0.31 \quad \lambda = 280$ nm		
		Meas. by Holmes, Daniels (1934) are consistent		
Hampson, et al (1973a) review		Survey of photochemistry including data listed above		

Reactions of $N_2O + M$ to $N_2O_5 + h\nu$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}		Notes and Reliability of log k
— N_2O_5 (+M) -> NO_2 + NO_3 (+M)		Elevation/km	k/s^{-1}	
*This survey (HSJ)	220	15	5.0 x 10^{-7}	±0.5
	217	20	1.8 x 10^{-7}	
	222	25	3.0 x 10^{-7}	
	227	30	5.5 x 10^{-7}	
	235	35	1.9 x 10^{-6}	
	250	40	1.6 x 10^{-5}	
	260	45	4.4 x 10^{-5}	
	Extrapolated from data taken between 273 and 353 K.			
— N_2O_5 + M -> NO_2 + NO_3 + M		see reverse reaction		
— N_2O_5 + H_2O -> 2HNO_3				
Hampson, et al (1973) review	300	k < 1 x 10^{-20}		
Morris, Niki (1973)	298	< 1.3 x 10^{-20}		
— NH_2 + H + M -> NH_3 + M				
Baulch, et al (1973) review	2000-3000	1.2 x 10^{-33} exp(11200/T) cm^6 molecule^{-2}s^{-1}, M = Ar		±0.3 (a)
		(a) $k_f = K_{eq}\, k_r$		
— NH_2 + HO -> NH_3 + O		see reverse reaction		
— NH_2 + H_2 -> NH_3 + H				
Baulch, et al (1973) review	800	< 10^{-16} $k_f = K_{eq}\, k_r$		approximate
— NH_2 + H_2O -> NH_3 + HO				
Baulch, et al (1973) review		no data, no recommendation		
— NH_3 + M = NH_2 + H + M				
Baulch, et al (1973) review	2000-3000	k = 1.5 x 10^{-8} exp(-42400/T) (M = Ar)		±0.3 (a)
		(a) To be used when P(M) < 4 atm.		

Reactions of N_2O_5 + M to NH_3 + M

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}$	Notes and Reliability of log k
— $NH_3 + H \rightarrow NH_2 + H_2$			
Baulch, et al (1973) review	800	$< 10^{-16}$	approximate
— $NH_3 + HO \rightarrow NH_2 + H_2O$			
Baulch, et al (1973) review		no recommendation. Data scatter badly products may be $NH_2OH + H$	
Hack, Hoyermann (1973)	300	2.8×10^{-13}	
Stuhl (1973a)	298	1.5×10^{-13}	± 0.1
Kurylo (1973)	298	4.1×10^{-14}	± 0.06
Smith (1973)	230–470	$2.3 \times 10^{-12} \exp(-800/T)$	

Reactions of NH_3 with H and HO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $H + H + M \rightarrow H_2 + M$ (f)			
— $H_2 + M \rightarrow H + H + M$ (r)			
Baulch, et al (1972) review	300	$k_f = 8.3 \times 10^{-33}$ $cm^6 molecule^{-2} s^{-1}$ $M = H_2$	±0.2
	1700-5000	$= 1.8 \times 10^{-30}$ T^{-1} $M = Ar$	±0.3
		Rel. efficiencies: $H_2(1.0)$, $Ar(0.25)$	
		$-d[H]/dt = 2k[H]^2[M]$	
	2500-5000	$k_r = 3.7 \times 10^{-10}$ exp(-48300/T)$cm^3 molecule^{-1} s^{-1}$,	±0.3
		$M = Ar$	
— $H + HO \rightarrow H_2 + O$		see reverse reaction	
— $H + HO + M \rightarrow H_2O + M$ (f)			
— $H_2O + M \rightarrow H + HO + M$ (r)			
*Baulch, et al (1972) review	1000-3000	$k_f = 6.1 \times 10^{-26} T^{-2} cm^6 molecule^{-2} s^{-1}$, $M = N_2$	±0.3
	2000-6000	$k_r = 5.8 \times 10^{-9}$ exp(-52900/T) $cm^3 molecule^{-1} s^{-1}$	±0.2
		$M = N_2$	
— $H + HO_2 \rightarrow HO + HO$ (1f)			
— $HO + HO \rightarrow H + HO_2$ (1r)			
— $H + HO_2 \rightarrow H_2 + O_2$ (2)			
— $H + HO_2 \rightarrow H_2O + O$ (3)			
Baulch, et al (1972) review	290-800	$k_{1f} = 4.2 \times 10^{-10}$ exp(-950/T)	±0.3 (a)
		$k_{1r} = k_{1f}/K_{eq} = 2.0 \times 10^{-11}$ exp(-20200/T)	±0.3
	290-800	$k_2 = 4.2 \times 10^{-11}$ exp(-350/T)	±0.4
		$k_{2r} = k_{2f}/K_{eq} = 9.1 \times 10^{-11}$ exp(-29100/T)	±0.4
		k_3 = no recommendation	
Lloyd (1973) review	300-1000	k_{1f} and k_2 - same as Baulch, et al	>±0.3 (a)
		$k_3 = 8.3 \times 10^{-11}$ exp(-500/T)	>±0.5 (b)

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3molecule^{-1}s^{-1}$	Notes and Reliability of log k
Moortgat, Allen (1973)	297	$k_{1f} = 8.3 \times 10^{-12}$	? (c)
		$k_2 = 1 \times 10^{-11}$	? (c)
		$k_3 = 6.7 \times 10^{-12}$	? (c)
		(a) Reaction 1 and rate ratios control values for reactions 2 and 3.	
		(b) Temperature coefficient estimated.	
		(c) Secondary reaction in $H + O_2 + M$ systems, fit of concentration vs. time plots.	
$H + H_2O \rightarrow H_2 + HO$			
Baulch, et al (1972) review	300-2500	$1.5 \times 10^{-10} \exp(-10250/T)$	±0.06 at 300K increasing to ±0.2 at high temp.
$H + H_2O_2 \rightarrow H_2 + HO_2$			
*Hampson, et al (1973) quoting	300-800	$2.8 \times 10^{-12} \exp(-1900/T)$	±0.3
Baulch, et al (1972) review			
$H + H_2O_2 \rightarrow H_2O + HO$			
*Hampson, et al (1973) quoting		no recommendation	
Baulch, et al (1972) review			
$H + HNO \rightarrow H_2 + NO$			
Hampson, et al (1973) review	211-703	$> 5 \times 10^{-14}$	±0.3
	2000	7×10^{-12}	±0.3
Baulch, et al (1973) review	300	$10^{-13} < k < 10^{-12}$	
	2000	8×10^{-12}	±0.2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1}s^{-1}$	Notes and Reliability of log k
— $H + HNO_2 \rightarrow$ products			
Hampson, et al (1973) review		No data	
Baulch, et al (1973) review		No recommendation	
— $H + HNO_3 \rightarrow$ products			
Hampson, et al (1973) review	300	$< 1 \times 10^{-13}$	
Wayne (1973)	300	$< 1 \times 10^{-15}$	estimate
Baulch, et al (1973) review	300	$< 10^{-13}$	approximate upper limit
— $H + CH_2O \rightarrow H_2 + CHO$			
Ridley, et al (1972)	297	5.4×10^{-14}	± 0.04
Westenberg, de Haas (1972)	297-652	$2.2 \times 10^{-11} \exp(-1890/T)$	
— $HO + M \rightarrow H + O + M$			
Baulch, et al (1972) review		no recommendation ($E/R > 50000$ K)	
— $HO + HO \rightarrow H + HO_2$		see reverse reaction	
— $HO + HO \rightarrow H_2 + O_2$			
Baulch, et al (1972) review		no recommendation	
— $HO + HO \rightarrow H_2O + O$ (f)			
— $O + H_2O \rightarrow HO + HO$ (r)			
*Baulch, et al (1972) review	300-2000	$k_f = 1.0 \times 10^{-11} \exp(-550/T)$	± 0.2
	300-2000	$k_r = 1.1 \times 10^{-10} \exp(-9240/T)$	± 0.2
Gardiner, et al (1973)	1200-2500	$k_f = 9.1 \times 10^{-11} \exp(-3500/T)$	
Westenburg, de Haas (1973a)	300	$k_f = 2.3 \times 10^{-12}$	± 0.06
— $HO + HO + M \rightarrow H_2O_2 + M$ (f)			
— $H_2O_2 + M \rightarrow HO + HO + M$ (r)			
Baulch, et al (1972) review	700-1500	$k_f = 2.5 \times 10^{-33} \exp(+2550/T) cm^6 molecule^{-2}s^{-1}$ $M = N_2$; $-d[OH]/dt = 2k[OH]^2[M]$	± 0.1 $700<T<950K$ increasing to

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
		$k_r = 2.0 \times 10^{-7} \exp(-22900/T) cm^3 molecule^{-1} s^{-1}$, $M = N_2$; $k_f = k_r K_{eq}$	±0.3 at 1500K
— $HO + HO_2 \rightarrow H_2O + O_2$			
Baulch, et al (1972) review		no recommendation	
Kaufman (1964) review	300	$k > 1 \times 10^{-11}$	estimate
Lloyd (1973) review	300-1000	$8.3 \times 10^{-11} \exp(-500/T)$	±0.3
Hochanadel, et al (1972)	300	2×10^{-10}	
*This survey (H.S.J.)		The range of values $2 \times 10^{-11} < k <$ $2 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ should be considered in models of the stratosphere	
— $HO + HO_2 \rightarrow H_2O_2 + O$			
Baulch, et al (1972) review		no recommendation	
— $HO + H_2 \rightarrow H_2O + H$			
Baulch, et al (1972) review	300-2500	$3.6 \times 10^{-11} \exp(-2590/T) cm^3 molecule^{-1} s^{-1}$	±0.08 at 300 K ±0.2 at high temp.
Wilson (1972) review	300-2000	$3.8 \times 10^{-11} \exp(-2600/T)$	±0.3
Stuhl, Niki (1972)	298	7.1×10^{-15}	+0.06
Westenberg (1973a)	298	7.6×10^{-15}	±0.04
	352	1.8×10^{-14}	
	403	3.2×10^{-14}	
	518	1.4×10^{-13}	
	628	3.6×10^{-13}	
	745	6.6×10^{-13}	
Smith, Zellner (1973a)	210-460	$1.8 \times 10^{-11} \exp(-2330/T)$	(a)

(continued on next page)

Reactions of HO with HO_2 and H_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
Paraskevopoulos (1973)	300	5.9×10^{-15}	
Gardiner, et al (1973)	1200-2500	$8.7 \times 10^{-11} \exp(-3250/T)$	
Greiner (1969)	300-500	$6.8 \times 10^{-12} \exp(-2020/T)$	±0.15
		(a) Reinterpretation by authors of reported data.	
— $HO + H_2O \rightarrow H_2O_2 + H$			
Baulch, et al (1972) review		no recommendation	
— $HO + H_2O_2 \rightarrow H_2O + HO_2$			
*Hampson (1973) quoting	300-800	$1.7 \times 10^{-11} \exp(-910/T)$	±0.2
Baulch, et al (1972) review			
Gorse, Volman (1972)	300	$k/k(HO + CO) = 8.13$	
— $HO + HNO \rightarrow H_2O + NO$			
Hampson, et al (1973) review	1600-2100	7×10^{-11}	±0.7
Baulch, et al (1973) reviw	2000	6×10^{-11}	±0.2
— $HO + HNO_2 \rightarrow H_2O + NO_2$			
Demerjian, et al (1972) review	300	6.8×10^{-12}	estimated, no data
Baulch, et al (1973) review	300	1.3×10^{-13}	±0.6 estimated
— $HO + HNO_3 \rightarrow H_2O + NO_3$			
Hampson, et al (1973) review	300-650	$6 \times 10^{-13} \exp(-400/T)$	±0.5
Johnston (1972) review	300-700	$(1.5 \text{ to } 2.0) \times 10^{-13}$	±0.2
*This survey (H.S.J.)	220-270	1.3×10^{-13}	
Wayne (1973)	300	1.5×10^{-13}	approximate
Baulch, et al (1973) review	300	1.3×10^{-13}	±0.3
Smith (1973)	300	8×10^{-14}	

Reactions of HO with H_2O to HNO_3

Reaction/Reference * = Preferred Value	Temp. Range/k	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $HO + SO_2 + M \rightarrow HSO_3 + M$			
*Payne, Stief, Davis (1973)	300	2×10^{-32} $cm^6 molecule^{-2} s^{-1}$ M = He	±0.3
Wayne (1973)	300	$4.5 \pm 1.5 \times 10^{-31}$ M = Ar	
— $HO + HCl \rightarrow H_2O + Cl$			
Takacs, Glass (1973)	295	$6.4 \pm 1.5 \times 10^{-13}$	±0.1
— $HO + CO \rightarrow CO_2 + H$			
*This survey (D.G.)	200-400	1.4×10^{-13}	±0.1 (a)
Wilson (1972) review	300-2000	5.1×10^{-13} exp(-300/T)	±0.3
Stuhl, Niki (1972)	300	1.35×10^{-13}	±0.06
Westenberg, de Haas (1973a)	298	1.33×10^{-13}	±0.04
	396	1.38×10^{-13}	
	523	1.44×10^{-13}	
	707	1.69×10^{-13}	
	915	2.17×10^{-13}	
Davis (1973)	220-370	2.05×10^{-13} exp(-75/T)	±0.04
Greiner (1969)	300-500	2.1×10^{-13} exp(-115/T)	±0.1
Smith and Zellner (1973)	300	1.45×10^{-13}	(b)
Paraskevopoulos (1973)	300	1.43×10^{-13}	
Peeters, Mahnen (1973)	1600-1900	4.7×10^{-13}	
Gardiner, et al (1973)	1200-2500	6.7×10^{-12} exp(-4000/T)	

(a) Small temperature coef. at low temperatures. Ignore in models

(b) Data reported 210 <T< 460 K. Slight positive temperature dependence, possibly curved.

Reactions of HO with SO_2 to CO

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3molecule^{-1}s^{-1}$	Notes and Reliability of log k
— $HO + CH_2O \rightarrow H_2O + CHO$			
*Morris, Niki (1971)	300	1.4×10^{-11}	±0.1
Wilson (1972) review	300-1600	8×10^{-11}	±1
Peeters, Mahnen (1973)	1400-1800	3.8×10^{-11}	
— $HO + CH_4 \rightarrow CH_3 + H_2O$			
Wilson (1972) review	300-2000	$4.7 \times 10^{-11} \exp(-2500/T)$	±0.7
*Davis (1973) (D.G., R.H.)	240-370	$2.95 \times 10^{-12} \exp(-1770/T)$	±0.04
Paraskevopoulos (1973)	300	8.3×10^{-15}	
Peeters, Mahnen (1973)	1100-1900	$5 \times 10^{-11} \exp(-3000/T)$	
Greiner (1970)	300-500	$5.5 \times 10^{-12} \exp(-1900/T)$	±0.1
— $HO + C_2H_2 \rightarrow$ products			
Smith and Zellner (1973)	210-460	$2.0 \times 10^{-12} \exp(-250/T)$	
Pastrana, Carr (1973)	300	1.47×10^{-13}	(a)
		(a) assumes stoichiometry of 2/1	
— $HO + C_2H_4 \rightarrow$ products			
Stuhl (1973c)	298	3×10^{-12}	±0.12
Smith and Zellner (1973)	210-460	$7.5 \times 10^{-12} \exp(-110/T)$	
— $HO + C_2H_6 \rightarrow$ products			
Paraskevopoulos (1973)	300	3.0×10^{-13}	
— $HO + C_3H_6 \rightarrow$ products			
Stuhl (1973c)	298	1.45×10^{-11}	±0.06
— $HO + C_4H_{10} \rightarrow$ products			
Stuhl (1973b)		2.35×10^{-12}	±0.06

Reactions of HO with CH_2O to C_4H_{10}

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $HO_2 + M \rightarrow H + O_2 + M$			
Baulch, et al (1972) review	300-2000	3.5×10^{-9} exp(-23000/T), M = Ar	±0.2 (a)
Lloyd (1973) review		same recommendation	
		(a) $k_f = k_r K_{eq}$	
— $HO_2 + M \rightarrow HO + O + M$			
Baulch, et al (1972) review		no recommendation	
— $HO_2 + H_2 \rightarrow H_2O_2 + H$			
Baulch, et al (1972) review	300-800	1.2×10^{-12} exp(-9400/T)	±0.3
Lloyd (1973) review	300-1000	same recommendation.	
		$k_f = k_r K_{eq}$	
— $HO_2 + H_2O \rightarrow H_2O_2 + HO$			
Baulch, et al (1972) review	300-800	4.7×10^{-11} exp(-16,500/T)	±0.2
Lloyd (1973) review	300-1000	same recommendation	
		$k_f = k_r K_{eq}$	
— $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$			
*Hampson (1973) review	300-1000	3×10^{-11} exp(-500/T) cm^3 $molecule^{-1} s^{-1}$	±0.3 at 300 K
Baulch, et al (1972) review	300	3.3×10^{-12}	
Lloyd (1973) review	300-1000	1.7×10^{-11} exp(-500/T)	±0.3 at 300 K
		$-d[HO_2]/dt = 2k[HO_2]^2$. Temperature coefficient estimated	larger at higher T
— $HO_2 + SO_2 \rightarrow SO_3 + HO$			
*Payne, Stief, Davis (1973)	300	9×10^{-16} $cm^3 molecule^{-1} s^{-1}$	±0.3
		(relative rate measurement - reference reaction: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$)	

Reactions of HO_2 with M to SO_2

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $HO_2 + CO \rightarrow CO_2 + HO$			
*This survey (D.D.D., H.I.S.)	300	$<10^{-19}$	a
Lloyd (1973) eval.	300-1000	$1.7 \times 10^{-13} \exp(-5000/T)$	b
Westenberg, de Haas (1972)	300	-1×10^{-12}	c,d
Davis, Payne, Stief (1972)	300	$<10^{-20}$	e
Wyrsch, et al (1973)	300	$<3 \times 10^{-18}$	
Simonaitis, Heickeln (1973)	373-473	$<5 \times 10^{-18}$	e
Volman, Gorse (1972)	330	$<10^{-15}$	f
Baldwin, Walker, Webster (1970)	713-773	$1 \times 10^{-10} \exp(-11500/T)$	e
Vardanyan, Dangyan, Sachyan (1972)	878-952	$2.2 \times 10^{-10} \exp(-11500/T)$	

NOTE: a. The low value of k selected in this evaluation is based on the evaluation by Lloyd and the measurements by Davis, Payne, Stief and Simonaitis, Heicklen.

b. Based on Davis, Payne and Stief (1972) and high T results. Temperature coef. probably maximum value.

c. Indirect measurement using a low-pressure discharge flow system.

d. Relative rate measurement - reference reaction: $H + HO_2 \rightarrow HO + HO$

e. Relative rate measurement - reference reaction: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

f. Relative rate measurement - reference reaction: $HO + CO \rightarrow CO_2 + H$

— $HO_2 + CH_2O \rightarrow H_2O_2 + CHO$			
*Lloyd (1973) review	200-1000	$1.7 \times 10^{-12} \exp(-4000/T)$	>±1 at 300K, ±0.2 at 800K
Baldwin, et al (1972)	773	1.6×10^{-15} (note on next page)	(a)

Reactions of HO_2 with CO and CH_2O

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
		(a) Derived by computer fit to data. Based on $k(HO_2 + HO_2 \rightarrow H_2O_2 + O_2) = 3.0 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$	
$HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$			
Demerjian et al (1972) review	300	6.7×10^{-14}	estimate
$HO_2 + C_2H_4 \rightarrow C_2H_4O + HO$?			
Walker (1973)	773	2.5×10^{-17}	(a)
		(a) Relative to k $(HO_2 + HCHO) = 1.6 \times 10^{-15}$	
$HO_2 + C_2H_4 \rightarrow$ addition products			
Lloyd (1973) review	300	$\sim 1.7 \times 10^{-17}$	> ±1 (a)
		(a) Suggestion. Data are irreconcilable.	
$HO_2 + C_2H_6 \rightarrow H_2O_2 + C_2H_5$			
Lloyd (1973) review	300–1000	$\sim 1.7 \times 10^{-12} \exp(-7000/T)$	±1 (a)
		(a) Relative rate data versus $2HO_2 \rightarrow H_2O_2 + O_2$ and $HO_2 + CO \rightarrow HO + CO_2$. Temp. coef. estimated.	
$HO_2 + C_3H_8 \rightarrow H_2O_2 + i\text{-}C_3H_7$			
Lloyd (1973) review	300–1000	$<3.3 \times 10^{-13} \exp(-5300/T)$	±1 (a)
		(a) Based on upper limit meas. Temp. coef. estimated.	
$HO_2 + n\text{-}C_4H_{10} \rightarrow H_2O_2 + s\text{-}C_4H_9$ (primarily)			
Lloyd (1973) review	300–1000	$8.3 \times 10^{-13} \exp(-5300/T)$	±1 (a)
		(a) Based on upper limit meas. Temp. coef. estimated.	

Reactions of HO_2 with CH_3O_2 to $n\text{-}C_4H_{10}$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $HO_2 + i\text{-}C_4H_{10} \rightarrow H_2O_2 + t\text{-}C_4H_9$			
Lloyd (1973) review	300-1000	$1.7 \times 10^{-13} \exp(-3500/T)$	±1 (a)
		(a) Based on upper limit meas. Temp. coef. estimated.	
— $H_2 + M \rightarrow H + H + M$		see reverse reaction	
— $H_2O_2 + h\nu \rightarrow HO + HO$			
*Hampson (1973) review		Absorption coefficient (cross section)	
		λ/nm $\sigma/cm^2 molecule^{-1}$, base e	
		190 80×10^{-20}	
		195 60×10^{-20}	
		200 54×10^{-20}	
		205 46×10^{-20}	
		210 40×10^{-20}	
		215 34×10^{-20}	
		220 28×10^{-20}	
		225 24×10^{-20}	
		254 7.4×10^{-20}	
		Quantum yields (primary)	
		$\phi(-H_2O_2) = 1.0$ $\lambda > 200$nm.	
		See ref. for other, minor, channels pertinent for $\lambda < 200$nm.	
— $H_2O_2 + M \rightarrow HO + HO + M$		see reverse equation	
— $HNO + M \rightarrow H + NO + M$			
*Baulch, et al (1973) review	230-700	$5 \times 10^{-8} \exp(-24{,}500/T)$ $M = H_2$	±0.2 (a)
		(a) No data. Value based on reverse rate	

Reactions of HO_2 with $i\text{-}C_4H_{10}$ to $HNO + M$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$			Notes and Reliability of log k
— $HNO + HNO \rightarrow H_2O + N_2O$					
*Baulch, et al (1973) review	300	4×10^{-15}			±0.3
— $HNO_2 + h\nu \rightarrow HO + NO$					
Johnston (1973)		$6.45 \times 10^{-4}\ s^{-1}$ (Daylight)			
		absorption: 300-400nm			
— $HNO_3 + h\nu \rightarrow HO + NO_2$		Elevation/km	$k(noon)/s^{-1}$	$k(24\ hr.\ av.)/s^{-1}$	
*Johnston, (1972) review	220	15	5.1×10^{-7}	1.5×10^{-7}	±0.15
	217	20	7.7×10^{-7}	2.3×10^{-7}	Rates are for
	222	25	2.8×10^{-6}	6.8×10^{-7}	45° latitude,
	227	30	1.4×10^{-5}	3.5×10^{-6}	solar equinox
	235	35	4.1×10^{-5}	1.2×10^{-5}	standard ozone
	250	40	7.6×10^{-5}	2.7×10^{-5}	background
	260	45	1.1×10^{-4}	4.2×10^{-5}	
*Hampson, et al (1973) review		Absorption coefficients. See also Text.			
Johnston, Chang (1973)		$\emptyset = 1 \quad 200 < \lambda < 315nm$			(a)
		(a) Products probably those shown above.			
— $HNO_3 + M \rightarrow HO + NO_2 + M$		see reverse reaction			
— $SO + SO \rightarrow SO_2 + S$					
*Schofield (1973) review (WHB)	300	$< 3 \times 10^{-15}$			
	1000	$< 2 \times 10^{-13}$			
		only upper limit estimates are available			
— $SO_2 + CH_3\ (+M) \rightarrow CH_3SO_2\ (+M)$					
James, et al (1973)	300	$3 \times 10^{-13}\ cm^3 molecule^{-1} s^{-1}$			±0.1

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
— $Cl + OClO \rightarrow 2ClO$			
Watson (1973) review	300	$5.9 \pm 0.9 \times 10^{-11}$ ($E = 0 \pm 1$ kJ/mol)	± 0.1
— $Cl + CH_4 \rightarrow HCl + CH_3$			
Davis, et al (1970)	300	$1.5 \pm 0.1 \times 10^{-13}$	
Fettis, Knox (1964)		$4 \times 10^{-11} \exp(-1930/T)$	
Clyne, Walker (1973)	300-686	$5.1 \times 10^{-11} \exp(-1790/T)$	
— $CO + CH_3O \rightarrow . . .$		see $CH_3O + CO$	
— $CH_2O + h\nu \rightarrow CHO + H$ (a) $\rightarrow CO + H_2$ (b)			
*Calvert, et al. (1972) (D.G.)		$\phi_a + \phi_b = 1$, $290 < \lambda < 360$ nm	

λ/nm	ϕ_a	ϕ_b	absn. cross section cm^2 molecule^{-1} base e**
290	0.81	0.19	31.8×10^{-21}
300	0.66	0.34	32.5
310	0.52	0.48	31.4
320	0.40	0.60	23.4
330	0.29	0.71	23.6
340	0.18	0.82	19.7
350	0.09	0.91	8.37
360	0.01	0.99	1.77

**Averaged for 10 nm bands. See McQuigg, Calvert (1969) for graph of absn. coefficient vs. wave length.

(continued on next page)

Reactions of $Cl + OClO$ to $CH_2O + h\nu$

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliability of log k
Sperling, Toby (1973)		λ/nm $Ø_a$ $Ø_b$	
		313 0.8 0.2	
		334 0.45 0.25	
		366 0.2 0.45	
— $CH_3O + O_2 \rightarrow CH_2O + HO_2$ (1)			
— $CH_3O + NO \rightarrow CH_3ONO$ (2a)			
$\rightarrow CH_2O + HNO$ (2b)			
— $CH_3O + NO_2 \rightarrow CH_3ONO_2$ (3a)			
$\rightarrow CH_2O + HNO_2$ (3b)			
— $CH_3O + CO \rightarrow$ products (4)			
Demerjian, et al (1972) review	300	$k_1 = 1.6 \times 10^{-17}$	
		$\sim 4.2 \times 10^{-13} \exp(-3000/T)$	
		adjusted to fit C_4H_{10}/NO_x simulation studies	
		$k_{2a} = 1.7 \times 10^{-13}$	
		$k_{2b}/k_{2a} = 0.17$	
		$k_{3b} = 3.3 \times 10^{-13}$	
		$k_{3b}/k_{3a} = 0.1$	
*Heicklen (1973)	298	$k_1 - 3 \times 10^{-18}$	
		$\sim 1.6 \times 10^{-13} \exp(-3300/T)$	
		$k_2 - 8 \times 10^{-14}$	
	298	$k_1/k_2 = 4.7 \times 10^{-5}$ ±20%	ratio probably is smaller at 220 K
		$k_{2b}/k_2 = 0.145$ ±0.015	
		$k_2/k_3 = 1.2$ ±0.1	

(continued on next page)

Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliability of log k
	298	$k_{2a}/k_{3a} = 1.1$	
	363	$= 1.8$	
	403	$= 2.7$	
	298	$k_{3a}/k_3 = 0.9 \pm 0.1$	k_{3a}/k_{3b}
	298	$k_{3b}/k_3 = 0.1 \pm 0.01$	probably constant
			300-400 K
	298-423	$k_4/k_2 = 5 \times 10^{-4}$	
— $CH_3O_2 + CH_3O_2 \rightarrow CH_3OOH + CH_2O_2$ (a)			
$\rightarrow 2CH_3O + O_2$ (b)			
Demerjian, et al (1972) review	300	$k_a = 6.8 \times 10^{-14}$, $k_a = k_b$	estimate
— $CH_3ONO + h\nu \rightarrow CH_3O^* + NO$ (a)			
$\rightarrow$ isomer (b)			
$\rightarrow CH_2O + HNO$ (c)			
$\rightarrow CH_2O + H + NO$ (d)			
*Heicklen (1973) review	298	$k_a/k = 0.76 \pm 0.02$, $\lambda = 366nm$	
	298	$k_b/k = 0.24 \pm 0.04$, $\lambda = 366nm$	
	298	$(k_c + k_d)/k < 0.02$, $\lambda = 366nm$	
		$k = k_a + k_b + k_c + k_d$	

Reactions of CH_3O_2

REFERENCES

Ahumada, J. J., Michael, J. V., and Osborne, D. T., "Pressure Dependence and Third Body Effects on The Rate Constants for H + O_2, H + NO, and H + CO," J. Chem. Phys. 57, 3736-3745 (1972)

Albers, E. A., Hoyermann, K., Wagner, H. Gg., and Wolfrum J., "Study of the Reaction of Ammonia with Oxygen Atoms," Symp. Combust. 12th(Combustion Institute, Pittsburgh, 1969) 313-321

Allen, E. R., and Moortgat, G. K., "Kinetic Studies of The Termolecular Reactions of Hydrogen Atoms with Nitric Oxide and with Molecular Oxygen," Third Intern. Symp. Gas Kinetics, Brussels (1973), Abstract D1

Anderson, J. G., and Kaufman, F., "Kinetics of the Reaction OH(v=0) + O_3 -> HO_2 + O_2," Chem. Phys. Lett. 19, 483-486 (1973)

Arin, L. M., and Warneck, P., "Reaction of Ozone with Carbon Monoxide," J. Phys. Chem. 76, 1514-1515 (1972)

Atkinson, R., and Cvetanovič, R. J., "Determination of the Rates of Hydrogen Atom Reaction with NO by a Modulation Technique," Can. J. Chem. 51, 370-372 (1973)

Baldwin, R. R., Gethin, A., and Walker, R. W., "Reaction of Hydrogen Atoms with Nitrous Oxide," J. Chem. Soc. Faraday Trans. I, 69, 352-358 (1973)

Baldwin, R. R., Fuller, A. R., Longthorn, D., and Walker, R. W., "Addition of Formaldehyde to Slowly Reacting Hydrogen + Oxygen Mixtures," J. Chem. Soc. Faraday Trans. I, 68, 1362-1367 (1972)

Baldwin, R. R., Walker, R. W., and Webster, S. J., "The Carbon Monoxide-Sensitized Decomposition of Hydrogen Peroxide," Combust. Flame 15, 167-172 (1970)

Basco, N., James, D. G. L., and James, F. C., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. II. Combination of the Methyl Radical with the Oxygen Molecule," Intern. J. Chem. Kinetics 4, 129-149 (1972)

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Baulch, D. L., Drysdale, D. D., and Horne, D. G., [Data sheets prepared for this survey] University of Leeds, 1973

Becker, K. H., Groth, W., and Schurath, U., "Reactions of $O_2(^1\Delta_g)$ with Ozone," Chem. Phys. Letts. 14, 489-492 (1972)

Becker, K. H., Groth, W., and Thran, D., "Mechanism of the Air Afterglow NO + O -> NO_2 + hν," Symp. Combust. 14th(Combustion Institute, Pittsburgh, 1973) 353-363

Bedford, G., and Thomas, J. H., "Reaction between Ammonia and Nitrogen Dioxide," J. Chem. Soc. Faraday Trans. I, 68, 2163-2170 (1972)

Benson, S. W. and O'Neal, H. E., "Kinetic Data on Gas Phase Unimolecular Reactions," NBS-NSRDS-21 (1970). (Supt. Doc., U.S. Govt. Printing Office, Washington, D.C. 20402)

Bemand, P. P., Clyne, M. A. A., and Watson, R. T., "Atomic Resonance Fluorescence and Mass Spectrometry for Measurement of the Rate Constants for Elementary Reactions: $O(^3P_J) + NO_2 \rightarrow NO + O_2$ and $NO + O_3 \rightarrow NO_2 + O_2$," typescript, submitted to J. Chem. Soc. Faraday Trans. II (1973)

Bevan, P. L., and Johnson, G. R. A., "Kinetics of Ozone Formation in the Pulse Radiolysis of Oxygen Gas," J. Chem. Soc. Faraday Trans. I., 69, 216-227 (1973)

Bishop, W. P. and Dorfman, L. M., "Pulse Radiolysis Studies. XVI. Kinetics of the Reaction of Gaseous Hydrogen Atoms with Molecular Oxygen by Fast Lyman-α Absorption Spectrophotometry," J. Chem. Phys. 52, 3210-3216 (1970)

Breckenridge, W. H., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of $SO(^1\Delta)$ in the Reaction of $O_2(^1\Delta_g)$ with $SO(^3\Sigma^-)$," J. Chem. Phys. 56, 465-474 (1972)

Bufalini, J. J. and Altshuller, A. P., "Kinetics of Vapor-Phase Hydrocarbon-Ozone Reactions," Can. J. Chem. 43, 2243-2250 (1965)

Calvert, J. G., Kerr, J. A., Demerjian, K. L., and McQuigg, R. D., "Photolysis of Formaldehyde as a Hydrogen Atom Source in the Lower Atmosphere," Science 175, 751-752 (1972)

Campbell, I. M., and Gray, C. N., "Rate Constants for $O(^3P)$ Recombination and Association with $N(^4S)$," Chem. Phys. Letts. 18, 607-609 (1973)

Clark, I. D., Jones, I. T. N., and Wayne, R. P., "The Kinetics of the Reaction Between $O_2(^1\Delta_g)$ and Ozone," Proc. Roy. Soc. London A <u>317</u>, 407-416 (1970)

Clyne, M. A. A., and Cruse, H. W., "Studies of Ground-State $^2P_{3/2}$ Halogen Atoms Using Atomic Resonance Absorption," Trans. Faraday Soc. <u>67</u>, 2869-2885 (1971)

Clyne, M. A. A. and Cruse, H. W., "Atomic Resonance Fluorescence Spectrometry for Rate Constants of Rapid Bimolecular Reactions. Part 1. Reactions O + NO_2, Cl + ClNO, Br + ClNO," J. Chem. Soc. Faraday Trans. II, <u>68</u>, 1281-1299 (1972)

Clyne, M. A. A., and Walker, R. F., "Absolute Rate Constants for Elementary Reactions in the Chlorination of CH_4, CD_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, $CDCl_3$ and $CBrCl_3$," J. Chem. Soc. Faraday Trans. I <u>69</u>, 1547-1567 (1973)

Collins, R. J., Husain, D., and Donovan, R. J., "Kinetic and Spectroscopic Studies of $O_2(a^1\Delta_g)$ by Time-resolved Absorption Spectroscopy in the Vacuum Ultra-violet," J. Chem. Soc. Faraday Trans. II <u>69</u>, 145-157 (1973)

Coltharp, R. N., Worley, S. D., and Potter, A. E., "Reaction Rate of Vibrationally Excited Hydroxyl with Ozone," Appl. Optics <u>10</u>, 1786-1789 (1971)

Davis, D. D., "New Rate Measurements on the Reaction of $O(^3P)$, O_3, and OH," AIAA Paper No. 73-501, AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, Colorado, June 11-13 (1973). Values revised by author

Davis, D. D., Braun, W., and Bass, A. M., "Reactions of $Cl^2P_{3/2}$: Absolute Rate Constants for Reaction with H_2, CH_4, C_2H_6, CH_2Cl_2, C_2Cl_4, and c-C_6H_{12}," Intern. J. Chem. Kinet. <u>2</u>, 101-114 (1970)

Davis, D. D., Herron, J. T., and Huie, R. E., "Absolute Rate Constants for the Reaction $O(^3P) + NO_2 \rightarrow NO + O_2$ Over the Temperature Range 230-339K," J. Chem. Phys. <u>58</u>, 530-535 (1973)

Davis, D. D., Payne, W., and Stief, L., "The Hydroperoxyl Radical in Atmospheric Chemical Dynamics: Reaction with Carbon Monoxide," Science 179, 280-282 (1973)

Davis, D. D., Wong, W., and Lephardt, J., "A Laser Flash Photolysis-Resonance Fluorescence Kinetic Study: Reaction of $O(^3P)$ with O_3," Chem. Phys. Lett. 22, 273-278 (1973)

Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," typescript, Ohio State University (1972) [to appear in Adv. in Environmental Sci. and Technology, J. N. Pitts, Jr. and R. L. Metcalf, editors, Wiley-Interscience (Vol. 4, 1974)]

DeMore, W. B., "Rate Constants for the Reactions of OH and HO_2 with Ozone," Science 180, 735-737 (1973)

DeMore, W. B., "Arrhenius Constants for the Reactions of Ozone with Ethylene and Acetylene," Intern. J. Chem. Kinetics 1, 209-220 (1969)

Dillemuth, F. J., Skidmore, D. R., and Schubert, C. C., "The Reaction of Ozone with Methane," J. Phys. Chem. 64, 1496-1499 (1960)

Donovan, R. J., Husain, D., and Kirsch, L. J., "Reactions of Atomic Oxygen. Part 1: The Rate of the Reaction $O + O_2 + M \rightarrow O_3 + M (M = He, Ar \text{ and } Kr)$," Trans. Faraday Soc. 66, 2551-2559 (1970)

Fettis, G. C., and Knox, J. H., "Rate Constants of Halogen Atom Reactions," G. Porter, Ed., Progress in Reaction Kinet. (Pergamon Press) 2, 1-38 (1964)

Findlay, F. D., and Snelling, D. R., "Temperature Dependence of The Rate Constant for the Reaction $O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$," J. Chem. Phys. 54, 2750-2755 (1971)

Fisher, E. R., and McCarty, M., Jr., "Study of the Reaction of Electronically Excited Oxygen Molecules with Carbon Monoxide," J. Chem. Phys. 45, 781-784 (1966)

Foner, S. N. and Hudson, R. L., "Mass Spectrometry of the HO_2 Free Radical," J. Chem. Phys. 36, 2681-2688 (1962)

Francis, P. D., "The Production of Oxygen Atoms in a Microwave Discharge and the Recombination Kinetics in a Gas Flow System," Brit. J. Appl. Phys. 2, 1717-1730 (1969)

Gaedtke, H., Glanzer, K., Hippler, H., Luther, K., and Troe, J., "Addition Reactions of Oxygen Atoms at High Pressures," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 295-303

Gardiner, W. C., Jr., Mallard, W. G., McFarland, M., Morinaga, L., Owen, J. H., Rawlins, W. T., Takeyama, T., and Walker, B. F., "Elementary Reaction Rates From Post-Induction-Period Profiles in Shock-Initiated Combustion," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 61-72

Ghormley, J. A., Ellsworth, R. L., and Hochanadel, C. J., "Reaction of Excited Oxygen Atoms with Nitrous Oxide. Rate Constants for Reaction of Ozone with Nitric Oxide and with Nitrogen Dioxide," J. Phys. Chem. 77, 1341-1345 (1973). Erratum furnished by author.

Glanzer, K., and Troe, J., Data sheets prepared for this survey, Ecole Polytechnique Federale de Lausanne (1973)

Gordon, R. J., and Lin, M. C., "The Reaction of Nitric Oxide with Vibrationally Excited Ozone," Chem. Phys. Lett. 22, 262-268 (1973)

Gorse, R. A. and Volman, D. H., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System: Rate Constants for Hydroxyl Radical Reactions with Hydrogen Peroxide and Isobutane by Competitive Kinetics," J. Photochem. 1, 1-10 (1972)

Gray, D., Lissi, E., and Heicklen, J., "The Reaction of Hydrogen Peroxide with Nitrogen Dioxide and Nitric Oxide," J. Phys. Chem. 76, 1919-1924 (1972)

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. V. Reactions with H_2 and CO in the Range 300-500°K," J. Chem. Phys. 51, 5049-5051 (1969)

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," J. Chem. Phys. 53, 1070-1076 (1970)

Hack, W., and Hoyermann, K., in press. Quoted in Gehring, M., Hoyermann, K., Schacke, H., and Wolfrum, J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Symp. Combust 14th (Combustion Institute, Pittsburgh, 1973) 99-105

Hampson, R. F. (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). these are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

Hampson, R. F. (editor), "Chemical Kinetics Data Survey VI. Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Atmospheric Chemistry," NBSIR 73-207 (1973a)

Hanst, P. L., Stephens, E. R., Scott, W. E., and Doerr, R. C., "Atmospheric Ozone-Olefin Reactions," (The Franklin Institute, Philadelphia, Pa. 1958)

Harker, A. and Johnston, H. S., "Photolysis of Nitrogen Dioxide to Produce Transient O, NO_3 and N_2O_5," J. Phys. Chem. 77, 1153-1156 (1973)

Heicklen, J., "Gas-Phase Reactions of Alkylperoxy and Alkoxy Radicals," Adv. Chem. Ser. (Am. Chem. Soc., Washington) 76, 23-39 (1968)

Heicklen, J., "Photochemistry of CH_3ONO, Reactions of CH_3O Radicals, Reactions of CH_3O_2 Radicals," reviews prepared for this survey, Penn. State University, January 1973

Herron, J. T., "An Evaluation of Rate Data for the Reactions of Atomic Oxygen (O^3P) with Methane and Ethane," Intern. J. Chem. Kinetics 1, 527-539 (1969)

Herron, J. T. and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," typescript, Natl. Bur. Std. (1972)

Hikida, T., Eyre, J. A., and Dorfman, L. M., "Pulse Radiolysis Studies. XX. Kinetics of Some Addition Reactions of Gaseous Hydrogen Atoms by Fast Lyman-α Absorption Spectrophotometry," J. Chem. Phys. 54, 3422-3428 (1971)

Hippler, H., and Troe, J., "Hochdruckbereich der Rekombination $O + O_2 \rightarrow O_3$, Ber. Bunsenges. Phys. Chem. 75, 27-32 (1971)

Hochanadel, C. J., Ghormley, J. A., and Ogren, P. J., "Absorption Spectrum and Reaction Kinetics of HO_2 Radical in the Gas Phase," J. Chem. Phys. 56, 4426-4432 (1972)

Holmes, H. H. and Daniels, F., "The Photolysis of Nitrogen Oxides: N_2O_5, N_2O_4 and NO_2," J. Am. Chem. Soc. 56, 630-637 (1934)

Huie, R. E., Herron, J. T., and Davis, D. D., "Absolute Rate Constants for the Reaction $O + O_2 + M \rightarrow O_3 + M$ over the Temperature Range 200-346°K," J. Phys. Chem. 76, 2653-2658 (1972)

Husain, D., Kirsch, L. J., and Donovan, R. J., "A Kinetic Study of $O(2^3P_j)$ by Atomic Absorption Spectroscopy Following the Flash Photolysis of Ozone," J. Photochem. 1, 69-73 (1972)

Jacob, A., and Winkler, C. A., "Kinetics of the Reactions of Oxygen Atoms and Nitrogen Atoms with Sulphur Trioxide," J. Chem. Soc. Faraday Trans. I 68, 2077-2082 (1972)

James , F. C., Kerr, J. A., and Simons, J. P., "A Direct Measurement of the Rate of Reaction of the Methyl Radical with Sulphur Dioxide," J. Chem. Soc. Faraday Trans. I 69, 2124-2129 (1973)

Johnston, H. S., "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York (1966), Chapter 1

Johnston, H. S., "Gas Phase Reaction Kinetics of Neutral Oxygen Species," NBS-NSRDS-20, 1968. (Supt. of Documents, U.S. Govt. Printing Office, Washington, D.C. 20402

Johnston, H. S., "Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides," typescript submitted to Adv. in Photochem. (1972)

Johnston, H. S., private communication (1973)

Johnston, H. S., and Chang, S-G., private communication (1973)

Jones, E. J. and Wulf, O. R., "Absorption Coefficient of Nitrogen Pentoxide in the Ultraviolet and the Visible Absorption Spectrum of NO_3," J. Chem. Phys. 5, 873-877 (1937)

Kaufman, F., "Aeronomic Reactions Involving Hydrogen. A Review of Recent Laboratory Studies," Ann. Geophys. 20, 106 (1964)

Kerr, J. A. and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds," (Butterworths, 1972)

Kondratiev, V. N., "Konstanty Skorosti Gazofaznykh Reaktsij Spravochnik," (Izdatelstvo "Nauka", Moskva, 1970); also issued as "Rate Constants of Gas Phase Reactions, Reference Book," R. M. Fristrom, Ed., Translated by L. J. Holtschlag COM-72-10014, Office of Standard Reference Data, NBS (1972). (Distributed by National Technical Information Service, Springfield, Va. 22151)

Kurylo, M. J., Hollinden, G. A., LeFevre, H. F., and Timmons, R. B., "ESR Study of the Kinetics of the Reactions of D Atoms and O Atoms with NH_3," J. Chem. Phys. 51, 4497-4501 (1969)

Kurylo, M. J., "Absolute Rate Constants for the Reaction $H + O_2 + M \rightarrow HO_2 + M$ Over the Temperature Range 203-404K," J. Phys. Chem. 76, 3518-3526 (1972)

Kurylo, M. J., "Kinetics of the Reactions $OH(v = 0) + NH_3 \rightarrow H_2O + NH_2$ and $OH(v = 0) + O_3 \rightarrow HO_2 + O_2$," typescript (to be published in Chem. Phys. Lett.) (1973)

Kurylo, M. J., Braun, W., Kaldor, A., Freund, S., and Wayne, R. P., Private communications (Sept-Oct 1973)

Lin, C. L., and DeMore, W. B., "$O(^1D)$ Production in Ozone Photolysis Near 3100Å," J. Photochem. 2, 161-164 (1973)

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for the Gas Phase Reactions of the Hydroperoxyl Radical," NBS Report 10447, 98 pp. (1971)

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Typescript, University of California, Riverside (Oct. 1973). Supersedes NBS Report 10447

Lundell, O. R., Ketcheson, R. D., and Schiff, H. I., "The Production of $O(^3P)$ Atoms, Free From Excited Molecules, and Their Reaction with O_3," Symp. Combust. 12th(Combustion Institute, Pittsburgh, 1969) 307-311

Mack, G. P. R., and Thrush, B. A., "Reaction of Oxygen Atoms with Carbonyl Compounds. Part 1. Formaldehyde," J. Chem. Soc. Faraday Trans. I 69, 208-215 (1973)

McCrumb, J. L. and Kaufman, F., "Kinetics of the $O + O_3$ Reaction," J. Chem. Phys. 57, 1270-1276 (1972)

McQuigg, R. D., and Calvert, J. G., "The Photodecomposition of CH_2O, CD_2O, CHDO and CH_2O-CD_2O Mixtures at Xenon Flash Lamp Intensities," J. Am. Chem. Soc. 91, 1590-1599 (1969)

Meaburn, G. M., Perner, D., LeCalve, J., and Bourene, M., "A Pulsed-Radiolysis Study of Atomic Oxygen Reactions in the Gas Phase," J. Phys. Chem. 72, 3920-3925 (1968)

Milks, D., and Matula, R. A., "A Single-Pulse Shock-Tube Study of the Reaction Between Nitrous Oxide and Carbon Monoxide," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 83-96

Moortgat, G. K., and Allen, E. R., "The Room Temperature Reactions of Hydrogen-Atoms in Molecular Oxygen," National Center for Atmospheric Research, Boulder (1973). Abstract of unpublished work.

Morley, C., and Smith, I. W. M., "Rate Measurements of Reactions of OH by Resonance Absorption. Part I. Reactions of OH with NO_2 and NO," J. Chem. Soc. Faraday Trans. II 68, 1016-1030 (1972)

Morris, E. D., Jr. and Niki, H., "Mass Spectrometric Study of the Reaction of Hydroxyl Radical with Formaldehyde," J. Chem. Phys. 55, 1991-1992 (1971)

Morris, E. D., Jr. and Niki, H., "Reaction of Methyl Radicals with Atomic Oxygen," Intern. J. Chem. Kinetics 5, 47-53 (1972)

Morris, E. D., Jr. and Niki, H., "The Reaction of N_2O_5 with H_2O," J. Phys. Chem. 77, 1929-1932 (1973)

Mulcahy, M. F. R. and Williams, D. J., "Kinetics of Combination of Oxygen Atoms with Oxygen Molecules," Trans. Faraday Soc. 64, 59-70 (1968)

Murphy, R. F., "The Ultraviolet Photolysis of the Nitrogen Oxides," Dissertation Abstr. Intern. B 31, 619 (1970)

Paraskevopoulos, G., "Reactions of $O(^1D)$ and OH with Organic Compounds," VII. Intern. Conference of Photochem., Abstracts, paper IIIA, p. 101 (Jerusalem, Israel, Aug. 29-Sept 4, 1973)

Pastrana, A. V., and Carr, R. W., Jr., "Rate of the Reaction of Hydroxyl Radical with Acetylene," XI Intern. Symp. on Free Radicals (Berchtesgaden-Konigssee, Sept. 4-7, 1973) Paper No. 35

Payne, W. A., Stief, L. J., and Davis, D. D., "A Kinetics Study of the Reaction of HO_2 with SO_2 and NO," J. Am. Chem. Soc. 95, 7614-7619 (1973)

Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," Symp. Combust . 14th (Combustion Institute, Pittsburgh, 1973) 133-141

Ridley, B. A., Davenport, J. A., Stief, L. J., and Welge, K. H., "Absolute Rate Constant for the Reaction H + H_2CO," J. Chem. Phys. 57, 520-523 (1972)

Sauer, M. C., Jr., "A Pulse-Radiolysis Study of the Dependence of the Reaction of Atomic Oxygen with Oxygen on the Nature of the Third Body," J. Phys. Chem. 71, 3311-3313 (1967)

Schofield, K., "An Evaluation of Kinetics Rate Data for Reactions of Neutrals of Atmospheric Interest," Planet. Space Sci. 15, 643-670, 1336 (1967)

Schofield, K., "The Rate of Destruction of $O_2(^1\Delta_g)$ by Atomic Hydrogen," Intern. J. Chem. Kinetics 4, 255-263 (1972)

Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

Simonaitis, R., and Heicklen, J., "The Reactions of HO_2 with Carbon Monoxide and Nitric Oxide and the Reaction of $O(^1D)$ with Water," J. Phys. Chem. 77, 1096-1102 (1973)

Simonaitis, R. and Heicklen, J., "The Reaction of HO_2 with O_3," J. Phys. Chem. 77, 1932-1935 (1973)

Simonaitis, R., and Heicklen, J., "The Reaction of HO_2 with NO and NO_2," Penn. State Univ. (Oct. 1973). Typescript

Slanger, T. G., and Black, G., "Reaction Rate Measurements of $O(^3P)$ Atoms by Resonance Fluorescence. I. $O(^3P) + O_2 + M \rightarrow O_3 + M$ and $O(^3P) + NO + M \rightarrow NO_2 + M$," J. Chem. Phys. 53, 3717-3721 (1970)

Slanger, T. G., Wood, B. J., and Black, G., "Investigation of the Rate Coefficient for $O(^3P) + NO_2 \rightarrow O_2 + NO$," Intern. J. Chem. Kinetics 5, 615-620 (1973)

Slanger, T. G. and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," Data sheets prepared for this survey, January 1973

Smith, I. W. M., private communication (1973)

Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by Resonance Absorption Part 2. Reactions of OH with CO, C_2H_4 and C_2H_2," J. Chem. Soc. Faraday Trans. II 69, 1617-1627 (1973)

Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of the OH Radical with H_2, CO, C_2H_4 and C_2H_2 between 210°K and 460°K," Proc. European Symp. Combust., 24 (1973a)

Sperling, H. P., and Toby, S., "The Photochemical Decomposition of Gaseous Formaldehyde," Can. J. Chem. 51, 471-475 (1973)

Stedman, D. H. and Niki, H., "Kinetics and Mechanism for the Photolysis of Nitrogen Dioxide in Air," J. Phys. Chem. 77, 2604-2609 (1973)

Stedman, D. H., Wu, C. H., and Niki, H., "Kinetics of Gas-Phase Reactions of Ozone with Some Olefins," J. Phys. Chem. 77, 2511-2514 (1973)

Stuhl, F., "Absolute Rate Constant for the Reaction $OH + NH_3 \rightarrow NH_2 + H_2O$," J. Chem. Phys. 59, 635-637 (1973a)

Stuhl, F., "Rate Constant for the Reaction of OH with n-C_4H_{10}," Z. Naturforsch. Pt A 28, 1383-1384 (1973b)

Stuhl, F., "Determination of Rate Constants for the Reactions of OH with Propylene and Ethylene by a Pulsed Photolysis-Resonance Fluorescence Method," Ber. Bunsenges. Physik. Chem. 77, 674-677 (1973c).

Stuhl, F. and Niki, H., "Detection of Oxygen (^3P) Atoms in Pulsed Vacuum UV Photolysis of NO and Its Application to O Atom Reactions," Chem. Phys. Lett. 7, 197-200 (1970)

Stuhl, F., and Niki, H., "Measurements of Rate Constants for Termolecular Reactions of $O(^3P)$ with NO, O_2, CO, N_2, and CO_2 Using a Pulsed Vacuum-uv Photolysis-Chemiluminescent Method," J. Chem. Phys. 55, 3943-3953 (1971)

Stuhl, F., and Niki, H., "Pulsed Vacuum-uv Photochemical Study of Reactions of OH with H_2, D_2, and CO Using a Resonance-Fluorescent Detection Method," J. Chem. Phys. 57, 3671-3677 (1972)

Takacs, G. A., and Glass, G. P., "Reactions of Hydroxyl Radicals with Some Hydrogen Halides," J. Phys. Chem. 77, 1948-1951 (1973)

Thrush, B. A., Letter to D. Garvin (Sept. 1973) reevaluating work in his laboratory

Tsang, W., "Comparison between Experimental and Calculated Rate Constants for Dissociation and Combination Reactions Involving Small Polyatomic Molecules," Intern. J. Chem. Kinetics 5, 947-963 (1973)

Vardanyan, I. A., Dangyan, T. M., and Sachyan, G. A., "Rate Constants for the Reaction $HO_2 + CO \rightarrow CO_2 + OH$," Dokl. Phys. Chem. 205, 632-634 (1972); tr. of Dokl Akad. Nauk SSSR 205, 619-621 (1972)

Volman, D. H., and Gorse, R. A., "Rate Constant for the Reaction of HO_2 with Carbon Monoxide," J. Phys. Chem. 76, 3301-3302 (1972)

Walker, R. W., "Activation Energies of the Reversible Reaction between Hydrogen Atoms and Methane to give Hydrogen and Methyl Radicals," J. Chem. Soc., Sect. A, 2391-2398 (1968)

Walker, R. W., Comments on "Gas-Phase Oxidation of Butene-2: The Role of Acetaldehyde in the Reaction," Ray, D. J. M., Diaz, R. R., and Waddington, D. J., Symp. Combust 14th (Combustion Institute, Pittsburgh, 1973) 265-266

Washida, N., and Bayes, K. D., "The Rate of Reaction of Methyl Radicals with Atomic Oxygen," Chem. Phys. Letts. 23, 373-375 (1973)

Washida, N., Martinez, R. I., and Bayes, K. D., "The Oxidation of Formyl Radicals," typescript, Univ. of California (Los Angeles) (1973)

Watson, R. T., [A Review of the Kinetics of the Reactions of the Chlorine-Oxygen System], University of California, Berkeley, Manuscript Tables (1973)

Wayne, R. P. private communication (1973)

Westenberg, A. A. and deHaas, N., "Steady-State Intermediate Concentrations and Rate Constants. Some HO_2 Results," J. Phys. Chem. 76, 1586-1593 (1972)

Westenberg, A. A., and deHaas, N., "Measurement of the Rate Constant for $H + H_2CO \rightarrow H_2 + HCO$ at 297-652°K," J. Phys. Chem. 76, 2213-2214 (1972)

Westenberg, A. A. and deHaas, N., "Rates of CO + OH and H_2 + OH Over an Extended Temperature Range," J. Chem. Phys. 58, 4061-4065 (1973a)

Westenberg, A. A. and deHaas, N., "Rate of the Reaction $OH + OH \rightarrow H_2O + O$," J. Chem. Phys. 58, 4066-4071 (1973b)

Wilson, Wm. E., Jr., "A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical," J. Phys. Chem. Ref. Data 1, 535-573 (1972)

Wong, W., and Davis, D. D., "A Flash Photolysis-Resonance Fluorescence Study of the Reaction of Atomic Hydrogen with Molecular oxygen: $H + O_2 + M \rightarrow HO_2 + M$," (to be published in Intern. J. Chem. Kinetics, 1973)

Wu, C. H., Morris, E. D., Jr., and Niki, H., "The Reaction of Nitrogen Dioxide with Ozone," J. Phys. Chem. 77, 2507-2511 (1973)

Wyrsch, D., Wendt, H. R., and Hunziker, H. E., "Modulation Kinetic Spectroscopy of $Hg/H_2/O_2/CO$ Mixtures: Reactions of HgH and HO_2," XI. Intern. Symp. on Free Radicals (Berchtesgaden-Konigssee, Sept. 4-7, 1973) Paper No. 36

4.2 Vibrational Energy Transfer Processes (R. L. Taylor)

4.2.1 Introduction

The rate constants are all listed for the exothermic reaction path. The form of the rate constants listed in the following table have been fitted to experimental data where available and either use a theoretical temperature dependence for extrapolation, or the general trend of the data itself has been used to suggest the temperature dependence. The table provided here was prepared in December 1973.

4.2.2 VIBRATIONAL ENERGY TRANSFER PROCESSES

(R. L. Taylor, December 1973)

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant-cm^3 $molecule^{-1}s^{-1}$
1	CO_2 (010) + M → CO_2 (000) + M Taylor and Bitterman (1969); Simpson et al (1969); Simpson and Chandler (1970); Buchwald and Bauer (1972); Sato and Tsuchiya (1972)	200 < T < 2000	M = CO_2 $k = 4.64 \times 10^{-10} \exp(-76.75/T^{1/3})$ M = N_2, O_2 $k = 6.69 \times 10^{-10} \exp(-84.07/T^{1/3})$
	Taylor and Bitterman (1969); Buchwald and Bauer (1972)	200 < T < 1200	M = H_2O $k = 3.22 \times 10^{-13} \exp(22.91/T^{1/3})$
2	N_2 (v = 1) + M → N_2 (v = 0) + M Millikan and White (1963); Taylor and Bitterman (1969); Kovacs and Mack (1972)	1000 < T < 5000	M = N_2, O_2, CO_2 $k = 8.53 \times 10^{-7} \exp(-273.10/T^{1/3})$
	Taylor and Bitterman (1969); vonRosenberg et al (1972); Evans (1972)	200 < T < 2000	M = H_2O $k = 1.07 \times 10^{-10} \exp(-69.90/T^{1/3})$
3	H_2O (010) + M → H_2O (000) + M Taylor and Bitterman (1969) Corrected by 0.1 Bauer (1968); Monk, (1969); Henderson et al (1969)	200 < T < 600	M = H_2O $k = 1.0 \times 10^{-11} + 2.68 \times 10^{-8} \exp(-70.00/T^{1/3})$
	Monk (1969)	200 < T < 400	M = N_2, CO_2 $k = 5.37 \times 10^{-10} \exp(-70.00/T^{1/3})$ M = O_2 (see process (9))
4	O_2 (v = 1) + M → O_2 (v = 0) + M Millikan and White (1963); Taylor and Bitterman (1969); Kovacs and Mack (1972)	200 < T < 5000	M = N_2, O_2, CO_2 $k = 4.81 \times 10^{-8} \exp(-169.60/T^{1/3})$
	Taylor and Bitterman (1969)		M = H_2O $k \leq 3.60 \times 10^{-10} \exp(-60.69/T^{1/3})$
5	CO_2 (001) + N_2 (v = 0) → CO_2 (000) + N_2 (v = 1) Rosser et al (1969); Taylor and Bitterman (1969); Margottin-Maclou et al (1971); Sato and Tsuchiya (1972)	200 < T < 2000	$k = 1.71 \times 10^{-6} \exp(-175.30/T^{1/3}) +$ $6.07 \times 10^{-14} \exp(15.27/T^{1/3})$

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant-cm^3 molecule^{-1}s^{-1}
6	H_2O (010) + O_2 (v = 0) → H_2O (000) + O_2 (v = 1) Taylor and Bitterman (1969)	200 < T < 400	$k = 1.00 \times 10^{-12}$
7	N_2 (v = 1) + O_2 (v = 0) → N_2 (v = 0) + O_2 (v = 1) Taylor and Bitterman (1969); Breshears and Bird (1968)	200 < T < 5000	$k = 1.74 \times 10^{-10} \exp(-124.00/T^{1/3})$
8	O_2 (v = 1) + CO_2 (000) → O_2 (v = 0) + CO_2 (010)	200 < T < 400	$k = 1.78 \times 10^{-12} \exp(-37.94/T^{1/3})$
9	CO_2 (100) + M → CO_2 (020) + M Taylor and Bitterman (1969); Sharma (1968); Moore (1973)	200 < T < 400	$M = N_2, O_2$ $k \geq 3.0 \times 10^{-11}$
10	CO_2 (001) + M → CO_2 (030) + M		
	Taylor and Bitterman (1969); Rosser et al (1969); Stephenson and Moore, (1972); Sato and Tsuchiya (1972)	200 < T < 2000	$M = N_2$ $k = 1.00 \times 10^{-15} + 5.16 \times 10^{-11} \exp(-76.75/T^{1/3})$
	Taylor and Bitterman (1969); Rosser and Gerry (1969); Stephenson and Moore (1972)		$M = O_2$ $k = 1.10 \times 10^{-15} + 7.31 \times 10^{-11} \exp(-76.75/T^{1/3})$
	Taylor and Bitterman (1969); Rosser and Gerry (1971); Sato and Tsuchiya (1972); Seery (1972 a)		$M = CO_2$ $k = 3.0 \times 10^{-15} + 1.72 \times 10^{-10} \exp(-76.75/T^{1/3})$
	Rosser et al (1971); Sato and Tsuchiya (1972); Stephenson and Moore (1972)		$M = CO$ $k = 2.20 \times 10^{-15} + 9.69 \times 10^{-11} \exp(-76.75/T^{1/3})$
	Taylor and Bitterman (1969); Rosser and Gerry (1969); Heller and Moore (1970)	200 < T < 1000	$M = H_2O$ $k = 4.0 \times 10^{-13}$
11	H_2O (100) + M → H_2O (020) + M Sarjeant et al (1972); Center and Kung (1973); Mechanism is author's prejudice	4000 < T < 2000	$M = H_2O$ $k = 2.50 \times 10^{-12}$ $T^{0.5}$ $M = N_2, O_2, CO_2$ $k \approx 1.0 \times 10^{-14}$ $T^{0.5}$
12	CO (v = 1) + M → CO (v = 0) + M Millikan and White (1963); Kovacs and Mack (1972)	200 < T < 5000	$M = CO, N_2, O_2$ $k = 6.67 \times 10^{-8} \exp(-208.30/T^{1/3})$
	vonRosenberg et al (1971)	1000 < T < 3000	$M = H_2O$ $k = 3.12 \times 10^{-10} \exp(-64.99/T^{1/3})$

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant - cm^3 $molecule^{-1}$ s^{-1}
13	N_2 (v = 1) + CO → N_2 (v = 0) + CO (v = 1) Sato et al (1969); vonRosenberg et al (1972); McLaren and Appleton (1971); Zittel and Moore (1972)	200 < T < 2000	$k = 1.78 \times 10^{-6} \exp(-209.90/T^{1/3}) +$ $6.98 \times 10^{-13} \exp(-25.60/T^{1/3})$
14	CO(v = 1) + O_2 (v = 0) → CO (v = 0) + O_2 (v = 1) Sato et al (1969); Center (1973)	1000 < T < 3000	$k = 3.50 \times 10^{-10} \exp(-124.00/T^{1/3})$
15	CO_2 (001) + CO (v = 0) → CO_2 (000) + CO (v = 1) Rosser et al (1971); Seery (1972); Stephenson and Moore (1972); Borrell and Millward (1972); Buchwald and Bauer (1972); Sato and Tsuchiya (1972)	1000 < T < 3000	$k = 1.56 \times 10^{-11} \exp(-30.12/T^{1/3})$
16	CO (v = 1) + H_2O (000) → CO (v = 0) + H_2O (000)		Data can be interpreted as either V-T or V-V process. See process (12) for V-T interpretation.
17	NO (v = 1) + M → NO (v = 0) + M Basco et al (1961); Taylor (1973)	200 < T < 2000	M = N_2, O_2 $k = 6.75 \times 10^{-7} \exp(-182.83/T^{1/3})$
	Robbens (1959); Bauer (1959); Basco et al (1961); Wray (1962); Kneser et al (1967); Breshears and Bird (1969); Bradley and Lewis (1969); Hochanadel and Ghormley (1969); Kamimoto and Matsui (1970); Billingsley and Callear (1969); Billingsley and Callear (1971); Green and Hancock (1973); Stephenson (1973)		M = NO $k = 2.49 \times 10^{-11} \exp(-40.19/T^{1/3})$
	Basco et al (1961)	200 < T < 400	M = CO_2 $k = 1.66 \times 10^{-11} \exp(-40.19/T^{1/3})$
	Basco et al (1961)		M = H_2O $k = 7.47 \times 10^{-10} \exp(-40.19/T^{1/3})$
	Basco et al (1961); Taylor et al (1967)		M = CO $k = 2.49 \times 10^{-12} \exp(-40.19/T^{1/3})$
18	N_2 (v = 1) + NO (v = 0) → N_2 (v = 0) + NO (v = 1) Taylor et al (1967); Basco et al (1961); Callear (1962)	200 < T < 2000	$k = 4.22 \times 10^{-10} \exp(-86.35/T^{1/3})$

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant - cm^3 molecule^{-1}s^{-}
19	$CO\ (v = 1) + NO\ (v = 0) \rightarrow CO\ (v = 0) + NO\ (v = 1)$ Basco et al (1961); Callear (1965); Taylor et al (1967)	$200 < T < 2000$	$k = 3.58 \times 10^{-11} \exp(-49.93/T^{1/3})$ $+ 1.26 \times 10^{-8} \exp(-115.13/T^{1/3})$
20	$N_2\ (v = 1) + N_2O\ (000) \rightarrow N_2\ (v = 0) + N_2O\ (001)$ Roach and Smith (1969); Yardley (1968); McNeal et al (1972); Stephenson and Moore (1972).	$200 < T < 2000$	$k = 5.4 \times 10^{-14} \exp(10.2/T^{1/3})$
21	$OH\ (v = 1) + M \rightarrow OH\ (v = 0) + M$ Worley et al (1971, 1972) Values are derived from the reported values for OH (v = 9)	$T = 300$	$M = O_2 \quad k(1) = 1 \times 10^{-15}$ $= N_2 \quad = 3.6 \times 10^{-16}$ $= NO \quad = 1.5 \times 10^{-14}$ $= N_2O \quad = 4.8 \times 10^{-15}$ $= CO_2 \quad = 2.4 \times 10^{-15}$ $= H_2O \quad = 2.0 \times 10^{-14}$
22	$N_2\ (v = 1) + O \rightarrow N_2\ (v = 0) = O$ Breshears and Bird (1968); McNeal et al (1972)	$200 < T < 3000$	$k = 1.07 \times 10^{-10} \exp(-69.90/T^{1/3})$
23	$O_2\ (v = 1) + O \rightarrow O_2\ (v = 0) + O$ Kiefer and Lutz (1967)	$200 < T < 2000$	$k = 6.88 \times 10^{-9} \exp(-76.75/T^{1/3})$
24	$CO\ (v = 1) + O \rightarrow CO\ (v = 0) + O$ Center (1973)	$200 < T < 3000$	$k = 9.9 \times 10^{-8} \exp(-118.07/T^{1/3})$
25	$CO_2\ (010) + O \rightarrow CO_2\ (000) + O$ Center (1973a)	$200 < T < 3000$	$k = 2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$
26	$O_3\ (100) + M \rightarrow O_3\ (001) + M$ Rosen and Cool (1973)	300	$M = N_2, O_2, O_3, CO_2 \quad k \geq 4.9 \times 10^{-12}$ Note: Data refers to $k_{26} + k_{27}$
27	$O_3\ (100) + O_3\ (001) \rightarrow O_3\ (101) + M$ Rosen and Cool (1973)	300	See Above

No.	Reaction/Reference	Temp. Range/^oK	Reaction Rate Constant-cm^3 $molecule^{-1} s^{-1}$
28	O_3 (100) + M → O_3 (000) + M	300	M = N_2 k = 2.4×10^{-14} M = O_2 k = 2.9×10^{-14} M = O_3 k = 1.1×10^{-13} M = CO_2 k = 1.9×10^{-13} Note: Data refer to $k_{28} + k_{29}$
29	O_3 (001) + M → O_3 (000) + M	300	See Above
30	O_3 (100) + M → O_3 (010) + M	300	Possible alternate mechanism for (28) + (29). See text.
31	O_3 (001) + M → O_3 (010) + M		
32	O_3 (010) + M → O_3 (000) + M		
33	O_3 (010) + CO_2 (000) → O_3 (000) + CO_2 (010)		
34	CO_2 (001) + O_3 (000) → CO_2 (100) + O_3 (100) Cool and Airey, (1973); vonRosenberg and Lowenstein (1973); Rosen and Cool (1973)	300	k = $7.6 - 12 \times 10^{-13}$

References

Basco, N., Callear, A. B. and Norrish, R. G. W., Proc. Roy. Soc. London A260, 459 (1961).

Bauer, H.-J., Kneser, H. O. and Sittig, E., J. Chem. Phys. 30, 1119 (1959).

Bauer, H.-J., J. Acoust. Soc. Amer. 44, 285 (1968).

Bevan, P. L. T. and Johnson, G. R. A., J. Chem. Soc. Faraday I69, 216 (1973)

Billingsley, J. and Callear, A. B., Nature 221, 1136 (1969).

Billingsley, J. and Callear, A. B., Trans. Faraday Soc. 67, 257 (1971).

Black, G., Submitted to J. Chem. Phys. (1973).

Black, G., Sharpless, R. L. and Slanger, T. G., J. Chem. Phys. 58, 4792 (1973).

Black, G., and Eckstrom, D. J., "Excitation and Deexcitation of Vibration in Gases by Oxygen and Nitrogen Atoms", Final Report. Contract DAHC04-72-C-0015, Stanford Research Institute, Menlo Park, California, February 16, 1973.

Borrell, P. and Millward, G. E., J. Chem. Phys. 57, 462 (1972).

Bradley, J. N. and Lewis, D., J. Chem. Phys. 50, 544 (1969).

Breshears, W. D. and Bird, P. F., J. Chem. Phys. 48, 4768 (1968).

Breshears, W. D. and Bird, P. F., Nature 224, 268 (1969).

Buchwald, M. I. and Bauer, S. H., J. Phys. Chem. 76, 3108 (1972).

Buchwald, M. I., McFarlane, R. and Bauer, S. H., Laboratory of Plasma Studies, Cornell University, Report No. 104, 1972a.

Callear, A. B., Disc. Faraday Soc. 33, 28 (1962).

Callear, A. B., Appl. Opt. Suppl. 2, 145 (1965).

Center, R. E., J. Chem. Phys. 58, 5230 (1973).

Center, R. E., Proceedings of the Ninth International Shock Tube Symposium, Stanford University, 1973a (to be published).

Center, R. E. and Kung, R., Avco Everett Research Laboratory, Inc., private communication, 1973.

Chen, H-L., Avco Everett Research Laboratory, Inc., private communication, 1973.

Cool, T. A. and Airey, J. R., Chem. Phys. Letters, 20, 67 (1973).

Delos, J. B., J. Chem. Phys. 59, 2365 (1973).

Eckstrom, D. J., J. Chem. Phys. 59, 2787 (1973).

Evans, L. B., J. Acoust. Soc. Amer. 50, 409 (1972).

Fisher, E. R. and Bauer, E., J. Chem. Phys. 57, 1966 (1972).

Fushiki, Y. and Tsuchiya, S., in press, J. Chem. Phys. (1973).

Gordon, R. G., Klemperer, W. and Steinfeld, J. I. Ann. Rev. Phys. Chem. 19, 215 (1968).

Green, W. H. and Hancock, J. K., J. Quantum Elec. QE-9, 50 (1973).

Heller, D. F. and Moore, C. B., J. Chem. Phys. 52, 1005 (1970).

Henderson, M. C., Herzfeld, K., Bry, J., Coakley, R. and Caviere, G., J. Acoust. Soc. Amer. 45, 109 (1969).

Herzfeld, K and Litovitz, T. A., Absorption and Dispersion of Ultrasonic Waves, Academic Press, Inc., New York 1959.

Hochanadel, C. J., Ghormley, J. A. and Boyle, J. W., J. Chem. Phys., 48, 2416 (1968).

Hochanadel, C. J. and Ghormley, J. A., J. Chem. Phys. 50, 3075 (1969).

Kamimoto, G. and Matsui, H., J. Chem. Phys. 53, 3987 (1970).

Kiefer, J. H. and Lutz, R. W., Proceedings of the Eleventh Symposium (International) on Combustion. The Combustion Institute, Pittsburg, Pa., 1967, p. 67

Kirsch, L. J. and Polanyi, J. C., J. Chem. Phys. 57, 4498 (1972).

Kneser, H. O., Bauer, H.-J. and Kosche, H., J. Acoust. Soc. Amer. 41, 1029 (1967).

Kovacs, M. A. and Mack, M. A., Appl. Phys. Letters 20, 487 (1972).

Margottin-Maclov, M., Doyenette, L. and Henry L., Appl. Opt. 10, 1768 (1971).

McCaa, D. J. and Shaw, J. H., M. Mol. Spect. 25, 374 (1968).

McLaren, T. I. and Appleton, J. P., Proceedings of the Eighth International Shock Tube Symposium, London, 1971, p. 27.

McNeal, R. J., Whitson, M. E., Jr. and Cook, G. R., Chem. Phys. Letters 16, 507 (1972).

McNeal, R. J., Whitson, M. E., Jr. and Cook, G. R., J. Chem. Phys. **57**, 4752 (1972a).

Millikan, R. C. and White, D. R., J. Chem. Phys. 39, 3209 (1963).

Monk, R. G., J. Acoust. Soc. Amer. 46, 580 (1969).

Moore, C. B., J. Chem. Phys. 43, 2979 (1965).

Moore, C. B., Advances Chem. Phys. 23, 41 (1973).

Moore, C. B., University of California at Berkeley, private communication, 1973 a.

Moore, C. B., Wood, R. E., Hu, B. L. and Yardley, J. T., J. Chem. Phys. 46, 4222 (1967).

Nikitin, E.G., Optics and Spectroscopy 9, 8 (1960).

Odiorne, T. J., Brooks, P. R. and Kasper, J. V. V., J. Chem. Phys. 55, 1980 (1971).

Roach, J. F. and Smith, W. R., J. Chem. Phys. 50, 4114 (1969).

Robben, F., J. Chem. Phys. 31, 420 (1959).

Rosen, D. I. and Cool, T. A., in press, J. Chem. Phys. (1973).

Rosser, W. A., Jr. and Gerry, E. T., J. Chem. Phys. 51, 2286 (1969).

Rosser, W. A., Jr. and Gerry, E. T., J. Chem. Phys. 54, 5131 (1971).

Rosser, W. A., Jr., Sharma, R. D. and Gerry, E. T., J. Chem. Phys. 54, 1196 (1971).

Rosser, W. A., Jr., Wood, A. D. and Gerry, E. T., J. Chem. Phys. 50, 4996 (1969).

Sarjeant, W. J., Kucerovsky, Z. and Brannen, E., Appl. Opt. 11, 725 (1972).

Sato, Y., Tsuchiya, S. and Kuratani, K., J. Chem. Phys. 50, 1911 (1969).

Sato, Y. and Tsuchiya, S., J. Phys. Soc. Japan 33, 1120 (1972).

Schwartz, R. N., Slawsky, Z. I. and Herzfeld, K., J. Chem. Phys. 20, 1591 (1952).

Seery, D. J., J. Chem. Phys. 56, 631 (1972).

Seery, D. J., J. Chem. Phys. 56, 4714 (1972 a)

Sharma, R. D., J. Chem. Phys. 49, 5195 (1968).

Sharma, R. D. and Brau, C. A., Phys. Rev. Letters 19, 1273 (1967).

Sharma, R. D. and Brau, C. A., J. Chem. Phys. 50, 924 (1969).

Simpson, C. J. S. M., Chandler, T. R. D. and Strawson, A. C., J. Chem. Phys. 51, 2214 (1969).

Simpson, C. J. S. M. and Chandler, T. R. D., Proc. Roy. Soc. London A317, 265 (1970).

Stephenson, J. C. and Moore, C. B., J. Chem. Phys. 56, 1295 (1972).

Stephenson, J. C., J. Chem. Phys. 59, 1523 (1973).

Taylor, R. L., Camac, M. and Feinberg, R. M., Proceedings of the Eleventh Symposium (International) on Combustion. The Combustion Institute, Pittsburgh, Pa., 1967, pp. 49-65.

Taylor, R. L. and Bitterman, S. A., Rev. Mod. Phys. 41, 26 (1969).

Taylor, R. L., Physical Sciences, Inc., unpublished data.

vonRosenberg, C. W., Bray, K. N. C. and Pratt, N. H., Proceedings of the Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburg, Pa., 1971, pp. 89-98.

vonRosenberg, C. W., Bray, K. N. C. and Pratt, N. H., J. Chem. Phys. 56, 3230 (1972).

vonRosenberg, C. W., Jr. and Lowenstein, A., J. Chem. Phys. 59, 2751 (1973).

vonRosenberg, C. W., Jr. and Trainor, D. W., J. Chem. Phys. 59, 2142 (1973).

vonRosenberg, C. W., Jr. and Trainor, D. W., Avco Everett Research Laboratory, Inc., private communication, 1973 a.

Welge, K. H., Filseth, S. V. and Davenport, J., J. Chem. Phys. 53, 502 (1970).

Worley, S. D., Coltharp, R. N. and Potter, A. E., J. Chem. Phys. 55, 2608 (1971).

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

Wray, K. L., J. Chem. Phys. 36, 2597 (1962).

Yardley, J. T., J. Chem. Phys. 49, 2816 (1968).

Zittel, P. F. and Moore, C. B., Appl. Phys. Letters 21, 81 (1972).

4.3 High Temperature Air Reactions (R. L. Taylor)

No.	Reaction	Temp. Range/K	Reaction Rate Constant, cm^3/molecule-sec	References
(1)	$O + O + M \rightarrow O_2 + M$	$2000 < T < 10,000$	$M = N_2$, $k = 1.7 \times 10^{-32} T^{-1/2}$	Lin + Teare (63)
			$M = O_2$, $k = 2.2 \times 10^{-28} T^{-3/2}$	Wray (62)
			$M = O$, $k = 6.2 \times 10^{-28} T^{-3/2}$	
			$M = N, NO$, $k = 8.3 \times 10^{-33} T^{-1/2}$	
(2)	$N + N + M \rightarrow N_2 + M$	$2000 < T < 10,000$	$M = N_2$, $k = 7.6 \times 10^{-32} T^{-1/2}$	Lin + Teare (63)
			$M = O_2, O, NO$, $k = 3.0 \times 10^{-32} T^{-1/2}$	Wray (62)
			$M = N$, $k = 6.5 \times 10^{-27} T^{-3/2}$	
(3)	$N + O + M \rightarrow NO + M$	$2000 < T < 10,000$	$M = N_2, O_2, N, O$, $k = 2.8 \times 10^{-28} T^{-3/2}$	Lin + Teare (63)
			$M = NO$, $k = 5.5 \times 10^{-27} T^{-3/2}$	Wray (62)
(4)	$N + NO \rightarrow N_2 + O$	$2000 < T < 10,000$	$k = 2.7 \times 10^{-11}$	Wray (62), Lin + Teare (63) Baulch et al (69)
(5)	$N + O_2 \rightarrow NO + O$	$2000 < T < 10,000$	$k = 2.2 \times 10^{-14} T \exp(-3560/T)$	Wray (62), Lin + Teare (63) Baulch et al (69)
(6)	$NO + NO \rightarrow N_2O + O$	$2000 < T < 10,000$	$k = 0.4 T^{-5/2} \exp(-43,000/T)$	Camac + Feinberg (67)

References

D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, High Temperature Reaction Rate Data, Report No. 4, Dept. of Physical Chemistry, The University, Leeds (1969).

M. Camac and R. M. Feinberg
Eleventh Symposium (International) on Combustion, p. 137 (1967).

S. C. Lin and J. D. Teare
Phys. Fluids 6, 355 (1963).

K. L. Wray, "Chemical Kinetics of High Temperature Air" Progress in Astronautics and Rocketry Vol. 7, p. 181, 1962.

4.4 Ion Molecule Reactions (E. E. Ferguson)

4.4.1 Explanation of Tables

The reactions are listed in the order: (1) atomic ions reacting with neutrals, (2) molecular ions reacting with neutrals. The ions are listed according to atomic number except that obviously related reactions may be grouped. No distinction is made between ion-atom interchange and charge-transfer reactions, i.e. those in which heavy particles are transferred as contrasted to electrons. The rate constant is defined as the coefficient k in the expression $-d[A^+]/dt = k[A^+][B]$ where $[A^+]$ and $[B]$ are the ion and neutral concentrations in the reaction $A^+ + B \rightarrow$ products.

The entries in the Tables are:

k : Rate constant in $cm^3\ sec^{-1}$ (molecule^{-1} implied)

Uncertainty: See Introduction for Discussion

Method : Indicated by the following abbreviations

FA Flowing Afterglow

This is a relatively high pressure experiment with many reactant ion collisions prior to reaction so that the reactants are almost always known to be in their ground states. This method has the greatest chemical versatility of all of the methods and so has produced a large fraction of the available data. FA data have been obtained in the temperature range 80 - 600 K.

SA Stationary Afterglow

This is a high pressure experiment in which reactant ions can safely be assumed to be in their ground states in most cases. The ionizing discharge may however produce excited or dissociated neutral reactants. Photoionization sources have alleviated this problem but have been very limited in their chemical versatility. Some SA experiments have covered a range of gas temperatures from about 180 - 600 K.

DT Drift Tube

This technique has only recently been applied to ion-molecule reactions with good results. The reactants are expected to be in their ground states. The method has the advantage of yielding reaction rate constants for ion translational energy going from thermal up into the several electron volt range. The data on energy dependences thus tends to augment thermal energy data in many cases.

MS Mass Spectrometer Ion Source

Most MS data in the literature have been obtained at low pressure (thin target conditions) and this raises the possibility that the ions may have been produced in excited states which can be quite misleading. Some MS experiments, particularly those of Kebarle have worked at relatively high pressure and have thereby avoided this problem. Low pressure mass spectrometer ion sources measure reaction cross sections rather than reaction rate constants. Since most applications require rate constants this introduces a small uncertainty. Essentially $\int\sigma(E)E^{\frac{1}{2}}dE$ must be approximated by $\bar{\sigma}(E)\bar{E}^{-\frac{1}{2}}$, while in rate constant measuring experiments (FA, SA, DT) the experiment itself accomplishes the integration. The low pressure MS experiments also involve a small electric field in the ion sampling so that the cross sections are measured somewhat above thermal energy.

B Beam

Beam data are always obtained at energies in excess of thermal. The extrapolations to low energy introduces some uncertainty into the low energy cross sections. This is more serious for ion-atom interchange reactions than for charge-transfer reactions in most cases. The beam technique has been a very versatile technique in the kinds of neutral reactants which can be studied, as for example metal atoms, and thus very important in aeronomy. Beam experiments of course provide ion kinetic energy dependences of the cross sections from fairly high ion kinetic energies to energies substantially in excess of thermal.

ICR Ion Cyclotron Resonance

The ICR technique has now been utilized for quantitative reaction rate constant measurements for several years and is proving to be a very valuable addition to the ion chemists armory. Since the ICR technique involves low pressure experiments the possibility of excited state reactant ions exists. Rate constants can in principle be measured as a function of ion kinetic energy in ICR but most reported values are essentially at thermal energy.

D Discharge

A gaseous discharge is a somewhat unwieldy and complicated device for determining individual reaction rate constants and very few such applications have been carried out.

In a few cases, binary ion-neutral reactions give more than one set of products, usually two. In such cases two reaction channels may be given and denoted by a and b for purposes of differentiating the separate rate constants k_a and k_b or to define a branching ratio, k_a/k_b. It is often the case that the overall ion loss rate, $k_a + k_b$, is much more precisely measured than is the branching ratio. There are cases where the reaction products are undetermined and simply listed as "Products". There are also cases where no reaction was detected to give <u>any</u> products and this is also indicated by "products" in order to exclude all possibilities.

References: Given at the end of each Table

The references are given by the first author of the paper and the year. All the papers of a given first author and year are further sequenced by a small letter a, b, c,... etc. following the year.

Remarks: Given at the end of each Table

The data refer largely to thermal energy (thermalized room temperature measurements) but in some cases energy or temperature dependencies are available and this is so indicated in the column headed "Remarks".

In many cases reactions have been measured by more than one method and/or in more than one laboratory. Measurements which have been improved or which are otherwise considered to be obsolete or in error have not been tabulated.

TABLE I. Binary Positive-Ion Reactions

Reaction	$k(cm^3 sec^{-1})$	Uncertainty	Method	Reference	Remarks
$H^+ + O \rightarrow O^+ + H$	3.8(-10)	± 50%	FA	Fehsenfeld 1972a	a
$H^+ + Fe \rightarrow Fe^+ + H$	7.4(-9)		B	Rutherford 1972c	g
$H^+ + NO \rightarrow NO^+ + H$	1.9(-9)	± 30%	FA	Fehsenfeld 1972a	
$H^+ + CO_2 \rightarrow COH^+ + O$	3.0(-9)	± 30%	FA	Fehsenfeld 1971a	
$He^+ + H_2 \rightarrow$ products	< 1 (-13)		FA	Fehsenfeld 1966a	
$He^+ + N_2 \rightarrow N^+ + N + He$ $\rightarrow N_2^+ + He$	1.2(-9)	± 30%	FA	Farragher 1970	k_a/k_b = 1.5, b
	1.0(-9)	+ 0.3, -0.2	DT	Heimerl 1969	k_a/k_b = 1.2; c
	1.85(-9)	± 15%	ICR	Laudenslager 1973	
	1.2(-9)	± 20%	FA	Dunkin 1968a	d
	1.5(-9)	± 30%	MS	Warneck 1967a	k_a/k_b = 1.1
			FA	Schmeltekopf 1968	k_a/k_b = 2.2, f
	1.45(-9)	± 15%	SA	Sayers 1964	
$He^+ + O_2 \rightarrow O^+ + O + He$ $\rightarrow O_2^+ + He$	1.0(-9)	± 30%	FA	Farragher 1970	k_a/k_b = 1.6
	8.5(-10)	+ 2.5, -2.0	DT	Heimerl 1969	k_a/k_b = 4, c
	1.5(-9)	± 25%	ICR	Laudenslager 1973	
	1.2(-9)	± 30%	MS	Warneck 1967	
	1.10(-9)	± 15%	SA	Sayers 1964	
$He^+ + CO \rightarrow C^+ + O + He$	1.7(-9)	± 30%	FA	Fehsenfeld 1966a	
	2.0(-9)	± 15%	ICR	Laudenslager 1973	
	1.6(-9)	± 30%	MS	Moran 1966	
$He^+ + NO \rightarrow N^+ + O + He$	1.7(-9)	± 30%	FA	Fehsenfeld 1966a	
	2.1(-9)	± 30%	MS	Moran 1966	
	2.0(-9)	± 15%	ICR	Laudenslager 1973	
$He^+ + H_2O \rightarrow$ products	5.6(-10)	± 0.5	FA	Howard 1970	
	4.5(-10)	± 30%	FA	Bolden 1972	
$He^+ + CO_2 \rightarrow O^+ + CO + He$ $\rightarrow CO^+ + O + He$	1.2(-9)	± 30%	FA	Fehsenfeld 1966a	
	1.6(-9)	± 15%	ICR	Laudenslager 1973	
$He^+ + CH_4 \rightarrow$ products	1.5(-9)	± 15%	ICR	Bowers 1972	
$He^+ + C_2H_6 \rightarrow$ products	2.3(-9)	± 15%	ICR	Bowers 1972	
$C^+ + O_2 \rightarrow CO^+ + O$	1.1(-9)	± 30%	FA	Fehsenfeld 1966b	
	9.0(-10)	± 30%	MS	Franklin 1965	
$C^+ + CO_2 \rightarrow CO^+ + CO$	1.9(-9)	± 30%	FA	Fehsenfeld 1966b	
	1.6(-9)	± 30%	D	Schildcrout 1970	

NOTE: In expressing the value of a rate constant the notation 3.8 (-10) is used to indicate 3.8 x 10^{-10}.

Table I Continued

Reaction	k(cm^{3}sec^{-1})	Uncertainty	Method	Reference	Remarks
$C^+ + H_2O \rightarrow COH^+ + H$	2.0(-9)	± 30%	FA	Bolden 1972	
$N^+ + Na \rightarrow Na^+ + N$	very small		B	Rutherford 1972a	g
$N^+ + Mg \rightarrow Mg^+ + N$	1.2(-9)		B	Rutherford 1971	g
$N^+ + Ca \rightarrow Ca^+ + N$	1.1(-9)		B	Rutherford 1972b	g
$N^+ + Fe \rightarrow Fe^+ + N$	1.5(-9)		B	Rutherford 1972c	g
$N^+ + H_2 \rightarrow NH^+ + H$	7 (-10)	± 30%	FA	Fehsenfeld 1967a	
$N^+ + CO \rightarrow CO^+ + N$	5 (-10)	± 30%	FA	Fehsenfeld 1967b	
$N^+ + NO \rightarrow NO^+ + N$	8 (-10)	± 30%	FA	Goldan 1966	
$N^+ + O_2 \rightarrow O_2^+ + N$ $\rightarrow NO^+ + O$	7 (-10)	± 30%	FA	Farragher 1970	
	5 (-10)	± 30%	DT	Johnsen 1970	h
	6 (-10)	± 30%	FA	Dunkin 1968	d,s
	6.1(-10)	± 30%	MS	Warneck 1967b	$k_a/k_b = 2.8$
			FA	Goldan 1966	$k_a \approx k_b$
	7 (-10)		MS	Aquilanti 1966	$k_a/k_b = 1.3$
$N^+ + H_2O \rightarrow H_2O^+ + N$	2.6(-9)	± 0.4	FA	Howard 1970	
	2.6(-9)	± 30%	FA	Bolden 1972	
$N^+ + CO_2 \rightarrow CO_2^+ + N$	1.3(-9)	± 30%	FA	Fehsenfeld 1967b	
$O^+ + H \rightarrow H^+ + O$	6.8(-10)	± 50%	1 and Keq	Fehsenfeld 1972a	a
$O^+ + Na \rightarrow Na^+ + O$	small		B	Rutherford 1972b	g
$O^+ + Mg \rightarrow Mg^+ + O$	small		B	Rutherford 1971	g
$O^+ + Ca \rightarrow Ca^+ + O$	7.6(-10)		B	Rutherford 1972b	g
$O^+ + Fe \rightarrow Fe^+ + O$	2.9(-9)		B	Rutherford 1972c	g
$O^+ + H_2 \rightarrow OH^+ + H$	2.0(-9)	± 30%	FA	Fehsenfeld 1967a	
$O^+ + N_2 \rightarrow NO^+ + N$	1.3(-12)	± 15%	FA	Schmeltekopf 1968	i
	1.2(-12)	± 10%	FA	Dunkin 1968	
			FA	Ferguson 1969	j,s
$O^+(^2D) + N_2 \rightarrow N_2^+ + O$	~1 (-9)		B	Rutherford 1971	g
$O^+ + NO \rightarrow NO^+ + O$	< 1 (-12)		FA	Dunkin 1971a	
$O^+ + O_2 \rightarrow O_2^+ + O$	2.0(-11)	± 15%	FA	Dunkin 1968	
	2.0(-11)	+0.4, -0.3	SA	Copsey 1966	
			SA	Smith 1968	k
			FA	Ferguson 1969	j,k,s
	2.0(-11)	± 0.5	MS	Warneck 1967b	
$O^+ + CO_2 \rightarrow O_2^+ + CO$	1.2(-9)	± 30%	FA	Fehsenfeld 1966c	
	1.0(-9)	± 30%	MS	Paulson 1966	

Table I Continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$O^+ + H_2O \rightarrow H_2O^+ + O$	2.3(-9)	± 0.25	FA	Howard 1970	
	2.4(-9)	± 30%	FA	Bolden 1972	
$O^+ + N_2O \rightarrow N_2O^+ + O$	2.2(-10)	± 1.3	MS	Ryan 1972	1
$\rightarrow NO^+ + NO$	2.3(-10)	± 1.4	MS	Ryan 1972	
$k_a + k_b =$	6.3(-10)	± 30%	FA	Dunkin 1971a	1
$O^+ + NO_2 \rightarrow NO_2^+ + O$	1.6(-9)	± 30%	FA	Dunkin 1971a	
$Na^+ + O_3 \rightarrow NaO^+ + O_2$	< 1 (-11)		FA	Ferguson 1968	m
$Mg^+ + O_3 \rightarrow MgO^+ + O_2$	2.3(-10)	± 50%	FA	Ferguson 1968	
$S^+ + NO \rightarrow NO^+ + S$	4.2(-10)	± 20%	FA	Fehsenfeld 1973a	
$S^+ + O_2 \rightarrow SO^+ + O$	1.6(-11)	± 20%	FA	Fehsenfeld 1973a	
$S^+ + CO_2 \rightarrow$ products	< 1 (-12)		FA	Fehsenfeld 1973a	
$Ar^+ + H_2 \rightarrow ArH^+ + H$	6.8(-10)	± 20%	ICR	Bowers 1969a	
	7.0(-10)	± 30%	FA	Adams 1970	
$Ar^+ + N_2 \rightarrow N_2^+ + Ar$	6.6(-11)	?	MS	Warneck 1967c	n
	5 (-11)	± 75%	ICR	Laudenslager 1973	
$Ar^+ + CO \rightarrow CO^+ + Ar$	1.2(-10)	± 30%	MS	Warneck 1967c	
	9.0(-11)	± 30%	FA	Fehsenfeld 1966d	
	5 (-11)	± 90%	ICR	Laudenslager 1973	
$Ar^+ + NO \rightarrow NO^+ + Ar$	3.9(-10)	± 30%	MS	Warneck 1967c	
	2.5(-10)	± 30%	ICR	Laudenslager 1973	
$Ar^+ + O_2 \rightarrow O_2^+ + Ar$	1.1(-10)	± 30%	MS	Warneck 1967c	
	5.0(-11)	± 30%	FA	Adams 1970	k
	7 (-11)	± 50%	ICR	Laudenslager 1973	
	5.0(-11)	± 25%	SA	Smith 1970	e
$Ar^+ + H_2O \rightarrow H_2O^+ + Ar$ $\rightarrow ArH^+ + OH$	1.4(-9)	± 0.1	FA	Howard 1970	
	1.6(-9)	± 30%	FA	Bolden 1972	
$Ar^+ + CO_2 \rightarrow CO_2^+ + Ar$	7.0(-10)	± 30%	MS	Warneck 1967c	
	7.6(-10)	± 30%	FA	Fehsenfeld 1966d	
	4.6(-10)	± 15%	ICR	Laudenslager 1973	
$Ar^+ + CH_4 \rightarrow CH_3^+ + H + Ar$	6.5(-10)	± 30%	MS	Jones 1971	
$\rightarrow CH_2^+ + H_2 + Ar$	1.4(-10)	± 30%	MS	Jones 1971	
$k_a + k_b =$	9.0(-10)	± 30%	FA	Bolden 1970	
$\rightarrow$ products	1.3(-9)	± 15%	ICR	Bowers 1972	
$Ar^+ + C_2H_6 \rightarrow$ products	1.1(-9)	± 15%	ICR	Bowers 1972	
$K^+ + O_3 \rightarrow KO^+ + O_2$	< 1 (-11)		FA	Ferguson 1968	m

Table I Continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$Cu^+ + O_3 \rightarrow CuO^+ + O_2$	1.6(-10)	± 50%	FA	Ferguson 1968	
$Fe^+ + O_3 \rightarrow FeO^+ + O_2$	1.5(-10)	± 50%	FA	Ferguson 1968	
$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.0(-9)	± 10%	MS	Reuben 1962	
	1.85(-9)		MS	Warneck 1967d	
	1.95(-9)	± 20%	ICR	Bowers 1969b	
$H_2^+ + N_2 \rightarrow N_2H^+ + H$	1.95(-9)	± 20%	ICR	Bowers 1969a	
$H_2^+ + Ar \rightarrow ArH^+ + H$	1.2(-9)	± 20%	ICR	Bowers 1969a	
$N_2^+ + N \rightarrow N^+ + N_2$	< 1 (-11)		FA	Ferguson 1965	
$N_2^+ + O \rightarrow NO^+ + N$	1.4(-10)	X2	FA	Fehsenfeld 1970	
$\rightarrow O^+ + N_2$	< 1 (-11)		FA	Ferguson 1965	t
$N_2^+ + H_2 \rightarrow N_2H^+ + H$	1.7(-9)	± 30%	FA	Fehsenfeld 1967a	
	1.4(-9)	± 20%	ICR	Bowers 1969	
$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	6.6(-11)	± 30%	FA	Farragher 1970	
	6 (-11)		DT	Johnsen 1970	h
	5 (-11)	± 30%	FA	Ferguson 1969	j,s
	6.5(-11)	± 1	MS	Aquilanti 1966	
$\rightarrow NO^+ + NO$	< 3 (-14)		MS	Warneck 1967b	
$N_2^+ + CO \rightarrow CO^+ + N_2$	7 (-11)	± 30%	FA	Fehsenfeld 1967b	
$N_2^+ + NO \rightarrow NO^+ + N_2$	3.3(-10)	± 30%	FA	Fehsenfeld 1970	
	4.8(-10)	± 30%	MS	Warneck 1967b	
$N_2^+ + H_2O \rightarrow H_2O^+ + N_2$	2.2(-9)	± 0.3	FA	Howard 1970	
$\rightarrow N_2H^+ + OH$	2.0(-9)	± 30%	FA	Bolden 1972	
$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$	9 (-10)	± 30%	FA	Fehsenfeld 1967b	
$N_2^+ + Na \rightarrow Na^+ + N_2$	5.8(-10)	± 50%	FA	Farragher 1969	
	1.9(-9)		B	Rutherford 1972a	g
$N_2^+ + Mg \rightarrow Mg^+ + N_2$	7.2(-10)		B	Rutherford 1971a	g
$N_2^+ + Ca \rightarrow Ca^+ + N_2$	1.8(-9)		B	Rutherford 1972b	g
$N_2^+ + Fe \rightarrow Fe^+ + N_2$	4.3(-10)		B	Rutherford 1972e	g
$O_2^+ + N \rightarrow NO^+ + O$	1.8(-10)	X2	FA	Goldan 1966	
$O_2^+ + N_2 \rightarrow NO^+ + NO$	< 1 (-15)		FA	Ferguson 1965	o
$O_2^+ + NO \rightarrow NO^+ + O_2$	6.3(-10)	± 30%	FA	Fehsenfeld 1970	
	7.7(-10)	± 30%	MS	Warneck 1967e	
	7.2(-10)	± 1.5	DT	Johnsen 1970	
$O_2^+ + NO_2 \rightarrow NO_2^+ + O_2$	6.6(-10)	± 30%	FA	Fehsenfeld 1973b	
$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$	2.4(-9)	± 30%	FA	Fehsenfeld 1973e	
$O_2^+ + Na \rightarrow Na^+ + O_2$	6.7(-10)	± 50%	FA	Farragher 1969	
	1.4(-9)		B	Rutherford 1972a	g

Table I Continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$O_2^+(a^4\Pi_u) + Na \rightarrow Na^+ + O_2$	2.0(-9)		B	Rutherford 1972a	g
$O_2^+ + Na \rightarrow NaO^+ + O$	1.2(-10)		B	Rol 1968	p
	< 7 (-11)		FA	Farragher 1969	
$O_2^+ + Mg \rightarrow Mg^+ + O_2$	1.2(-9)		B	Rutherford 1971a	g
$O_2^+(a^4\Pi_u) + Mg \rightarrow Mg^+ + O_2$	> 3 (-9)		B	Rutherford 1971a	q,g
$O_2^+ + Ca \rightarrow Ca^+ + O_2$	1.8(-9)		B	Rutherford 1972b	g
$O_2^+(a^4\Pi_u) + Ca \rightarrow Ca^+ + O_2$	3.5(-9)		B	Rutherford 1972b	g
$O_2^+ + Fe \rightarrow Fe^+ + O_2$	1.1(-9)		B	Rutherford 1972c	g
$NO^+ + Na \rightarrow Na^+ + NO$	7.7(-11)	± 50%	FA	Farragher 1969	
$NO^+ + Mg \rightarrow Mg^+ + NO$	8.1(-10)		B	Rutherford 1971a	g
$NO^+ + Ca \rightarrow Ca^+ + NO$	4.0(-9)		B	Rutherford 1972b	g
$NO^+ + Fe \rightarrow Fe^+ + NO$	9.2(-10)		B	Rutherford 1972c	g
$NO^+ + O_3 \rightarrow NO_2^+ + O_2$	< 1 (-14)		FA	Fehsenfeld 1973b	
$CO^+ + O \rightarrow O^+ + CO$	1.4(-10)	± 50%	FA	Fehsenfeld 1972a	
$CO^+ + N \rightarrow$ products	< 2 (-11)		FA	Fehsenfeld 1972a	
$CO^+ + NO \rightarrow NO^+ + CO$	3.3(-10)	± 30%	FA	Fehsenfeld 1972a	
$CO^+ + H_2 \rightarrow COH^+ + H$	2.0(-9)	± 30%	FA	Fehsenfeld 1967a	
$CO^+ + O_2 \rightarrow O_2^+ + CO$	2.0(-10)	± 30%	FA	Fehsenfeld 1966b	
$CO^+ + CO_2 \rightarrow CO_2^+ + CO$	1.1(-9)	± 30%	FA	Fehsenfeld 1966b	
$CO^+ + H_2O \rightarrow$ products	2.2(-9)	± 30%	FA	Bolden 1972	
$SiO^+ + O \rightarrow Si^+ + O_2$	~ 2 (-10)		FA	Fehsenfeld 1969a	
$SiO^+ + N \rightarrow Si^+ + NO$	~ 2 (-10)		FA	Fehsenfeld 1969a	
$\rightarrow NO^+ + Si$	~ 1 (-10)		FA	Fehsenfeld 1969a	
$MgO^+ + O \rightarrow Mg^+ + O_2$	~ 1 (-10)		FA	Ferguson 1968	
$SO^+ + CO \rightarrow S^+ + CO_2$	< 1 (-12)		FA	Fehsenfeld 1973a	
$H_3^+ + N_2 \rightarrow N_2H^+ + H_2$	1.5(-9)	± 30%	FA	Burt 1970	
	1.0(-9)	± 30%	MS	Aquilanti 1965	
$H_3^+ + CO \rightarrow COH^+ + H_2$	1.4(-9)	± 30%	FA	Burt 1970	
$H_3^+ + NO \rightarrow NOH^+ + H_2$	1.4(-9)	± 30%	FA	Burt 1970	
$H_3^+ + CO_2 \rightarrow CO_2H^+ + H_2$	1.9(-9)	± 30%	FA	Burt 1970	
$H_3^+ + NO_2 \rightarrow NO^+ + OH + H_2$	7 (-10)	± 30%	FA	Burt 1970	
$H_3^+ + N_2O \rightarrow N_2OH^+ + H_2$	1.8(-9)	± 30%	FA	Burt 1970	
$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2$	1.6(-9)	± 30%	FA	Burt 1970	
	7.5(-10)	± 30%	MS	Aquilanti 1966a	
$H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + H_2$	1.9(-9)	± 30%	FA	Burt 1970	
$\rightarrow C_2H_3^+ + 2H_2$	1.2(-10)	± 30%	FA	Burt 1970	

Table 1 Continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$H_3^+ + C_2H_2 \rightarrow C_2H_3^+ + H_2$	1.9(-10)	± 30%	FA	Burt 1970	
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	~ 3.0(-9)		FA	Burt 1970	
$H_3^+ + NH_3 \rightarrow NH_4^+ + H_2$	~ 3.6(-9)		FA	Burt 1970	
$N_2H^+ + CO_2 \rightarrow CO_2H^+ + N_2$	9.2(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + N_2O \rightarrow N_2OH^+ + N_2$	7.9(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2$	8.9(-10)	± 30%	FA	Burt 1970	
$N_2H^+ + H_2O \rightarrow H_3O^+ + N_2$	~ 5 (-10)		FA	Burt 1970	
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	1.7(-9)	± 30%	FA	Bolden 1972	
	1.8(-9)	± 30%	MS	Good 1970	
	1.6(-9)	± 20%	MS	Gupta 1967	
$H_2O^+ + Na \rightarrow Na^+ + H_2O$	1.9(-9)		B	Rutherford 1972a	g
$H_2O^+ + Ca \rightarrow Ca^+ + H_2O$	4.0(-9)		B	Rutherford 1972b	g
$H_2O^+ + Fe \rightarrow Fe^+ + H_2O$	1.5(-9)		B	Rutherford 1972c	g
$CO_2^+ + H \rightarrow HCO^+ + O$	6 (-10)	± 50%	FA	Fehsenfeld 1971a	$k_a/k_b \sim 5$
$\rightarrow H^+ + CO_2$					
$CO_2^+ + O \rightarrow O_2^+ + CO$	2.6(-10)	X 2	FA	Fehsenfeld 1970	$k_a/k_b \sim 1.7$
$\rightarrow O^+ + CO_2$					
$CO_2^+ + N \rightarrow$ products	< 1 (-11)		FA	Fehsenfeld 1970	
$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$	1.4(-9)	± 30%	FA	Fehsenfeld 1967a	
$CO_2^+ + NO \rightarrow NO^+ + CO_2$	1.2(-10)	± 30%	FA	Fehsenfeld 1970	
$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	5.0(-11)	± 30%	FA	Fehsenfeld 1970	
$NO_2^+ + NO \rightarrow NO^+ + NO_2$	2.9(-10)	± 30%	FA	Fehsenfeld 1969b	
$SO_2^+ + CO \rightarrow SO^+ + CO_2$	3.0(-10)	± 20%	FA	Fehsenfeld 1973a	
$SO_2^+ + O_2 \rightarrow O_2^+ + SO_2$	2.8(-10)	± 20%	FA	Fehsenfeld 1973a	
$H_3O^+ + Ca \rightarrow Ca^+ + H_2O + H$	4.4(-9)		B	Rutherford 1972b	g
$N_4^+ + O_2 \rightarrow O_2^+ + 2N_2$	4 (-10)	± 30%	FA	Dunkin 1971b	
$O_4^+ + O \rightarrow O_2^+ + O_3$	3 (-10)	± 2	FA	Fehsenfeld 1972b	
$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$	1.5(-9)	± 0.5	FA	Howard 1972	
	1.3(-9)	± 50%	MS	Good 1970	
	2.2(-9)	± 50%	FA	Fehsenfeld 1971b	
$O_2^+ \cdot N_2 + H_2O \rightarrow O_2^+ \cdot H_2O + N_2$	4 (-9)	± 2	FA	Howard 1972	
$O_2^+ \cdot N_2 + O_2 \rightarrow O_4^+ + N_2$	> 5 (-11)		FA	Adams 197b	80°K
$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+ \cdot H_2O + OH$	1.4(-9)	± 0.5	FA	Howard 1972	
	> 1 (-9)		MS	Good 1970	
	~ 3.2(-9)		FA	Fehsenfeld 1971b	

Table I Continued

Reaction	k(cm^{3}sec^{-1})	Uncertainty	Method	Reference	Remarks
$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$	1.0(9)	± 0.4	FA	Howard 1972	
	9 (-10)	± 50%	MS	Good 1970	
	1.9(-9)	± 50%	FA	Fehsenfeld 1971b	
$\rightarrow H_3O^+ + OH + O_2$	2 (-10)	± 1	FA	Howard 1972	
	3 (-10)	± 1	MS	Good 1970	
	≤ 3 (-10)		FA	Fehsenfeld 1971b	
$NO^+ \cdot CO_2 + H_2O \rightarrow NO^+ \cdot H_2O + CO_2$	~ 1 (-9)		FA	Dunkin 1971b	
$NO^+(H_2O)_3 + H_2O \rightarrow H_3O^+(H_2O)_2 + HNO_2$	7 (-11)	± 2	FA	Howard 1972	
	8 (-11)	± 50%	FA	Fehsenfeld 1971c	
	7 (-11)	± 30%	SA	Puckett 1971a	r
$NO^+ \cdot NO + H_2O \rightarrow NO^+ \cdot H_2O + NO$	1.4(-9)	± 0.3	SA	Puckett 1971a	
$NO^+ \cdot NO + NH_3 \rightarrow NO^+ \cdot NH_3 + NO$	1.3(-9)	± 0.2	SA	Puckett 1971a	
$NO^+ \cdot H_2O + NO \rightarrow NO^+ \cdot NO + H_2O$	9 (-14)	± 2	SA	Puckett 1971a	
$NO^+ \cdot H_2O + NH_3 \rightarrow NH_4^+ + HNO_2$	1.0(-9)	± 30%	FA	Fehsenfeld 1971d	
$NO_2^+ \cdot H_2O + NH_3 \rightarrow NH_4^+ + HNO_3$	1.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$NO^+ \cdot NH_3 + NH_3 \rightarrow NH_4^+ + ONNH_2$	9.1(-10)	± 30%	SA	Puckett 1971b	
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	1.9(-9)	± 0.2	ICR	Huntress 1971a	
	1.5(-9)	± 30%	MS	Melton 1966	
	1.7(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	2.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O) + NH_3 \rightarrow$ products	2.6(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O)_2 + NH_3 \rightarrow$ products	1.6(-9)	± 30%	FA	Fehsenfeld 1973c	
$H_3O^+(H_2O)_3 + NH_3 \rightarrow$ products	2.1(-9)	± 30%	FA	Fehsenfeld 1973c	
$NH_4^+(H_2O) + NH_3 \rightarrow NH_4^+(NH_3) + H_2O$	1.2(-9)	± 30%	FA	Fehsenfeld 1973c	
$NH_4^+(H_2O)_2 + NH_3 \rightarrow NH_4^+(NH_3)(H_2O) + H_2O$	≥ 9 (-10)	± 30%	FA	Fehsenfeld 1973c	

FOOTNOTES

a) Agrees well with extrapolated beam measurements

b) Farragher gives $k_a = 6.5(-10) \pm 1.3$, $k_b = 4.2(-10) \pm 0.9$

c) Heimerl gives k as a function of ion kinetic energy to ~ 0.1 eV

d) Rate constant found to be independent of temperature, 300-600 K

e) Rate constant proportional to T^{-1} in thermal range

f) Rate constant independent of N_2 vibrational temperature from 300-600°K but ratio k_a/k_b increases with T_v

g) Extrapolated from beam energies. This leads to additional uncertainty in k, probably reliable to within factor of 2.

h) Johnsen gives k as function of ion kinetic energy to ~ 1 eV

i) Schmeltekopf gives k as function of N_2 vibrational temperature from 300-6000 K

j) Rate constant given for temperature range 80-600 K

k) Gives rate constant proportional to $T^{-\frac{1}{2}}$ in thermal range.

l) Ryan gives $k_a + k_b = 4.3(-10) \pm 0.6$. Dunkin 1971 erroneously neglects channel b

m) Probably endothermic

n) Measurements on this reaction have given rate constants ranging from 4(-12) to 6.6(-11), depending on experimental conditions. This is almost surely due to the near resonance involved and the difficulties are elaborated in Adams 1970b where a pressure dependent k is observed. This is also discussed by Adams, Dean, and Smith, Int. J. Mass Spectrometry and Ion Phys. 10, 63, 1972.

o) It has also been shown (FA) that $k < 10^{-15}$ cm^3 sec^{-1} at 600 K

p) More details of this experiment, including the rate constant cited are given by Rol and Entemann in a General Dynamics/Convair Report GDC-DBE69-002 of January 1969

q) Rate constant is not given but cross section data down to 10 eV shows clearly that rate constant is quite large

r) Reaction is endothermic

s) The energy dependence of this reaction is given in McFarland, et al, J. Chem. Phys. 60, Jan. 1, 1974. (The full reference is M. McFarland, D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson and A. L. Schmeltekopf, and all known data is summarized in figures in this paper).

t) Current measurements in progress suggest that this rate constant may be slightly larger than 10^{-11}

REFERENCES TABLE I

N. G. Adams, D. K. Bohme, D. B. Dunkin, and F. C. Fehsenfeld, J. Chem. Phys. 52, 1951 (1970a)

N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 52, 3133 (1970b)

V. Aquilanti, A. Galli, A. Ciardini Guidoni, and G. G. Volpi, J. Chem. Phys. 43 1969 (1965)

V. Aquilanti and G. G. Volpi, J. Chem. Phys. 44, 2307 (1966a)

V. Aquilanti and G. G. Volpi, Ricerca Sci. 36 259 (1966b)

R. C. Bolden and, R. S. Hemsworth, M. J. Shaw, and N. D. Twiddy, J. Phys. B 3, 45 (1970)

R. C. Bolden and N. D. Twiddy, Faraday Disc. 53, 192 (1972)

M. T. Bowers and D. D. Elleman, J. Chem. Phys. 51, 4606 (1969a)

M. T. Bowers, D. D. Elleman, and J. King, Jr., J. Chem. Phys. 50, 4787 (1969b)

M. T. Bowers and D. D. Elleman, Chem. Phys. 16, 486 (1972)

J. A. Burt, J. L. Dunn, M. J. McEwan, M. M. Sutton, A. E. Roche, and H. I. Schiff, J. Chem. Phys. 52, 6062 (1970)

M. J. Copsey, D. Smith, and J. Sayers, Planet. Space Sci. 14, 1047 (1966)

D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 49, 1365 (1968)

D. B. Dunkin, M. McFarland, F. C. Fehsenfeld, and E. E. Ferguson, J. Geophys. Res. 76, 3820 (1971a)

D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 54, 3817 (1971b)

A. L. Farragher, J. A. Peden, and W. L. Fite, J. Chem. Phys. 50, 287 (1969)

A. L. Farragher, Trans. Faraday Soc. 66, 1411 (1970)

F. C. Fehsenfeld, A. L. Schmeltekopf, P. D. Goldan, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4087 (1966a)

F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 45, 23 (1966b)

F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. 44, 3022 (1966c)

F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. 45, 404 (1966d)

F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 46, 2802 (1967a)

F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 46, 2019 (1967b)

F. C. Fehsenfeld, Can. J. Chem. 47, 1808 (1969a)

F. C. Fehsenfeld, E. E. Ferguson, and M. Mosesman, Chem. Phys. Letters 4, 73 (1969b)

F. C. Fehsenfeld, D. B. Dunkin, and E. E. Ferguson, Planet. Space Sci 18, 1267 (1970)

F. C. Fehsenfeld and E. E. Ferguson, J. Geophys. Res. 76, 8453 (1971a)

F. C. Fehsenfeld, M. Mosesman, and E. E. Ferguson, J. Chem. Phys. 55, 2115 (1971b)

F. C. Fehsenfeld, M. Mosesman, and E. E. Ferguson, J. Chem. Phys. 55, 2120 (1971c)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. 54, 439 (1971d)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. 56, 3066 (1972a)

F. C. Fehsenfeld and E. E. Ferguson, Radio Sci. 7, 113 (1972b)

F. C. Fehsenfeld and E. E. Ferguson, J. Geophys. Res. 78, 1169 (1973a)

F. C. Fehsenfeld, E. E. Ferguson, and C. J. Howard, J. Geophys. Res. 78, 327 (1973b)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. (1973c) in press

E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and H. I. Schiff, Planet. Space Sci. 13, 823 (1965)

E. E. Ferguson and F. C. Fehsenfeld, J. Geophys. Res. 73, 6215 (1968)

E. E. Ferguson, D. K. Bohme, F. C. Fehsenfeld, and D. B. Dunkin, J. Chem. Phys. 50, 5039 (1969)

J. L. Franklin and M. S. B. Munson, Tenth Combustion Symposium, p. 561, Combustion Institute, Pittsburgh, Pa. (1965)

P. D. Goldan, A. L. Schmeltekopf, F. C. Fehsenfeld, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4095 (1966)

A. Good, D. A.Durden, and P. Kebarle, J. Chem. Phys. 52, 212, 222 (1970)

S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, Can. J. Chem. 45, 3107 (1967)

J. Heimerl, R. Johnsen, and M. A. Biondi, J. Chem. Phys. 51, 5041 (1969)

C. J. Howard, H. W. Rundle, and F. Kaufman, J. Chem. Phys. 53, 3745 (1970)

C. J. Howard, H. W. Rundle, and F. Kaufman, J. Chem. Phys. 55, 4772 (1971)

C. J. Howard, V. M. Bierbaum, H. W. Rundle, and F. Kaufman, J. Chem. Phys. 57, 3491 (1972)

W. T. Huntress, M. Mosesman, and D. D. Elleman, J. Chem. Phys. 54, 843 (1971)

R. Johnsen, H. L. Brown, and M. A. Biondi, J. Chem. Phys. 52, 5080 (1970)

E. G. Jones and A . Harrison, Int. J. Mass Spectro. Ion Phys. 6, 77 (1971)

J. B. Laudenschlager and M. T. Bowers, Chem. Phys. Letters (1973) in press

E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson, and L. Friedman, *Ion-Molecule Reactions*, Wiley, New York 1970

T. F. Moran and L. Friedman, J. Chem. Phys. 45, 3837 (1966)

C. E. Melton, J. Chem. Phys. 45. 5515 (1966)

J. F. Paulson, R. L. Mosher, and F. Dale, J. Chem. Phys. 44, 3025 (1966)

L. J. Puckett and M. W. Teague, J. Chem. Phys. 54, 2564 (1971a)

L. J. Puckett and M. W. Teague, J. Chem. Phys. 54, 4860 (1971b)

B. G. Reuben and L. Friedman, J. Chem. Phys. 37, 1636 (1962)

P. K. Rol and E. A. Entemann, J. Chem. Phys. 49, 1430 (1968)

J. A. Rutherford, R. F. Mathis, B. R. Turner, and D. A. Vroom, J. Chem. Phys. 55, 3785 (1971a)

J. A. Rutherford and D. A. Vroom, J. Chem. Phys. 55, 5622 (1971b)

J. A. Rutherford, R. F. Mathis, B. R. Turner, and D. A. Vroom, J. Chem. Phys. 56, 4654 (1972a)

J. A. Rutherford, R. F. Mathis, B. R. Turner, and D. A. Vroom, J. Chem. Phys. 57, 3087 (1972b)

J. A. Rutherford and D. A. Vroom, J. Chem. Phys. 57, 3091 (1972c)

K. R. Ryan, J. Chem. Phys. 57, 271 (1972)

J. Sayers and D. Smith, Disc. Faraday Soc. 37, 167 (1964)

S. M. Schildcrout, J. G. Collins, and J. L. Franklin, J. Chem. Phys. 52, 5767 (1970)

A. L. Schmeltekopf, E. E. Ferguson, and F. C. Fehsenfeld, J. Chem. Phys. 48, 2966 (1968)

D. Smith and R. A. Fouracre, Planet. Space Sci. 16, 243 (1968)

D. Smith, C. V. Goodall, N. G. Adams, and A. G. Dean, J. Phys. B 3, 34 (1970)

P. Warneck, J. Chem. Phys. 47, 4279 (1967a)

P. Warneck, J. Geophys. Res. 72, 1651 (1967b)

P. Warneck, J. Chem. Phys. 46, 513 (1967c)

P. Warneck, J. Chem. Phys. 46, 502 (1967d)

P. Warneck, Planet. Space Sci. 15, 1349 (1967e)

4.4.3 TABLE II. Binary Negative-Ion Reactions

Reaction	k(cm^3sec^{-1})	Uncertainty	Method	Reference	Remarks
$H^- + H \rightarrow H_2 + e$	1.3(-9)	± 50%	FA	Schmeltekopf 1967	a
	1.8(-9)	X2	FA	Fehsenfeld 1973a	
$H^- + CO \rightarrow HCO + e$	~ 5 (-11)		FA	Dunkin, 1970	
$H^- + NO \rightarrow HNO + e$	4.6(-10)	± 30%	FA	Dunkin, 1970	
$H^- + O_2 \rightarrow HO_2 + e$	1.2(-9)	± 0.2	FA	Dunkin, 1970	
$\rightarrow O^- + OH$	< 1 (-11)		FA	Dunkin, 1970	
$\rightarrow O_2^- + H$	< 1 (-11)		FA	Dunkin, 1970	
$\rightarrow OH^- + O$	< 1 (-11)		FA	Dunkin, 1970	
$H^- + N_2O \rightarrow OH^- + N_2$	1.1(-9)	± 0.3	FA	Dunkin, 1970	
$H^- + NO_2 \rightarrow NO_2^- + H$	2.9(-9)	± 30%	FA	Ferguson, 1969	
$H^- + H_2O \rightarrow OH^- + H_2$	3.8(-9)	± 30%	MS	Melton, 1971	
$C^- + H_2 \rightarrow$ products	< 1 (-13)		FA	Fehsenfeld 1970	
$C^- + CO \rightarrow C_2O + e$	4.1(-10)	± 30%	FA	Fehsenfeld,1970	
$C^- + O_2 \rightarrow O^- + CO$	4.0(-10)	± 30%	FA	Fehsenfeld, 1970	
$C^- + N_2O \rightarrow CO + N_2 + e$	9.0(-10)	± 30%	FA	Fehsenfeld, 1970	
$C^- + CO_2 \rightarrow 2CO + e$	4.7(-11)	± 30%	FA	Fehsenfeld, 1970	
$O^- + O \rightarrow O_2 + e$	1.9(-10)	X2	FA	Fehsenfeld, 1967	
$O^- + N \rightarrow NO + e$	2.2(-10)	X2	FA	Fehsenfeld, 1967	
$O^- + H_2 \rightarrow H_2O + e$	7.0(-10)	± 0.5	DT	Parkes, 1972a	
	6.0(-10)	± 30%	FA	Ferguson, 1969	
	7.2(-10)	± 1	DT	Moruzzi, 1968	
$\rightarrow OH^- + H$	3.3(-11)	± 0.5	DT	Parkes, 1972a	
$O^- + CO \rightarrow CO_2 + e$	6.5(-10)	± 1	DT	Moruzzi, 1968	
	4.4(-10)	± 30%	FA	Ferguson, 1969	
	7.3(-10)	± 0.7	DT	Parkes, 1972a	
$O^- + NO \rightarrow NO_2 + e$	2.2(-10)	± 0.5	DT	Moruzzi, 1968	
	1.6(-10)	± 30%	FA	Ferguson, 1969	
$O^- + N_2 \rightarrow N_2O + e$	< 5 (-13)		DT	Moruzzi, 1968	c
	< 1 (-12)		FA	Fehsenfeld, 1966	
$O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$	~ 3 (-10)		FA	Fehsenfeld, 1969a	
$O^- + H_2O \rightarrow OH^- + OH$	1.4(-9)	± 30%	MS	Melton, 1971	b
$O^- + N_2O \rightarrow NO^- + NO$	2.2(-10)	± 0.4	FA	Marx, 1973	d
	2.5(-10)	± 0.5	ICR	Marx, 1973	
	1.95(-10)	± 0.06	DT	Parkes 1973	
$O^- + NO_2 \rightarrow NO_2^- + O$	1.2(-9)	± 30%	FA	Ferguson, 1969	
$O^- + O_3 \rightarrow O_3^- + O$	5.3(-10)	X2	FA	Ferguson, 1969	
$O^- + CH_4 \rightarrow OH^- + CH_3$	1.1(-10)	± 0.1	DT	Parkes, 1972a	
	1.0(-10)	± 20%	FA	Bohme, 1969	

Table II continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$O^- + C_2H_4 \rightarrow C_2H_4O + e$	4.05(-10)	± 0.5	DT	Parkes, 1972a	
$\rightarrow C_2H_2^- + H_2O$	1.9(-10)	± 0.3	DT	Parkes, 1972a	
$O^- + C_2H_2 \rightarrow C_2H_2O + e$	1.3(-9)	± 0.09	DT	Parkes, 1972a	
$\rightarrow C_2H^- + OH$	8.0(-10)	± 0.5	DT	Parkes, 1972a	
$\rightarrow C_2OH + H$	8 (-11)	± 1	DT	Parkes, 1972a	
$O^- + C_2H_6 \rightarrow OH^- + C_2H_5$	7.0(-10)	± 20%	FA	Bohme, 1969	
$O^- + C_3H_8 \rightarrow OH^- + C_3H_7$	9.3(-10)	± 20%	FA	Bohme, 1969	
$O^- + n - C_4H_{10} \rightarrow OH^- + C_4H_9$	1.2(-9)	± 20%	FA	Bohme, 1969	
$F^- + H \rightarrow HF + e$	1.6(-9)	X2	FA	Fehsenfeld, 1973a	
$S^- + H_2 \rightarrow H_2S + e$	< 1 (-15)		FA	Fehsenfeld, 1969b	
$S^- + O_2 \rightarrow SO_2 + e$	3.0(-11)	± 30%	FA	Fehsenfeld, 1969b	
$Cl^- + H \rightarrow HCl + e$	9.0(-10)	X2	FA	Ferguson, 1969	
	1.0(-9)	X2	FA	Fehsenfeld, 1973a	
$OH^- + H \rightarrow H_2O + e$	1.0(-9)	X2	FA	Ferguson, 1969	
	1.8(-9)	X2	FA	Fehsenfeld, 1973a	
$OH^- + O \rightarrow HO_2 + e$	2.0(-10)	± 50%	FA	Fehsenfeld, 1966	
$OH^- + N \rightarrow HNO + e$	< 1 (-11)		FA	Fehsenfeld, 1966	
$OH^- + NO_2 \rightarrow NO_2^- + OH$	1.9(-9)	± 30%	FA	Ferguson, 1969	
$HS^- + H \rightarrow H_2S + e$	1.3(-9)	X2	FA	Fehsenfeld, 1973a	
$CN^- + H \rightarrow HCN + e$	8.0(-10)	X2	FA	Fehsenfeld, 1973a	
$NO^- + O_2 \rightarrow O_2^- + NO$	5.0(-10)	± 30%	FA	McFarland, 1972	e
$NO^- + N_2O \rightarrow NO_2^- + N_2$	2.8(-14)	± 0.2	DT	Parkes, 1973	
$NO^- + NO_2 \rightarrow NO_2^- + NO$	7.4(-10)	± 30%	DT	McFarland, 1972	
$O_2^- + H \rightarrow$ products	1.5(-9)	X2	FA	Fehsenfeld, 1973a	
$O_2^- + N \rightarrow NO_2 + e$	4.0(-10)	± 50%	FA	Fehsenfeld, 1967	
$O_2^- + O \rightarrow O_3 + e$	3.3(-10)	± 50%	FA	Fehsenfeld, 1967	
$O_2^- + H_2 \rightarrow$ products	< 1 (-12)		FA	Fehsenfeld, unpublished	
$O_2^- + O_2(^1\Delta_g) \rightarrow 2O_2 + e$	~ 2 (-10)		FA	Fehsenfeld, 1969a	
$O_2^- + N_2O \rightarrow O_3^- + N_2$	< 1 (-12)		DT	Parkes, 1973	
$O_2^- + NO_2 \rightarrow NO_2^- + O_2$	8.0(-10)	± 30%	FA	Ferguson, 1969	
$O_2^- + O_3 \rightarrow O_3^- + O_2$	3.0(-10)	± 30%	FA	Fehsenfeld, 1967	
$O_2^- + SO_2 \rightarrow SO_2^- + O_2$	4.8(-10)	± 30%	FA	Fehsenfeld, 1973b	
$NO_2^- + H \rightarrow OH^- + NO$	3.0(-10)	X2	FA	Fehsenfeld, 1972	
	4.0(-10)	X2	FA	Fehsenfeld, 1973a	
$NO_2^- + O \rightarrow$ products	< 1 (-11)		FA	Fehsenfeld, unpublished	
$NO_2^- + N \rightarrow$ products	< 1 (-11)		FA	Fehsenfeld, unpublished	

Table II continued

Reaction	k($cm^3 sec^{-1}$)	Uncertainty	Method	Reference	Remarks
$NO_2^- + NO_2 \rightarrow NO_3^- + NO$	~ 4 (-12)		FA	Fehsenfeld, 1969c	
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	1.8(-11)	± 50%	FA	Fehsenfeld, 1968	
$O_3^- + H \rightarrow OH^- + O_2$	8.4(-10)	X2	FA	Fehsenfeld, 1973a	
$O_3^- + N_2 \rightarrow$ products	< 1 (-15)		FA	Fehsenfeld, unpublished	
$O_3^- + NO \rightarrow$ products	1.0(-11)	± 50%	FA	Fehsenfeld, 1967	f
$O_3^- + CO_2 \rightarrow CO_3^- + O_2$	4.0(-10)	± 30%	FA	Fehsenfeld, 1967	
	5.5(-10)	± 0.5	DT	Parkes, 1972b	
$O_3^- + NO_2 \rightarrow$ products	2.8(-10)	± 30%	FA	Dunkin, 1972	
$O_3^- + SO_2 \rightarrow SO_3^- + O_2$	1.7(-9)	± 30%	FA	Fehsenfeld, 1973b	
$CO_3^- + O \rightarrow O_2^- + CO_2$	8.0(-11)	± 50%	FA	Fehsenfeld, 1967	
$CO_3^- + NO \rightarrow NO_2^- + CO_2$	9.0(-12)	X2	FA	Fehsenfeld, 1967	
	1.8(-11)	± 30%	FA	Fehsenfeld, 1973b	
$CO_3^- + NO_2 \rightarrow$ products	2 (-10)	X2	FA	Fehsenfeld, 1973b	
$CO_3^- + SO_2 \rightarrow SO_3^- + CO_2$	2.3(-10)	± 30%	FA	Fehsenfeld, 1973b	
$NO_3^- + N \rightarrow$ products	< 1 (-11)		FA	Fehsenfeld, 1969c	
$NO_3^- + O \rightarrow$ products	< 1 (-11)		FA	Fehsenfeld, 1969c	
$O_4^- + O \rightarrow O_3^- + O_2$ $\rightarrow O^- + 2O_2$	4.0(-10)	± 50%	FA	Fehsenfeld, 1969c	$k_a > k_b$
$O_4^- + CO \rightarrow CO_3^- + O_2$	< 2 (-11)		FA	Adams, 1970	
$O_4^- + NO \rightarrow NO_3^{-*} + O_2$	2.5(-10)	± 30%	FA	Adams, 1970	h
$O_4^- + CO_2 \rightarrow CO_4^- + O_2$	4.3(-10)	± 30%	FA	Adams, 1970	
$O_4^- + H_2O \rightarrow O_2^- \cdot H_2O + O_2$	1.5(-9)		MS	Payzant, 1972	
	1.4(-9)		DT	Pack, 1971	
$CO_4^- + O \rightarrow CO_3^- + O_2$ $\rightarrow O_3^- + CO_2$	1.5(-10)	± 50%	FA	Fehsenfeld, 1969c	$k_a > k_b$
$CO_4^- + NO \rightarrow NO_3^{-*} + CO_2$	4.8(-11)	± 30%	FA	Fehsenfeld, 1969c	h
$O_2^- \cdot H_2O + NO \rightarrow NO_3^- + H_2O$	3.1(-10)	± 30%	FA	Adams, 1970	
$O_2^- \cdot H_2O + CO_2 \rightarrow CO_4^- + H_2O$	5.8(-10)	± 30%	FA	Adams, 1970	
$O_2^- \cdot H_2O + O_3 \rightarrow$ products	3 (-10)	± 30%	FA	Fehsenfeld, 1973b	
$O_2^-(H_2O)_2 + O_3 \rightarrow$ products	3.4(-10)	± 30%	FA	Fehsenfeld, 1973b	
$NO_3^{-*} + NO \rightarrow NO_2^- + NO_2$	1.5(-11)	X2	FA	Adams, 1970	h
$NO_3^- + NO \rightarrow NO_2^- + NO_2$	~ 3 (-15)		DT	Parkes, 1972c	i
$O_2^- \cdot H_2O + O_2 \rightarrow O_4^- + H_2O$	2.5(-15)	± 1	DT	Parkes, 1971	i
$O_3^-(H_2O) + CO_2 \rightarrow$ products	3 (-10)	X2	FA	Fehsenfeld, 1973b	
$O_3^-(H_2O)_2 + CO_2 \rightarrow$ products	2 (-10)	X2	FA	Fehsenfeld, 1973b	

Table II continued

Reactions	$k(cm^3 sec^{-1})$	Uncertainty	Method	Reference	Remarks
$CO_3^-(H_2O) + NO \rightarrow$ products	1.8(-11)	X2	FA	Fehsenfeld, 1973b	
$CO_3^-(H_2O) + NO_2 \rightarrow$ products	1.5(-10)	X2	FA	Fehsenfeld, 1973b	
$NO_2^-(H_2O) + SO_2 \rightarrow NO_2^-(SO_2) + H_2O$	1.5(-9)	± 30%	FA	Fehsenfeld, 1973b	
$SO_4^- + NO_2 \rightarrow NO_2^- + SO_2 + O_2$	2.5(-10)	X2	FA	Fehsenfeld, 1973b	
$\rightarrow NO_3^- + SO_3$	1 (-10)	X2	FA	Fehsenfeld, 1973b	
$SO_3^- + H_2O \rightarrow H_2SO_4 + e$	< 1 (-12)		FA	Fehsenfeld, 1973b	j

FOOTNOTES

a) There is a theoretical value for k by J. C. Browne and A. Dalgarno, J. Phys. B. (Atomic and Molec. Phys. 2, 885, 1969). The value at thermal energy is 2.0(-9) and the energy dependence is also given.

b) k independent of ion energy, 0-5 eV.

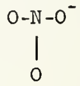
c) F. Kaufman, J. Chem. Phys. 46, 2449, 1967 points out that a detailed balancing argument can be used to calculate $k < 10^{-13}$ cm^3 sec^{-1} from dissociative electron attachment data for N_2O.

d) Because this reaction has often been measured with energetic O^- ions for which the rate constant is lower than for thermal ions, there has been a spread in published rate constants. This effect leads to a pressure dependence for k when the O^- is produced from N_2O as has usually been the case. This problem is resolved in Marx 1973 and all earlier measurements are rationalized.

e) The electron affinity of NO is so low (~ 0.024 eV $\approx$ kT) that collisional detachment is rapid in almost all gases. Such data for a number of gases are given in McFarland 1972.

f) Products reported to be $NO_3^- + O$ in reference. This is uncertain, it is more likely that products are $NO_2^- + O_2$.

g) Products uncertain, either NO_2^- or NO_3^- or both.

h) There are two forms of NO_3^-, suggested as being the stable nitrate ion  $\underset{\overset{|}{\mathrm{O}}}{\mathrm{O{-}N{-}O^-}}$ and the higher energy peroxide ion $O{-}N{-}O{-}O^-$ (which is denoted NO_3^{-*}).

i) Reaction is endothermic

j) Probably endothermic.

REFERENCES, TABLE II

N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 52, 3133 (1970)

D. K. Bohme and F. C. Fehsenfeld, Can. J. Chem. 47, 2717 (1969)

D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 53, 987 (1970).

D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, Chem. Phys. Letters 15, 257 (1972)

F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. 45, 1844 (1966)

F. C. Fehsenfeld, A. L. Schmeltekopf, H. I. Schiff, and E. E. Ferguson, Planet. Space Sci. 15, 373 (1967)

F. C. Fehsenfeld and E. E. Ferguson, Planet. Space Sci. 16, 701 (1968)

F. C. Fehsenfeld, D. L. Albritton, J. A. Burt, and H. I. Schiff, Can. J. Chem. 47, 1793 (1969a)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. 51, 3512 (1969b)

F. C. Fehsenfeld, E. E. Ferguson, and D. K. Bohme, Planet. Space Sci. 17, 1759 (1969c)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. 53, 2614 (1970)

F. C. Fehsenfeld and E. E. Ferguson, Planet. Space Sci. 20, 295 (1972)

F. C. Fehsenfeld, C. J. Howard, and E. E. Ferguson, J. Chem. Phys., 58, 5841 (1973a)

F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. Vol. 59 (1973b) in press

E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Adv. in Chem. Series 80, 83 (1969)

R. Marx, G. Mauclaire, F. C. Fehsenfeld, D. B. Dunkin, and E. E. Ferguson, J. Chem. Phys. 58, 3267 (1973)

M. McFarland, D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 56, 2358 (1972)

C. E. Melton and G. A. Neece, J. Am. Chem. Soc. 93, 6757 (1971).

J. L. Moruzzi, J. W. Ekin, and A. V. Phelps, J. Chem. Phys. 48, 3070 (1968)

J. L. Pack and A. V. Phelps, Bull. Am. Phys. Soc. 16, 214 (1971)

D. A. Parkes, Trans. Faraday Soc. 67, 711 (1971)

D. A. Parkes, J. Chem. Soc. Faraday Trans. I. 68, 613 (1972a)

D. A. Parkes, J. Chem. Soc. Faraday Trans. I. 68, 627 (1972b)

D. A. Parkes and T. M. Sugden, J. Chem. Soc. Faraday Trans. II, 68, 600 (1972c)

D. A. Parkes, J. Chem. Soc. Faraday Trans., I. 68, 2103 (1973)

J. D. Payzant and P. Kebarle, J. Chem. Phys. 56, 3482 (1972)

A. L. Schmeltekopf, F. C. Fehsenfeld, and E. E. Ferguson, Astrophys. J., 148, L155 (1967)

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM.
BIBLIOGRAPHIC DATA SHEET

1. PUBLICATION OR REPORT NO.
NBSIR 74-430

2. Gov't Accession No.

3. Recipient's Accession No.

4. TITLE AND SUBTITLE
Chemical Kinetics Data Survey VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)

5. Publication Date
January 1974

6. Performing Organization Code

7. AUTHOR(S)
David Garvin, R. F. Hampson

8. Performing Organ. Report No.
NBSIR 74-430

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

Climatic Impact Assessment Program
Department of Transportation
Washington D. C. 20590

13. Type of Report & Period Covered
Interim

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Chemical kinetic and photochemical data for gas phase reactions pertinent to the chemistry of the stratosphere are presented in four tables. These tables give recommended values and also cite recent experimental work. They give data in the following subject areas: chemical reactions and photochemistry of neutral species, energy transfer reactions, high temperature air reactions, and ion-molecule reactions.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Atmospheric chemistry; chemical kinetics; data evaluation; energy transfer; gas phase; high temperature air chemistry; ion-molecule reactions; optical absorption cross sections; photochemistry; quantum yield; rate constants

18. AVAILABILITY ☒ Unlimited

☐ For Official Distribution. Do Not Release to NTIS

☐ Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13

☐ Order From National Technical Information Service (NTIS) Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)
UNCLASSIFIED

20. SECURITY CLASS (THIS PAGE)
UNCLASSIFIED

21. NO. OF PAGES
101

22. Price


AMERICAN REVOLUTION BICENTENNIAL
1776-1976