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NBSIR-203

Chemical Kinetics Data Survey IV. Preliminary Tables of Chemical Data for Modelling of the Stratosphere

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David Garvin, Editor

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

May 1973

Interim Report

Prepared for
Climatic Impact Assessment Program, Department of Transportation

NBSIR 73-203

ERRATA (Supersedes errata dated 27 July 73)

1) On report cover change NBSIR-203 to NBSIR 73-203.

2) In table 1 (pages 8-51) make the following changes or additions. In each case a complete line for the table is shown and is identified by page number and reaction. The corrections or additions are underlined.

Page No.	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3\ molecule^{-1}s^{-1}$	Notes and Reliability of log k
44	$O_3 + SO \rightarrow O_2 + SO_2$			
	Schofield (1971) review	223-303	$2.5 \times 10^{-12}\ \exp(-1050/T)$	±0.5
46	$HO + CH_4 \rightarrow CH_3 + H_2O$			
	*Wilson (1972) review	300-2000	$4.7 \times 10^{-11}\ \exp(-2500/T)$	±0.7
47	$CH_2O + O \rightarrow CHO + OH$			
	*Demerjian, et al (1972) review	300	1.6×10^{-13}	
47	$HO + CH_2O \rightarrow H_2O + CHO$			
	*Morris, Niki	300	1.4×10^{-11}	±0.1
	Wilson (1972) review	300-1600	8×10^{-11}	±1
47,48	$HO_2 + CH_2O \rightarrow H_2O_2 + CHO$			
	*Lloyd (1971) review	300-1000	$8 \times 10^{-13}\ \exp(-3300/T)$	$\rangle$±1
48	$CH_3O + O_2 \rightarrow CH_2O + HO_2$ (1)			
	etc.			
	Demerjian, et al (1972) review	300	$k_{2b}/k_{2a} = 0.17$ $k_{3b} = 3.3 \times 10^{-13}$	

NBSIR 73-203
ERRATA (Supersedes errata dated 27 July 73)

Page No.	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^3 $molecule^{-1}$ s^{-1}	Notes and Reliability of log k
49	$HO_2 + CH_3O \rightarrow CH_3O_2H + O_2$			
	Change reaction to read: $HO_2 + \underline{CH_3O_2} \rightarrow CH_3O_2H + O_2$			
49	$CH_3O_2 + NO \rightarrow CH_3O_2NO$ (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
50	$O_3 + C_2H_4 \rightarrow$ products			
	Demerjian, et al (1972) review	300	2.7×10^{-18}	
51	$O_3 + C_3H_6 \rightarrow C_3H_6O_3$			
	DeMore (1969)	183, 193, 300	$1.65 \times 10^{-15} \exp(-1600/T)$	(b)
	*This survey (D.G.)	200-300	$2 \times 10^{-15} \exp(-1600/T)$	(a)

Add the following references:

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

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

7 Aug 73

NBSIR 73-203

CHEMICAL KINETICS DATA SURVEY IV. PRELIMINARY TABLES OF CHEMICAL DATA FOR MODELLING OF THE STRATOSPHERE

David Garvin, Editor

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

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IV. Tables

Second Printing - July 1973

Chemical Kinetics Data Survey

IV. Preliminary Tables of Chemical Data for Modelling of the Stratosphere

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.

Keywords: 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.

I. 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, R. J. Cvetanovic, D. D. Davis, E. E. Ferguson, D. Garvin, R. D. Hudson, H. I. Schiff and R. Taylor, in "The Natural Stratosphere" E. Reiter, editor, Climatic Impact Assessment Program Monograph No. 1. The first draft was prepared in November 1972.

The tables as distributed here have been revised to include new data and also to include contributions of rate evaluations by other scientists. These contributers represented in the present edition are D. L. Baulch, D. D. Drysdale and D. G. Horne (University of Leeds), J. Heicklen (Pennsylvania State University), W. H. Breckenridge (University of Utah), T. G. Slanger (Stanford Research Institute) and K. H. Welge (York University).

The tables are in several parts:

(1) Chemical reactions and photochemistry of neutral species (by the entire group).

(2) Energy transfer reactions (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.

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.

II. 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 at NBS have been distributed in NBS Report 10692 (January 1972) and NBS Report 10828 (April 1972).

These will appear, in slightly revised form, in J. Phys. Chem. Ref. Data 2 No. 2 (Summer 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). 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).

III. 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 listed as not evaluated in this report (immediately before Table I). These will be incorporated in the tables. Detailed evaluations will be issued in companion reports (such as NBS Report 73-206). We will also welcome comments and corrections of any of the recommendations.

I. Tables of Rate and Photochemical Data

Introduction

These tables provide current (May. 1973) best estimates for reaction rate constants, quantum yields and absorption cross sections. The reactions reviewed and other reactions for which selected data are needed are listed in a table of contents at the beginning of the table itself. Some of the reactions reviewed are not classed as important. Data are given for them for purpose of comparison. Other sections of the chapter also include data. See "High temperature air chemistry" for nitrogen oxide formation reactions in that regime, "Energy transfer kinetics for the stratosphere" and "Ionic reactions". Evaluations of data and remarks on specific chemical problems are gathered into section G "Special cases of important reaction systems".

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.

(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.

The persons making new selections or syntheses are usually identified by initials.
These selections are necessarily tentative because there it 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 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. D. Baulch, D. D. Drysdale and D. G. Horne, University of Leeds; J. Heicklen, Pennsylvania State University; T. G. Slanger, Stanford Research Institute and K. H. Welge, York University and W. H. Breckenridge, University of Utah.

Conventions Concerning Rate Constants for Some 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 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 $k[HNO_3]$. The units given for the k's, s^{-1} for first order, and cm^{-3} molecule 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.

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 (atm at 273 K)$^{-1}$ cm^{-1}, base e, multiply by 2.69×10^{19}.

Arrangement of the Table

1. Reactions are listed only once. They are in groups in this order:

   (a) Reactions among oxygen species: O, O_2, $O_2(^1\Delta)$, $O_2(^1\Sigma)$ and O_3 and reactions of O^* with all species.*

   (b) Reactions of hydrogen/oxygen species: H, H_2, HO, HO_2, H_2O, H_2O_2 among themselves and with group a, above.

   (c) Reactions of nitrogen/hydrogen/oxygen species: N, NO, NO_2, NO_3, N_2O, N_2O_5, NH, NH_2, NH_3, HNO, HNO_2, HNO_3 among themselves and with molecules in earlier groups.

   (d) Reactions of sulfur compounds: SO, SO_2, SO_3, H_2SO_4 among themselves and with molecules in earlier groups.

   (e) Reactions of carbon compounds, CO, CH_3, CH_4, CHO, CH_2O, CH_3O, CH_3O_2, C_2H_4, C_2H_6, C_3H_6.

2. A reaction is placed in the <u>last group</u> to which any <u>reactant</u> belongs, e.g. $NO + O_3 = NO_2 + O_2$ in group c.

3. Within a group, reactions are filed with the <u>reactant</u> <u>later</u> in the list for the group $NO_2 + NO_3 \rightarrow N_2O_5$ under NO_3.

4. All reactions of a substance with those before it in the filing order appear together. The sequence is reaction with the earliest substance in the sequence first, e.g. $NO + O$, then $NO + O_2$, ... $NO + N$.

(The order of substances in a group is atom, compounds of only the primary element, then those with O, those with H, those with H and O etc. That is, combinations with the element in each earlier group in order.)

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*Note: the placement of all reactions of $O(^1D)$ and (^1S) in group 1 is an exception to the general rules.

Contents of the Table and Other Reactions of Interest

a. Reactions among Oxygen Species

Reactions reviewed

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

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

$O(^1D) + O_2,\ O_3,\ CO,\ CO_2,\ N_2,$

$N_2O,\ NO,\ NO_2,\ H_2,\ H_2O,\ CH_4,$

$C_2H_6,\ NH_3,\ H_2O_2$

$O(^1S) + O,\ O_2,\ O_3,\ CO_2,$

$N_2,\ N_2O,\ NH_3,\ NO,\ NO_2,\ H_2O,\ CH_4$

$O_2(^1\Delta) + M \rightarrow O_2 + M$

$O_2(^1\Sigma) + M \rightarrow O_2 + M$

$O_3 + h\nu \rightarrow O + O_2$

$O_3 + O \rightarrow O_2 + O_2$

Reactions not reviewed for which selections are needed

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

$O_2(^1\Delta) + O_3 \rightarrow$

b. Reactions of hydrogen/oxygen species

Reactions reviewed

$H + O_2 + M \rightarrow HO_2 + M$

$H + O_3 \rightarrow HO + O_2$

$HO + HO \rightarrow H + HO_2$

$H_2 + O_2$ *

$H_2O + O$

$HO + M \rightarrow H + O + M$

$HO + O \rightarrow H + O_2$

$HO + O_3 \rightarrow HO_2 + O_2$

$HO + H \rightarrow H_2 + O$

$HO + H + M \rightarrow H_2O + M$

$HO_2 + O_3 \rightarrow HO + 2O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$HO_2 + M \rightarrow H + O_2 + M$

$\rightarrow HO + O + M$

$HO_2 + H \rightarrow H_2 + O_2$

$\rightarrow H_2O + O$ *

$\rightarrow HO + HO$

$HO_2 + HO \rightarrow H_2O + O_2$

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

$H_2O_2 + O(^3P) \rightarrow HO_2 + HO$

$\rightarrow H_2O + O_2$

$H_2O_2 + H \rightarrow H_2 + HO_2$

$\rightarrow H_2O + HO$ *

$H_2O_2 + HO \rightarrow H_2O + HO_2$

Reactions not reviewed for which selections are needed

$H + O + M \rightarrow HO + M$

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

$HO^* + M \rightarrow HO + M$

$HO_2 + h\nu \rightarrow$

$HO_2 + O \rightarrow HO + O_2$

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

* Selection needed.

c. Reactions of nitrogen/hydrogen/oxygen species

Reactions reviewed

$N + O + M \rightarrow NO + M$

$N_2 + O \rightarrow NO + N$

$N + O_2 \rightarrow NO + O$

$N + O_3 \rightarrow NO + O_2$

$N + HO \rightarrow NO + H$

$NO + O \rightarrow O_2 + N$

$NO + O + M \rightarrow NO_2 + M$

$NO + O_2 + M \rightarrow NO_3 + M$ *

$O_2 + NO + NO \rightarrow NO_2 + NO_2$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO + H + M \rightarrow HNO + M$

$NO + H_2 \rightarrow HNO + H$

$NO + HO_2 \rightarrow NO_2 + HO$

$NO + H_2O \rightarrow HNO + HO$

$NO + H_2O_2 \rightarrow HO + HNO_2$

$N + NO \rightarrow N_2 + O$

$NO + NO \rightarrow N_2O + O$

$NO_2 + M \rightarrow N + O + M$

$NO_2 + O + M \rightarrow NO_3 + M$

$NO_2 + N \rightarrow$ Products

$NO_2 + O \rightarrow NO + O_2$

$NO_2 + O_2 \rightarrow NO + O_3$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_2 + NO_2 \rightarrow NO + NO_3$ *

$NO_2 + NO + O_2 \rightarrow NO_2 + NO_3$

$H + NO_2 \rightarrow HO + NO$

$HO + NO_2\ (+M) \rightarrow HNO_3\ (+M)$

$H_2O + NO + NO_2 \rightarrow 2HNO_2$

$NO_3 + h\nu \rightarrow NO + O_2$ *

$NO_3 + M \rightarrow NO_2 + O + M$

$NO_3 + O_2 \rightarrow NO_2 + O_3$

$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$

$NO_3 + NO \rightarrow NO_2 + NO_2$

$NO_3 + NO_2 \rightarrow NO_2 + NO + O_2$

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

$N_2O + O \rightarrow NO + NO$

$\rightarrow N_2 + O_2$

$N_2O_5 + h\nu \rightarrow O + \ldots$ *

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

$N_2O_5 + H_2O \rightarrow 2HNO_3$

$O + NH_3 \rightarrow HO + NH_2$

$HNO + M \rightarrow H + NO + M$

$O_2 + HNO \rightarrow NO + HO_2$

$H + HNO \rightarrow H_2 + NO$

$HO + HNO \rightarrow H_2O + NO$

$HNO + HNO \rightarrow H_2O + N_2O$

$HNO_2 + h\nu \rightarrow HO + NO$ *

*Selections needed.

$O + HNO_2 \rightarrow HO + NO_2$ *

$HNO_2 + H \rightarrow$ products *

$HO + HNO_2 \rightarrow H_2O + NO_2$

$HNO_3 + h\nu \rightarrow HO + NO_2$

$O + HNO_3 \rightarrow HO + NO_3$

$H + HNO_3 \rightarrow$ products

$HO + HNO_3 \rightarrow H_2O + NO_3$

<u>Reactions not reviewed for which selections are needed</u>

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

$NO + HO\ (+M) \rightarrow HNO_2 + M$

$NO + HO_2\ (+M) \rightarrow HNO_3 + M$

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

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

$NO_2 + HO_2 \rightarrow HO + NO_3$

$NO_3 + h\nu \rightarrow NO + O_2$

$N_2O + h\nu \rightarrow N_2 + O(^1D)$

$O + N_2O_5 \rightarrow \ldots$

$N_2O_5 + HO \rightarrow$

$O + NH \rightarrow$

$O_2 + NH \rightarrow$

$O + NH_2$

$O_2 + NH_2 \rightarrow$

$HO + NH_3 \rightarrow H_2O + NH_2$

$HNO + h\nu \rightarrow H + NO$

$HNO_2 + HNO_2 \rightarrow NO + NO_2 + H_2O$

$HNO_3 + NH_3 \rightarrow$

$HNO_2 + HNO_3 \rightarrow$

d. Reactions of sulfur/nitrogen/hydrogen/oxygen species

Reactions reviewed

$O_3 + SO \rightarrow O_2 + SO_2$

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

$HO_2 + SO_2 \rightarrow SO_3 + HO$

Reactions not reviewed for which selections are needed

$SO + h\nu \rightarrow S + O$

$O_2 + SO \rightarrow SO_2 + O$

$SO_2 + h\nu \rightarrow SO + O$

$\rightarrow SO_2^*$

$O + SO_2 \rightarrow$

$O_3 + SO_2 \rightarrow$

$HO + SO_2\ (+M) \rightarrow HOSO_2$

$SO_3 + h\nu \rightarrow SO_2 + O$

$O + SO_3 \rightarrow$

$HO + SO_3\ (+M) \rightarrow H_2SO_4$

$H_2O + SO_3 \rightarrow H_2SO_4$

$O_3 + S_2O \rightarrow$

H_2SO_4 (aerosols) $+ h\nu \rightarrow$

$O(^1D) + H_2SO_4$ (aerosols)

$N_2O_5 + H_2SO_4$

$NH_3 + H_2SO_4\ (+M) \rightarrow NH_4HSO_4$

*Selection needed.

e. Reactions of carbon species

Reactions reviewed

$O_3 + CO \rightarrow CO_2 + O_2$

$CO + HO \rightarrow CO_2 + H$

$CO + HO_2 \rightarrow CO_2 + HO$

$CH_3 + O_2 \rightarrow CH_2O + HO$

$O_2 + CH_3 + M \rightarrow CH_3O_2 + M$

$O + CH_4 \rightarrow$ products

$O_3 + CH_4 \rightarrow$ products

$HO + CH_4 \rightarrow CH_3 + H_2O$

$CHO + O_2 \rightarrow CO + HO_2$

$CH_2O + h\nu \rightarrow CHO + H$

$\rightarrow CO + H_2$

$O + CH_2O \rightarrow CHO + HO$

$CH_2O + HO \rightarrow H_2O + CHO$

$CH_2O + HO_2 \rightarrow H_2O_2 + CHO$

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

$CH_3O + NO \rightarrow CH_2O + HNO$

$\rightarrow CH_3ONO$

$CH_3O + NO_2 \rightarrow CH_2O + HNO_2$

$\rightarrow CH_3ONO_2$

$CH_3O + CO \rightarrow$ products

$CH_3O_2 + CH_3O_2 \rightarrow CH_3OOH + CH_2O_2$

$\rightarrow 2CH_3O + O_2$

$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$\rightarrow CH_3O_2NO$

$\rightarrow CH_2O + HONO$

$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$

$\rightarrow CH_2O + HONO_2$

$\rightarrow CH_3O + NO_3$

$C_2H_4 + O \rightarrow$ products

$C_2H_4 + O_3 \rightarrow$ products

$C_2H_6 + O \rightarrow$ products

$C_3H_6 + O \rightarrow$ products

$C_3H_6 + O_3 \rightarrow C_3H_6O_3$

$CH_3ONO + h\nu$

$\rightarrow CH_3O^* + NO$

$\rightarrow$ Isomer

$\rightarrow CH_2O + HNO$

$\rightarrow CH_2O + H + NO$

Reactions not reviewed for which selections are needed

$CH_3 + NO (+ M) \rightarrow CH_3NO + M$

$CH_3O_2 + h\nu \rightarrow$

$O + CH_3O_2 \rightarrow$

$O_2 + CH_3O_2 \rightarrow$

$CH_3OOH + h\nu \rightarrow CH_3O + HO$

$CH_3ONO \rightarrow CH_3O + NO$

$CH_3ONO_2 + h\nu \rightarrow$

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{6}molecule^{-2}s^{-1}	Notes and Reliablity 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
	$O_2 + O(^3P) + M \rightarrow O_3 + M$			
	*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)	±.07
	Johnston (1968) eval.	200-1000	$4.6 \times 10^{-35} \exp(1050/T)$ M = O_3 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(3.1) O_2(1.1)	
	Meaburn, et al (1968)	300	1.0×10^{-33} M = CO_2 Rel. M efficiencies: CO_2(1.0), CO(4.4), N_2O(8.8)	
	Stuhl, Niki (1971)	300	5.4×10^{-34} 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)**	

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Notes and Reliablity of log k
	Hippler, Troe (1971)	300	8×10^{-34} $cm^6 molecule^{-2} s^{-1}$	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	
	$O(^1D_2) + O_2 \rightarrow O_2(^1\Sigma_g^+) + O(^3P)$	298	7.5×10^{-11} $cm^3 molecule^{-1} s^{-1}$		±0.1 a
	$O(^1D_2) + O_3 \rightarrow O_2(^3\Sigma_u^-) + O_2$ (?) (a)	"	5.0×10^{-10} $k_a/k_b \sim 1$		±0.3 a,c
	$\rightarrow O_2 + 2O(^3P)$ (b)	"			
	$O(^1D_2) + CO \rightarrow CO + O(^3P)$	"	7.5×10^{-11}		±0.1 a
	$O(^1D_2) + CO_2 \rightarrow CO_2 + O(^3P)$	"	1.8×10^{-10}		±0.1 a
	$O(^1D_2) + N_2 \rightarrow N_2 + O(^3P)$	"	5.5×10^{-11}		±0.15 a
	$O(^1D_2) + N_2 + M \rightarrow N_2O + M$	"	2.8×10^{-36} $cm^6 molecule^{-2} s^{-1}$		b
	$O(^1D_2) + N_2O \rightarrow N_2 + O_2$ (a)	"	1.1×10^{-10} $cm^3 molecule^{-1} s^{-1}$		±0.1 a
	$\rightarrow 2NO$ (b)	"	1.1×10^{-10}		±0.1 a
	$O(^1D_2) + NO \rightarrow NO + O(^3P)$	"	2.1×10^{-10}		±0.1 a
	$O(^1D_2) + NO_2 \rightarrow NO + O_2$	"	2.8×10^{-10}		±0.1 a
	$O(^1D_2) + H_2 \rightarrow HO + H$	"	2.9×10^{-10}		±0.1 a
	$O(^1D_2) + H_2O \rightarrow 2HO$	"	3.5×10^{-10}		±0.1 a
	$O(^1D_2) + CH_4 \rightarrow CH_3 + HO$ (a) $\rightarrow CH_2O + H_2$ (b)	"	4.0×10^{-10}. $k_a/k_b = 10$		±0.1 a
	$O(^1D_2) + C_2H_6 \rightarrow C_2H_5 + HO$ (a) $\rightarrow CH_3 + CH_2O$ (b)	"	4.8×10^{-10}		±0.1 a
	$O(^1D_2) + NH_3 \rightarrow NH_2 + HO$	298	(Probably about 3×10^{-10} No measurements available)		a,d

Reaction of $O(^1D_2)$

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k	
	$O(^1D_2) + H_2O_2$ -> $HO + HO_2$	"	$>3 \times 10^{-10}$		d
	a. *Evaluation for this survey (R.J.C.). See details in text "Reactions of $O(^1D_2)$ Atoms," section G.				
	b. Gaedtke, et al (1972)				
	c. Further determinations are desirable. See details of evaluation.				
	d. Estimated, Experimental determination is necessary.				
	$O(^1S) + O(^3P)$ -> ?	300	7.5×10^{-12}	±0.2	a
	$O(^1S) + O_2$ -> ?	200-377	$4.3 \times 10^{-12} \exp(-850/T)$	±0.15	a
	$O(^1S) + O_3$ -> ?	300	5.8×10^{-10}	±0.07	a
	$O(^1S) + CO_2$ -> ?	200-450	$3.1 \times 10^{-11} \exp(-1320/T)$	±0.15	a
	$O(^1S) + N_2$ -> ?	200-380	$< 5 \times 10^{-17}$		a
	$O(^1S) + N_2O$ -> ?	300	1.4×10^{-11}	±0.1	a
	$O(^1S) + NH_3$ -> ?	300	5×10^{-10}	±0.2	a
	$O(^1S) + NO$ -> ?	200-291	$3.2 \times 10^{-11} (T)^{0.5}$	±0.05	a
	$O(^1S) + NO_2$ -> ?	300	5×10^{-10}	±0.2	a
	$O(^1S) + H_2O$ -> ?	300	$> 10^{-10}$	±1	a
	$O(^1S) + CH_4$ -> ?	300	2×10^{-14}	±0.4	a
			a) Rate constants evaluated for this survey by T. G. Slanger and K. H. Welge		
	$O_2(^1\Delta) + M$ -> $O_2 + M$				
	*Hampson (1973) review	285-322	$2.2 \times 10^{-18} (T/300)^{0.8}$, $M = O_2$	±0.1	
		300	$<2 \times 10^{-20}$, $M = N_2$		

Reaction of $O_2(^1\Delta)$

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$O_2(^1\Sigma) + M \rightarrow O_2 + M$			
	*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
	$O_2(^1\Delta) + M \rightarrow O_2 + M$			
	*Breckenridge, Miller (1972) (WHB)	300	$< 2 \times 10^{-15}$ $M = SO_2$	
	*Fisher, McCarty (1966) (WHB)	300	$< 3 \times 10^{-16}$ $M = CO$	
			total rate, quenching and reaction	
	$O_2(^1\Delta) + SO \rightarrow O_2 + SO(^1\Delta)$			
	Breckenridge, Miller (1972) (WHB)	300	$3.5 \pm 0.36 \times 10^{-13}$	
	$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$			
	*Hampson, et al. (1973) review		$\emptyset = 1$, $450 < \lambda < 750$ nm - Chappuis bands	See Comment
			$\emptyset = 0$ $250 < \lambda < 350$ nm	in text.
	$O_3 + h\nu \rightarrow O(^3P) + O_2(^1\Delta$ or $^1\Sigma)$			
	*Hampson, et al. (1973) review		$\emptyset = 1$, $310 < \lambda < 350$ nm - Huggins bands	
			$\emptyset = 0$, $\lambda < 310$ nm	
	$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$			
	*Hampson, et al. (1973) review		$\emptyset = 1$, $250 < \lambda < 310$ nm - Hartley bands	
			$\emptyset = 0$, $\lambda > 310$ nm	

Reaction of O_3

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Sigma_g^+)$			
	*Hampson, et al. (1973) review		$\phi = 0$, $250 < \lambda < 350$ nm	
	$O_3 + O(^3P) \rightarrow O_2 + O_2$			
	Hampson (1973) eval.	188-1000	$1.9 \times 10^{-11} \exp(-2300/T)$	
	*This Survey			
	(D.D.D., H.I.S, and H.J.)	220-1000	$1.9 \times 10^{-11} \exp(-2300/T)$	±0.1 (a)
	McCrumb, Kaufman (1972)	269-409	$1.1 \times 10^{-11} \exp(-2155/T)$	
	Lundell, Ketcheson, Schiff (1969)	300	1.5×10^{-14}	
	Husain, Kirsch, Donovan (1972)	300	1.3×10^{-14}	
	Davis, Wong, Lephardt (1972)	220-353	$2.2 \times 10^{-11} \exp(-2350/T)$	
	(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.			
	$H + O_2 + M \rightarrow HO_2 + M$			
	*This Survey (D.D.D.)	203-404	$6.7 \times 10^{-33} \exp(290/T)$ $cm^6 molecule^{-2} s^{-1}$ 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)	±.07 (a)
		(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 Rel. M efficiencies: Ar(1.0), He(1.0), N_2(1.3), O_2(1.3), H_2O(21)	±.2
	Bishop, Dorfman (1970)	300	2.35×10^{-32} M = Ar	
	Hikida, Eyre, Dorfman (1971)	300	1.64×10^{-32} M = Ar	

Reaction of H

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliablity of log k
	Ahumada, Michael, Osborne	300	0.75×10^{-32} M = He	
			Rel. M efficiencies: He(1.0), Ar(0.8)	
	Kurylo (1972)	203-404	6.7×10^{-33} exp(235/T)	
			Rel. M efficiencies:	
			Ar(1.0), He(1.0), N_2(3.4)	
	Wong, Davis (1972)	220-360	6.8×10^{-33} exp(340/T)	
			Rel. M efficiencies:	
			Ar(1.0), He(1.0), N_2(2.9)	
	Westenberg, DeHaas (1972)	300	1.9×10^{-32} M = Ar or He	
	$H + O_3 \rightarrow HO + O_2$			
	*Hampson, et al (1973) review	300	2.6×10^{-11} cm^3 molecule^{-1}s^{-1}	±0.1
	$HO + HO \rightarrow H + HO_2$			
	Baulch, et al (1972) review	290-800	2.0×10^{-11} exp(-20200/T)	±0.3
	$HO + HO \rightarrow H_2 + O_2$			
	Baulch, et al (1972) review		no recommendation	
	$HO + HO \rightarrow H_2O + O$			
	*Baulch, et al (1972) review	300-2000	1.0×10^{-11} exp(-550/T)	±0.2
	$HO + M \rightarrow H + O + M$			
	Baulch, et al (1972) review		no recommendation (E/R > 50000)	

Reaction of HO

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$HO + O \rightarrow H + O_2$			
	Baulch, et al (1972) review	300	$3.8 \pm 1.7 \times 10^{-11}$	± 0.17
	*Wilson (1972) review	300-1000	$4.2 \pm 1.7 \times 10^{-11}$,	± 0.17
	$HO + O_3 \rightarrow HO_2 + O_2$			
	DeMore (1973)	300	8×10^{-14}	
	Anderson, Kaufman (1973)	220-450	$1.3 \times 10^{-12} \exp(-956/T)$	
	*Hampson et al (1973) review		$1.6 \times 10^{-12} \exp(-1000/T)$	± 0.3
	$HO + H \rightarrow H_2 + O$			
	*Baulch, et al (1972) review	400-2000	$1.4 \times 10^{-14} (T)\exp(-3500/T)$	± 0.15
	$HO + H + M \rightarrow H_2O + M$			
	*Baulch, et al (1972) review	1000-3000	$3.9 \times 10^{-25} T^{-2} cm^6 molecule^{-2} s^{-1}$, $M = N_2$	± 0.3
	$HO_2 + O_3 \rightarrow (HO + 2O_2)$			
	DeMore (1973)	300	$3 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$	
	Anderson (1973)	220-450	$k/k(HO + O_3 \rightarrow HO_2 + O_2) \lesssim 0.1$	
	*This Survey (D.G.)	225-298	$1 \times 10^{-13} \exp(-1250/T)$	± 0.3
	Simonaitis, Heicklen (1973)	225-298	$3.3 \times 10^{-14} \exp(-1000/T)$	± 0.3
	$HO_2 + M \rightarrow H + O_2 + M$			
	Baulch, et al (1972) review	300-2000	$3.5 \times 10^{-9} \exp(-23000/T)$, $M = Ar$	± 0.2

Reaction of HO_2

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$HO_2 + M \rightarrow HO + O + M$			
	Baulch, et al (1972) review		no recommendation	
	$HO_2 + H \rightarrow H_2 + O_2$			
	*Baulch, et al (1972) review	290-800	$4.2 \times 10^{-11} \exp(-350/T)$	±0.4
	$HO_2 + H \rightarrow H_2O + O$			
	Baulch, et al (1972) review		no recommendation	
	$HO_2 + H \rightarrow HO + HO$			
	*Baulch, et al (1972) review	290-800	$4.2 \times 10^{-10} \exp(-950/T)$	±0.3
	$HO + HO_2 \rightarrow H_2O + O_2$			
	Kaufman (1964) review	300	$k > 1 \times 10^{-11}$	estimate
	Lloyd (1971) review	300-1000	$1.7 \times 10^{-11} \exp(-500/T)$	estimate
	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	
	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$			
	*Hampson (1973) review	300-1000	$3 \times 10^{-11} \exp(-500/T)$ cm^3 $molecule^{-1} s^{-1}$	±0.3 at 300 K
	Baulch, et al (1972) review	300	3.3×10^{-12}	

Reaction of HO_2

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$H_2O_2 + hv \rightarrow HO + HO$			
	*Hampson (1973) review		Absorption coefficient (cross section)	

λ/nm	σ/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)

$\varnothing (-H_2O_2) = 1.0$ $\lambda > 200$nm.

See ref. for other, minor, channels pertinent for $\lambda < 200$nm.

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant	Notes and Reliablity of log k
	$H_2O_2 + O(^3P) = HO_2 + OH$ (a) $= H_2O + O_2$ (b)			
	*This Survey (D.D.D.)	283-373	$k(a+b) = 3.6 \times 10^{-11} \exp(-2950/T) cm^3 molecule^{-1} s^{-1}$	±0.07 (a)
	Foner, Hudson (1962)	300	$\lesssim 4 \times 10^{-15}$	
	Baulch, et al (1972) eval.		No recommendation, because of a lack of data.	
	Davis, Wong, Schiff, Lephardt (1972)	283-373	$k(a+b) = 3.6 \times 10^{-11} \exp(-2950/T)$	
		300	$k(a+b) = 1.6 \times 10^{-15}$	

(a) There is presently no basis for assigning relative k values to the two possible channels for this reaction.

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$H_2O_2 + H \rightarrow H_2 + HO_2$			
	*Hampson, et al (1973) quoting	300-800	$2.8 \times 10^{-12} \exp(-1900/T)$	±0.3
	Baulch, et al (1972) review			
	$H_2O_2 + H \rightarrow H_2O + HO$			
	*Hampson, et al (1973) quoting		no recommendation	
	Baulch, et al (1972) review			
	$H_2O_2 + HO \rightarrow H_2O + HO_2$			
	*Hampson (1973) quoting	300-800	$1.7 \times 10^{-11} \exp(-910/T)$	±0.2
	Baulch, et al (1972) review			
	Gorse, Volman (1972)	300	$k/k(HO + CO) = 8.13$	
	$N + O + M \rightarrow NO + M$			
	*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
	$N + O_2 \rightarrow NO + O$			
	*Baulch, et al (1973) review	300-3000	$1.1 \times 10^{-14} T \exp(-3150/T)$, $cm^3 molecule^{-1} s^{-1}$	±0.12, 300<T<1500K increasing to ±0.3 at 3000K
	$N + O_3 \rightarrow NO + O_2$			
	*Baulch, et al (1973) review	300	5.7×10^{-13}	±0.2

Reaction of N

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$N + HO \rightarrow NO + H$			
	*Baulch, et al (1973) review	300	5.3×10^{-11}	±0.3
	$N + N + M \rightarrow N_2 + M$			
	*Baulch, et al (1973) review	100-600	$8.3 \times 10^{-34} \exp(+500/T) cm^6 molecule^{-2} s^{-1}$, $(M = N_2)$ where $-d[N]/dt = 2k[N]^2[M]$	±0.2(200-600) <0.2 (T<200K)
	$N_2 + M \rightarrow N + N + M$			
	*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
	$N_2 + O \rightarrow N + NO$			
	Baulch, et al (1973) review	2000-5000	$1.3 \times 10^{-10} \exp(-38000/T)$	±0.3
	$N_2 + O_2 \rightarrow N_2O + O$			
	*Baulch, et al (1973) review	1200-2000	$1.0 \times 10^{-10} \exp(-52.2 \times 10^3/T)$	±0.4
	$N_2 + HO \rightarrow N_2O + H$			
	*Baulch, et al (1973) review	700-2500	$2.5 \times 10^{-12} \exp(-39.1 \times 10^3/T)$	±0.2
	$NO + M \rightarrow N + O + M$			
	*Baulch, et al (1973) review	4200-6700	Insufficient data for a reliable recommendation. Use, with caution: $6.6 \times 10^{-4} T^{-1.5} \exp(-75.5 \times 10^3/T)\ cm^3\ molecule^{-1} s^{-1}$ $(M = Ar, O_2, N_2)$ $k(M = NO, N, O)/k(Ar) \sim 18$	

Reaction of NO

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$NO + O \rightarrow N + O_2$			
	Baulch, et al (1973) review	1000–3000	2.5×10^{-15} T exp (−19500/T)	±0.12 at 1000 K increasing to ±0. at 3000K
	$NO + O + M \rightarrow NO_2 + M$			
	*Baulch, et al (1973) review	200–500	3.0×10^{-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), $N_2(1.4)$	
	NBS data sheet (1973) review	200–500	accepts above recommendation	
	Slanger, Wood, Black (1973)	296	6.0×10^{-32} M = Ar	
		241	13.0×10^{-32} M = Ar	
	$NO + O_2 + M \rightarrow NO_3 + M$			
	Baulch, et al (1973) review		No recommendation	
	$NO + O_3 \rightarrow NO_2 + O_2$			
	*Hampson, et al (1973) review	198–330	9×10^{-13} exp(−1200/T) cm^3 $molecule^{-1} s^{-1}$	±0.11
	Stedman, Niki (1972)	300	1.73×10^{-14}	±0.2
	Baulch, et al (1973) review	200–350	1.5×10^{-12} exp(−1330/T)	±0.2
	$NO + H + M \rightarrow HNO + M$			
	*Baulch, et al (1973) review	230–700	1.5×10^{-32} exp(300/T) $cm^6 molecule^{-2} s^{-1}$ M = H_2	±0.2

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$NO + H_2 \to HNO + H$			
	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	
	$NO + HO \to NO_2 + H$			
	Baulch, et al (1973) review	298-633	$2.8 \times 10^{-12} \exp(-15.1 \times 10^3/T)$	±0.2(298K)
		based on $k = 5.8 \times 10^{-10} \exp(-740/T)$ for reverse reaction		increasing to
				±0.3(633K)
	$NO + HO_2 \to NO_2 + OH$			
	* This survey (D.D.D.)	300	2×10^{-13}	±0.5
	Davis, Payne, and Stief (1973)	300	3×10^{-13}	±0.5 (a)
	Simonaitis and Heicklen (1973)	300	$> 1.5 \times 10^{-13}$	±0.5 (a)
		(a) $k/k(2HO_2 \to H_2O_2)$ measured		
	$NO + H_2O \to HNO + HO$			
	Baulch, et al (1973) review	2000	3×10^{-18}	±0.2 (a)
			(a) No data. Value based on reverse rate.	
	$NO + H_2O_2 \to HO + HNO_2$			
	*Hampson, et al (1973) review	300	$< 5 \times 10^{-20}$	
		500	$\sim 2 \times 10^{-20}$	
	Gray, et al (1972)	300	$< 5 \times 10^{-20}$	
	$NO + N \to N_2 + O$			
	*Baulch, et al (1973) review	300-5000	2.7×10^{-11}	±0.1 at 300K
				increasing to ±0.3
				$2000 < T < 5000$

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$NO + NO \rightarrow N + NO_2$			
	Baulch, et al (1973) review	Endothermic.	Unimportant compared to $NO + NO \rightarrow N_2O + O$	
	$NO + NO + O_2 \rightarrow NO_2 + NO_2$			
	*Baulch, et al (1970) review	270-660	$3.3 \times 10^{-39} \exp(526/T)$ cm^6 $molecule^{-2} s^{-1}$	
	Stedman, Niki (1972)	300	2.0×10^{-38}	±0.1
			where $d[NO_2]/dt = 2k[NO]^2[O_2]$	
	$NO + NO \rightarrow N_2O + O$			
	Baulch, et al (1973) review	1200-2000	$2.2 \times 10^{-12} \exp(-32.1 \times 10^3/T)$ $cm^3 molecule^{-1} s^{-1}$	±0.3
			$-d[NO]/dt = 2k[NO]^2$	
	$NO_2 + M \rightarrow NO + O + M$			
	Baulch, et al (1973) review	1400-2400	$1.8 \times 10^{-8} \exp(-33{,}000/T)$ $M = Ar$	±0.1
	$NO_2 + O(^3P) \rightarrow NO + O_2$			
	*This survey (D.D.D.)	230-550	9.1×10^{-12}	±0.06
	Baulch, et al (1973)	300-550	$1.7 \times 10^{-11} \exp(-300/T)$	
	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)

Reaction of NO_2

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliablity of log k
	Clyne, Cruse (1972)	298	6.1×10^{-12}	
	Slanger, et al (1973)	300	9.3×10^{-12}	(b)
		240	10.5×10^{-12}	
	NBS data sheet (1973) review	220-500	9.1×10^{-12}	±0.08
	Stuhl, Niki (1970)	300	4.4×10^{-12}	(b)
		(a) $k/k(O + NO + M)$ measured, where $k(ref) = 6.9 \times 10^{-32}$		
		(b) The same technique was used by Slanger and by Stuhl and Niki: Flash photolysis - chemiluminescence.		
	$NO_2 + O + M \rightarrow NO_3 + M$			
	*NBS data sheet (1973) review	298	1.0×10^{-31} cm^6 molecule^{-2}s^{-1} $M = N_2$	±0.2
	Baulch, et al (1973) review	295	6.3×10^{-32} $M = N_2$	±0.4
	$NO_2 + O_2 \rightarrow NO + O_3$			
	*Baulch, et al (1973) review	200-350	$2.8 \times 10^{-12} \exp(-25{,}400/T)$	±0.2 (a)
			(a) No data. Value based on reverse rate	
	$NO_2 + O_3 \rightarrow NO_3 + O_2$			
	*This survey (H.S.J. and D.G.)	220-300	$6.3 \times 10^{-12}\exp(-3500/T)$ cm^{3}molecule^{-1}s^{-1}	±0.2 at 300K ±0.3-1.0 at 220K (a)
	Hampson, et al (1973) review	298	5×10^{-17}	±0.2
	Johnston, Yost (1949)	286-302	$9.8 \times 10^{-12} \exp(-3500/T)$	
	Baulch, et al (1973) review	286-302	$9.8 \times 10^{-12} \exp(-3500/T)$	±0.3
	Niki (1972) private comm.	299	4.4×10^{-17}	(b)

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
			(a) High uncertainty assigned at 220K because of long extrapolation from 300K. The room temperature recommendation of Hampson, et al has been combined with Johnston and Yost's activation energy. (b) Revision, based on later experiments of value reported by Stedman and Niki (1972)	
	$NO_2 + N \rightarrow$ 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: $\rightarrow NO + NO$, $\rightarrow N_2O + O$, $\rightarrow N_2 + O_2$, $\rightarrow N_2 + O + O$	
	$NO_2 + NO_2 \rightarrow NO + NO_3$			
	Baulch, et al (1973) review		No recommendation	
	$NO_2 + NO + O_2 \rightarrow NO_2 + NO_3$			
	*Baulch, et al (1973) review	300-500	$8 \times 10^{-41} \exp(400/T)$ $cm^6 molecule^{-2} s^{-1}$ (a) No reliable data. Value based on reverse rate.	±0.4 (a)
	$NO_2 + H \rightarrow HO + NO$			
	*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	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Notes and Reliablity of log k at 633K
	$NO_2 + HO (+M) \rightarrow HNO_3 (+M)$				
	*Tsang (1972) review		Elevation/km	k(T,M)	
		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	9.6×10^{-13}	another ±5%
		235	35	5.5×10^{-13}	$M = N_2$
		250	40	2.7×10^{-13}	
		260	45	1.4×10^{-13}	
	$NO_2 + NO + H_2O \rightarrow 2HNO_2$				
	Hampson, et al (1973) review	300	$<1.1 \times 10^{-55} cm^9 molecule^{-3} s^{-1}$ where k is defined as: $-d[NO_2]/dt = k[NO][NO_2][H_2O]^2$ main reaction probably is heterogeneous		
	$NO_3 + h\nu \rightarrow NO + O_2$				
	*Johnston (1972) review	300	$10^{-2} s^{-1}$ (Daylight) Very strong absorption spectrum 600-700 nm. 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.		±1.0

Reaction of NO_3

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/$cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$NO_3 + M \rightarrow NO_2 + O + M$			
	*Baulch, et al (1973) review	295	~8 x 10^{-42} $M = N_2$	(a)
			(a) No reliable data. Value based on reverse rate	
	$NO_3 + O_2 \rightarrow NO_2 + O_3$			
	*Baulch, et al (1973) review	300	7 x 10^{-34}	±0.3 (a)
			(a) No data. Value based on reverse rate.	
	$NO_3 + NO \rightarrow 2NO_2$			
	*Baulch, et al (1973) review	300	~2 x 10^{-11}	±0.7
	*Johnston (1966) review	300	8.3 x 10^{-12}	
	Harker, Johnston (1972)	300	8.7 x 10^{-12}	
		Temperature effect is probably zero or very small.		
	$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO$			
	*Baulch, et al (1973) review	300-850	2.3 x 10^{-13} exp(-1000/T)	±0.4
	Johnston (1966) review	300-1100	3.8 x 10^{-13} exp(-2200/T)	
	$NO_3 + NO_2 (+M) \rightarrow N_2O_5 (+M)$			
	*Johnston (1966) review			

	Elevation/km	k (T,M) $cm^3 molecule^{-1} s^{-1}$	Log (M)
220	15	1.9 x 10^{-12}	18.60
217	20	1.1 x 10^{-12}	18.27
222	25	6.6 x 10^{-13}	17.93
227	30	4.5 x 10^{-13}	17.58

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/$cm^3 molecule^{-1} s^{-1}$			Notes and Reliablity of log k
		235	35	2.7×10^{-13}	17.26	
		250	40	1.5×10^{-13}	16.92	
		260	45	7.1×10^{-14}	16.60	
	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$					
	*Johnston (1966) review	600-1100	$4.3 \times 10^{-12} \exp(-3850/T)$			±0.3
	*Baulch, et al (1973) review	293-309	$5 \times 10^{-12} \exp(-3000/T)$			±0.5 (a)
			(a) $-d[NO_3]/dt = 2k[NO_3]^2$			
	$N_2O + O \rightarrow N_2 + O_2$					
	Baulch, et al (1973) review	1200-2000	$1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$			±0.4
	$N_2O + O \rightarrow NO + NO$					
	Baulch, et al (1973) review	1200-2000	$1.7 \times 10^{-10} \exp(-14.1 \times 10^3/T)$			±0.3
	$N_2O + H \rightarrow N_2 + HO$					
	Baulch, et al (1973) review	700-2500	$1.26 \times 10^{-10} \exp(-7600/T)$			±0.2
	$NH_2 + H_2O \rightarrow NH_3 + HO$					
	Baulch, et al (1973) review		no data, no recommendation			
	$N_2O_5 + h\nu \rightarrow O + . . .$					
	*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}		
	Reaction of N_2O_5					

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3molecule^{-1}s^{-1}$		Notes and Reliablity of log k
			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	18×10^{-20}	
			280	8.3×10^{-20}	
			>302	Zero	
	Murphy (1969)		$0.5 \times \emptyset(-N_2O_5) = \emptyset(O) = 0.31$ $\lambda = 280nm$ Meas. by Holmes, Daniels (1934) are consistent		
	NBS Data Sheets (1972)		Survey of photochemistry including data listed above.		
	N_2O_5 (+M) -> NO_2 + NO_3 (+M)		Elevation/km	k/s-1	
	*Johnston (1966) review	220	15	5.0×10^{-7}	±0.5
		217	20	1.8×10^{-7}	
		222	25	3.0×10^{-7}	
		227	30	5.5×10^{-7}	
		235	35	1.9×10^{-6}	
		250	40	1.6×10^{-5}	
		260	45	4.4×10^{-5}	
		Extrapolated from data taken between 273 and 353 K.			

Reaction of N_2O_5

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3molecule^{-1}s^{-1}$	Notes and Reliablity of log k
	$N_2O_5 + H_2O \rightarrow 2HNO_3$			
	Hampson, et al (1973) review	300	$k < 1 \times 10^{-20}$ See also discussion in text "Nitric Acid and Nitrous Acid," section G.	
	$NH_2 + H_2 \rightarrow NH_3 + H$			
	Baulch, et al (1973) review	800	$< 10^{-17}$ $k_f = K_{eq} k_r$	approximate
	$NH_2 + H + M \rightarrow NH_3 + M$			
	Baulch, et al (1973) review	2000-3000	$1.3 \times 10^{-33} \exp(+8300/T)$ cm^6 $molecule^{-2}s^{-1}$ M = Ar (a) $k_f = K_{eq} k_r$	±0.3 (a)
	$NH_2 + HO \rightarrow NH_3 + O$			
	Baulch, et al (1973) review	300-1000	$1 \times 10^{-13} \exp(-2500/T)$ $cm^3molecule^{-1}s^{-1}$ (a) $k_f = K_{eq} k_r$ channel forming $NH + H_2O$ may be favored	0.2 (a)
	$NH_3 + M = NH_2 + H + M$			
	Baulch, et al (1973) review	2000-3000	$k = 1.5 \times 10^{-8} \exp(-42400/T)$ (M = Ar) (a) To be used when $P(M) < 4$ atm.	±0.3 (a)
	$NH_3 + O \rightarrow HO + NH_2$			
	*Baulch, et al (1973) review	300-1000	$2.5 \times 10^{-12} \exp(-3020/T)$	±0.2
	Kurylo, et al (1969) (D.G.)	361-677	$6.6 \times 10^{-12} \exp(-3300/T)$	±0.3
	Albers, et al (1969)	300-1000	$2 \times 10^{-12} \exp(-3000/T)$	
	Reaction of NH_3			

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	Kondratiev (1970) review	350-1000	$1.8 \times 10^{-12} \exp(-2500/T)$	
			Data of Albers, et al provide an upper limit when extrapolated to 220K	
	$NH_3 + H \rightarrow NH_2 + H_2$			
	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	
	Stuhl (1973)	298	1.5×10^{-13}	±0.1
	Kurylo (1973)	298	4.2×10^{-14}	±0.1 (a)
			(a) preliminary value	
	$HNO + M \rightarrow H + NO + M$			
	*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	
	$O_2 + HNO \rightarrow NO + HO_2$			
	Demerjian, et al (1972) review	300	2.1×10^{-20}, $E/R \sim 5000$	estimated
	$H + HNO \rightarrow H_2 + NO$			
	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

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3molecule^{-1}s^{-1}$			Notes and Reliablity of log k
	$HO + HNO \rightarrow H_2O + NO$					
	Hampson, et al (1973) review	1600-2100	7×10^{-11}			± 0.7
	Baulch, et al (1973) review	2000	6×10^{-11}			± 0.2
	$HNO + HNO \rightarrow H_2O + N_2O$					
	*Baulch, et al (1973) review	300	4×10^{-15}			± 0.3
	$HNO_2 + h\nu \rightarrow HO + NO$					
	NBS data sheets (1972)		No quantum yield or absorption coefficient data.			
	$HNO_2 + O \rightarrow HO + NO_2$					
	This survey (D.G.)		No data. Probably faster than $O + HNO_3$, since it is 94 kJ/mol more exothermic.			
	$HNO_2 + H \rightarrow$ products					
	Hampson, et al (1973) review		No data			
	$HNO_2 + HO \rightarrow H_2O + NO_2$					
	Demerjian, et al (1972) review	300	6.8×10^{-12}			estimated, no data
	$HNO_3 + h\nu \rightarrow HO + NO_2$		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,

Reaction of HNO_3

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/$cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
		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}	
			See text on "Nitric Acid and Nitrous Acid," section G, for absorption cross sections.	
	$HNO_3 + O \rightarrow HO + NO_3$			
	Morley, Smith (1972)	300	$<1.3 \times 10^{-14}$	
	*Hampson, et al (1973) review	300	$<1.5 \times 10^{-14}$	
	$HNO_3 + H \rightarrow$ products			
	Hampson, et al (1973) review	300	$< 1 \times 10^{-13}$	
	$HNO_3 + HO \rightarrow H_2O + NO_3$			
	Hampson, et al (1973) review	300-650	6×10^{-13} exp(-400/T)	±0.5
	Johnston (1972) review	300-700	(1.5 to 2.0) $\times 10^{-13}$	±0.2
	*This survey (H.S.J.)	220-270	1.3×10^{-13}	
			See text "Nitric Acid and Nitrous Acid," section G for a summary of data.	
	$SO + O_2 \rightarrow SO_2 + O$			
	*Breckenridge, Miller (1972) (WHB)	300	$<8 \times 10^{-17}$	
	*Schofield (1973) review (WHB)	400-2500	3.0×10^{-13} exp(-2800/T)	

Reaction of SO

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/\mathrm{cm^3 molecule^{-1} s^{-1}}$	Notes and Reliablity of log k
	$SO + SO \rightarrow SO_2 + O$			
	*Schofield (1973) review (WHB)	300	$<3 \times 10^{-15}$	
		1000	$<2 \times 10^{-13}$	
	$O_3 + SO \rightarrow O_2 + SO_2$			
	Schofield (1971) review	220-300	2.5×10^{-12}	
	$O + SO_2 + M \rightarrow SO_3 + M$			
	*Schofield (1971) review	250-1000	$1 \times 10^{-33} \exp(+1000/RT)\ \mathrm{cm^6\ molecule^{-2} s^{-1}}$, $M = O_2$	±0.3
	$HO_2 + SO_2 \rightarrow SO_3 + HO$			
	*Davis, Payne, Stief (1972)	300	$3 \times 10^{-16}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$ (relative rate measurement - reference reaction: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$)	±0.3
	$O_3 + CO \rightarrow CO_2 + O_2$			
	Arin, Warneck (1972)	296	$<4 \times 10^{-25}$	
	$HO + CO \rightarrow CO_2 + H$			
	*This survey (D.G.)	200-400	1.33×10^{-13}	±0.1
	Wilson (1972) review	300-2000	$5.1 \times 10^{-13} \exp(-300/T)$	±0.3
	Stuhl, Niki (1972)	300	1.35×10^{-13}	±0.06
	Westenberg, de Haas (1973)	298	1.33×10^{-13}	±0.04
		396	1.38×10^{-13}	
		523	1.44×10^{-13}	

Reaction of CO

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
		707	1.69×10^{-13}	
		915	2.17×10^{-13}	
	$HO_2 + CO \rightarrow CO_2 + HO$			
	*This survey (D.D.D., H.I.S.)	300	$<10^{-19}$	a
	Lloyd (1971) eval.	300	$\sim 1 \times 10^{-24}$	b
	Westenberg, de Haas (1972)	300	$\sim 1 \times 10^{-12}$	c,d
	Davis, Payne, Stief (1972)	300	$<10^{-20}$	e
	Simonaitis, Heicklen (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 earlier evaluation by Lloyd and the more recent measurements by Davis, Payne, Stief and Simonaitis, Heicklen. Also see note in text.

b. Based on high temperature data of Baldwin, Walker, Webster and an assumed value of the "A" factor.

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: $HO + CO \rightarrow CO_2 + H$

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant	Notes
	$O_2^{\cdot} + CH_3 \rightarrow CH_2O + HO$			
	Basco, et al (1972)	295	3×10^{-16}	estimated (a)

Reaction of CH_3

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
			a. Based on negative result and sensitivity limit. Other measurements at higher T suggest an appreciable activation energy.	
	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$			
	Basco, et al (1972) (D.G.)	295	2.6×10^{-31}, cm^6 $molecule^{-2} sec^{-1}$, $M = N_2$ (low pressure limit)	
	$CH_3 + O_2 (+M) \rightarrow CH_3O_2$			
	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.	
	$O + CH_4 \rightarrow$ products			
	*Herron, Huie (1972) review	350-1000	$3.5 \times 10^{-11} \exp(-4550/T)$	±0.11
	$O_3 + CH_4 \rightarrow$ products			
	Dillemuth, et al (1960)	310-340	$2.7 \times 10^{-13} \exp(-7700/T)$	(a)
		(a) as quoted by Kondratiev (1970)		
	$HO + CH_4 \rightarrow CH_3 + H_2O$			
	*Wilson (1972) review	300-2000	$4.77 \times 10^{-11} \exp(-2500/T)$	±0.3
	$O_2 + CHO \rightarrow CO + HO_2$			
	Demerjian, et al (1972) review	300	1.7×10^{-13}	estimated

Reaction of CHO

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	CH_2O + hv -> CHO + H (a)			
	-> 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. Se McQuigg, Calvert (1969) for graph of absn. coefficient vs. wave length.

	CH_2O + O -> CHO + OH			
	*Demerjian, et al (1972) review	300-1000	8×10^{-12} exp (-3300/T)	
	HO + CH_2O -> H_2O + CHO			
	*Wilson (1972) review	300	1.6×10^{-13}	
	HO_2 + CH_2O -> H_2O_2 + CHO			
	Reaction of CH_2O			

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliablity of log k
	*Lloyd (1971) review	700-1600	7.9 x 10^{-9} exp (-6500/T)	
	$CH_3O + O_2 \rightarrow CH_2O + HO_2$ (1)			
	$CH_3O + NO \rightarrow CH_3ONO$ (2a)			
	$\rightarrow CH_2O + HNO$ (2b)			
	$CH_3O + NO_2 \rightarrow CH_3ONO_2$ (3a)			
	$\rightarrow CH_2O + HONO_2$ (3b)			
	$CH_3O + CO \rightarrow$ products (4)			
	Demerjian et al (1972) review	300	$k_1 = 1.6 \times 10^{-17}$, E/R = 3000	
			adjusted to fit C_4H_{10}/NO_x simulation studies	
			$k_{2a} = 1.7 \times 10^{-13}$	
			$k_{2b}/k_{2a} = 0.165$	
			$k_{3b} = 3.3 \times 10^{-14}$	
			$k_{3b}/k_{3a} = 0.1$	
	*Heicklen (1973)	298	$k_1 \sim 3 \times 10^{-18}$	
			$\sim 1.6 \times 10^{-13}$ exp(-3300/T)	
			$k_2 \sim 8 \times 10^{-14}$	
		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	
		298	$k_{2a}/k_{3a} = 1.1$	
		363	= 1.8	
		403	= 2.7	
		298	$k_{3a}/k_3 = 0.9$ ±0.1	k_{3a}/k_{3b}

Reaction of CH_3O

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
		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
	$HO_2 + CH_3O \rightarrow CH_3O_2H + O_2$			
	Demerjian et al (1972) review	300	6.7×10^{-14}	estimate
	$CH_3O_2 + NO \rightarrow CH_3O_2NO$ (a)			
	$\rightarrow CH_2O + HONO$ (b)			
	$\rightarrow CH_3O + NO_2$ (c)			
	Demerjian, et al (1972) review	300	$k_a = 1.7 \times 10^{-11} \exp(-500/T)$	estimate
	*Heicklen (1973) review	298	$k_a/k = 0.6 \pm 0.1$	
			$k_b/k = 0.4 \pm 0.1$	
			$k_c/k < 0.02$	
			$(k = k_a + k_b + k_c)$	
	$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$ (a)			
	$\rightarrow CH_2O + HONO_2$ (b)			
	$\rightarrow CH_3O + NO_3$ (c)			
	*Heicklen (1973) review	298	$k_a/k = 0.75 \pm 0.05$	
			$k_b/k = 0.25 \pm 0.1$	
			$k_c/k < 0.1$	

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Notes and Reliablity of log k
	$CH_3ONO + h\nu \rightarrow CH_3O^* + NO$ (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	$(k_c + k_d)/k < 0.02$, $\lambda = 366nm$	
			$k = k_a + k_b + k_c + k_d$	
	$O + C_2H_4 \rightarrow$ products			
	*Herron, Huie (1972) evaluation	200-500	$5.5 \times 10^{-12} \exp(-565/T)$	± 0.08
	$O + C_2H_6 \rightarrow$ products			
	*Herron, Huie (1972) evaluation	300-650	$4.1 \times 10^{-11} \exp(-3200/T)$	± 0.11
	$O + C_3H_6 \rightarrow$ products			
	*Herron, Huie (1972) evaluation	200-500	$4.1 \times 10^{-12} \exp(-38/T)$	± 0.08
	$O_3 + C_2H_4 \rightarrow$ products			
	Demerjian, et al. (1972) review	300K	2.7×10^{-10}	
	DeMore (1969)	178-233	$3.2 \times 10^{-15} \exp(-2400/T)$	
	Reaction of C_2H_4			

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliablity of log k
	*This survey (D.G.)	200-300	7.8×10^{-15} exp (-2400/T)	(a)

(a) The room temperature recommendation of Demerjian et al has been combined with DeMore's activation energy.

No	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Notes and Reliablity of log k
	$O_3 + C_3H_6 \rightarrow C_3H_6O_3$			
	Demerjian et al (1972) review	300K	1.0×10^{-17}	
	DeMore (1969)	183, 193, 300	1.65×10^{-13} exp (-1600/T)	(b)
	*This survey (D.G.)	200-300	2×10^{-13} exp (-1600/T)	(a)

(a) The room temperature recommendation of Demerjian et al has been combined with DeMore's activation energy.

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

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Chemical Kinetics Data Survey

Rates of Energy Transfer Processes

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.

R. L. Taylor
May 1973

RATES OF ENERGY TRANSFER PROCESSES

Reaction/Reference	Temp. Range/K	Reaction Rate Constant - $cm^3 molecule^{-1} s^{-1}$
$CO_2(010) + M \rightarrow CO_2(000) + M$	$200 < T < 2000$	$M = CO_2$ $k = 4.64 \times 10^{-10} exp(-76.75/T^{1/3})$
Taylor, Bitterman (69), Simpson, Chandler (70), Buchwald, Bauer (72), Sato, Tsuchiya (72)		$M = N_2, O_2$ $k = 6.69 \times 10^{-10} exp(-84.07/T^{1/3})$
Taylor, Bitterman (69), Buchwald, Bauer (72)	$200 < T < 700$	$M = H_2O$ $k = 3.22 \times 10^{-13} exp(22.91/T^{1/3})$
$N_2(v = 1) + M \rightarrow N_2(v = 0) + M$	$1000 < T < 5000$	$M = N_2, O_2, CO_2$ $k = 8.53 \times 10^{-7} exp(-273.10/T^{1/3})$
Millikan, White (63), Taylor, Bitterman (69), Kovacs, Mack (72)		$M = H_2O$ (see Ref. 22)
$H_2O(010) + M \rightarrow H_2O(000) + M$	$200 < T < 600$	$M = N_2, CO_2, H_2O$ $k = 5.93 \times 10^{-14} exp(32.69/T^{1/3})$
Taylor, Bitterman (69) Corrected		$M = O_2$ (see Ref. 22)
$O_2(v = 1) + M \rightarrow O_2(v = 0) + M$	$200 < T < 5000$	$M = N_2, O_2, CO_2$ $k = 4.81 \times 10^{-8} exp(-169.60/T^{1/3})$
Millikan, White (63), Taylor, Bitterman (69), Kovacs, Mack (72)		
Bitterman, Taylor (69)		$M = H_2O$ $k = 3.60 \times 10^{-10} exp(-60.69/T^{1/3})$
$CO_2(001) + N_2(v = 0) \rightarrow CO_2(000) + N_2(v = 1)$	$200 < T < 2000$	$k = 1.71 \times 10^{-6} exp(-175.30/T^{1/3}) +$ $6.07 \times 10^{-14} exp(15.27/T^{1/3})$
Rosser, et al (69), Taylor, Bitterman (69), Margottin-Maclou, et al (71), Moore, et al (67), Sato, Tsuchiya (72)		
$N_2(v = 1) + H_2O(000) \rightarrow N_2(v = 0) + H_2O(010)$	$200 < T < 2000$	$k = 3.48 \times 10^{-9} exp(-95.94/T^{1/3})$
Taylor, Bitterman (69)		

Reaction/Reference	Temp. Range/K	Reaction Rate Constant - $cm^3 molecule^{-1} s^{-1}$
$H_2O(010) + O_2(v = 0) \rightarrow H_2O(000) + O_2(v = 1)$ Taylor, Bitterman (69)	$200 < T < 400$	$k = 1.00 \times 10^{-12}$
$N_2(v = 1) + O_2(v = 0) \rightarrow N_2(v = 0) + O_2(v = 1)$ Taylor, Bitterman (69)	$200 < T < 5000$	$k = 1.74 \times 10^{-10} \exp(-124.00/T^{1/3})$
$CO_2(100) + M \rightarrow CO_2(020) + M$ Taylor, Bitterman (69)	$200 < T < 400$	$M = N_2, O_2, CO_2, H_2O$ $k = 1.0 \times 10^{-10}$
$CO(v = 1) + M \rightarrow CO(v = 0) + M$ Millikan, White (63), Kovacs, Mack (72)	$200 < T < 5000$	$M = CO, N_2, O_2$ $k = 6.67 \times 10^{-8} \exp(-208.30/T^{1/3})$
vonRosenberg, et al (71)	$1000 < T < 3000$	$M = H_2O$ $k = 3.12 \times 10^{-10} \exp(-64.99/T^{1/3})$
$N_2(v = 1) + CO \rightarrow N_2(v = 0) + CO(v = 1)$ Sato, et al (69), Moore (71), vonRosenberg, et al (72)	$200 < T < 2000$	$k = 1.78 \times 10^{-6} \exp(-209.90/T^{1/3}) +$ $6.98 \times 10^{-13} \exp(-25.60/T^{1/3})$
$CO(v = 1) + O_2(v = 0) \rightarrow CO(v = 0) + O_2(v = 1)$ Sato, et al (69)	$1000 < T < 3000$	$k = 3.50 \times 10^{-10} \exp(-124.00/T^{1/3})$
$CO_2(001) + CO(v = 0) \rightarrow CO_2(000) + CO(v = 1)$ Rosser, et al (71), Seery (72), Stephenson, Moore (72), Borrell, Millward (72), Buchwald, Bauer (72), Sato, Tsuchiya (72)	$200 < T < 2000$	$k = 1.56 \times 10^{-11} \exp(-30.12/T^{1/3})$
$CO(v = 1) + H_2O(000) \rightarrow CO(v = 0) + H_2O(000)$		Data can be interpreted as either V-T or V-V process. See (ref. 23) for $M = H_2O$

Reaction/Reference	Temp. Range/K	Reaction Rate Constant - $cm^3 molecule^{-1} s^{-1}$
$OH(v = 1) + M \rightarrow OH(v = 0) + M$ Worley, et al (71,72)	$T = 200$	$M = O_2 \quad k(1) = 1 \times 10^{-15}$ $= N_2 \quad = 3.6 \times 10^{-16}$ $= NO \quad = 1.5 \times 10^{-14}$ $= N_2O \quad = 4.8 \times 10^{-15}$ $= CO_2 \quad = 2.4 \times 10^{-15}$ $= H_2O \quad = 2.0 \times 10^{-14}$
$N_2(v = 1) + O \rightarrow N_2(v = 0) + O$ Breshears, Bird (65), McNeal, et al (72)	$200 < T < 3000$	$k = 1.57 \times 10^{-5} \exp(-259.00/T^{1/3})$
$O_2(v = 1) + O \rightarrow O_2(v = 0) + O$ Kiefer, Lutz (67)	$200 < T < 2000$	$k = 5.95 \times 10^{-6} \exp(-166.20/T^{1/3})$
$CO(v = 1) + O \rightarrow CO(v = 0) + O$ Center (72)	$200 < T < 3000$	$k = 1.01 \times 10^{-8} \exp(-95.91/T^{1/3})$
$CO_2(010) + O \rightarrow CO_2(000) + O$ Center (72)	$200 < T < 3000$	$k = 2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$
$CO_2(001) + M \rightarrow CO_2(030) + M$ Rosser, Gerry (69), Moore et al (67), Stephenson, Moore (72)	$200 < T < 2000$	$M = N_2, O_2 \quad k = 4.12 \times 10^{23} T^{-5.89} \exp(-4223/T - 672.67/T^{1/3} + 2682.9/T^{2/3})$
Buchwald, Bauer (72), Sato, Tsuchiya (72), Seery (72), Rosser, Gerry (71)		$M = CO_2 \quad k = 9.16 \times 10^{23} T^{-5.89} \exp(-4223/T - 672.67/T^{1/3} + 2682.9/T^{2/3})$
Heller, Moore (70)	$200 < T < 1000$	$M = H_2O \quad k = 4.71 \times 10^{-40} T^{4.54} \exp(2082/T + 454.06/T^{1/3} - 1729.2/T^{2/3})$

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High Temperature Air Kinetics

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)

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REACTION-RATE TABLES

I. Binary Positive-Ion Reactions

II. Binary Negative-Ion Reactions

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	
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 $\bar{\sigma}(E)\ E^{-\frac{1}{2}}$, 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	

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
	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
$O^+(^2D) + N_2 \rightarrow N_2^+ + O$	~ 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
	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
$Ca^+ + O_3 \rightarrow CaO^+ + O_2$	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	
$N_2^+ + H_2 \rightarrow N_2H^+ + H$	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
	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 1972c	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 1973c	
$O_2^+ + Na \rightarrow Na^+ + O_2$	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	$k(cm^3sec^{-1})$	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
$CO_2^+ + H \rightarrow HCO^+ + O$ $\rightarrow H^+ + CO_2$	6 (-10)	± 50%	FA	Fehsenfeld 1971a	$k_a/k_b \sim 5$
$CO_2^+ + O \rightarrow O_2^+ + CO$ $\rightarrow O^+ + CO_2$	2.6(-10)	X 2	FA	Fehsenfeld 1970	$k_a/k_b \sim 1.7$
$CO_2^+ + N \rightarrow$ 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^3sec^{-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

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TABLE II. Binary Negative-Ion Reactions

Reaction	k(cm^{3}sec^{-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	
$O_4^- + O \rightarrow O_3^- + O_2$	4.0(-10)	± 50%	FA	Fehsenfeld, 1969c	$k_a > k_b$
$\rightarrow O^- + 2O_2$					
$O_4^- + CO \rightarrow CO_3^- + O_2$	< 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	
$CO_4^- + O \rightarrow CO_3^- + O_2$	1.5(-10)	± 50%	FA	Fehsenfeld, 1969c	$k_a > k_b$
$\rightarrow O_3^- + CO_2$					
$CO_4^- + NO \rightarrow NO_3^{-*} + CO_2$	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.

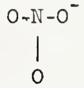
c) F. Kaufman, J. Chem. Phys. 46, 2449, 1967 points out that a detailed balancing argument can be used to calculate $k < 10^{-13}$ cm^3 sec^{-1} from dissociative electron attachment data for N_2O.

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  $O{-}\underset{\underset{O}{|}}{N}{-}O^-$ and the higher energy peroxide ion $O{-}N{-}O{-}O^-$ (which is denoted NO_3^{-*}).

i) Reaction is endothermic

j) Probably endothermic.

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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.

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