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NBSIR 73-206

# Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions

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Physical Chemistry Division
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Interim Report

Prepared for
**Climatic Impact Assessment Program, Department of Transportation,**
**Office of Standard Reference Data, N.B.S.,**
**and**
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# V. SIXTY-SIX CONTRIBUTED RATE AND PHOTOCHEMICAL DATA EVALUATIONS ON NINETY-FOUR REACTIONS

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

ERRATA-NBSIR 73-206, second printing

page 13 Reaction Mechanism, 5th line: delete $\underline{\text{and } NO_2}$

page 17 Table III:
Heading for columns D, E, F, G, H and I should read:
Absolute rate constants, $k/10^{-10}\ cm^3\ molecule^{-1}s^{-1}$

page 38 Table I:
1) The values given for $\epsilon(T \leq 300\ K)$ for $\lambda = 230$, 240, 250, 260, and 270 nm are in units of $10^5\ cm^2/mol$

2) The value of $\epsilon(T = 1100\ K)$ at $\lambda = 260$ nm should be $1.9 \times 10^5\ cm^2/mol$

July 24, 1973

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IV. Evaluations

E. $H + H_2O_2$

Reactions of the $H_2$-$N_2$-$O_2$ system for which data sheets have been contributed by D. L. Baulch, D. D. Drysdale and D. G. Horne

$N + N + M \rightarrow N_2 + M$

$N_2 + M \rightarrow N + N + M$

$N + NO \rightarrow N_2 + O$

$N_2 + O \rightarrow N + NO$

$N + NO_2 \rightarrow NO + NO$

$NO + NO \rightarrow N + NO_2$

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

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

$N + O_2 \rightarrow NO + O$

$NO + O \rightarrow N + O_2$

$N + O_3 \rightarrow NO + O_2$

$N_2 + O_2 \rightarrow N_2O + O$

$N_2O + O \rightarrow N_2 + O_2$

$NO + NO \rightarrow N_2O + O$

$N_2O + O \rightarrow NO + NO$

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

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

$NO + NO_3 \rightarrow NO_2 + NO_2$

$NO_2 + NO_2 \rightarrow NO + NO_3$

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

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

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

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O_2 \rightarrow NO + O_3$

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

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

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

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

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + O_2 \rightarrow NO_2 + O_3$

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

$N + OH \rightarrow NO + H$

$N_2 + HO \rightarrow N_2O + H$

$N_2O + H \rightarrow N_2 + HO$

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

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

$H_2 + NO \rightarrow HNO + H$

$H + HNO \rightarrow H_2 + NO$

$NO + HO \rightarrow NO_2 + H$

$NO_2 + H \rightarrow NO + HO$

$H_2O + NO \rightarrow HNO + OH$

$HO + HNO \rightarrow H_2O + NO$

$HNO + HNO \rightarrow H_2O + N_2O$

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

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

$NH_3 + H \rightarrow NH_2 + H_2$

$NH_2 + H_2 \rightarrow NH_3 + H$

$NH_3 + O \rightarrow NH_2 + HO$

$NH_2 + HO \rightarrow NH_3 + O$

$NH_3 + HO \rightarrow NH_2 + H_2O$

$NH_2 + H_2O \rightarrow NH_3 + HO$

# Chemical Kinetics Data Survey

# V. Sixty-Six Contributed Rate and Photochemical Data Evaluations on Ninety-Four Reactions

## Abstract

This report records the data evaluations contributed to the Climatic Impact Assessment Program chemical kinetics survey during the period Nov 1972 - April 1973 by various kineticists and photochemists. Data are included on reactions of $O(^1D)$, $O(^1S)$, $O_2(^1\Delta)$, $CH_3ONO$, $CH_3O$, $CH_3O_2$, $H_2O_2$, $HO_2$, $SO$, $SO_2$ and the $H_2$-$N_2$-$O_2$ system.

Keywords: atmospheric chemistry, chemical kinetics, data evaluation, gas phase reactions, optical absorption cross sections, photochemistry, quantum yields, rate constants.

# I. Introduction

This report is a collection of rate constant evaluations contributed to the Climatic Impact Assessment Program survey of rate and photochemical data. These evaluations, data sheets and comments are background material explaining some of the evaluations in the CIAP rate and photochemical data tables that are being issued in a separate report (NBS Report 73-203).

The evaluations have been contributed by kineticists and data analysts familiar with the available experimental data. The preferred values given reflect the current state of the art and provide guidance for modellers on rate constants and photochemical mechanisms.

All of the recommendations given here have been incorporated in the CIAP tables.

We are indebted to the following persons for the contributions to this survey that appear in this report:

R. J. Cvetanovic, Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

T. Slanger, Stanford Research Institute, Menlo Park, California.

K. H. Welge, Centre for Research in Experimental Space Science and Chemistry Department, York University, Toronto, Canada.

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*D. L. Baulch*, *D. D. Drysdale*, *D. G. Horne*, Department of Physical Chemistry, University of Leeds, Leeds, England.

## II. Related Reports

1. Hampson, R. F. (editor) Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry. To appear in J. Phys. Chem. Ref. Data 2 No. 2 (Summer 1973). These are slightly revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

2. Garvin, D. (editor) Chemical Kinetics Data Survey IV. Preliminary Tables of Chemical Data for Modelling of the Stratosphere, NBS Report 73-203 (May 1973). This is a collection of tables from the preliminary draft of a chapter on Stratospheric Chemistry for "The Natural Stratosphere" E. Reiter, editor, Climatic Impact Assessment Program Monograph 1. (1973).

3. Johnston, H. and Garvin, D., Working Papers for a Survey of Rate Data for Chemical Reactions in the Stratosphere NBS Report 10931 (October 1972). This describes the survey of rate data being undertaken for CIAP.

4. Hampson, R. F. (editor) Chemical Kinetics Data Survey VI. Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Stratospheric Chemistry, NBS Report 73-207 (May 1973). These are newly prepared data sheets. They supplement reference 1, above, and the present report.

## 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 NBS Report 73-203 (immediately before Table I). These will be incorporated in the tables. Detailed evaluations will be issued in companion reports (such as this report).

We will also welcome comments and corrections of any of the recommendations.

## G. Special Cases

### G.1. REACTIONS OF O($^1D_2$) ATOMS (R.J. Cvetanovic)

Relative Rate Constants at 300 K

O($^1D_2$) atoms have long radiative life time and are in general extremely reactive chemically and susceptible to rapid collisional deexcitation. They are therefore difficult to observe directly in laboratory experiments. As a consequence, with relatively few exceptions, all the available kinetic information in the literature is in the form of relative rate constants obtained in competitive experiments. As a rule measurements of several rates relative to a single reference reaction are reported but a substantial variety of reference reactions has been used in different investigations. While, fortunately, it is the relative rates which are usually of primary interest for stratospheric modeling, absolute values are necessary in some cases. A satisfactory conventional evaluation of the rate data for a single elementary reaction at a time is clearly not possible. The present evaluation has therefore been carried out with the main object of deriving first from the experimental relative values in the literature a consistent and reliable set of average relative rate constants. The set is then placed on an absolute scale by adopting for one of the reactions an absolute rate constant consistent with the available experimental absolute values.

The experimental values of the relative rate constants considered are listed in Table I. Some reactions not of stratospheric interest are also included so that the relative values can be reduced more readily to a common basis for direct comparison and test of mutual consistency. To test the mutual consistency of the data and obtain representative average values three different procedures can be used: 1) separate assessment of groups of sets with a common experimental reference reaction (e.g. all the sets of rates measured relative to $O_2$ or $N_2O$, etc.), 2) reduction of all the sets (in as much as possible) to a common basis by adopting an arbitrary single reference reaction, and 3) computer evaluation of the mean relative rates by a least squares method. The latter two procedures have been adopted for the present evaluation.The second procedure has the advantage of being capable of revealing quickly any data which show gross inconsistencies and should be rejected. Thus, for example, in relative rate measurements a constant systematic error may sometimes affect appreciably the value for the reference reaction itself but cancels out when the other relative rates in the set are compared between themselves. Some examples of this will be pointed out. An important justification for the adopted procedures is provided by the, on the whole, remarkable mutual consistency of the data from very diverse sources when treated in this manner.

Table II gives the recalculated relative rate constants reduced to a common basis by taking the reaction with $CO_2$ as the standard reference reaction. In a few cases the sets did not contain the $CO_2$ reaction itself or it was felt that the $CO_2$ value was less reliable. The underlined mean values of other ratios of rate constants (e.g. $^{k}\text{neopentane}/^{k}CO_2$, $^{k}\text{Xe}/^{k}CO_2$, etc.) have then been used to carry out an indirect reduction to the common $CO_2$ base. These underlined values were not used in the computations of the averages. It is evident that some sets listed in Table I have been omitted from Table II. This has been done either because a meaningful recalculation relative to $CO_2$ could not be made or because the reduced data were obviously in gross disagreement with the other values. However, the omissions are relatively minor and Table II contains essentially all of the comprehensive sets of relative rate data in the literature. The values in parentheses in Table II have not been used in the computation of the averages because there appears to be some indication that they may involve considerably more than the random errors. (The value in parentheses for $C_3H_8$ in the Yamazaki, Cvetanovic 64b set is no doubt an example of the type discussed above of a substantial, perhaps interpretative, systematic error in a reference reaction in a series of relative determinations).

The mean values of the relative rates in Table II and their standard deviations are shown in the last two rows. The standard deviations are relatively moderate in most cases and the mean values represent a reasonably consistent set of relative rate constants. Two blank columns have been left in Tables I and II, for $NH_3$ and $H_2O_2$, to show that rate constants are not available for these two compounds and should be determined. In the meantime it may be assumed that the value for $NH_3$ is probably between that for $H_2$ and $CH_4$, and the value for $H_2O_2$ is likely to be as large as that for $H_2O$ and could be appreciably larger.

The mean values of the relative rate constants have been also computed using a N.B.S. program (code name "Omnitab") for the linear least squares analysis. The computations have been carried out by Dr. Robert F. Hampson at the National Bureau of Standards. Omnitab computations for the sets of data used in Table II, but omitting the values in parentheses for $O_2$ and $C_3H_8$ and all the values for Kr, Ar and $SF_6$, give the mean relative rate constants in Column B of Table III. With some minor exceptions they are very similar to the mean values in Column A, taken from Table II. The mean values in Column C of Table III have been obtained for the same data as in B plus the nine absolute values in the literature (listed in Columns D, E and F of Table III). The mean relative values obtained are again very similar, with the notable exception of the mean value for ozone, which is reduced by about 30 percent. This difference indicates a significant disparity between the relative and the absolute rate measurements for ozone and shows the need for additional determinations.

## Absolute Rate Constants at 300K

The available absolute rate constants of $O(^1D_2)$ reactions are listed in Columns D-F of Table III. The earlier values for $O_2$ of Noxon (1970) and for $O_3$ of Gilpin, Schiff and Welge (1971) are consistent with the recent measurements of Heidner and Husain (1973). The previous value for $O_3$ of Heidner, Husain and Wiesenfeld (1972) is somewhat larger.

To make best use of the available absolute rate constants to set all the relative rate constants on an absolute scale, the following three Omnitab computations have been compared between themselves and with the absolute values in the literature. 1) The set of the relative Omnitab values from Column B of Table III has been converted to absolute scale by adopting the value $k_{CO_2} = 2.1 \times 10^{-10}$ of Heidner and Husain (1973) - the absolute values obtained are given in Column G of Table III. 2) Omnitab computations of the absolute rate constants for the data of Column B plus the nine absolute values (in Columns D-F) are given in Column H of Table III. 3) Omnitab computations as in the preceding case but without the $k_{O_3}$ value of Heidner, Husain and Wiesenfeld (1972) gave almost uniformly

1 to 3 percent larger absolute values than in Column H of Table III - the results of these computations are therefore not shown separately in Table III. From a comparison of these three computed sets of absolute values with the measured absolute values a "recommended" set of absolute values was derived and is listed, together with an estimate of the likely uncertainties, in Column I of Table III. The estimated uncertainties are relatively moderate in all cases except for ozone, for which it may be as large as a factor of two. Further determinations for ozone are evidently highly desirable.

## Temperature Dependence

The temperature dependence of the rate constants of the $O(^1D_2)$ reactions is not known although it is likely to be generally very small or negligible. This is supported by the observed rapid occurrence of some of these reactions at cryogenic temperatures. At the same time, Simonaitis and Heicklen (1972) have recently reported a slight increase in $k_{CO}$ with temperature, as indicated in Table I. Evidently further work is required. In the meantime it is probably best to assume that the set of absolute values listed in Table III holds also at the typical stratospheric temperatures.

## Hot Atom Effect

Heicklen and his coworkers (Goldman, Greenberg, Heicklen (1971), Greenberg and Heicklen (1972), Simonaitis, Greenberg, Heicklen (1972)) have recently postulated involvement and a measurable kinetic contribution of "hot" $O(^1D_2)$ atoms in some $O(^1D_2)$ reactions. Unpublished subsequent work to verify this postulate (Paraskevopoulos et al. 1972, unpubl.) has shown at best very minor effects, bordering on the experimental error. Further work is needed. In the meantime it would not seem justifiable to recommend any corrections in stratospheric modelling for potential "hot" $O(^1D_2)$ atom effects.

Reaction Mechanism

All the available evidence shows that at atmospheric (and stratospheric) pressures there is no stable adduct formation (i.e. only deexcitation of $O(^1D_2)$ occurs) in the $O(^1D_2)$ reactions with such simple gases as $N_2$, $O_2$, CO, $CO_2$ and the same is probably also true for NO and $NO_2$. In agreement with this Gaedtke et al. (H. Gaedtke, et al. (1972)) have found an extremely small third order rate constant for the formation of $N_2O$ from $N_2$ and $O(^1D_2)$ in the presence of excess $N_2$ as the third body ($k=3 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$). In the reaction of $O(^1D_2)$ with $O_2$ the products appear to be $O(^3P)$, $O_2(^1\Sigma_g{}^+)$ and $O_2{}^\ddagger$ (vibrationally excited ground electronic state of $O_2$). McCullough and McGrath (1973) believe that the production of $O_2{}^\ddagger$ is quite extensive but Snelling (unpubl.) finds that $O_2(^1\Sigma_g{}^+)$ is produced in at least 75% of the $O(^1D_2)$ + $O_2$ reactive collisions and Gauthier and Snelling (unpubl.) find that approximately 25 to 50% of it is formed in the first vibrational level. The products of the reaction of $O(^1D_2)$ with $O_3$ appear to be $O_2{}^\ddagger$, $O_2$ and $O(^3P)$. Davenport, Schiff and Welge (1972) have shown that the ratio of ($O_2 + O_2$) to ($O_2 + O + O$) reaction channels is approximately unity. In the case of $NO_2$, abstraction of an oxygen atom no doubt occurs but the electronic (or vibrational) state of the $O_2$ formed is uncertain. $O(^1D_2)$ attack on $N_2O$ proceeds along two reaction paths: a) to form $N_2 + O_2$ and b) to form 2NO; the ratio $k_a/k_b$ is very close to one (P.M. Scott, et al. 1971).

In the reactions of $O(^1D_2)$ with $H_2$, $H_2O$ and paraffins little or no (<ca 3%) deactivation to $O(^3P)$ occurs. $H_2$ gives HO + H, $H_2O$ gives 2HO and in the case of paraffins there are two predominant reaction channels: insertion into the CH bonds to form "hot" alcohols and abstraction of H to form HO and alkyl radicals. The "hot" alcohols are collisionaly stabilized at sufficiently high pressures, especially so in the case of larger paraffin molecules. With $CH_4$ and $C_2H_6$, on the other hand, no collisional stabilization can be expected at the low atmospheric and stratospheric pressure and the products are HO and $CH_3$ from $CH_4$ and HO, $C_2H_5$, $CH_3$ and $CH_2OH$ from ethane. With some paraffins there is also a small amount of molecular elimination i.e. direct formation of two stable molecules from the initial adduct. In the case of $CH_4$ the products of the molecular elimination are $H_2$ and $CH_2O$ and its yield is 9% of the total reaction (Lin and DeMore (1972)).

TABLE I. Experimental values of the relative rate constants of $O(^1D_2)$ atoms at 298 K

| Experimental set of data | $O_2$ | $O_3$ | CO | $CO_2$ | $N_2$ | $N_2O$ | NO | $NO_2$ | $NH_3$ | $H_2$ | $H_2O$ | $H_2O_2$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ | Neo-$C_5H_{12}$ | Xe | Kr | Ar | $SF_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Yamazaki, Cvetanovic (64a) | | | | 1 | | 1.6(a) | | | | | | | | | | | .82 | | | 0 |
| Yamazaki, Cvetanovic (64b) | | | | | .15 | | | | | | | | | | 1 | | .47 | .054 | | 0 |
| Preston, Cvetanovic (66) | | | | 1 | .24 | 1.10 | | 1.62 | | | | | | | 4.67 | | .78 | .060 | .011 | 0 |
| Katakis (67) | | 1 | | | | | | | | | .25 | | | | | | | | | |
| Snelling, Bair (67) | | 1 | | | .065 | | | | | | | | | | | | .175 | | .0003 | |
| Young et al. (68) | .23 | | | 1.32 | .28 | 1 | .85 | | | | | | | | | | | | | |
| Young et al. (68) | .23 | | | .77 | .21 | | .79 | | | 1 | | | 1.20 | | | | | | | |
| Paraskevopoulos, Cvetanovic (69) | | | .074 | .126 | .039 | | | | | .254 | | | .315 | | | 1 | .128 | | | 0 |
| Biedenkapp, Bair (70)<br>Biedenkapp et al. (70) | | 1 | | | .5 | | | | | | .45 | | | | | | 1.25 | | | |
| DeMore (70) | .20 | | .36 | .88 | .20 | 1 | | | | | | | | | | | | | | |
| Donovan et al. (70) | | | | .63 | .23 | 1 | | | | 2.0 | | | 2.3 | | | | | | | |
| Yamazaki (70) | | | .75 | .94 | .27 | 1 | | | | | | | | | | | .94 | .08 | .01 | |
| Noxon (70) | 1 | | | (.04)(b) | 1.43 | | | | | | | | | | | | | | | |
| Ellenrieder et al. (71)<br>Castellano, Schumacher (71) | .23 | 1 | | | .20 | | | | | | | | | | | | .18 | .04 | | |
| Loewenstein (71) | 1 | | | 1.8 | .64 | | | | | | | | | | | | | | | |
| Gilpin et al. (71) | 1 | ~5 | | | | | | | | | | | | | | | | | | |
| Goldman et al. (71) | | 2.6(c)<br>4.1 | | | | 1 | | | | | | | | | | | | | | |
| Langley, McGrath (71a,b) | .79 | 1 | | | | | | | | | .5 | | | | | | | | | |
| Paraskevopoulos, Cvetanovic (71) | | | | | | | | | | | .38 | | | | | 1 | | | | |
| Paraskevopoulos et al. (71a) | .30 | | | .81 | | 1 | | 1.21 | | | | | | | | | .54 | | | |
| Paraskevopoulos et al. (71b) | .035 | | | | | | | | | | | | | | | 1 | | | | |
| Scott, Cvetanovic (71) | .36 | | | .54 | | 1 | | | | | 1.50 | | | | | 4.29 | .59 | | | 0.00 |
| Slanger, Black (71) | | | | 1 | .26 | | | | | 1.28 | | | | | | | | | | |
| Clark, Noxon (72) | 1 | | .36 | 1.82 | .78 | | | | | | | | | | | | | | | |
| Fortin et al. (72) | | | | | 1 | | | | | | 3.5 | | | | | | | | | |
| Greenberg, Heicklen (72) | | | | | | 1 | | | | | | | 2.28(c)<br>1.35 | | | | | | | |
| Lissi, Heicklen (72) | | 1 | | .45 | .1 | | | | | | 1.5 | | | | | | | | | |
| Paraskevopoulos et al. (72) | | | | | | .145 | | | | | | | | | | 1 | | | | |
| Simoniatis, Heicklen (72) | | | .33(d) | | | .48 | | | | | 1 | | | | | | | | | |
| Michaud et al. | | | | | | | | | | | | | | .388 | .605 | 1 | | | | |
| Gauthier, Snelling | 1 | 8.0 | .95 | 2.7 | .72 | 3.3 | | | | 4.0 | 5.0 | | 5.1 | | 10.8 | 14.0 | | | | |
| Snelling | 1 | | | | .70 | | | | | | | | | | | | | | | |

a) See Paraskevopoulos et al. (1972) for reinterpretation. b) See Clark and Noxon (1972) for retraction. c) Different values at different wave lengths of $N_2O$ photolysis: involvement of "hot" $O(^1D_2)$ postulated. d) A value of 0.60 obtained at 423 K.

TABLE II. Rate constants of $O(^1D_2)$ reactions at 298 K expressed relative to $CO_2$ taken as unity (for basic data, see Table I)

| Set of Data | $O_2$ | $O_3$ | CO | $CO_2$ | $N_2$ | $N_2O$ | NO | $NO_2$ | $NH_3$ | $H_2$ | $H_2O$ | $H_2O_2$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ | Neo-$C_5H_{12}$ | Xe | Kr | Ar | $SF_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Yamazaki, Cvetanovic (64a) | | | | 1 | | 1.6 | | | | | | | | | | | .82 | | | 0 |
| Yamazaki, Cvetanovic (64b) | | | | | .28 | | | | | | | | | | (1.89) | | $\underline{.89}$ | .102 | | 0 |
| Preston, Cvetanovic (66) | | | | 1 | .24 | 1.10 | | 1.62 | | | | | | | 4.67 | | .78 | .060 | .011 | 0 |
| Snelling, Bair (67) | | 4.61 | | | $\underline{.30}$ | | | | | | | | | | | | .81 | | .0012 | |
| Young et al. (68) | .29 | | | (1.72) | .37 | $\underline{1.31}$ | 1.11 | | | | | | | | | | | | | |
| Young et al. (68) | .30 | | | 1 | .27 | | 1.03 | | | 1.30 | | | 1.56 | | | | | | | |
| Paraskevopoulos, Cvetanovic (69) | | | .59 | 1 | .31 | | | | | 2.0 | | | 2.5 | | | 7.9 | 1.00 | | | 0 |
| DeMore (70) | .23 | | .41 | 1 | .23 | 1.14 | | | | | | | | | | | | | | |
| Donovan et al. (70) | | | | 1 | .37 | 1.6 | | | | 3.2 | | | 3.7 | | | | | | | |
| Yamazaki (70) | | | .79 | 1 | .29 | 1.06 | | | | | | | | | | | 1.00 | .09 | .01 | |
| Loewenstein (71) | .56 | | | 1 | .36 | | | | | | | | | | | | | | | |
| Paraskevopoulos, Cvetanovic (71) | | | | | | | | | | | 2.64 | | | | | $\underline{7.0}$ | | | | |
| Paraskevopoulos et al. (71a) | .37 | | | 1 | | 1.24 | | 1.50 | | | | | | | | | .67 | | | |
| Paraskevopoulos et al. (71b) | .25 | | | | | | | | | | | | | | | $\underline{7.0}$ | | | | |
| Scott, Cvetanovic (71) | (.66) | | | 1 | | 1.84 | | | | | 2.75 | | | | | 7.9 | 1.09 | | | 0 |
| Slanger, Black (71) | | | | 1 | .26 | | | | | 1.28 | | | | | | | | | | |
| Clark, Noxon (72) | .39 | | .14 | (.71) | $\underline{.30}$ | | | | | | | | | | | | | | | |
| Fortin et al. (72) | | | | | $\underline{.30}$ | | | | | | 1.07 | | | | | | | | | |
| Paraskevopoulos et al. (72) | | | | | | 1.02 | | | | | | | | | | $\underline{7.0}$ | | | | |
| Simonaitis, Heicklen (72) | | | | | | $\underline{\underline{1.31}}$ | | | | | 2.75 | | | | | | | | | |
| Michaud et al. | | | | | | | | | | | | | | 2.72 | 4.24 | $\underline{7.0}$ | | | | |
| Gauthier, Snelling | .37 | 2.96 | .35 | 1 | .27 | 1.22 | | | | 1.5 | 1.85 | | 1.9 | | 4.0 | 5.2 | | | | |
| Snelling | .42 | | | | $\underline{.30}$ | | | | | | | | | | | | | | | |
| Mean values[a)] | .35 | 3.79 | .46 | 1 | .30 | 1.31 | 1.07 | 1.56 | | 1.86 | 2.21 | | 2.42 | 2.72 | 4.30 | 7.00 | .89 | .08 | .008 | 0 |
| Standard deviation | .10 | 1.03 | .23 | - | .05 | .31 | .05 | .08 | | .75 | .75 | | .86 | - | .31 | 1.50 | .17 | .02 | .005 | - |

a) The values in parentheses and the underlined values are not used in the calculations of mean values.

TABLE III. Summary of the mean relative rates and the absolute rate constants of reactions of O($^1D_2$) atoms at 298 K

| | Mean relative rates[a] | | | Absolute rate constants ($10^{10}$cc.molec$^{-1}$sec$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Table II[b] | Omnitab[c] | | Noxon (1970) | Gilpin et al (1971) | Heidner, Husain (1973) | Omnitab[c] | | Recommended Values |
| | A | B | C | D | E | F | G | H | I |
| $O_2$ | .35 | .42 | .41 | .6±.3 | | .70±.05 | .88 | .61 | .75±.15 |
| $O_3$ | 3.79 | 4.21 | 2.82 | | 2.5±1 | 3.5±.3[d]<br>2.7±.2 | 8.8 | 4.2 | 5.0±2.5 |
| CO | .46 | .42 | .42 | | | .73±.07 | .87 | .62 | .75±.15 |
| $CO_2$ | 1 | 1 | 1 | | | 2.1±.2 | 2.10 | 1.48 | 1.8±.3 |
| $N_2$ | .30 | .30 | .30 | | | .69±.06 | .64 | .44 | .55±.15 |
| $N_2O$ | 1.31 | 1.23 | 1.21 | | | | 2.57 | 1.79 | 2.2±.4 |
| NO | 1.07 | 1.16 | 1.14 | | | | 2.44 | 1.69 | 2.1±.4 |
| $NO_2$ | 1.56 | 1.55 | 1.54 | | | | 3.26 | 2.28 | 2.8±.5 |
| $NH_3$ | | | | | | | | | |
| $H_2$ | 1.86 | 1.63 | 1.61 | | | | 3.43 | 2.39 | 2.9±.5 |
| $H_2O$ | 2.21 | 1.94 | 1.94 | | | 3.0±.3 | 4.09 | 2.86 | 3.5±.6 |
| $H_2O_2$ | | | | | | | | | |
| $CH_4$ | 2.42 | 2.26 | 2.22 | | | | 4.74 | 3.29 | 4.0±.7 |
| $C_2H_6$ | 2.72 | 2.71 | 2.67 | | | | 5.68 | 3.94 | 4.8±.9 |
| $C_3H_8$ | 4.30 | 4.47 | 4.42 | | | | 9.38 | 6.53 | 8.0±1.5 |
| neo-$C_5H_{12}$ | 7.0 | 6.94 | 6.84 | | | | 14.6 | 10.1 | 12.3±2.3 |
| Xe | .89 | .83 | .78 | | | | 1.74 | 1.16 | 1.4±.3 |

a) Expressed relative to the $CO_2$ rate taken as unity.

b) Mean values from Table II.

c) Least squares computations of the mean relative and absolute rate constants carried out at the National Bureau of Standards by Dr. Robert F. Hampson. Column B: Omnitab computations for the sets of data used in Table II (omitting all the values for Kr, Ar and $SF_6$ and the values in parentheses for $O_2$ and $C_3H_8$). Columns C and H: Omnitab computations of the mean relative and absolute rate constants, respectively, using the same data as in B plus the nine absolute values in Columns D, E and F. Column G: The relative data of Column B placed on an absolute scale by taking for $CO_2$ the value of 2.1 x $10^{-10}$cc.molec$^{-1}$sec$^{-1}$.

d) Heidner, Husain and Wiesenfeld (1972).

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Gauthier, M., and Snelling, D. R., (Private Communication)

Gilpin, R., Schiff, H. I., and Welge, K. H., "Photodissociation of $O_3$ in the Hartley Band. Reactions of $O(^1D)$ and $O_2(^1\Sigma_g^+)$ with $O_3$ and $O_2$," J. Chem. Phys. 55, 1087 (1971)

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## The reaction of $O(^1S)$ with $CO_2$

(1) $O(^1S) + CO_2 \rightarrow ?$

Preferred value:

$k_1 = 3.1 \times 10^{-11} \exp(-2630/RT)\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $200\ K < T < 450\ K$

Reliability: $A = 3.1 \pm 0.5 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1}$

$E = 2630 \pm 200$ cal/mole

thus, $\log k \pm 0.15$

Remarks:

The data of Atkinson and Welge (c) is used essentially intact, as it is the only temperature-variant experiment. Two other 300 K experimental points are considered (a,b) which serve to slightly modify and set reliability limits on the expression.

References considered:

(a) E. C. Zipf, Can. J. Chem. 47, 1863 (1969)
(b) S. V. Filseth, F. Stuhl and K. H. Welge, J. Chem. Phys. 52, 239 (1970)
(c) R. Atkinson and K. H. Welge, J. Chem. Phys. 57, 3689 (1972)

Evaluator:

Tom G. Slanger

Date: February 1973

## The reaction of $O(^1S)$ with $O_3$

(1) $O(^1S) + O_3 \rightarrow ?$

Preferred value:

$k_1 = 5.8 \times 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$
T = 300 K; probably temperature independent
Reliability: k $\pm$ 1 x $10^{-10}$, thus log k $\pm$ 0.07

Remarks:

There has been only a single measurement of $k_1$.

References considered:

G. London, R. Gilpin, H. I. Schiff, and K. H. Welge, J. Chem. Phys. 54, 4512 (1971)

Evaluator:

Tom G. Slanger

Date: February 1973

## The reaction of $O(^1S)$ with $N_2O$

(1) $O(^1S) + N_2O \rightarrow ?$

Preferred value:

$k_1 = 1.4 \times 10^{-11}$ cm$^3$molecule$^{-1}$s$^{-1}$

T = 300 k

Reliability: $k \pm 0.3 \times 10^{-11}$, thus $\log k \pm 0.1$

Remarks:

Four measurements have been reported: $5.9 \times 10^{-13}$ (ref. a), $1.6 \times 10^{-11}$ (ref. b), $1.5 \times 10^{-11}$ (ref. c), $1.1 \times 10^{-11}$ (ref. d). The preferred value and the reliability are derived from the values of ref. b,c,d giving equal weight to each of them. Ref. (a) has been disregarded.

References considered:

- (a) R. A. Young and G. Black, J. Chem. Phys. 44, 3741 (1966)
- (b) R. A. Young, G. Black and T. G. Slanger, J. Chem. Phys. 49, 4769 (1968)
- (c) F. Stuhl and K. H. Welge, Can. J. Chem. 47, 1870 (1969)
- (d) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52, 239 (1970)

Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $O_2$

(1) $O(^1S) + O_2 \rightarrow ?$

**Preferred value:**

$k_1 = 4.3 \times 10^{-12} \exp(-1700/RT)\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $200\ K < T < 377\ K$

Reliability: $A = 4.3 \pm 0.7 \times 10^{-12}\ cm^3 molecule^{-1} s^{-1}$

$E = 1700 \pm 200$ cal/mole

thus, $\log k \pm 0.15$

**Remarks:**

Two temperature-variant data sets, those of Atkinson and Welge (e) and of Slanger, Wood and Black (f) were combined. Four 300 K measurements (a,b,c,d) were also considered.

**References considered:**

(a) E. C. Zipf, Bull. Am. Phys. Soc. 12, 225 (1967)
(b) R. A. Young, G. Black and T. G. Slanger, J. Chem. Phys. 50, 309 (1969)
(c) S. V. Filseth and K. H. Welge, J. Chem. Phys. 51, 839 (1969)
(d) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52, 239 (1970)
(e) R. Atkinson and K. H. Welge, J. Chem. Phys. 57, 3689 (1972)
(f) T. G. Slanger, B. J. Wood and G. Black, Chem. Phys. Letters 17, 401 (1972)

**Evaluator:**

Tom G. Slanger

Date: February 1973

## The reaction of $O(^1S)$ with $CH_4$

(1) $O(^1S) + CH_4 \rightarrow ?$

Preferred value:

$k_1 = 2 \times 10^{-14}\ cm^3 molecule^{-1} s^{-1}$

T = 300 K

Reliability: log k ± 0.4

Remarks:

The preferred value is based on two works (ref. a,b). One work (a) yielded $k(CH_4) = 4.7 \times 10^{-14}$. The other (b) yielded a relative value $k(CH_4)/k(N_2O) = 6 \times 10^{-4}$. Using for $k(N_2O)$ the preferred value $1.4 \times 10^{-11}$ yields $k(CH_4) = 8.4 \times 10^{-15}$. For a more accurate value another measurement is indicated.

References considered:

(a) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52, 239 (1970)
(b) R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50, 309 (1968)

Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $H_2O$

(1) $O(^1S) + H_2O \rightarrow ?$

### Preferred value:

$k_1 \gtrsim 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$

T = 300 K

Reliability: log k ± 1

### Remarks:

Two measurements have been reported: ~ 4 x $10^{-10}$ (ref. a) and 7 x $10^{-11}$ (ref. b). Reliability limited mostly by $H_2O$ concentration measurement. Recent experience indicates that the rate constant is more likely a few times $10^{-10}$.

### References considered:

(a) F. Stuhl and K. H. Welge, Can. J. Chem. 47, 1870 (1969)
(b) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52, 239 (1970)

### Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $NH_3$

(1) $O(^1S) + NH_3 \rightarrow ?$

### Preferred value:

$k_1 = 5 \times 10^{-10}\ cm^3 molecule^{-1} s^{-1}$

T = 300 K

Reliability: k ± 50 %, thus log k ± 0.2

### Remarks:

There exists only one measurement (ref. a). The reliability is an educated guess. The accuracy of the measurements was limited by $NH_3$ concentration measurement.

### References considered:

(a) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52 239 (1970)

### Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $O(^3P)$

(1) $O(^1S) + O(^3P) \rightarrow ?$

### Preferred value:

$k_1 = 7.5 \times 10^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$

T = 300 K

Reliability: k ± 50%, log k ± 0.2

### Remarks:

There has been only a single measurement of $k_1$. Products are probably 2 $O(^1D)$; for this reaction $\Delta H(300) = -24.6$ kJ mol$^{-1}$ ($-5.9$ kcal mol$^{-1}$)

### References considered:

W. Felder and R. A. Young, J. Chem. Phys. 56, 6028 (1972)

### Evaluator:

Tom G. Slanger

Date: February 1973

## The reaction of $O(^1S)$ with NO

(1) $O(^1S) + NO \rightarrow ?$

Preferred value:

$k_1 = 3.2 \times 10^{-11} T^{1/2}$ cm$^3$molecule$^{-1}$s$^{-1}$

Temperature range: $200 < T < 291$ K

Reliability: k ± 10 %, log k ± 0.05

Remarks:

The preferred value is based on measurements (ref. a) at 200 K, $k(200 = (5.0 \pm 0.6) \times 10^{-10}$, at 291 K, $k(291) = (5.7 \pm 0.6) \times 10^{-10}$ and (ref. b) at room temperature, k (room) = $5.5 \times 10^{-10}$. Two other measurements (ref. c and d) at room temperature have been disregarded. Ref.(c)reported $8 \times 10^{-10}$. Ref.(d)reported $k(NO)/k(N_2O) = 60$ yielding $k(NO) = 8.4 \times 10^{-10}$ using for $k(N_2O)$ the preferred value $1.4 \times 10^{-11}$. Rejection of ref. (c) and (d) is somewhat arbitrary. The lower values have been chosen because they include T-variant measurement. Because NO is important in auroral events, another investigation may be appropriate to measure the degree of reliability. Averaging all values yields an arithmetic mean of $6.5 \times 10^{-10}$.

References considered:

(a) R. Atkinson and K. H. Welge, J. Photochem., in press (1973)
(b) G. Black, T. G. Slanger, G. A. St. John and R. A. Young, Can. J. Chem. 47, 1872 (1969)
(c) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52, 239 (1970); ibid, erratum 57, 4064 (1972)
(d) R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys. 50, 309 (1969)

Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $NO_2$

(1) $O(^1S) + NO_2 \rightarrow ?$

Preferred value:

$k_1 = 5 \times 10^{-10}\ cm^3 molecule^{-1} s^{-1}$

T = 300 K

Reliability: k ± 50 %, log k ± 0.2

Remarks

There exists only one measurement (ref. a). The error limit is an educated guess. The accuracy was determined mainly by $NO_2$ concentration measurement uncertainty.

References considered:

(a) S. V. Filseth, F. Stuhl, and K. H. Welge, J. Chem. Phys. 52 239 (1970)

Evaluator:

Karl H. Welge

Date: February 1973

## The reaction of $O(^1S)$ with $N_2$

(1) $O(^1S) + N_2 \rightarrow ?$

Preferred value:

$k_1 < 5 \times 10^{-17}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 200 K $< T <$ 380 K

Remarks

Same upper limit measured in both papers considered (a,b).

References considered:

(a) F. Stuhl and K. H. Welge, Can. J. Chem. 47, 1870 (1969)
(b) R. Atkinson and K. H. Welge, J. Chem. Phys. 57, 3689 (1972)

Evaluator:

Tom G. Slanger

Date: February 1973

## Rate constants for reactions of $O_2(^1\Delta)$ and of sulfur monoxide

| Reaction | $k/cm^3\ molecule^{-1}s^{-1}$ | T/K | Ref. |
|---|---|---|---|
| $CO + O_2(^1\Delta) \rightarrow$ quenching or reaction | $< 3 \times 10^{-16}$ | 300 | 1 |
| $CO + O_2(^1\Delta) \rightarrow CO_2 + O$ | $< 9 \times 10^{-27}$ | 300 | 2 |
| $SO + O_2(^1\Delta) \rightarrow SO(^1\Delta) + O_2$ | $(3.5 \pm 0.36) \times 10^{-13}$ | 300 | 1 |
| $SO_2 + O_2(^1\Delta) \rightarrow$ quenching | $< 2 \times 10^{-15}$ | 300 | 1 |
| $SO + O_2 \rightarrow SO_2 + O$ | $< 8 \times 10^{-17}$ | 300 | 1 |
| | $3.0 \times 10^{-13} \exp(-2800/T)$ | 400-2500 | 3 |
| $SO + SO \rightarrow SO_2 + S$ | $< 3 \times 10^{-15}$ | 300 | 3 |
| | $< 2 \times 10^{-13}$ | 1000 | 3 |

References

1. W. H. Breckenridge and T. A. Miller, J. Chem. Phys. 56, 465 (1972).
2. E. R. Fisher and M. McCarty, Jr., J. Chem. Phys. 45, 781 (1966).
3. Evaluations of K. Schofield, to be published in Journal of Physical and Chemical Reference Data, Issue No. 1, Vol. 2, 1973.

Evaluator:

W. H. Breckenridge
February, 1973

## Chemical Kinetics Data Survey

### 1. Primary Photochemical Transitions

| Reaction | $\Delta H_0^o$ kJ/mol | kcal/mol | λ threshold (nm) |
|---|---|---|---|
| $HO_2(X^2A'') \rightarrow H + O_2(X^3\Sigma_g^-)$ | 192 | (45.9) | 623 (1) |
| $\rightarrow H + O_2\ (a^1\Delta_g)$ | 286 | (68.4) | 417 (2) |
| $\rightarrow H + O_2(b^1\Sigma_g^+)$ | 349 | (83.4) | 343 (3) |
| $\rightarrow OH + O(^3P)$ | 262 | (62.6) | 456 (4) |
| $\rightarrow OH + O(^1D)$ | 453 | (108.0) | 265 (5) |

$\Delta H_0^o$ calculated using values from ref. (a).

### 2. Data

#### 2a. Absorption Spectrum and Absorption Coefficient

| Wavelength Range | Observation |
|---|---|
| 195 - 245 nm | Continuous abs. spectrum with maximum at 200 - 210 nm, obtained at 300 K from photolysis of $H_2O_2$, photolysis of $H_2O_2$ in the presence of $O_3$ and photolysis of $Cl_2$ in the presence of $H_2O_2$ (b) |

| | |
|---|---|
| 195 - 290 nm | Continuous abs. spectrum with maximum at 195 - 210 nm, obtained at 1100 K from pyrolysis of $H_2O_2$ (c, d) |
| 185 - 260 nm | Continuous abs. spectrum with maximum at 200 - 210 nm, obtained at 300 K from photolysis of water (e) |
| 210 - 300 nm | Continuous abs. spectrum with maximum at 230 - 240 nm, obtained at 300 K in aqueous solution from pulse radiolysis (f) |

### 2b. Quantum yields

| | |
|---|---|
| 200 - 260 nm | No direct measurements; estimate: $\phi_4 \sim 1$, derived from temperature dependence and shape of absorption spectrum in (d) |

## 3. Preferred Values

### a. Absorption coefficients

$195 < \lambda < 290$ nm. Evaluation of ref. (d) Data for $T \leq 300$ K and $T = 1100$ K given in Table I and Fig. 1. Data of ref. (b) according to ref. (d) may be represented as

$$\ln\left(\frac{\varepsilon(\upsilon)}{\upsilon}\right) \approx \ln\left(\frac{\varepsilon(\upsilon_{max})}{\upsilon_{max}}\right) - \alpha(\upsilon_{max} - \upsilon)^2$$

with $\lambda = \frac{1}{\upsilon}$, $\varepsilon(\upsilon_{max}) = 1.2 \cdot 10^6$ $cm^2/mol$, $\upsilon_{max} = 48780$ $cm^{-1}$

and $\alpha \approx 1.9 \cdot 10^{-8}$ $cm^2$.

b. Quantum yields

$200 < \lambda < 250$ nm: $\phi_4(-HO_2) \sim 1$

$\lambda < 200$ nm : no recommendation

## 4. Remarks

a. Absorption coefficients

The evaluation of ref. (d) is used. The aequous solution data show a solvent shift of about + 30 nm compared to the gas phase. The integrated absorptions (at the right of the maximum) for the solution (f), the gas phase at 300 K (b) and the gas phase at 1100 K (c) agree within about 10%. The gas phase 300 K data of ref. (e) are about 30% higher than those of ref. (b). The gas phase 1100 K data (after accounting for the temperature dependence) are about 10% higher than those of ref. (b). The causes of the discrepancies are problems in calculating the $HO_2$ concentrations in the different systems. All authors state an uncertainty of a factor of 2. The consistency, however, points to an uncertainty of atmost 30%. Absorption spectra to lower excited states as postulated in ref. (g) have not been detected.

### b. Quantum yields

The estimate of a total quantum yield of 1 is based on the completely continuous shape of the absorption at energies highly in excess of the threshold energies for reactions (1) - (4). The estimate of a predominant photolysis path to OH + O is based on the temperature dependence of the absorption spectrum: The steep slope of the potential surface of the excited state vertically above the ground state minimum is predominantly in the direction of the normal vibration $\nu_3$, which corresponds to an O - O stretching. The steep slope of the upper potential surface and the absence of any structure near the threshold of reaction (5), points to reaction (4) as predominant channel instead of reaction (5)

Table I

Values of absorption coefficient of $HO_2$, 185 - 290 nm

| $\lambda$(nm) | $\varepsilon$($T \leq 300$ K), $cm^2/mol$ | Ref | $\varepsilon$($T = 1100$ K), $cm^2/mol$ | Ref |
|---|---|---|---|---|
| 185 | $1.0 \cdot 10^6$ | e* | | |
| 195 | 1.1 · | b | $8 \cdot 10^5$ | d |
| 200 | 1.2 · | b | 8.5 · | d |
| 210 | 1.2 · | b | 8.5 · | d |
| 220 | 1.0 · | b | 7.5 · | d |
| 230 | 6.7 · | b | 6.3 · | d |
| 240 | 3.6 · | b | 4.3 · | d |
| 250 | 1.8 | d | 3.0 · | d |
| 260 | 1 · | d | 4.9 · | d |
| 270 | 0.5 · | d | 1.1 · | d |

The absorption coefficient is defined by the equ.:

$$\varepsilon = \frac{1}{Cl} \log_{10}(I_o/I)$$

with l in cm and C in $mol/cm^3$

*) fitted to the data of ref. b using equal $\varepsilon$-values at 210 nm

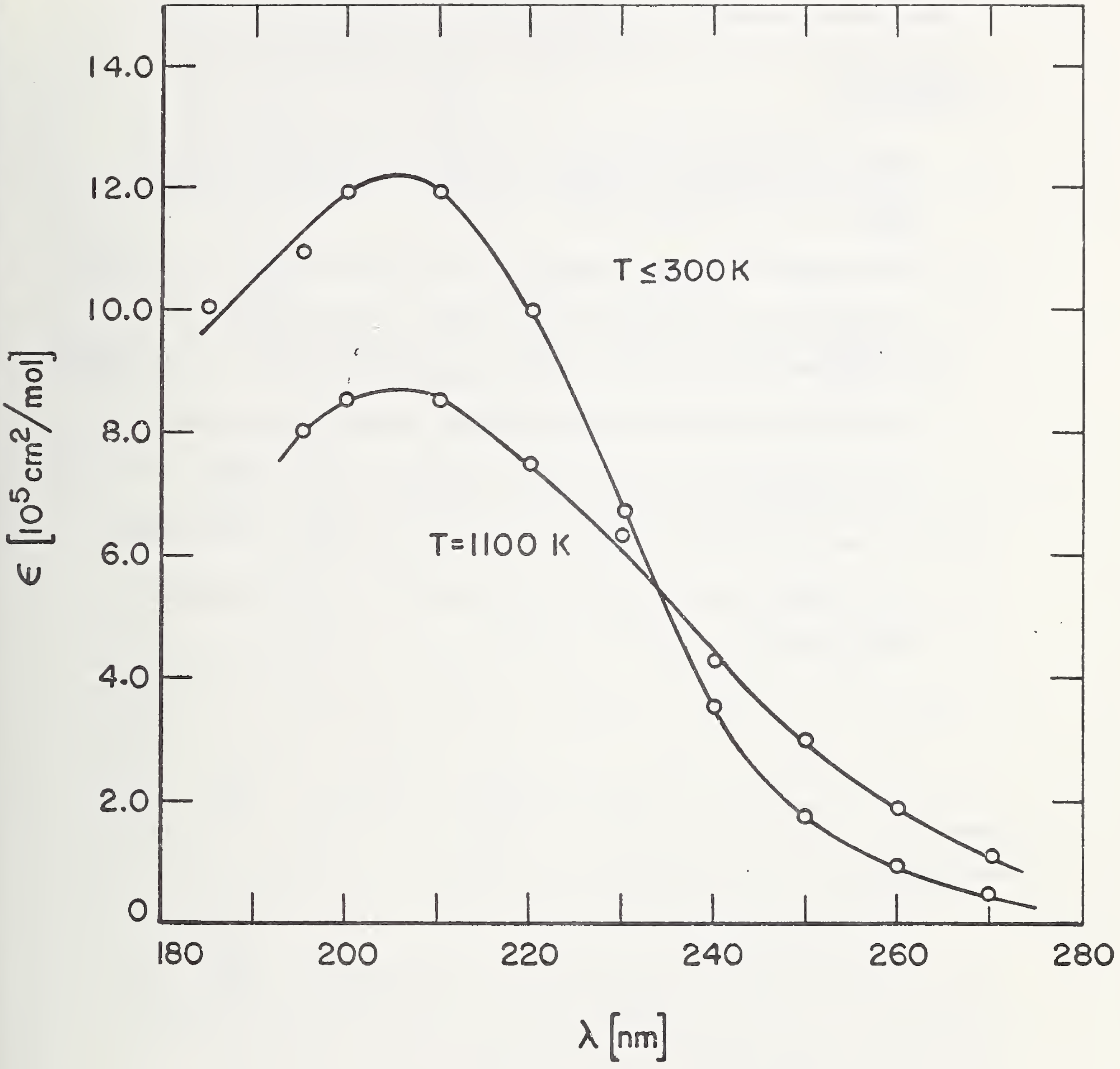

Figure 1. Absorption coefficient ε for $HO_2$ vapor. Same data as in Table I. Units of ε are $cm^2$/mol (see Table I).

## 5. References

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J. Troe
January 1973

## Comments on the reaction $H + H_2O_2 \rightarrow H_2 + HO_2$

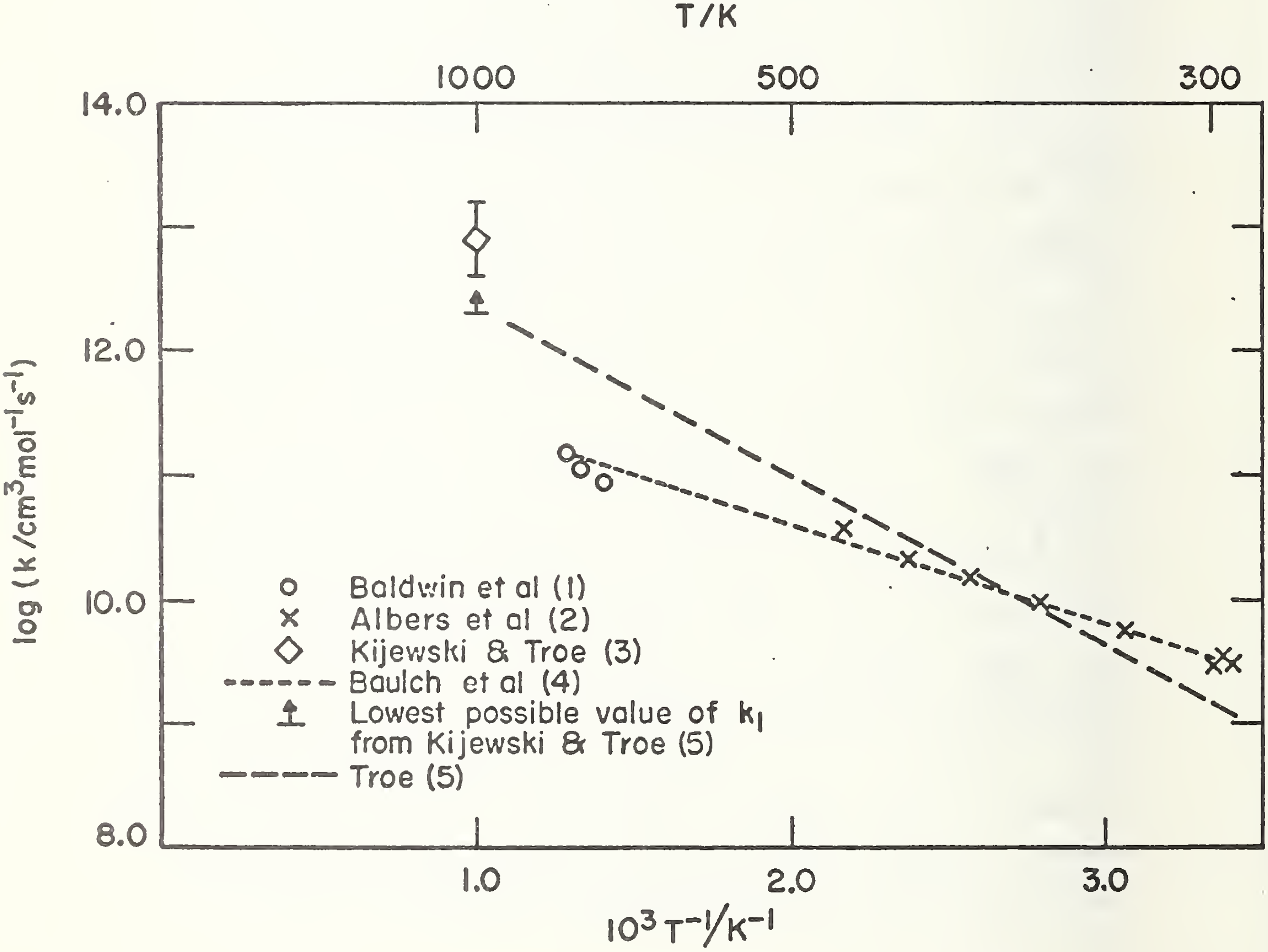
The preferred value for this reaction as shown in the CIAP Monograph No. 1 Tables (preliminary) is that of Baulch, Drysdale, Horne and Lloyd. J. Troe has commented on this selection in the light of his more recent experiments. These comments are given below together with a reply by D. D. Drysdale.

> Since the Leeds evaluation, we have measured rates and $HO_2$ profiles in the $H_2$ - and CO - catalyzed pyrolysis of $H_2O_2$ (H. Kijewski and J. Troe, Int. J. Chem. Kin. <u>3</u>, 223 (1971)). Our data allow one to derive $k_1 \simeq (k_3 + k_4) \times (0.09 \pm 0.04)$, where $H + H_2O_2 \rightarrow H_2 + HO_2$ $(k_1)$ $H + HO_2 \rightarrow H_2 + O_2$ $(k_3)$ and $H + HO_2 \rightarrow 2\ OH$ $(k_4)$ at 900 - 1100 K, in this limit independent of $k_2$. For the rate constant $k_2$ of $H + H_2O_2 \rightarrow OH + H_2O$, all ratios $k_2/k_1$ which are smaller than 20 are compatible with our results. Using $k_4 \simeq 7 \cdot 10^{13}$ $\mathrm{cm^3/mol\ sec}$ and $k_4/k_3 \simeq 5$ (see Refs. in the article cited above), we obtain $k_1$ (1000 K) $\simeq 10^{12.9 \pm 0.3}$ $\mathrm{cm^3/mol\ sec}$. With the lowest possible $k_3 + k_4$ value of about $2 \cdot 10^{13}$ $\mathrm{cm^3/mol\ sec}$, we would obtain $k_1(1000\ K) \simeq 10^{12.3 \pm 0.3}$ $\mathrm{cm^3/mol\ sec}$. The data preferred in the data sheet, as adopted from the Leeds evaluation, would give at 1000 K $k_1 \simeq 10^{11.4}$ $\mathrm{cm^3/mol\ sec}$ and are thus far outside of our range. With the value of Albers et al. of $k_1 = 0.43 \cdot (7 \pm 4) \cdot 10^{12} \exp(-\frac{4200}{RT}) = 3 \cdot 10^{12} \exp(-\frac{4200}{RT})$ $\mathrm{cm^3/mol\ sec}$, one would obtain $k_1(1000\ K) \simeq 10^{11.6 \pm 0.3}$ $\mathrm{cm^3/mol\ sec}$, which is not much better. A consistent picture could only be obtained with a larger activation energy of $k_1$. A rate expression of e.g. $\underline{k_1 = 5 \cdot 10^{13} \exp(-\frac{6200}{RT})\ \mathrm{cm^3/mol\ sec}}$ would agree with the data of Albers et al. reasonably well and meet our lowest possible value of $k_1(1000\ K) \simeq 10^{12.3}$ $\mathrm{cm^3/mol\ sec}$. We estimate the uncertainty worse than given in the data sheet, perhaps a factor of 4. For $k_2$ we have no recommendation, except that $k_2(1000\ K) < 10^{14}$ $\mathrm{cm^3/mol\ sec}$ and that we also realize the inconsistency between the data of Albers et al. and of Baldwin et al.
>
> J. Troe
> February, 1973

$H + H_2O_2 \rightarrow H_2 + HO_2$

Dr. Troe's recent results are in conflict with our evaluation and other data in this temperature region. Both Troe's and Baldwin's results were obtained from studies of complex kinetic systems and it is difficult to resolve which of these is the more reliable. We prefer for the moment to base our evaluation on the extensive data of Albers et. al. with which Baldwin's results also agree. However, in the light of Dr. Troe's results we feel that our recommended expression should be used only in the temperature range 300 - 500 K with error limits in log k of ± 0.3

D. L. Baulch, D. D. Drysdale
May, 1973



$H + H_2O_2 \rightarrow H_2 + HO_2$ Rate constant as a function of temperature (Baulch, Drysdale)

# Photochemical and Rate Data for Methyl nitrite, Methoxy and Methylperoxy

Julian Heicklen

## PHOTOCHEMISTRY OF $CH_3ONO$

The photolysis of $CH_3ONO$ has been studied extensively. The results have been reviewed and extended by Wiebe and his coworkers.[1,2] All investigators agree that the principal primary process is

$$CH_3ONO + h\nu \rightarrow CH_3O^* + NO \qquad 1a$$

where the $CH_3O$ radical product can have considerable excess energy and decompose to $CH_2O + H$ if not stabilized.

It was Napier and Norrish[3] who first showed that photodecomposition is not the sole reaction when radiation is absorbed. Part of the time an isomer is formed which reverts back to $CH_3ONO$.

$$CH_3ONO + h\nu \rightarrow \text{Isomer} \rightarrow CH_3ONO \qquad 1b$$

Other possible reactions of $CH_3ONO$ photolysis are

$$CH_3ONO + h\nu \rightarrow CH_2O + HNO \qquad 1c$$

$$\rightarrow H + CH_2O + NO \qquad 1d$$

Wiebe et al.[2] determined the relative importance of reactions 1a-1d with 3660A incident radiation by studying the photolysis of $CH_3O^{14}NO$ in the presence of $^{15}NO$ and measuring the production of $CH_3O^{15}NO$, $^{30}N_2O$, $^{29}N_2O$, and $^{28}N_2O$. The $N_2O$ is produced from the reaction

$$2HNO \rightarrow H_2O + N_2O \qquad 2$$

Wiebe et al. found that no $^{29}N_2O$ or $^{28}N_2O$ was produced, from which they concluded that reactions 1c and 1d do not occur. From the quantum yields of $CH_3O^{15}NO$ and $^{30}N_2O$, they deduced that reaction 1a proceeds with 76% efficiency. With 3660A incident radiation, the efficiencies are for reaction 1a, $0.76 \pm 0.02$, for reaction 1b, $0.24 \pm 0.04$, for reactions 1c and 1d combined $< 0.02$. The relative importance of these reactions with other incident wavelengths is not known.

## REACTIONS OF $CH_3O$ RADICALS

The reactions of $CH_3O$ radicals which might be important in the stratosphere are those with $O_2$, $O_3$, NO, $NO_2$, and CO. Unfortunately, the measurements are few and mostly at room temperature. No absolute measurements have been made for any of these rate constants. However, some relative rate constants do exist.

Consider the reactions

$CH_3O + O_2 \rightarrow HO_2 + CH_2O$ 3

$CH_3O + NO \rightarrow CH_3ONO$ 4a

$CH_3O + NO \rightarrow CH_2O + HNO$ 4b

$CH_3O + NO_2 \rightarrow CH_3ONO_2$ 5a

$CH_3O + NO_2 \rightarrow CH_2O + HONO$ 5b

$CH_3O + CO \rightarrow$ products 6

Wiebe and Heicklen[1] studied the photolysis of $CH_3ONO$ in the presence of NO-CO mixtures and estimated $k_6/k_4 \sim 5 \times 10^{-4}$ for temperatures between 25 and 150°C. Presumably, under stratospheric conditions, the ratio [NO]/[CO] is sufficiently large, so that reaction 6 is unimportant.

The relative importance of reactions 3, 4, and 5 were examined at room temperature by Wiebe et al.[2] by examining the photolysis of $CH_3ONO$ in the presence of NO-$O_2$ and NO-$NO_2$ mixtures. From these studies they found that $k_3/k_4 = 4.7 \times 10^{-5}$ (± 20%) and $k_4/k_5 = 1.2 \pm 0.1$. Reaction 3 probably proceeds with an activation energy of about 6 kcal/mole.[4] Thus at stratospheric temperatures (∿ 200°K), $k_3/k_4$ should be even smaller. Two values of $k_{4a}/k_{5a}$ have been reported at higher temperatures from pyrolysis studies. Phillips and Shaw[5] reported $k_{4a}/k_{5a} = 1.8$ at 90°C, whereas Baker and Shaw[6] found $k_{4a}/k_{5a} = 2.7$ at 130°C. The value of $k_{4a}/k_{5a}$ from Wiebe et al.[2] is 1.1 at

25° C. Thus the ratio $k_{4a}/k_{5a}$ appears to be temperature dependent.

The value for the branching ratio $k_{4b}/k_4$ is obtained from the $N_2O$ quantum yield in the photolysis of $CH_3ONO$, since all the $N_2O$ is produced from reaction 2. Surprisingly, a consistent value of this ratio has been difficult to obtain and values from 0 to 0.5 have been reported.[7] The difficulty has arisen because of the decomposition of the energetic $CH_3O^*$ radical produced in the photolysis. Recently three studies done at high pressures to stabilize the $CH_3O$ radicals have all found the same value of 0.055 for the quantum yield of $N_2O$ production.[1,2,8] Two of the studies[2,8] were done at 25°C, but the other extended the results to 150°C. When the quantum yield data for $N_2O$ are combined with the efficiency for reaction 1a, then $k_{4b}/k_4 = 0.145 \pm 0.015$ from 25-150°C.

The branching ratio $k_{5b}/k_5$ is not firmly established. Only two experimental studies give information on this ratio. Baker and Shaw[6] pyrolized $(CH_3O)_2$ at 130°C in the presence of $NO_2$ and obtained $k_{5b}/k_5 = 0.10 \pm 0.01$. Wiebe et al.,[2] in their studies, found $k_{5a}/k_5 = 0.9 \pm 0.1$ at 25°C, which is consistent with the Baker and Shaw finding and suggests that $k_{5a}/k_{5b}$ has little if any temperature dependence.

Two estimates have been made for absolute rate coefficients of the above reactions. Arden et al.[9] estimated $k_4 \sim 0.8 \times 10^{-13}$ cm$^3$/molecule sec. Heicklen[4] deduced that $k_3 = 0.27 \times 10^{-17}$ cm$^3$/molecule sec at 25° C. The ratio of these two numbers gives $k_3/k_4 \sim 3.4 \times 10^{-5}$ in good agreement with the measured value[2] of $4.7 \times 10^{-5}$.

## REACTIONS OF $CH_3O_2$ RADICALS

Even less is known about the reactions of $CH_3O_2$ radicals than about those of $CH_3O$ radicals. The reactions of importance should be those with $O_3$, NO, $NO_2$, and CO. Of these only the reactions with NO and $NO_2$ have been studied.[10] The rate coefficients are not known, but some information is available on the branching ratios. The possible reaction channels are

$$CH_3O_2 + NO \rightarrow CH_3O_2NO \qquad 7a$$

$$\rightarrow CH_2O + HONO \qquad 7b$$

$$\rightarrow CH_3O + NO_2 \qquad 7c$$

$$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2 \qquad 8a$$

$$\rightarrow CH_2O + HONO_2 \qquad 8b$$

$$\rightarrow CH_3O + NO_3 \qquad 8c$$

Spicer et al.[10] examined the above reactions and found that when $CH_3O_2$ was reacted with either NO or $NO_2$ at 25°C, the major product was $CH_3ONO_2$. They interpreted the $CH_3ONO_2$ production to represent that fraction of the reaction that proceeded either via reaction 7a or reaction 8a. It was deduced that reaction 7c occurred $< 2\%$ of the time since $CH_3ONO$ was not produced in the $CH_3O_2$-NO system, as it surely would have been if $CH_3O$ were present. Reaction 8c was considered unlikely since it is endothermic by $\sim 4.5$ kcal/mole. Thus it was concluded that the efficiencies of reactions 7a, 7b, and 7c are $0.6 \pm 0.1$, $0.4 \pm 0.1$, and $< 0.02$. Likewise, the efficiencies for reactions 8a, 8b, and 8c are $0.75 \pm 0.05$, $0.25 \pm 0.1$, and $< 0.1$.

Table I: Best estimates of rate coefficients.

| Rate Coefficient | Value | Units | T,°C | Reference |
|---|---|---|---|---|
| $k_{1a}/k_1$[a] | 0.76 ± 0.02 | None | 25 | 2 |
| $k_{1b}/k_1$[a] | 0.24 ± 0.04 | None | 25 | 2 |
| $(k_{1c} + k_{1d})/k_1$[a] | $< 0.02$ | None | 25 | 2 |
| $k_6/k_4$ | $5 \times 10^{-4}$ | None | 25-150 | 1 |
| $k_3/k_4$ | $4.7 \times 10^{-5}$ (±20%) | None | 25 | 2 |
| $k_4$ | $\sim 0.8 \times 10^{-13}$ | $cm^3/sec$ | -- | 9 |
| $k_3$[b] | $\sim 0.3 \times 10^{-17}$ | $cm^3/sec$ | 25 | 4 |
| $k_4/k_5$ | 1.2 ± 0.1 | None | 25 | 2 |
| $k_{4a}/k_{5a}$ | 1.1 | None | 25 | 2 |
| $k_{4a}/k_{5a}$ | 1.8 | None | 90 | 5 |
| $k_{4a}/k_{5a}$ | 2.7 | None | 130 | 6 |
| $k_{4b}/k_4$ | 0.145 ± 0.015 | None | 25-150 | 1,2,8 |
| $k_{5b}/k_5$ | 0.10 ± 0.01 | None | 130 | 6 |
| $k_{5a}/k_5$ | 0.9 ± 0.1 | None | 25 | 2 |
| $k_{7a}/k_7$ | 0.6 ± 0.1 | None | 25 | 10 |
| $k_{7b}/k_7$ | 0.4 ± 0.1 | None | 25 | 10 |
| $k_{7c}/k_7$ | $< 0.02$ | None | 25 | 10 |
| $k_{8a}/k_8$ | 0.75 ± 0.05 | None | 25 | 10 |
| $k_{8b}/k_8$ | 0.25 ± 0.1 | None | 25 | 10 |
| $k_{8c}/k_8$ | $< 0.1$ | None | 25 | 10 |

a) $\lambda = 3660A$

b) $k_3 \sim 1.6 \times 10^{-13}$ exp. $(-6500/RT)$ $cm^3/sec$ (Ref. 9). R = 1.987 cal/mole-°K.

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The combination of nitrogen atoms

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| 1. | $N + N + N_2 \rightarrow N_2 + N_2$ | -945.3 | (-225.9) |

Preferred value:

$k_1 = 8.3 \times 10^{-34} \exp[+500/T]\ cm^6 molecule^{-2} s^{-1}$

where $\frac{-d[N]}{dt} = 2k[N]^2[N_2]$

Temperature range: $100 < T < 600$ K

Reliability: Uncertainty in log k ± 0.2 (200-600 K: the uncertainty is greater below 200 K)

Remarks:

The large scatter of the data at 300 K is due to a lack of appreciation of the complex nature of the surface decay of N atoms in the experimental systems studied. The expression is based on data obtained in the temperature range 100-600 K by (28,32,33,36-38,41 and 44): only in these papers are the effects of both first and second order surface recombination considered. All other data are rejected.

Campbell and Thrush's relative efficiencies ($N_2$: Ar: He = 1: 1: 1.4 at 298 K) (32) are probably the most reliable.

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## $N + N + N_2 \rightarrow N_2 + N_2$

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Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

# Chemical Kinetics Data Survey

## The dissociation of nitrogen

| | | $\Delta H(300)$ kJ $\mathrm{mol}^{-1}$ | (kcal $\mathrm{mol}^{-1}$) |
|---|---|---|---|
| (1) | $N_2 + N_2 \rightarrow N + N + N_2$ | 945.3 | (225.9) |

### Preferred value:

$k_1 = 6.1 \times 10^{-3} T^{-1.6} \exp[-113\ 200/T]$ $\mathrm{cm^3 molecule^{-1} s^{-1}}$

Temperature range: $6000 < T < 15\ 000$ K

Reliability: $\log k \pm 0.5$

Definition: $-d[N_2]/dt = k_1[N_2]^2$

### Remarks:

The dissociation of $N_2$ has been studied by shock tube, following the reaction by interferometry (1,2), by pressure changes at the end wall (4) and by monitoring v.u.v. absorption at 117.6 nm ($N_2(X^1\Sigma_g^+)_{v''} \simeq 10$) (3). We prefer the expression obtained in the latter work by Appleton et al (3): it is in good agreement with theoretical calculations by Shui et al (5).

The results of (2 and 3) suggest that $k(M = Ar)/k(M = N_2) \simeq 0.4$ at 6400 K, but no firm conclusion can be drawn about the relative efficiencies of N and $N_2$ except that $k(M = N) > k(M = N_2)$. Hanson and Baganoff (4) found $k(M = N)/k(M = N_2)$ to vary with temperature.

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### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions on the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of N with NO

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $N + NO \rightarrow N_2 + O$ | -313.7 | (-74.98) |

### Preferred value:

$k_1 = 2.7 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $300\ K < T < 5000\ K$

Reliability: log k ± 0.1 at 300 K increasing to log k ± 0.3 in range 2000-5000 K

### Remarks:

Expression based on room temperature data for $k_1$ (primarily those of (11) and (13)) and the data above 2000 K for $k_2$ ($k_2 = 1.3 \times 10^{-10} \exp\{-38.0 \times 1000/T\}\ cm^3 molecule^{-1} s^{-1}$; $\log K_{12}(2000) = 7.57$, $\log K_{12}(3000) = 4.82$, $\log K_{12}(4000) = 3.45$, $\log K_{12}(5000) = 2.62$).

(1) $N + NO \rightarrow N_2 + O$

(2) $N_2 + O \rightarrow N + NO$

### References considered:

1. C. P. Fenimore and G. W. Jones, J. Phys. Chem. 61, 654 (1957)
2. P. Harteck and S. Dondes, J. Chem. Phys. 27, 546 (1957)
3. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 28, 665 (1958)
4. F. Kaufman and L. J. Decker, 7th Combustion Symp., 57 (1959)
5. G. J. Verbeke and C. A. Winkler, J. Phys. Chem. 64, 319 (1960)
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10. C. B. Kretschmer, Aerojet-General Corp., AN-671 (1962)
11. L. F. Phillips and H. I. Schiff, J. Chem. Phys. 36, 1509 (1962)
12. Y. Takezaki and S. Mori, Bull. Inst. Chem. Res. Kyoto, 45, 388 (1967)
13. C. Lin, D. A. Parkes, and F. Kaufman, J. Chem. Phys. 53, 3896 (1970)

### Evaluator:

D. L. Baulch, D. D. Drysdale, and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of $N_2$ with O

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $N_2 + O \rightarrow N + NO$ | 313.7 | (74.98) |

### Preferred value:

$k_1 = 1.3 \times 10^{-10} \exp\{-38.0 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 2000 K $< T <$ 5000 K

Reliability: log k ± 0.3

### Remarks:

The expression is based on the data of (1,2 and 4) and is compatible with the room temperature data for $k_{-1}$ ($2.7 \times 10^{-11}$ $cm^3$ $molecule^{-1} s^{-1}$) and a zero activation energy for reaction (-1). (log K(300) = -54.0)

(1) $N_2 + O \rightarrow N + NO$

(-1) $N + NO \rightarrow N_2 + O$

The satisfactory [NO] profiles calculated in (3 and 5) using similar expressions for $k_1$ substantiate the above choice for $k_1$.

### References considered:

1. R. E. Duff and N. Davidson, J. Chem. Phys. 31, 1018 (1959)
2. K. L. Wray and J. D. Teare, J. Chem. Phys. 36, 2582 (1962)
3. C. T. Bowman, Combustion Sci. Tech. 3, 37 (1971)
4. J. B. Livesey, A. L. Roberts and A. Williams, Combustion Sci. Tech. 4, 9 (1971)
5. H. K. Newhall and S. M. Shahed, 13th Combustion Symp. 381 (1971)

### Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of N with $NO_2$ to form NO

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $N + NO_2 \rightarrow NO + NO$ | -325.2 | (-77.72) |

### Preferred value:

None. See remarks
k defined by $-d[NO_2]/dt = 1/2\ d[NO]/dt = k[N][NO_2]$

### Remarks:

There are insufficient data to merit the recommendation of a rate constant expression. The most reliable determination of the overall rate constant is that of Phillips and Schiff (5) who estimated

$k = k_1 + k_2 + k_3 + k_4 = (1.8_5 \pm 0.2_2) \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ at 300 K

(1) $NO_2 + N \rightarrow NO + NO$
(2) $NO_2 + N \rightarrow N_2O + O$
(3) $NO_2 + N \rightarrow N_2 + O_2$
(4) $NO_2 + N \rightarrow N_2 + O + O$

However their estimate that $k_1/k = 0.33$ (300 K) is high relative to the value of $k_1/k = 0.12$ (~298 K) obtained by Dmitriev et al (6). Furthermore it can be inferred from the results of Clyne and Thrush (3) that $(k_2 + 2k_4)/k_1 = 4.7 \pm 1.2$ (300-700 K) and this also implies that Phillips and Schiff's value for $k_1/k$ may be too high. There is an obvious need for more data on reactions 1-4.

### References considered:

1. P. Harteck and S. Dondes, J. Chem. Phys. 27, 546 (1957)
2. G. J. Verbeke and C. A. Winkler, J. Phys. Chem. 64, 319 (1960)
3. M.A.A. Clyne and B. A. Thrush, Trans. Faraday Soc. 57, 69 (1961)
4. J. P. Doering and B. H. Mahan, J. Chem. Phys. 34, 1617 (1961)
5. L. F. Phillips and H. I. Schiff, J. Chem. Phys. 42, 3171 (1965)
6. L. A. Dmitriev, S. A. Kamenetskaya and S. Ya. Pshezhetskii, Khim. Vys. Energ. 1, 205 (1967), English translation p. 175

### Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

| The reaction of NO with NO to form N and $NO_2$ | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|
| (1) $NO + NO \rightarrow N + NO_2$ | 325.2 | (77.72) |

Preferred value:

None. See remarks

Remarks:

There are no experimental data for this reaction. Thermodynamically this reaction is unfavored and it will be exceeded by the parallel reaction

(2) $NO + NO \rightarrow N_2O + O$

at all temperatures.

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The combination of N and O

| | | ΔH(300) kJ $\mathrm{mol}^{-1}$ | ($\mathrm{kcal\ mol}^{-1}$) |
|---|---|---|---|
| (1) | $N + O + M \rightarrow NO + M$ | -631.6 | (-150.96) |

Preferred value:

$k_1 = 1.8 \times 10^{-31} T^{-0.5}$ $\mathrm{cm}^6 \mathrm{molecule}^{-2} \mathrm{s}^{-1}$ ($M = N_2$)

Temperature range: $200\ K < T < 400\ K$

Reliability: log k ± 0.2

Remarks:

The expression is that suggested by Campbell and Thrush (7). The results from (4) and, to a lesser extent, (5) are in agreement with this expression.

There are too few data to enable the recommendation of third body efficiencies. However the efficiencies determined by Campbell and Thrush (7,8 and 9) should be fairly reliable: they are listed in the following table.

Relative Efficiencies of Third Bodies, Determined by Campbell and Thrush

| M | 298K | 196K | Reference |
|---|---|---|---|
| $N_2$ | 1 | 1 | |
| Ar | 0.77 | 0.73 | 7 |
| He | 0.35 | - | 7 |
| $H_2$ | - | 2.2 | 8 |
| $H_2O$ | 6.7 | - | 9 |
| $CO_2$ | - | 3.0 | 9 |
| $N_2O$ | - | 2.2 | 9 |

References considered:

1. P. Harteck, R. R. Reeves and G. Manella, private communication to F. Kaufman, Prog. Reaction Kinetics 1, 1 (1961)
2. C. Mavroyannis and C. A. Winkler, Can. J. Chem. 39, 1601 (1961)
3. K. L. Wray, J. D. Teare, B. Kivel and P. Hammerling, 8th Combustion Symp. 328 (1962)
4. C. B. Kretschmer and H. L. Petersen, J. Chem. Phys. 39, 1772 (1963)
5. C. A. Barth, Ann. Geophys. 20, 182 (1964)
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8. I. M. Campbell and B. A. Thrush, Trans. Faraday Soc. 64, 1265 (1968)

## References (contd.)

9. I. M. Campbell and B. A. Thrush, Trans. Faraday Soc. 64, 1275 (1968)
10. S. Takahashi, Mem. Defense Acad. Japan 8, 611 (1968)
11. V. H. Shui, J. P. Appleton and J. C. Keck, 13th Combustion Symp., 21 (1971)

## Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The dissociation of NO

| | | $\Delta H(300)$ kJ mol$^{-1}$ | (kcal mol$^{-1}$) |
|---|---|---|---|
| (1) | $NO + M \rightarrow N + O + M$ | 631.6 | (150.96) |

Preferred value:

None. See remarks

Remarks:

There are insufficient data to enable a reliable recommendation to be made. The rate constant expressions of Wray and Teare (3) are probably the best available and we suggest that they be used until further data are available. They are

(4200-6700 K) $6.6 \times 10^{-4} T^{-1.5} \exp\{-75.5 \times 10^3/T\}$ cm$^3$molecule$^{-1}$s$^{-1}$ (M = Ar, $O_2$, $N_2$)

(4000-6600 K) $1.3 \times 10^{-2} T^{-1.5} \exp\{-75.5 \times 10^3/T\}$ cm$^3$molecule$^{-1}$s$^{-1}$ (M = NO, N, O)

These expressions should be used with caution. They were derived on the assumption that k (M = $N_2$, $O_2$) = k(M = Ar) and k(M = N, O) = k(M = NO). Furthermore they were obtained from a data analysis in which it was assumed that the bimolecular reaction of NO gave $N_2$ and $O_2$ directly as products,

(2) $NO + NO \rightarrow N_2 + O_2$

whereas Camac and Feinberg (5) have subsequently demonstrated that the alternative reaction

(3) $NO + NO \rightarrow N_2O + O$

occurs to a significant extent.

References considered:

1. E. Freedman and J. W. Daiber, J. Chem. Phys. 34, 1271 (1961)
2. W. G. Vincenti, Arnold Engineering Development Center, AEDC TN-61-65 (1961). AD 256 239
3. K. L. Wray and J. D. Teare, J. Chem. Phys. 36, 2582 (1962)
4. R. L. McKenzie, Natl. Aeron. Space Admin., NASA TN D-3287 (1966)
5. M. Camac and R. M. Feinberg, 11th Combustion Symp. 137 (1967)

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of N with $O_2$

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $N + O_2 \rightarrow NO + O$ | -133.2 | (-31.83) |

Preferred value:

$k_1 = 1.1 \times 10^{-14} T \exp\{-3.15 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 300 K $< T <$ 3000 K

Reliability: log k ± 0.12 in the range 300-1500 K increasing to log k ± 0.3 at 3000 K

Remarks:

The majority of the data for this reaction are in excellent agreement. The selected expression is based primarily on the discharge-flow results of (6,11,14 and 15). This expression is substantiated by the data at higher temperatures of (5, 16 and 18) and is in excellent agreement with the data for the reverse reaction. An Arrhenius expression cannot describe the data as adequately as the expression chosen here.

References considered:

1. K. Vetter, Z. Elektrochem. 53, 369 (1949)
2. C. P. Fenimore and G. W. Jones, J. Physic. Chem. 61, 654 (1957)
3. P. Harteck and S. Dondes, J. Chem. Phys. 27, 546 (1957)
4. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 27, 1411 (1957)
5. F. Kaufman and L. J. Decker, 7th Combustion Symp. 57 (1959)
6. M.A.A. Clyne and B. A. Thrush, Proc. Roy. Soc. A261, 259 (1961)
7. M.A.A. Clyne and B. A. Thrush, Nature 189, 56 (1961)
8. C. Mavroyannis and C. A. Winkler, Chemical Reactions in the Lower and Upper Atmosphere (Interscience, N.Y., 1961) p. 287
9. C. B. Kretschmer and H. L. Petersen, J. Chem. Phys. 39, 1772 (1963)
10. A. S. Vlastaras and C. A. Winkler, Can. J. Chem. 45, 2837 (1967)
11. W. E. Wilson, J. Chem. Phys. 46, 2017 (1967)
12. S. Miyazaki and S. Takahaski, Mem. Defense Acad. Japan 8, 469 (1968)
13. K. H. Becker, W. Groth and D. Kley, Z. Naturforschung 24A, 1280 (1969)
14. I. D. Clark and R. P. Wayne, Proc. Roy. Soc. A316, 539 (1970)
15. A. A. Westenberg, J. M. Roscoe and N. DeHaas, Chem. Phys. Letts. 7, 597 (1970)
16. C. T. Bowman, Combustion Sci. Tech. 3, 37 (1971)
17. J. B. Livesey, A. L. Roberts and A. Williams, Combustion Sci. Tech. 4, 9 (1971)
18. H. K. Newhall and S. M. Shahed, 13th Combustion Symp. 381 (1971)

## $N + O_2 \rightarrow NO + O$

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of NO with O

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO + O \rightarrow N + O_2$ | 133.2 | (31.83) |

### Preferred value:

$k_1 = 2.5 \times 10^{-15}\ T \exp\{-19.5 \times 10^3/T\}\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $1000\ K < T < 3000\ K$

Reliability: log k ± 0.12 at 1000 K increasing to log k ± 0.3 at 3000 K

### Remarks:

The expression is calculated from the reverse rate constant, $1.1 \times 10^{-14}\ T \exp\{-3.15 \times 10^3/T\}\ cm^3 molecule^{-1} s^{-1}$, and equilibrium data, log K(1000) = -7.66, log K(1500) = -5.34, log K(2000) = -4.17, log K(3000) = -3.00. It is in excellent agreement with the data of (2 and 5). $K = k_1/k_{-1}$

### References considered:

1. F. Kaufman and J. R. Kelso, J. Chem. Phys. 23, 1702 (1955)
2. F. Kaufman and L. J. Decker, 7th Combustion Symp. 57 (1959)
3. K.G.P. Sulzmann and C.B. Ludwig, General Dynamics Corp./Convair Division, Report ZPh-087 (1961), AD 269 383.
4. K. L. Wray and J. D. Teare, J. Chem. Phys. 36, 2582 (1962)
5. T. C. Clark, S. H. Garnett and G. B. Kistiakowsky, J. Chem. Phys. 51, 2885 (1969)

### Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitrogen atom with ozone

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $N + O_3 \rightarrow NO + O_2$ | -525.4 | (-125.6) |

Preferred value:

$k_1 = 5.7 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 298K

Reliability: Uncertainty in log $k_1$: ± 0.2 at 298K

Remarks:

Two determinations of $k_1$ have been made in discharge-flow systems. Chen and Taylor (1) found $N_2O$ as the only stable product and deduced a value for $k_1$ by assuming a detailed mechanism giving rise to $N_2O$. However, Phillips and Schiff (2) could not detect $N_2O$ in the products of the $O_3$ + N reaction. They determined $k_1$ by monitoring the removal of $O_3$ by mass spectrometry and applying a second order derivation. Their value of $k_1$ at 298 K is recommended above.

References considered:

1. M. C. Chen and H. A. Taylor, J. Chem. Phys. 34, 1344 (1961)
2. L. F. Phillips and H. I. Schiff, J. Chem. Phys. 36, 1509 (1962)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of $N_2$ with $O_2$ to form $N_2O$ and O

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $N_2 + O_2 \rightarrow N_2O + O$ | 331.3 | (79.18) |

Preferred value:

$1.0 \times 10^{-10} \exp\{-55.2 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 1200 K $<$ T $<$ 2000 K

Reliability: log k ± 0.4

Remarks:

There are no experimental data for the rate of this reaction. The above expression is calculated from our recommendation for the rate of the reverse reaction ($k_{rev} = 1.7 \times 10^{-10} \exp\{-14.1 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$, 1200-2000 K) and equilibrium constant data (log K(1000) = -17.98, log K(1500) = -12.10 and log K(2000) = -9.12).

References considered:

None

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of $N_2O$ with O to form $N_2$ and $O_2$

| | | $\Delta H(300)$ kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $N_2O + O \rightarrow N_2 + O_2$ | -331.3 | (-79.18) |

Preferred value:

$k_1 = 1.7 \times 10^{-10} \exp\{-14.1 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: 1200 K $< T <$ 2000 K

Reliability: log k ± 0.4

Remarks:

The data from (1,6,8,9,10 and 11) indicate that $k_1/k_2 = 1.0 \pm 0.2$ in the range 1000-2800 K.

(1) $N_2O + O \rightarrow N_2 + O_2$

(2) $N_2O + O \rightarrow NO + NO$

The recommended rate constant expression is based on this ratio and our recommendation for $k_2$, i.e. the expression derived by Fenimore and Jones (5), $k_2 = 1.7 \times 10^{-10} \exp\{-14.1 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$ (1200-2000 K).

References considered:

1. F. Kaufman, N. J. Gerri and R. E. Bowman, J. Chem. Phys. 25, 106 (1956)
2. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 27, 1141 (1957)
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6. W. Jost, K. W. Michel, J. Troe and H. Gg. Wagner, Z. Naturforschung 19a, 59 (1964)
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8. D. Gutman, R. L. Belford, A. J. Hay and R. Pancirov, J. Phys. Chem. 70, 1793 (1966)
9. A. A. Borisov, Kin. i Kat. 9, 482 (1968). English translation p. 399.
10. S. C. Barton and J. E. Dove, Can. J. Chem. 47, 521 (1969)
11. H. Henrici and S. H. Bauer, J. Chem. Phys. 50, 1333 (1969)

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

| The reaction of NO with NO to form $N_2O$ and O | $\Delta H(300)$ kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|
| (1) $NO + NO \rightarrow N_2O + O$ | 150.7 | (36.02) |

Preferred value:

$k_1 = 2.2 \times 10^{-12} \exp\{-32.1 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

k defined by $-d[NO]/dt = 2k[NO]^2$

Temperature range: $1200 \text{ K} < T < 2000 \text{ K}$

Reliability: log k ± 0.3

Remarks:

This is the expression derived by Kaufman and Kelso (6). Kaufman and Kelso (6) and Freedman and Daiber (8) monitored the rate of NO removal but assumed that the reaction gave $N_2 + O_2$ as products.

(2) $NO + NO \rightarrow N_2 + O_2$

Yuan et al (7) also followed the removal of NO but did not specify the reaction products. However Camac and Feinberg (10) have demonstrated that the products of the bimolecular reaction of NO were $N_2O + O$.

(1) $NO + NO \rightarrow N_2O + O$

An Arrhenius expression plotted through the data from (5,6,7,8 and 10) gives an anomalously high A-factor and predicts values of $k_{-1}$ which disagree with the direct data for $k_{-1}$. We consider that the high temperature data (7,8 and 10) represent upper limits for $k_1$ because of the occurrence of other NO-consuming reactions which were not adequately allowed for in the data analyses. The expression of Kaufman and Kelso (6) satisfactorily describes the data of (5 and 6) and also is in agreement with the data of Fenimore and Jones (9) for $k_{-1}$.

(-1) $N_2O + O = NO + NO$

References considered:

1. S. Dushman, J. Am. Chem. Soc. 43, 397 (1921)
2. J. Zeldovich, Acta Physicochim. URSS, 21, 577 (1946)
3. K. Vetter, Z. Elektrochem. 53, 369, 376 (1949)
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8. E. Freedman and J. W. Daiber, J. Chem. Phys. 34, 1271 (1961)
9. C. P. Fenimore and G. W. Jones, 8th Combustion Symp. 127 (1962)
10. M. Camac and R. M. Feinberg, 11th Combustion Symp. 137 (1967)

## $NO + NO \rightarrow N_2O + O$

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of $N_2O$ with O to form NO

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $N_2O + O \rightarrow NO + NO$ | -150.7 | (-36.02) |

**Preferred value:**

$k_1 = 1.7 \times 10^{-10} \exp\{-14.1 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$

$k_1$ defined by $-d[N_2O]/dt = 1/2\ d[NO]/dt = k_1[N_2O][O]$

Temperature range: $1200\ K < T < 2000\ K$

Reliability: $\log k \pm 0.3$

**Remarks:**

The expression is that suggested by Fenimore and Jones (8). The experimental data are scattered. The results from (6 and 12) refer to the removal of $N_2O$ by reactions 1 and 2.

(1) $N_2O + O \rightarrow NO + NO$

(2) $N_2O + O \rightarrow N_2 + O_2$

The available evidence (2,11,13,14,15 and 16) suggests that $k_1/k_2 = 1.0 \pm 0.2$ in the temperature range 1200-2000 K and so we have divided the data from (6 and 12) by two. The flame study of Fenimore and Jones (8) utilized a relatively direct technique for monitoring reaction 1 and their rate expression is in excellent agreement with our recommendation for reaction (-1) (1200-2000 K).

(-1) $NO + NO \rightarrow N_2O + O$

**References considered:**

1. F. C. Henriques, A.B.F. Duncan and W. A. Noyes, J. Chem. Phys. 6, 518 (1938)
2. F. Kaufman, N.J. Gerri and R. E. Bowman, J. Chem. Phys. 25, 106 (1956)
3. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. 27, 1141 (1957)
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10. C. B. Kretschmer, Aerojet-General Corp., Report AN-671 (1962)
11. W. Jost, K. W. Michel, J. Troe and H. Gg. Wagner, Z. Naturforschung 19a, 59 (1964)
12. E. S. Fishburne and R. Edse, J. Chem. Phys. 44, 515 (1966)

References (contd):

13. D. Gutman, R. L. Belford, A. J. Hay and R. Pancirov, J. Phys. Chem. 70, 1793 (1966)
14. A. A. Borisov, Kin. i Kat. 9, 482 (1968), English translation p. 399.
15. S. C. Barton and J. E. Dove, Can. J. Chem. 47, 521 (1969)
16. H. Henrici and S. H. Bauer, J. Chem. Phys. 50, 1333 (1969)

Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitric oxide, nitrogen dioxide and oxygen

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO + NO_2 + O_2 \rightarrow NO_2 + NO_3$ | -19.2 | (-4.59) |

($NO_3$ is the symmetric nitrate radical)

### Preferred value:

$k_1 = 8 \times 10^{-41} \exp[+400/T]$ $cm^6 molecule^{-2} s^{-1}$

Temperature range: $300 < T < 500$ K

Reliability: Uncertainty in log $k_1$: ±0.4 in temperature range quoted

### Remarks:

The above expression is based entirely on the rate constant for the reverse reaction and equilibrium data. Above 500 K, the activation energy steadily increases and becomes positive above ~ 800 K. The value of $k_1$ deduced from a study of the $NO_2$ catalysed oxidation of ClNO at 298 K by Ray and Ogg (1) is within a factor of two of the above expression.

### References considered:

1. J. D. Ray and R. A. Ogg, J. Chem. Phys. 26, 984 (1957)

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitrogen dioxide with nitrogen trioxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ | 19.2 | (4.59) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1 = 2.3 \times 10^{-13} \exp(-1600/T)\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $300 < T < 850$ K

Reliability: Uncertainty in log $k_1$: ±0.4 in the temperature range quoted

Remarks:

Reaction 1 is analogous to reaction 2 and is not a simple dissociation of $NO_3$ to NO and $O_2$.

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2 \qquad (1)$$

$$NO_2 + NO_2 \rightarrow NO + NO + O_2 \qquad (2)$$

The existing data on $k_1$ were derived from analyses of the kinetics of (a) the thermal decomposition of $N_2O_5$ (1,2,5) and (b) the initial stages of the bimolecular $NO_2$ decomposition reaction (3,6). The approximate value of $k_1$ deduced by Berces and Forgeteg (7) from a study of the photolysis of $HNO_3$ vapor is not considered.

The first order rate constant for $N_2O_5$ disappearance ($k_o$) can be related to the product of $k_1$ and the equilibrium constant $k_3/k_{-3}$.

$$N_2O_5 + M \rightleftarrows NO_2 + NO_3 + M \qquad (3,-3)$$

Expressions for $k_1$ have been calculated from data on $k_o$ of Johnston and Tao (2) and Daniels and Johnston (1). In a shock tube study of $N_2O_5$/Ar mixtures, Schott and Davidson (5) monitored $NO_3$ and interpreted the decay in terms of reactions 1,-3 and 4.

$$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2 \qquad (4)$$

However, in view of some inconsistencies in their final results, their value should not be considered reliable.

Remarks (cont'd):

Ashmore and co-workers (3,6) investigated the early stages of the decomposition of $NO_2$ in which $NO_3$ contributes to the kinetics. First, they obtained an order of magnitude estimate for $k_1/k_5$.

$$NO + NO_3 \rightleftarrows NO_2 + NO_2 \qquad (5,-5)$$

but subsequently derived an expression for $k_5/k_1k_{-5}$ which, combined with thermodynamic data from (4 and 5) yielded $k_1 = 2.0 \times 10^{-13} \exp[-1600/T]\ cm^3 molecule^{-1} s^{-1}$.

We suggest that the data derived from Ashmore and Burnett (6) and Johnston and Tao (2) are the most reliable and base the recommended expression on them.

References considered:

1. F. Daniels and E. H. Johnston, J. Am. Chem. Soc. 43, 53 (1921)
2. H. S. Johnston and Y.-S. Tao, J. Am. Chem. Soc. 73, 2949 (1951)
3. P. G. Ashmore and B. P. Levitt, Research (Correspondence) 9, S25 (1956)
4. J. D. Ray and R. A. Ogg, J. Chem. Phys. 26, 984 (1957)
5. G. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)
6. P. G. Ashmore and M. G. Burnett, Trans. Faraday Soc. 58, 253 (1962)
7. T. Berces and S. Forgeteg, Trans. Faraday Soc. 66, 640 (1970)
8. H. S. Johnston, J. Am. Chem. Soc. 73, 4542 (1951)

Evaluators:

D. L. Baulch, D. D. Drysdale, D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitric oxide with nitrogen trioxide

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO + NO_3 \rightarrow NO_2 + NO_2$ | -95.2 | (-22.75) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1 \approx 2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$

$- d[NO]/dt = (1/2) d[NO_2]/dt = k_1 [NO][NO_3]$

Temperature: 300 K

Reliability: Uncertainty in log $k_1$: ±0.7

Remarks:

Values of $k_1$ have been obtained only from analyses of complex systems. Johnston (1) and Hisatsune et al (3) examined the kinetics of the $N_2O_5/NO$ system and estimated $k_1k_2/k_{-2}$

$$NO + NO_3 \rightarrow NO_2 + NO_2 \qquad (1)$$

$$N_2O_5 + M \rightleftarrows NO_2 + NO_3 + M \qquad (2,-2)$$

Using equilibrium data on reaction 2, the results of Hisatsune et al (3) lead to $1.8 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$, close to Johnston's lower limit ($k > 1.6 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$).

Ford et al (5) analysed the photolysis of $NO_2/O_3$ mixtures and interpreted the results in terms of a mechanism comprising six reactions. They deduced $k_1k_{-2}/k_2$ at 300 K, but their value depended on values of $k_3$ and $k_4$ (2) which are probably unreliable. The value of $k_1$ calculated from their result ($6.5 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$) is about a factor of two less than Hisatsune's result (3).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (3)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4)$$

The remaining data are very scattered. Ashmore and Burnett (6) examined the kinetics of the early stages of $NO_2$ decomposition in which reaction-1 contributes to the initial removal of $NO_2$. The expression deduced for $k_{-1}$ (473-707 K) gives $k_1$ about a factor of ten less than the room temperature values described above. The reason for this is not clear. Husain and Norrish (7) studied the flash photolysis of $NO_2/N_2$ mixtures, monitoring $NO_3$ by kinetic spectroscopy, and deduced a value of the ratio $k_1/k_5$.

Remarks (cont'd):

$$NO_2 + O + M \rightarrow NO_3 + M \qquad (5)$$

The value of $k_5$ assumed in this work may be a factor of five too high and consequently $k_1$ may be considerably less than their value ($1.4 \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$. Finally, Morrison et al (9) interpreted the thermal oxidation of NO in terms of a complex mechanism involving the species $NO_3$, $N_2O_3$, $N_2O_4$ and $N_2O_5$ and deduced a value for the ratio $k_1k_6/k_{-6}$ at 300 K.

$$NO + O_2 \rightleftarrows NO_3 \qquad (6,-6)$$

In view of the complexity of this system no reliance can be placed on the value of $k_1$ obtained by combining this ratio with equilibrium data on reaction 6, assuming $NO_3$ to be the symmetric nitrate radical.

We suggest that the consensus value $k_1 \approx 2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ be used at 300 K, but recommend wide error limits.

References considered:

1. H. S. Johnston, J. Am. Chem. Soc. 73, 4542 (1951)
2. H. W. Ford, G. J. Doyle and N. Endow, J. Chem. Phys. 26, 1336 (1957)
3. I. C. Hisatsune, B. Crawford and R. A. Ogg, J. Am. Chem. Soc. 79, 4648 (1957)
4. G. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)
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Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The disproportionation of nitrogen dioxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + NO_2 \rightarrow NO + NO_3$ | 95.2 | (22.75) |

($NO_3$ is the symmetric nitrate radical)

### Preferred value:

None

### Remarks:

There are few data specifically concerning reaction 1. An approximate value of $2.2 \times 10^{-18}$ $cm^3 molecule^{-1} s^{-1}$ (707 K) was obtained by Ashmore and Levitt (1) in a study of the early stages of $NO_2$ decomposition. In similar work Ashmore and Burnett (4) and Graham (5) obtained expressions for $k_1$ in close agreement with each other and with (1). However, the available data on the reverse reaction cannot be reconciled with these expressions, and although we suggest an approximate value for $k_{-1}$ at 300 K, it is not possible with the existing data, to recommend an expression for $k_1$.

$$NO_2 + NO_2 \rightleftarrows NO + NO_3 \qquad (1,-1)$$

### References considered:

1. P. G. Ashmore and B. P. Levitt, Research (Correspondence) 9, S25 (1956)
2. I. C. Hisatsune, B. Crawford and R. A. Ogg, J. Am. Chem. Soc. 79, 4648 (1957)
3. G. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)
4. P. G. Ashmore and M. G. Burnett, Trans. Faraday Soc. 58, 253 (1962)
5. E. W. Graham, Ph.D. Thesis, University of California, Berkeley (1963)
6. N. Davidson and G. L. Schott, J. Chem. Phys. 27, 317 (1957)

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Voluem 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The combination of NO and O

| | $\Delta H(300)$ | |
|---|---|---|
| | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) $NO + O + M \rightarrow NO_2 + M$ | -306.4 | (-73.23) |

Preferred value:

$k_1 = 3.0 \times 10^{-33} \exp\{+0.94 \times 10^3/T\}$ $cm^6 molecule^{-2} s^{-1}$ $(M = Ar, O_2)$

Temperature range: $200\ K < T < 500\ K$

Reliability: log k ± 0.08

Remarks:

The selected expression is based primarily on the data of Clyne and Thrush (9), Kaufman and Kelso (13) and Hartley and Thrush (15) and also the data of Klein and Herron (11) after taking into account the relative third body efficiencies of $N_2$ and $O_2$. The following table lists the relative third body efficiencies that we recommend for use at ~300 K.

| M = $O_2$ | $N_2$ | Ar | He | $CO_2$ | $N_2O$ | $H_2O$ | $D_2O$ | $CH_4$ | $CF_4$ | $SF_6$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.4 | 1.0 | $0.7_5$ | 2.1 | 2.1 | 6.1 | 5.0 | 2.2 | 2.2 | 2.6 |

These efficiencies are derived primarily from the data in (13); the data in (5,6,7,9 and 15) were also considered. There is no information available on the variation of efficiencies with temperature.

References considered:

1. F. Kaufman, N. J. Gerri and R. E. Bowman, J. Chem. Phys. 25, 106 (1956)
2. H. W. Ford and N. Endow, J. Chem. Phys. 27, 1156 (1957)
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5. F. Kaufman, Proc. Roy. Soc. A247, 123 (1958)
6. F. Kaufman, J. Chem. Phys. 28, 352 (1958)
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8. D. Garvin, P. P. Gwyn and J. W. Moskowitz, Can. J. Chem. 38, 1795 (1960)
9. M.A.A. Clyne and B. A. Thrush, Proc. Roy. Soc. A269, 404 (1962)
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11. F. S. Klein and J. T. Herron, J. Chem. Phys. 41, 1285 (1964)
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## $NO + O + M \rightarrow NO_2 + M$

### References (contd.)

15. D. B. Hartley and B. A. Thrush, Proc. Roy. Soc. A297, 520 (1967)
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22. F. Stuhl and H. Niki, J. Chem. Phys. 55, 3943 (1971)
23. R. Atkinson and R. J. Cvetanovic, J. Chem. Phys. 56, 432 (1972)

### Evaluator:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The dissociation of $NO_2$ to NO and O

| | | $\Delta H(300)$ kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + M \rightarrow NO + O + M$ | 306.4 | (73.23) |

Preferred value:

$k_1 = 1.8 \times 10^{-8} \exp\{-33 \times 10^3/T\}$ $cm^3 molecule^{-1} s^{-1}$ (M = Ar)

Temperature range: 1400 K $< T <$ 2400 K

Reliability: log k ± 0.1

Remarks:

This is the expression derived by Troe (9). Apart from the preliminary results presented in (1), the various experimental determinations of this rate constant are in remarkable agreement (2,4,6,7,9 and 10). The only information on the relative efficiencies of different collision partners is the estimate by Fishburne and Edse (8) that $k(M = O_2) = k(M = Ar)$, 1600-2000 K, but this is not borne out by their own experimental results and is therefore not recommended.

References considered:

1. M. Steinberg and T. F. Lyon, 131st Natl. Meeting Am. Chem. Soc. 51R (1957)
2. R. E. Huffman and N. Davidson, J. Am. Chem. Soc. 81, 2311 (1959)
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9. J. Troe, Ber. Bunsenges. Physik. Chem. 73, 144 (1969)
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Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: February 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The combination of nitric oxide and molecular oxygen

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO + O_2 + M \rightarrow NO_3 + M$<br>($NO_3$ is the symmetric nitrate radical) | -19.2 | (-4.59) |

Preferred value:

None

Remarks:

This reaction has been invoked occasionally in the literature but there appears to be no direct evidence for it: only circumstantial evidence exists for the alternative process giving rise to the unsymmetric ONOO radical (2). Bahn (1) has confused reaction 1 with reaction 2, implying that $NO_2$ acts only as a collision partner

$$NO + O_2 + M \rightarrow NO_3 + M \qquad (1)$$

$$NO + NO_2 + O_2 \rightarrow NO_2 + NO_3 \qquad (2)$$

but it is likely that the mechanism is more complex than a simple three body collision: it is possibly similar to the nitric oxide oxidation reaction 3 (2).

$$NO + NO + O_2 \rightarrow NO_2 + NO_2 \qquad (3)$$

References considered:

1. G. S. Bahn, "Reaction Rate Compilation for the H-O-N System," (Gordon and Breach, New York, 1968) p. 65
2. D. L. Baulch, D. D. Drysdale and D. G. Horne, Evaluated Kinetic Data for High Temperature Reactions, Vol. II, (Butterworths, London, 1973) p. 285

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in reference (2).

## The oxidation of nitric oxide by ozone

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO + O_3 \rightarrow NO_2 + O_2$ | -199.9 | (-47.78) |

Preferred value:

$k_1 = 1.5 \times 10^{-12} \exp(-1330/T)$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $200 \text{ K} < T < 350 \text{ K}$

Reliability: Uncertainty in log $k_1$: ± 0.2 in temperature range quoted

Remarks:

Reaction 1 has been studied principally in flow systems, following reaction by u.v. absorption photometry (3,5), mass spectrometry (4, 10) and by monitoring the emission from the excited product $NO_2^*$ (6,7).

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

A stopped-flow technique (1) and a static photolysis system ($NO_2$ in air) (2) have also been used. The determinations by Thrush and his co-workers (6,7) appear to be the most reliable: the above expression is based principally on their work. Apart from the work of Ford (2) and Borok (3), which are unreliable on experimental grounds, the remaining data lie within a factor of 1.6 of our recommendation.

The chemiluminescent reaction has been studied in detail by Clyne et al (6) and Clough and Thrush (7) at low pressures (~ 2 mm Hg). Clyne et al (6) showed that the emission intensity was described by the relationship

$$I = I_o[NO][O_3]/[M]$$

where $I_o$ is dependent on the nature of M (7). They determined $I_o$ = 20.7 exp[-2100/T] $s^{-1}$ for $M = N_2, O_2$ in the spectral range 600-875 nm. Assuming a linear increase in intensity to 1100 nm, the pre-exponential factor becomes $1.2 \times 10^2 s^{-1}$ for the wider spectral range 600-1100 nm. Clough and Thrush (7) resolved the overall rate constant $k_1$ into two components $k_{1a}$ and $k_{1b}$ where

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1a)$$

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (1b)$$

The temperature dependence of $k_{1b}$ was assumed identical to that of $I_o$ (6).

Remarks (cont'd):

Fontijn et al (9) have shown how the chemiluminescent reaction may be used to monitor NO (or $O_3$) in polluted air. They used Clyne's expression for $I_o(M = N_2,O_2)$ in the range 600-875 nm, but quote the pre-exponential factor as 12 instead of 20.7 (6).

References considered:

1. H. S. Johnston and H. J. Crosby, J. Chem. Phys. 19, 799 (1951); 22, 689 (1954)
2. H. W. Ford, G. J. Doyle and N. Endow, J. Chem. Phys. 26, 1337 (1957)
3. M. T. Borok, Russ. J. Phys. Chem. 35, 1123 (1961)
4. L. F. Phillips and H. I. Schiff, J. Chem. Phys. 36, 1509 (1962); 37, 924 (1962)
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7. P. N. Clough and B. A. Thrush, Trans. Faraday Soc. 63, 915 (1967)
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Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitrogen dioxide with oxygen

|  |  | ΔH(300) |  |
|---|---|---|---|
|  |  | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO_2 + O_2 \rightarrow NO + O_3$ | 199.9 | (47.78) |

### Preferred value:

$k_1 = 2.8 \times 10^{-12} \exp[-25,400/T]$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $200 < T < 350$ K

Reliability: Uncertainty in log $k_1$: ±0.2 in temperature range quoted

### Remarks:

There are no data available on the rate of this reaction. The above expression is based on the rate constant for the reverse reaction and equilibrium data; it cannot be recommended for use at the high temperatures at which the reaction may be significant.

### References considered:

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the H -N -O System" (Butterworths, 1973 in press) by these authors.

# Chemical Kinetics Data Survey

## The association of nitrogen dioxide and nitrogen trioxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ | -92.9 | (-22.2) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1^o = 2.8 \times 10^{-30}\ cm^6 molecule^{-2} s^{-1}$ ($M=N_2O_5 + NO$) at 300 K

$k_1^\infty = 3.8 \times 10^{-12}\ cm^3 molecule^{-1} s^{-1}$

Temperature: 300 K

Reliability: Uncertainty in log $k_1^o$: ±0.3

Uncertainty in log $k_1^\infty$: ±0.4

Remarks:

There are no data available on the rate of this reaction. The values of $k_1^o$ and $k_1^\infty$ suggested above have been calculated from data on the reverse reaction (references 1 and 2 respectively) and the equilibrium constant.

References considered:

1. H. S. Johnston and R. L. Perrine, J. Am. Chem. Soc. 73, 4782 (1951)
2. R. L. Mills and H. S. Johnston, J. Am. Chem. Soc. 73, 938 (1951)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The dissociation of nitrogen pentoxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ | 92.9 | (22.2) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1^o = 2.2 \times 10^{-5} \exp(-9700/T)\ cm^3 molecule^{-1} s^{-1}$, ($M = N_2O_5 + NO$)

Temperature range: $300 < T < 340$ K

$k_1^\infty = 5.7 \times 10^{14} \exp(-10\,600/T)\ s^{-1}$

Temperature range: $273 < T < 300$ K

Reliability: Uncertainty in log $k_1^o$: ±0.3 in temperature range quoted

Uncertainty in log $k_1^\infty$: ±0.4 in temperature range quoted

Remarks:

The decomposition of $N_2O_5$ proceeds with the dissociation reaction 1

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \qquad (1)$$

which is in its second order region at pressures below 0.1 mm Hg (3). Data on the second order rate constant $k_1^o$ were derived by three methods: (a) kinetic analysis (8) of low pressure ($< 2 \times 10^{-3}$ mm Hg) data on $N_2O_5$ decomposition (1), (b) kinetic analysis of the decomposition of $N_2O_5$ in the presence of NO (2,3,5,6) and (c) extrapolation of shock tube data on the apparent second order rate constant to zero pressure (7). The value derived by method(c)cannot be considered reliable as the extrapolation was based on only two experimental points. The remaining data are in satisfactory agreement: in view of the observation (2) that Mills and Johnston's results (3) may be high on account of heterogeneous effects, we prefer Johnston and Perrine's data (2) and recommend their expression for $k_1^o$.

Mills and Johnston (3) provide the only reliable data on the limiting high pressure first order rate constant $k_1^\infty$, obtained by extrapolating the apparent first order rate constant to infinite pressure. Amell and Daniels (4) and Hisatsune et al (6) quote first order rate constants, but these were obtained in the fall-off region and cannot be given any weight in this evaluation. We recommend the expression derived by Mills and Johnston (3).

## $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

References considered:

1. E. F. Linhorst and J. H. Hodges, J. Am. Chem. Soc. 56, 836 (1934)
2. H. S. Johnston and R. L. Perrine, J. Am. Chem. Soc. 73, 4782 (1951)
3. R. L. Mills and H. S. Johnston, J. Am. Chem. Soc. 73, 938 (1951)
4. A. R. Amell and F. Daniels, J. Am. Chem. Soc. 74, 6209 (1952)
5. H. S. Johnston, J. Am. Chem. Soc. 75, 1567 (1953)
6. I. C. Hisatsune, B. Crawford and R. A. Ogg, J. Am. Chem. Soc. 79, 4648 (1957)
7. G. L. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)
8. R. A. Ogg, J. Chem. Phys. 18, 572 (1950)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The combination of $NO_2$ and O atoms

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + O + M \rightarrow NO_3 + M$ | -211.2 | (-50.5) |

($NO_3$ is the symmetric nitrate radical)

**Preferred value:**

$k_1^\infty = 1.8 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$

$k_1^o = 6.3 \times 10^{-32}$ $cm^6 molecule^{-2} s^{-1}$ ($M=N_2$)

Temperature: 295 K

Reliability: Uncertainty in log $k_1^\infty$ and log $k_1^o$: ±0.4 at 295 K

**Remarks:**

The O-atom addition and abstraction reactions 1 and 2 become competitive only at pressures of the order of one atmosphere.

$$NO_2 + O + M \rightarrow NO_3 + M \qquad (1)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (2)$$

Early work on the photolysis of $NO_2$ in the presence of nitrogen at 1 atm assumed that reaction 1 occurred but did not investigate its pressure dependence (1,2). Troe (4) studied the photolysis of $NO_2$ at 366 nm in $N_2$ at pressures up to 200 atm and determined the ratio $k_1/k_2$. He found reaction 1 to be in its third order region below 8 atm and in its fall off region at 10 atm. He obtained $k_1^o/k_2 = 1.1 \times 10^{-20}$ $cm^3 molecule^{-1}$ and $k_1^\infty/k_2 = 3$. The values of $k_1^o$ and $k_1^\infty$ recommended above were calculated using $k_2$ from (5). Smith (3) also found a pressure effect in the relative rates of the reactions of O with $NO_2$ and $CS_2$ which he attributed to reaction 1: values of $k_1$ at 298 and 410 K indicated a pronounced negative temperature coefficient. However, in view of the complexity of the system studied, we do not place any weight on Smith's results.

**References considered:**

1. H. W. Ford and N. Endow, J. Chem. Phys. 27, 1156, 1277 (1957)
2. E. A. Schuck, E. R. Stephens and R. R. Schrock, J. Air Poll. Control Assocn. 11, 695 (1966)
3. I.W.M. Smith, Trans. Faraday Soc. 64, 378 (1968)
4. J. Troe, Ber. Bunsenges. Physik. Chem. 73, 906 (1969)
5. D. L. Baulch, D. D. Drysdale and D. G. Horne, Evaluated Kinetic Data for High Temperature Reactions, Vol. II (Butterworths, 1973), p. 271

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

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in reference (5).

## The dissociation of nitrogen trioxide

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO_3 + M \rightarrow NO_2 + O + M$ | 211.2 | (50.5) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1 \simeq 8 \times 10^{-42}$ $cm^3 molecule^{-1} s^{-1}$ $M=N_2$

Temperature: 295 K

Remarks:

There are no reliable data on the rate of reaction 1.

$$NO_3 + M \rightarrow NO_2 + O + M \qquad (1)$$

The above value is calculated from the recommended value for the reverse rate constant and equilibrium data. Schott and Davidson (1) estimated $k_1$ (M=Ar) = $4.2 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$ at 1216 K from results on the rate of disappearance of $NO_3$ from shocked $N_2O_5$/Ar mixtures: little reliance can be placed on this figure as reaction 1 made only a minor contribution to the overall removal of $NO_3$.

References considered:

1. G. L. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The oxidation of nitrogen dioxide by ozone

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_2 + O_3 \rightarrow NO_3 + O_2$ | -104.6 | (-25.0) |

($NO_3$ is the symmetric nitrate radical)

### Preferred value:

$k_1 = 9.8 \times 10^{-12} \exp(-3500/T)$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $286 < T < 302$ K

Reliability: Uncertainty in log $k_1$: ± 0.3 in temperature range quoted

### Remarks:

Direct determinations of $k_1$ have been made by stopped-flow (1) and stirred-flow (2) methods, monitoring reaction by absorption photometry. The results, which differed by a factor of two, cannot easily be reconciled. However, in view of the apparent precision of Johnston and Yost's data (1) we recommend that their expression for $k_1$ (shown above) be used, although with wide error limits. A recent paper by Scott et al (3) describes an indirect determination of $k_1$ obtained in a study of the flash photolysis of $NO_2/O_3$ mixtures. In view of the complexity of the system studied, we place no weight on their value which lies a factor of 5 below the data of Johnston and Yost.

### References considered:

1. H. S. Johnston and D. M. Yost, J. Chem. Phys. 17, 386 (1949)
2. H. W. Ford, G. J. Doyle and N. Endow, J. Chem. Phys. 26, 1336 (1957)
3. P. M. Scott, K. F. Preston, R. J. Andersen and L. M. Quick, Can. J. Chem. 49, 1808 (1971)
4. M. Nicolet, J. Geophys. Res. 70, 679 (1965)

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitrogen trioxide with oxygen

|  |  | ΔH(300) |  |
|---|---|---|---|
|  |  | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO_3 + O_2 \rightarrow NO_2 + O_3$ | 104.6 | (25.0) |

($NO_3$ is the symmetric nitrate radical)

Preferred value:

$k_1 = 7 \times 10^{-34}$ $cm^3 molecule^{-1} s^{-1}$

Temperature: 300 K

Reliability: Uncertainty in log $k_1$: ±0.3 at 300 K

Remarks:

$$NO_3 + O_2 \rightarrow NO_2 + O_3 \qquad (1)$$

There are no data on the rate of this reaction. The recommended expression for $k_{-1}$ predicts $k_1 \simeq 7 \times 10^{-34}$ $cm^3 molecule^{-1} s^{-1}$ at 300 K and an activation energy of ~ 32 kcal $mol^{-1}$. Clearly this reaction will be unimportant at ambient temperatures.

References considered:

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The decomposition of nitrogen trioxide

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$ | -76.0 | (-18.16) |

($NO_3$ is the symmetric nitrate radical)

**Preferred value:**

$k_1 = 5 \times 10^{-12} \exp(-3000/T)$ $cm^3 molecule^{-1} s^{-1}$

$-d[NO_3]/dt = 2k_1[NO_3]^2$

Temperature range: $293 < T < 309$ K

Reliability: Uncertainty in log $k_1$: ±0.5 in temperature range quoted

**Remarks:**

Schott and Davidson (2) estimated $k_1$ from data of Schumacher and Sprenger (1) on the decomposition of $O_3$ in the presence of $N_2O_5$ at 293 and 309 K. Their expression is used by Johnston et al (3) and is recommended above, but only in the narrow temperature range quoted. The error at higher temperatures could be large. Schott and Davidson also estimated $k_1 = 3.8 \times 10^{-14}$ $cm^3 molecule^{-1} s^{-1}$ at 820 K by monitoring the decay of $NO_3$ in shocked $N_2O_5/NO_2/Ar$ mixtures. However, little reliance can be placed on this figure.

**References considered:**

1. H. J. Schumacher and G. Sprenger, Z. Physik. Chem. B2, 267 (1929)
2. G. Schott and N. Davidson, J. Am. Chem. Soc. 80, 1841 (1958)
3. H. S. Johnston, J. Lewis and L. Zafonte, Project Clean Air, Task Force 7, Preliminary report, 1970

**Evaluators:**

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of nitrogen atom with hydroxyl

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $N + OH \rightarrow NO + H$ | -203.8 | (-48.7) |

Preferred value:

$k_1 = 5.3 \times 10^{-11}\ cm^3 molecule^{-1} s^{-1}$

Temperature range: 300 K

Reliability: Uncertainty in log $k_1$: ± 0.3 at 300 K

Remarks:

The two available data on reaction 1 were obtained in discharge flow systems. Garvin and Broida (1) estimated $k_1 > 10^{-11}\ cm^3 molecule^{-1} s^{-1}$ at 300 K from observations of the effect of H atoms on the $O_3 + N$ reaction. Campbell and Thrush (2) studied the reaction of mixtures of N and O atoms with $H_2$ and deduced $k_1/k_2 = 1.4 \pm 0.1$ from analyses of the atom decay rates. Taking $k_2$ from (3), we obtain $k_1 = 5.3 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$, which is recommended above. No information is available on the temperature dependence, although it is likely to be small.

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

References considered:

1. D. Garvin and H. P. Broida, 9th Combustion Symp. 678 (1963)
2. I. M. Campbell and B. A. Thrush, Trans. Faraday Soc. 64, 1265 (1968)
3. D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions. Vol. I (Butterworths, 1972) p. 37

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydroxyl with nitrogen molecules

| | | $\Delta H(300)$ kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $N_2 + HO \rightarrow N_2O + H$ | 261.0 | (62.38) |

Preferred value:

$k_1 = 2.5 \times 10^{-12} \exp[-39\ 100/T]$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $700 < T < 2500$ K

Reliability: Uncertainty in log k: ± 0.2 in the temperature range quoted

Remarks:

No experimental data are available on the rate of reaction 1. The preferred expression was obtained by combining $k_{-1}$ (q.v.) with equilibrium data.

(-1) $N_2O + H \rightarrow N_2 + HO$

Clearly reaction 1 will become significant only at very high temperatures ($T > 3000$ K) at which the error in $k_1$ calculated from the above expression is unknown and may be large.

References considered:

None

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

The reaction of hydrogen atoms with nitrous oxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $N_2O + H \rightarrow N_2 + HO$ | -261.0 | (-62.38) |

Preferred value:

$k_1 = 1.2_6 \times 10^{-10} \exp[-7600/T]\ cm^3 molecule^{-1} s^{-1}$

Temperature range: 700 $< T <$ 2500 K

Reliability: Uncertainty in log k: ± 0.2 in temperature range quoted.

Remarks:

Recent results by Baldwin et al (6) and Albers (reported in (7)) have established that the activation energy is higher than previously supposed (3,8). If the early data of Fenimore and Jones, obtained in flame studies, are recalculated using a revised calibration of the H-atom concentration, then, with the exception of two order of magnitude determinations at 400 K (2,4), the above expression adequately describes all the data. These data arise from a variety of sources viz. shock tube (5), flame (1,3), and discharge-flow systems (7) and a study of the reactions of $N_2O$ added to slowly reacting $H_2/O_2$ mixtures (6).

References considered:

1. C. P. Fenimore and G. W. Jones, J. Phys. Chem. 63, 1154 (1959)
2. M. Schiavello and G. G. Volpi, J. Chem. Phys. 37, 1510 (1962)
3. G. Dixon-Lewis, M. M. Sutton and A. Williams, 10th Combustion Symp. 495 (1965); J. Chem. Soc. 5724 (1965)
4. G.R.A. Johnson and M. Simic, J. Phys. Chem. 71, 1118 (1967)
5. H. Henrici and S. H. Bauer, J. Chem. Phys. 50, 1333 (1969)
6. R. R. Baldwin, A. Gethin and R. W. Walker, JCS Faraday I, 69, 352 (1973)
7. M. Gehring, K. Hoyermann, H. Schacke and J. Wolfrum,. 14th Combustion Symp. (1972)
8. K. Schofield, Planet. Space Sci. 15, 643 (1967)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The combination of hydrogen atom with nitric oxide

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $H + NO + M \rightarrow HNO + M$ | -208.7 | (-49.9) |

Preferred value:

$k_1 = 1.5 \times 10^{-32} \exp(+\ 300/T)\ cm^6 molecule^{-2} s^{-1}$, $(M = H_2)$

Temperature range: $230 < T < 700$ K

Reliability: Uncertainty in log $k_1$: ± 0.2 in temperature range quoted

Remarks:

There is good agreement between the five independent determinations of $k_1$

$$NO + H + M \rightarrow HNO + M \qquad (1)$$

The recommended expression is that derived by Kaufman (4) from the discharge-flow data of Clyne and Thrush (1,2). Subsequent work has supported the latter data at 300 K; in particular, Hikida's value of $k_1$ (7), obtained in a pulse radiolysis study, is in excellent agreement. The values obtained by Simonaitis (3) and Hartley and Thrush (5) are within a factor of four of the above expression: we do not place any weight on Callear and Wood's approximate value obtained by flash photolysis (6). Limited data on the relative efficiencies are given by Hartley and Thrush (5).

References considered:

1. M.A.A. Clyne and B. A. Thrush, Trans. Faraday Soc. 57, 1305 (1961)
2. M.A.A. Clyne and B. A. Thrush, Disc. Faraday Soc. 33, 139 (1962)
3. R. Simonaitis, J. Phys. Chem. 67, 2227 (1963)
4. F. Kaufman, Ann. Geophys. 20, 106 (1964)
5. D. B. Hartley and B. A. Thrush. Proc. Roy. Soc. A297, 520 (1967)
6. A. B. Callear and P. Wood. Trans. Faraday Soc. 67, 3399 (1971)
7. T. Hikida, J. A. Eyre and L. M. Dorfman, J. Chem. Phys. 54, 3422 (1971)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The dissociation of HNO

|  |  | $\Delta H(300)$ |  |
|---|---|---|---|
|  |  | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $HNO + M \rightarrow NO + H + M$ | 208.7 | (49.9) |

### Preferred value:

$k_1 = 5 \times 10^{-8} \exp[-24{,}500/T]$ $cm^3 molecule^{-1} s^{-1}$ $M = H_2$

Temperature range: $230 < T < 700$ K

Reliability: Uncertainty in log $k_1$: ±0.2 in temperature range quoted

### Remarks:

There are no experimental data on the rate of reaction 1.

$$HNO + M \rightarrow NO + H + M \qquad (1)$$

The above expression is based on the recommended expression for the reverse rate constant and equilibrium data. The uncertainty in log k at temperatures above 700 K cannot be estimated.

### References considered:

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydrogen with nitric oxide

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $H_2 + NO \rightarrow HNO + H$ | 227.3 | (54.3) |

Preferred value:

$k_1 = 5.3 \times 10^{-18}\ cm^3 molecule^{-1} s^{-1}$

Temperature: 2000 K

Reliability: Uncertainty in log $k_1$: ±0.2 at 2000 K

Remarks:

There are no experimental data on reaction 1

$$NO + H_2 \rightarrow HNO + H \qquad (1)$$

The above value is based on the recommended value of $k_{-1}$ (1) and equilibrium data. The temperature dependence of $k_1$ is not known.

References considered:

1. C. J. Halstead and D. R. Jenkins, Chem. Phys. Letts. 2, 281 (1968)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydrogen atom with HNO

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $H + HNO \rightarrow H_2 + NO$ | -227.3 | (-54.3) |

Preferred value:

$k_1 = 8.0 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 2000 K

$10^{-13} < k_1 < 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 300 K

Reliability: Uncertainty in log $k_1$: ±0.2 at 2000 K

Remarks:

Studies of the NO-catalysed recombination of H atoms in flames have given values of $k_1$ in the region of 2000 K. We recommend $k_1$ = $8 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ obtained by Halstead and Jenkins from $H_2/O_2$ flames (5). Smith (6) has recently reported a value of $4 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ from $C_3H_8/O_2/N_2$ flames: the reason for this discrepancy is not obvious.

$$HNO + H \rightarrow H_2 + NO \qquad 1$$

At low temperatures, reaction 1 is fast and difficult to measure. Clyne and Thrush (1) estimated a lower limit of $5 \times 10^{-14}$ $cm^3$ $molecule^{-1} s^{-1}$ from a discharge-flow study of the H + NO reaction. Kohout and Lampe (4), studying the mercury photosensitised reaction between $H_2$ and NO, monitoring HNO and the product $N_2O$ by mass spectrometry, obtained an order of magnitude estimate of $k_1$ which we cautiously recommend above. However, it must be noted that Callear and Carr (7) have criticized Kohout and Lampe's experimental arrangement.

References considered:

1. M.A.A. Clyne and B. A. Thrush, Disc. Faraday Soc. 33, 139 (1962)
2. E. M. Bulewicz and T. M. Sugden, Proc. Roy. Soc. A277, 143 (1964)
3. R. M. Lambert, Chem. Comm. 850 (1966)
4. F. C. Kohout and F. W. Lampe, J. Chem. Phys. 46, 4075 (1967)
5. C. J. Halstead and D. R. Jenkins, Chem. Phys.Letts. 2, 281 (1968)
6. M. Y. Smith, Combustion and Flame 18, 293 (1972)
7. A. B. Callear and R. W. Carr, private communication (1972)

## $H + HNO \rightarrow H_2 + NO$

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydroxyl with nitric oxide to form nitrogen dioxide and hydrogen atoms

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $NO + HO \rightarrow NO_2 + H$ | 121.3 | (28.99) |

Preferred value:

$k_1 = 2.8 \times 10^{-12} \exp[-15\ 100/T]\ cm^3 molecule^{-1} s^{-1}$

Temperature range: $298 < T < 633$ K

Reliability: Uncertainty in log k: ± 0.2 at 298 K increasing to ±0.3 at 633 K

Remarks:

No experimental data are available on the rate of reaction 1

1. $NO + OH \rightarrow NO_2 + H$

-1. $NO_2 + H \rightarrow NO + OH$

The preferred expression was obtained by combining $k_{-1} = 5.8 \times 10^{-10} \exp(-740/T)$ with equilibrium data. Clearly reaction 1 will become significant only at high temperatures ($T > 1500$ K) at which the error in $k_1$ calculated from the above expression is unknown and may be large.

References considered:

None

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydrogen atoms with nitrogen dioxide to form nitric oxide and hydroxyl

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $NO_2 + H \rightarrow NO + HO$ | -121.3 | (-28.99) |

Preferred value:

$k_1 = 5.8 \times 10^{-10} \exp[-740/T]$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $298 < T < 633$ K

Reliability: Uncertainty in log k: ±0.2 in temperature range quoted

Remarks:

The most reliable value of $k_1$ is that of Phillips and Schiff (3) who examined reaction 1 in a discharge flow system, using mass spectrometry.

$$NO_2 + H \rightarrow NO + OH \qquad (1)$$

Rosser and Wise (1) obtained $k_1/k_2$ from a study of the $H_2/Cl_2/NO_2$ reaction:

$$Cl_2 + H \rightarrow HCl + Cl \qquad (2)$$

taking $k_2$ from (4) we obtain $k_1 = 1.5 \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$ at 500K. Ashmore and (2) examine the behaviour of $NO_2$ in slowly reacting $H_2/O_2$ mixtures and deduced a value of $k_3/k_1$: combining this with $k_3$ from (5) we obtain $k_1 = 1.8 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ at 633 K.

$$O_2 + H + H_2 \rightarrow HO_2 + H_2 \qquad (3)$$

The recommended expression is based on the latter value and $k_1 = 5 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ at 300 K (3): the value calculated from Rosser and Wise's data (1) lies within 12% of this expression at 500 K.

## $NO_2 + H \rightarrow NO + HO$

References considered:

1. W. A. Rosser and Wise, J. Chem. Phys. 65, 532 (1961); 65, 2277 (1961)
2. P. G. Ashmore and B. J. Tyler, Trans. Faraday Soc. 58, 1108 (1962)
3. L. F. Phillips and H. I Schiff, J. Chem. Phys. 37, 1233 (1962)
4. V. N. Kondratiev, Rate Constants of Gas Phase Reactions, (Science Publishing House, Moscow (1970)
5. D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions, Vol. 1 (Butterworths, London, 1972) p. 377

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of water with nitric oxide

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| (1) | $H_2O + NO \rightarrow HNO + OH$ | 290.6 | (69.46) |

Preferred value:

$k_1 = 3 \times 10^{-18}$ $cm^3 molecule^{-1} s^{-1}$

Temperature: 2000 K

Reliability: Uncertainty in log $k_1$: ±0.2 at 2000 K

Remarks:

There are no experimental data on reaction 1.

$$H_2O + NO \rightarrow HNO + OH \qquad (1)$$

The above value is based on the recommended value of $k_{-1}$ (1) and equilibrium data. The temperature dependence of $k_1$ is not known.

References considered:

1. C. J. Halstead and D. R. Jenkins, Chem. Phys. Letts. 2, 281 (1968)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of hydroxyl with HNO

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $OH + HNO \rightarrow H_2O + NO$ | -290.6 | (-69.46) |

**Preferred value:**

$k_1 = 6 \times 10^{-11}\ cm^3\ molecule^{-1}s^{-1}$

Temperature: 2000 K

Reliability: Uncertainty in log $k_1$: ±0.2 at 2000 K

**Remarks:**

Studies of the NO-catalysed recombination of atoms and radicals in flames have given data on $k_1$ in the region of 2000 K. We recommend $k_1 = 6 \times 10^{-11}\ cm^3 molecule^{-1}s^{-1}$ obtained by Halstead and Jenkins from $H_2/O_2$ flames (2) but point out that Smith (3) has recently determined $k_1 = 1.8 \times 10^{-11}\ cm^3 molecule^{-1}s^{-1}$ at 2117 K in $C_3H_8/O_2/N_2$ flames. The reason for this discrepancy is not clear.

**References considered:**

1. E. M. Bulewicz and T. M. Sugden, Proc. Roy. Soc. A277, 143 (1964)
2. C. J. Halstead and D. R. Jenkins, Chem. Phys. Letts. 2, 281 (1968)
3. M. Y. Smith, Combustion and Flame 18, 293 (1972)

**Evaluators:**

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The disproportionation of HNO

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| (1) | $HNO + HNO \rightarrow H_2O + N_2O$ | -358.9 | (-85.8) |

### Preferred value:

$k_1 = 4 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$

Temperature: 300 K

Reliability: Uncertainty in log $k_1$: ±0.3 at 300 K

### Remarks:

Kohout and Lampe (2) provided the first conclusive evidence for this reaction in a mass spectrometric study of the mercury-photosensitised $H_2/NO$ reaction

$$HNO + HNO \rightarrow H_2O + N_2O \qquad (1)$$

Their value for $k_1 = 6.7 \times 10^{-16}$ $cm^3 molecule^{-1} s^{-1}$ was obtained by comparing the decays of HNO and $N_2O$ following a period of photolysis. Callear and Carr (3) obtained $k_1 = 4 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$ by studying the flash photolysis and mercury-sensitised flash photolysis of $H_2/NO$ mixtures, monitoring HNO by kinetic spectroscopy. They attribute this discrepancy to a systematic error in Kohout and Lampe's work, arising from non-homogenous production of HNO in their photolysis cell. We recommend that Callear and Carr's value be used at 300 K.

### References considered:

1. M.A.A. Clyne, 10th Combustion Symp. 311 (1965)
2. F. C. Kohout and F. W. Lampe, J. Chem. Phys. 46, 4075 (1967)
3. A. B. Callear and R. W. Carr, private communication

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: April 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The dissociation of ammonia

| | | ΔH(300) kJ mol$^{-1}$ | (kcal mol$^{-1}$) |
|---|---|---|---|
| (1) | $NH_3 + Ar \rightarrow NH_2 + H + Ar$ | 452.3 | (108.1) |

Preferred value:

$k_1 = 1.5 \times 10^{-8} \exp[-42\,400/T]$ cm$^3$molecule$^{-1}$s$^{-1}$

Unimolecular reaction in its second order region below 4 atm (3-6).

Temperature range: $2000 < T < 3000$ K

Reliability: Uncertainty in log k: ± 0.3 in temperature range quoted

Remarks:

The decomposition of $NH_3$ has been studied in the temperature range 2000-3300 K by shock tube techniques. The results are scattered, particularly below 2500 K where induction periods (4,5,6) and fractional orders (1) have been reported. Clearly, the mechanism is complex (2). Henrici (4) monitored the removal of $NH_3$ during the induction period and deduced values of k($NH_3$ + Ar) from experiments with very dilute $NH_3$/Ar mixtures. At low temperatures (2000-2500 K) and concentrations (0.03% $NH_3$) his results lie significantly lower than the other data (1,3,5,6): an Arrhenius expression based on these results is consistent with the data at 3000 K obtained at higher $NH_3$ concentrations (3,4). However, until this work is confirmed, we cannot recommend Henrici's expression for k($NH_3$ + Ar) and instead suggest the expression given above which is a compromise between the low concentration data (4) and the data of Michel and Wagner (3). More work is required to resolve the kinetics of ammonia decomposition between 2000 and 2500 K.

Of the remaining work, Jacobs (1) found a fractional order for $NH_3$ removal, reflecting a complex mechanism, and his data cannot be used directly to define k($NH_3$ + Ar). Takeyama and Miyama's results (5) lie somewhat higher than all the others, which may be due to the presence of impurities in their reagent gases. Bradley's data (6) are very scattered, perhaps as a consequence of the very high $NH_3$ concentrations used: he quotes an expression for k($NH_3$ + Ar) but gives no details of its calculation.

References considered:

1. T. A. Jacobs, J. Phys. Chem. 67, 665 (1963)
2. H. E. Avery and J. N. Bradley, Trans. Faraday Soc. 60, 857 (1964)
3. K. W. Michel and H. Gg. Wagner, 10th Combustion Symp. 353 (1965)
4. H. Henrici, Ph.D. Thesis, Göttingen (1966)

References considered (cont'd):

5. T. Takeyama and H. Miyama, Bull. Chem. Soc. Japan 39, 2352 (1966)
6. J. N. Bradley, R. N. Butlin and D. Lewis, Trans. Faraday Soc. 63, 2962 (1967)
7. M. C. Branch and R. F. Sawyer, Dept. Mech. Eng., Thermal Systems Division, Univeristy of California, Berkeley, Report TS-71-1 (1971)
8. K. Schofield, General Motors Corp., Delco Electronic Division, Report TR-71-57 (1971)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Voluem 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterowrths, 1973 in press) by these authors.

## The combination of amino with hydrogen atoms to form ammonia

| | | ΔH(300) kJ $mol^{-1}$ | ($kcal\ mol^{-1}$) |
|---|---|---|---|
| (1) | $NH_2 + H + Ar \rightarrow NH_3 + Ar$ | -452.3 | (-108.1) |

### Preferred value:

$k_1 = 1.2 \times 10^{-33} \exp[11200/T]\ cm^6 molecule^{-2} s^{-1}$

Temperature range: $2000 < T < 3000$ K

Reliability: Uncertainty in log k: ± 0.3 in temperature range quoted

### Remarks:

The above expression is based entirely on the rate constant of the reverse reaction and equilibrium data. Gordon et al (1) reported a value of k($NH_2$ + H + M) at 300 K but this cannot be considered reliable as they assumed that the competing reaction $NH_2 + NH_2 \rightarrow N_2H_4$ was in its second order region below 1 atm pressure. This is probably incorrect.

### References considered:

1. S. Gordon, W. Mulac and P. Nangia, J. Phys. Chem. 75, 2087 (1971)

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of ammonia with hydrogen atoms

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| 1. | $NH_3 + H \rightarrow NH_2 + H_2$ | 16.2 | (3.87) |

Preferred value:

$k_1 < 10^{-16}$ $cm^3 molecule^{-1} s^{-1}$ at 800 K

Reliability: Approximate upper limit only

Remarks:

The metathetical reaction 1 has been invoked a number of times in a variety of systems (2,4,7,8,9) and $k_1$ deduced from kinetic analyses of complex mechanisms (2,7,9).

1. $NH_3 + H \rightarrow NH_2 + H_2$

However, discharge-flow studies have revealed that the true rate constant may be as much as two orders of magnitude less than the values obtained in the other studies. Thus Albers et al (5) and Kurylo et al (6) could detect no net consumption of hydrogen atoms when ammonia was added to a stream of H-atoms in a discharge-flow system (800 and 750 K respectively). In subsequent experiments, Kurylo et al (6) observed a substitution reaction to take place when D-atoms were reacted with $NH_3$.

2. $NH_3 + D \rightarrow NH_2D + H$

More work on this system would be merited.

References considered:

1. M. Schiavello and G. G. Volpi, J. Chem. Phys. 37, 1510 (1962)
2. K. T. Aganesyan and A. B. Nalbandyan, Dokl. Akad. Nauk SSSR 160, 162 (1965)
3. R. Tunder, S. Mayer, E. Cook and L. Schieler, Aerospace Corp. Report TR-100(9210-02)-1 (1966)
4. F. T. Jones and T. J. Sworski, Trans. Faraday Soc. 63, 2411, 2426 (1967)
5. E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, 12th Combustion Symp. 313 (1969)
6. M. J. Kurylo, G. A. Hollinden, H. F. LeFevre and R. B. Timmons, J. Chem. Phys. 51, 4497 (1969)
7. C. Willis, A. W. Boyd and O. A. Miller, Can. J. Chem. 47, 3007 (1969)
8. J. A. Eyre and D. Smithies, Trans. Faraday Soc. 66, 2199 (1970)
9. A. W. Boyd, C. Willis and O. A. Miller, Can. J. Chem. 49, 2283 (1971)
10. M. C. Branch and R. F. Sawyer, University of California, Berkeley, Dept. Mech. Eng., Thermal Systems Div., Report TS-71-1 (1971)

## The reaction of amino with hydrogen molecules

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| 1. | $NH_2 + H_2 \rightarrow NH_3 + H$ | -16.2 | (-3.87) |

### Preferred value:

$k_1 < 10^{-16}$ $cm^3$ $molecule^{-1}s^{-1}$ at 800 K

Reliability: Approximate upper limit only

### Remarks:

There are no data available on this reaction. The above upper limit is based on an estimate of the upper limit of the rate constant

(-1) $NH_3 + H \rightarrow NH_2 + H_2$

for the reverse reaction, $k_{-1} < 10^{-16}$ $cm^3 molecule^{-1}s^{-1}$ at 800 K, and equilibrium data.

### References considered:

1. E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, 12th Combustion Symp. 313 (1969)

### Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## $NH_3 + H \rightarrow NH_2 + H_2$

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of ammonia with oxygen atoms to form amino and hydroxyl

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| 1. | $NH_3 + O \rightarrow NH_2 + HO$ | 23.8 | (5.7) |

Preferred value:

$k_1 = 2.5 \times 10^{-12} \exp[-3020/T]$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $300 < T < 1000$ K

Reliability: Uncertainty in log k: ± 0.2 in temperature range quoted.

Remarks:

The reaction between ammonia and oxygen atoms has been studied mainly in discharge-flow systems (2,3,5,7,8): the stoichiometry was considered in each case (except 2) and assumed to remain constant over the temperature range studied. Despite a surprising variation in the stoichiometries observed ($m = \Delta[O]/\Delta NH_3 = 8(3), 4.4(5)$ and $2.9(7)$), the agreement of the data from (3,5,7 and 8) is good although only the results of Albers et al (7) for a linear relationship on an Arrhenius plot (300-1000 K). The curvature in (3 and 8) may be due to the presence of $O_2$ in the system: molecular oxygen was absent from (5 and 7) but a curved Arrhenius plot was also obtained in (5). Heicklen and Cohen (9) have pointed out some inconsistencies in the kinetic treatment used by Wong and Potter (3,5) and accordingly we favor the work of Albers et al (7) and recommend above the rate constant which is based on their data.

Of the remaining determinations we reject Avramenko's data (2) as there appears to have been some impurity in their system. Fenimore and Jones' crude estimate (1) was based on NO yields in a $NH_3/H_2/O_2$ flame at 1600 K and cannot be considered reliable. Finally, although the expression derived by Aganesyan and Nalbandyan(4) from a study of the inhibition of the $CO/O_2$ lower explosion limit is in reasonable agreement with the other data, it is not possible to give it much weight in this evaluation.

References considered:

1. C. P. Fenimore and G. W. Jones, J. Phys. Chem. 65, 298 (1961)
2. L. I. Avramenko, R. V. Kolesnikova and N. L. Kuznetsova, Izvest. Akad. Nauk. SSSR, Otd. Khim, Nauk, 6, 983 (1962)
3. E. L. Wong and A. E. Potter, J. Chem. Phys. 39, 2211 (1963)
4. K. T. Aganesyan and A. B. Nalbandyan, Dokl. Akad. Nauk SSSR, 160, 162 (1965). English translation, p. 18.

## References considered (cont'd)

5. E. L. Wong and A. E. Potter, J. Chem. Phys. 43, 3371 (1965)
6. R. Tunder, S. Mayer, E. Cook and L. Schieler, Aerospace Corp. Report, TR-100 (9210-02)-1 (1966)
7. E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, 12th Combustion Symp. 313 (1969)
8. M. J. Kurylo, G. A. Hollinden, H. F. LeFevre and R. B. Timmons, J. Chem. Phys. 51, 4497 (1969)
9. J. Heicklen and N. Cohen, Comprehensive Chemical Kinetics, Vol. 6, editors C. H. Bamford and C.F.H. Tipper (Elsevier, Amsterdam, 1972) p. 1.

## Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of amino with hydroxyl to form ammonia and oxygen atoms

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| 1 | $NH_2 + HO \rightarrow NH_3 + O$ | -23.8 | (-5.7) |

**Preferred value:**

$k_1 = 1 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$

Temperature range: $300 < T < 1000$ K

Reliability: Uncertainty in log k: ± 0.2 in temperature range quoted

**Remarks:**

There are no data available on this reaction: the above expression is based on the rate constant for the reverse reaction (1).

(-1) $NH_3 + O \rightarrow NH_2 + HO$

$k_{-1} = 2.5 \times 10^{-12} \exp(-3020/T)$ $cm^3 molecule^{-1} s^{-1}$ and equilibrium data

The alternative reaction $NH_2 + HO \rightarrow H_2O + NH$ may be favored.

**References considered:**

1. E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, 12th Combustion Symp. 313 (1969)

**Evaluators:**

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

## The reaction of ammonia with hydroxyl to form amino and water

| | | ΔH(300) | |
|---|---|---|---|
| | | kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
| 1. | $NH_3 + HO \rightarrow NH_2 + H_2O$ | -47.1 | (-11.26) |

Preferred value:

No recommendation. See remarks

Remarks:

The few estimates of the rate constant of this reaction are badly scattered and cannot be usefully evaluated. A room temperature value of 3 x $10^{-13}$ $cm^3 molecule^{-1} s^{-1}$ by Wolfrum (5) seems high and at variance with recent results of Worley et al (6) which suggest that the reaction may proceed by an exchange, generating H atoms analogous to the $NH_3$ + D reaction (4).

2. $NH_3 + OH \rightarrow NH_2OH + H$

Further data on this reaction are required.

References considered:

1. C. P. Fenimore and G. W. Jones, J. Phys. Chem. 65, 298 (1961)
2. R. Tunder, S. Mayer, E. Cook and L. Schieler, Aerospace Corp. TR-100 (9210-02)-1 (1966)
3. E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, 12th Combustion Symp. 313 (1969)
4. M. J. Kurylo, G. A. Hollinden, H. F. LeFevre and R. B. Timmons, J. Chem. Phys. 51, 4497 (1969)
5. K. Hoyermann, W. Hack and J. Wolfrum (private communication, 1972)
6. S. D. Worley, R. N. Coltharp and A. E. Potter, Jr., J. Phys. Chem. 76, 1511 (1972)

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

The reaction of amino with water

| | | ΔH(300) kJ $mol^{-1}$ | (kcal $mol^{-1}$) |
|---|---|---|---|
| 1. | $NH_2 + H_2O \rightarrow NH_3 + OH$ | 47.1 | (11.26) |

Preferred value:

No recommendation. See remarks

Remarks:

There are no data available on this reaction and there are insufficient reliable data on its reverse for any estimate of the rate constant.

References considered:

None

Evaluators:

D. L. Baulch, D. D. Drysdale and D. G. Horne

Date: March 1973

Additional information on this reaction may be found in "Evaluated Kinetic Data for High Temperature Reactions. Volume 2. Homogeneous Gas Phase Reactions of the $H_2$-$N_2$-$O_2$ System" (Butterworths, 1973 in press) by these authors.

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| | |
|---|---|
| 4. TITLE AND SUBTITLE<br>CHEMICAL KINETICS DATA SURVEY<br>V. Sixty-Six Contributed Rate and Photochemical Data Evaluations on Ninety-Four Reactions | 5. Publication Date<br>6. Performing Organization Code |
| 7. AUTHOR(S)<br>Dr. David Garvin | 8. Performing Organization<br>NBSIR 73-206 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>NATIONAL BUREAU OF STANDARDS<br>DEPARTMENT OF COMMERCE<br>WASHINGTON, D.C. 20234 | 10. Project/Task/Work Unit No.<br>3160409<br>11. Contract/Grant No. |
| 12. Sponsoring Organization Name and Address<br>Climatic Impact Assessment Program<br>Department of Transportation<br>Washington D. C. 20590<br>and National Bureau of Standards | 13. Type of Report & Period Covered<br>Interim<br>14. Sponsoring Agency Code |

15. SUPPLEMENTARY NOTES

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

This report records the data evaluations contributed to the Climatic Impact Assessment Program chemical kinetics survey during the period Nov. 1972 - April 1973 by various kineticists and photochemists. Data are included on reactions of $O(^1D)$, $O(^1S)$, $O_2(^1\Delta)$, $CH_3ONO$, $CH_3O$, $CH_3O_2$, $H_2O_2$, $HO_2$, SO, $SO_2$ and the $H_2$-$N_2$-$O_2$ system.

17. KEY WORDS (Alphabetical order, separated by semicolons) Atmospheric chemistry; Chemical kinetics; Data evaluation; Gas phase reactions; Optical Absorption cross sections; Photochemistry; Quantum yields; Rate constants

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| | 20. SECURITY CLASS (THIS PAGE)<br>UNCLASSIFIED | 22. Price |