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Kinetic and Photochemical Data for Atmospheric Chemistry Reactions of the Nitrogen Oxides

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Kinetic and Photochemical Data for Atmospheric Chemistry Reactions of the Nitrogen Oxides

R. F. Hampson, Jr.

Center for Thermodynamics and Molecular Science
National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234

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This report contains 24 individual data sheets for thermal and photochemical reactions of importance in the atmospheric chemistry of the nitrogen oxides. For each reaction the available experimental data are summarized and critically evaluated, and a preferred value of the rate coefficient is given. The selection of the preferred value is discussed and an estimate of its accuracy is given. For the photochemical process the data are summarized, and preferred values for the photoabsorption cross section and primary quantum yields are given. These data sheets were prepared by the author for the evaluation by the CODATA Task Group on Chemical Kinetics to be published in the Journal of Physical and Chemical Reference Data.

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TABLE OF CONTENTS

Kinetic and Photochemical Data for Atmospheric Chemistry Reactions of the Nitrogen Oxides

R. F. Hampson

This report contains 24 individual data sheets for thermal and photochemical reactions of importance in the atmospheric chemistry of the nitrogen oxides. For each reaction the available experimental data are summarized and critically evaluated, and a preferred value of the rate coefficient is given. The selection of the preferred value is discussed and an estimate of its accuracy is given. For the photochemical process the data are summarized, and preferred values for the photoabsorption cross section and primary quantum yields are given. These data sheets were prepared by the author for the evaluation by the CODATA Task Group on Chemical Kinetics to be published in the Journal of Physical and Chemical Reference Data.

This work was supported in part by the High Altitude Pollution Program of the Office of Environmental Quality, Federal Aviation Adminstration and the Upper Atmospheric Physics Section of the National Aeronautics and Space Administration. It was also supported in part by the Office of Standard Reference Data, NBS.

Key words: Atmospheric chemistry, chemical kinetics, data evaluation, nitrogen oxides, photoabsorption cross section, photochemistry, quantum yield, rate coefficient.

1. Introduction

This report contains individual data sheets for 16 chemical reactions and 8 photochemical processes of importance in the atmospheric chemistry of the nitrogen oxides. These data sheets were prepared by the author for the evaluation by the CODATA Task Group on Chemical Kinetics to be published in the Journal of Physical and Chemical Reference Data. The Task Group convened to prepare this evaluation in a series of working sessions, the last held in May 1979 to put the manuscript in final form prior to submission for publication. The last meeting at which new data was considered for evaluation was held in December 1978. At that time the Task Group restricted its consideration to data published in the scientific literature, preprints of journal articles and significant new results presented at open scientific meetings. The evaluations contained in this report reflect the combined judgment of the entire Task Group whose membership consists of: J. A. Kerr (Chairman), D. L. Baulch, R. A. Cox, R. F. Hampson, J. Troe and R. T. Watson.

2. Guide to the Data Sheets

The data sheets are of two types, (i) those for the thermal reactions and (ii) those for the photochemical reactions.

2.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K.

The available kinetic data on the reactions are summarized under three headings, (i) Absolute Rate Coefficients, (ii) Relative Rate Coefficients and (iii) Reviews and Evaluations. Some of the earlier data summarized in previous evaluations have been omitted, except where the data have a direct bearing on the preferred data selected here. Under all three of the headings above the data are presented as absolute rate coefficients. If the temperature coefficient has been measured the results are given in a temperature-dependent form over a stated range of temperatures. For bimolecular reactions the temperature dependence is expressed in the normal Arrhenius form, $k = A \exp(-C/T)$ where $C = E/R$.

Single temperature data are presented as such and wherever possible the rate coefficient at 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The data listed under Reviews and Evaluations are from the most recent source if that source contains the same recommendations as earlier reviews.

The tables of data are supplemented by a series of comments summarizing the experimental details. For measurements of relative rate coefficients the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data is that preferred in the present evaluation.

The preferred rate coefficients are presented, (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated range of temperatures. This is followed by a statement of the error limits in log k at 298 K and in (E/R) for the temperature range of the preferred rate coefficient. Some comments on the assignment of errors are given later in this Introduction.

The "Comments" on the preferred values describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

2.2 Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K and calculated threshold wavelengths. This is followed by tables summarizing the avilable experimental data on, (i) absorption cross sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross section data and the preferred quantum yields at wavelength intervals of 5 nm where possible. The comments again describe how the preferred data were selected and include any other relevant points. The photochemical data sheets are also concluded with a list of references.

2.3 Asignment of Errors

Under the heading "reliability", estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$.

The assignment of these absolute error limits in k and E/R is a subjective assessment of the evaluators. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurements, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of ± 10% or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of two or even more. This can only mean that one or more of the studies has involved large systematic errors which are difficult to detect. This is hardly surprising since, unlike say molecular reactions, it is not possible to study atomic and free radical reactions in isolation and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of errors made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations made and the number of different techniques used. On the whole, our assessment of error limits errs towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum error limits of ± 100% are appropriate. At the present time we do not feel justified in assigning error limits to the parameters reported for the photochemical reactions.

$N + O_2 \rightarrow NO + O$

$\Delta H° = - 133.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.38 \times 10^{-11} \exp(-3570/T)$	412-755	Clyne and Thrush, 1961 [1]	(a)
8.6×10^{-17}	298*		
$(2.34 \pm 0.12) \times 10^{-11} \exp(-(3975 \pm 100)/T)$	300-910	Wilson, 1967 [2]	(b)
$(8.0 \pm 1.0) \times 10^{-17}$	300		
$5.5 \times 10^{-12} \exp(-3220/T)$	280-333	Becker, Groth and Kley, 1969 [3]	(c,g)
11.1×10^{-17}	298		
$(10.8 \pm 1.0) \times 10^{-17}$	302	Clark and Wayne, 1970 [4]	(d)
$(7.5 \pm 0.5) \times 10^{-17}$	298	Westenberg, Roscoe and de Haas, 1970 [5]	(b)
Reviews and Evaluations			
$1.1 \times 10^{-14}(T) \exp(-3150/T)$	300-3000	Baulch, et al, 1973 [6]	(e)
$5.5 \times 10^{-12} \exp(-3220/T)$	200-300	NASA, 1977 [7]	(f,g)

Comments

(a) Discharge flow, [N] monitored by titration with NO.

(b) Discharge flow, [N] monitored by ESR.

(c) Static system, [N] monitored by decay of N_2 first positive band intensity.

(d) Discharge flow, [N] monitored by titration with NO.

(e) Evaluation for temperature range 300-3000 K. Considered all studies listed here. Recommended in Hampson and Garvin, 1975 [8].

(f) Accepted results of Becker, et al, 1969 [3].

(g) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k = 8.9 \times 10^{-17}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

$k = 4.4 \times 10^{-12} \exp(-3220/T)$ over range 280-333 K

Reliability

$\Delta \log k = \pm 0.1$ at 298 K

$\Delta (E/R) = \pm 350$ K

Comments on Preferred Value

Preferred value at room temperature given as simple average of 298 K values in references [1-5]. The value of E/R is that of Becker et al, 1969 [3] and is accepted as most reliable value for use in this low temperature region.

References

[1] Clyne, M. A. and Thrush, B., Proc. R. Soc. London, Ser. A: 261, 259 (1961).

[2] Wilson, W. E., Jr., J. Chem. Phys. 46, 2017 (1967).

[3] Becker, K. H., Groth, W. and Kley, D., Z. Naturforsch., Teil A: 24, 1280 (1969).

[4] Clark, I. D. and Wayne, R. P., Proc. R. Soc. London, Ser. A: 316, 539 (1970).

[5] Westenberg, A. A., Roscoe, J. M. and de Haas, N., Chem. Phys. Lett. 7, 597 (1970).

[6] Baulch, D. L., Drysdale, D. A. and Horne, D. G., "Evaluated Kinetics Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System" Butterworths, London (1973).

[7] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

[8] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[9] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Pub. 513 (1978).

$N + O_3 \rightarrow NO + O_2$

$\Delta H^\circ = -525$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 1.4) \times 10^{-13}$	300	Phillips and Schiff, 1962 [1]	(a)
$\leq 5 \times 10^{-16}$	300	Stief, et al, 1979 [2]	(b)
Reviews and Evaluations			
5.7×10^{-13}	300	Baulch, et al, 1973 [3]	(c)
$2 \times 10^{-11} \exp(-1070/T)$	200-300	NASA, 1977 [4]	(d)

Comments

(a) Discharge flow, [N] and [O_3] monitored by mass spectrometric detection, results derived by 2nd order kinetics analysis.

(b) Flash photolysis and discharge flow experiments, [N] monitored by resonance fluorescence. No decay observed, upper limit given based on detection sensitivity.

(c) Accepted results of Phillips and Schiff, 1962 [1] with increased error limits.

(d) Accepted room temperature results of Phillips and Schiff, 1962 [1]. Pre-exponential factor assigned value similar to that for reactions of O_3 with O and with Cl; E/R value derived from fit to room temperature value.

Preferred Value

$k \leq 5 \times 10^{-16}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

Comments on Preferred Value

Preferred value is based on results reported by Stief et al, 1979 [2]. It is possible that the value reported by Phillips and Schiff, 1962 [1] is due to the rapid disappearance of O_3 initiated by H atom impurities according to the following catalytic cycle, which is equivalent to the reaction of N with O_3:

$$H + O_3 \rightarrow OH + O_2$$

$$N + OH \rightarrow NO + H$$

In this reagard it may be noted that in a study of flame spectra by Garvin and Broida, 1963 [5], visible and ultraviolet emission from possible excited products of reaction of N with O_3 was not observed unless H atoms were also present in the reaction zone, in which case visible and ultraviolet emission was observed from the species HO, NH, NO, N_2 and NH_2.

Reference

[1] Phillips, L. F. and Schiff, H. I., J. Chem. Phys. <u>36</u>, 1509 (1962).

[2] Stief, L. J., Payne, W. A., Lee, J. H. and Michael, J. V., J. Chem. Phys. <u>70</u>, 5241 (1979).

[3] Baulch, D. L., Drysdale, D. D. and Horne, D. G., data sheet in D. Garvin, Ed., Nat. Bur. Stand. (U.S.), NBSIR 73-206 (1973).

[4] NASA Reference Publication 1010, R. D. Hudson, Ed, Chapter 1 (1977).

[5] Garvin, D. and Broida, H. P., Ninth Symposium on Combustion, Academic Press, NY p. 678 (1963).

$N + NO \rightarrow N_2 + O$

$\Delta H^\circ = -313.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(8.2 \pm 1.4) \times 10^{-11} \exp(-(410 \pm 120)/T)$	298-670	Clyne and McDermid, 1975 [1]	(a,g)
$(2.2 \pm 0.2) \times 10^{-11}$	298		
$(2.7 \pm 0.4) \times 10^{-11}$	196-370	Lee, et al, 1978 [2]	(b)
$(4.0 \pm 0.2) \times 10^{-11}$	233-400		(c)
$(3.4 \pm 0.9) \times 10^{-11}$	196-400		(d)
<u>Reviews and Evaluations</u>			
2.7×10^{-11}	300-5000	Baulch, et al, 1973 [3]	(e)
$8.2 \times 10^{-11} \exp(-410/T)$	200-300	NASA 1977, [4]	(f,g)

Comments

(a) Discharge flow. [N] monitored by mass spectrometry.

(b) Discharge flow, [N] monitored by resonance fluorescence.

(c) Flash photolysis of N_2O, [N] monitored by resonance fluorescence.

(d) Reported value. Derived as mean value of results of two independent methods.

(e) Evaluation, based on all previously reported data. Recommended in Hampson and Garvin, 1975 [5].

(f) Accepted results of Clyne and McDermid, 1975 [1].

(g) Recommended in Hampson and Garvin, 1978 [6].

Preferred Value

$k = 3.4 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ over range 200-400 K

Reliability

$\Delta \log k = \pm 0.15$ at 298 K

$\Delta E/R = \pm 100$ K

Comments on Preferred Value

Preferred value is based on results of Lee et al, 1978 [2]. Reliability at room temperature based on consideration of these data and the 298 K results of Clyne and McDermid, 1975 [1]. Based on a critical reexamination of the high temperature data reported in reference [1], the temperature dependence reported therein is rejected.

References

[1] Clyne, M. A. A. and McDermid, I. S., J. Chem. Soc. Faraday Trans. 1 71, 2189 (1975).

[2] Lee, J. H., Michael J. V., Payne, W. A. and Stief, L. J., J. Chem. Phys. 69, 3069 (1978).

[3] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System" Butterworths, London (1973).

[4] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

[5] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.) Tech. Note 866 (1975).

[6] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.) Spec. Publ. 513 (1978).

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

$\Delta H°\ (1) = -\ 175\ kJ\ mol^{-1}$

$\Delta H°\ (2) = -\ 325\ kJ\ mol^{-1}$

$\Delta H°\ (3) = -\ 506\ kJ\ mol^{-1}$

$\Delta H°\ (4) = -\ \ 8\ kJ\ mol^{-1}$

Rate coefficient data $\qquad k = k_1 + k_2 + k_3 + k_4$

$k/cm^3\ molecule^{-1}s^{-1}$	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(1.85 \pm 0.22) \times 10^{-11}$	298	Phillips and Schiff, 1965 [1]	(a)
$(1.4 \pm 0.2) \times 10^{-12}$	298	Clyne and McDermid, 1975 [2]	(b)
<u>Reviews and Evaluations</u>			
no recommendation		Baulch, et al, 1973 [3]	(c)
1.4×10^{-12}	300	Hampson and Garvin, 1975 [4]	(d)
$2 \times 10^{-11} \exp(-800/T)$	200-300	NASA, 1977 [5]	(e,f)

Comments

(a) Discharge flow system, mass spectrometric detection. Monitored [NO_2] in excess N. From stoichiometric relationships measured under different experimental conditions, the following relative contributions of the primary reaction channels were derived: $k_1/k \approx 0.43$; $k_2/k = 0.33$; $k_3/k = 0.10$; $k_4/k = 0.13$.

(b) Discharge flow system, mass spectrometric detection. In separate experiments monitored [N] in excess NO_2 and monitored [NO_2] in excess N. Found significant increase in apparent rate constant value as initial stoichiometry was lowered. Measured yield of N_2O. Computer simulation of system used only the reaction channel to yield N_2O + O and the reactions of O with NO_2 and N with NO.

(c) Evaluation in 1973 of all previously published data. No recommendation given.

(d) Accepted results of Clyne and McDermid, 1975 [2]. Accepted both the value of k and the indicated products (i.e. N_2O + O).

(e) Accepted 298 K results in reference [2]. "A-factor" selected at 2×10^{-11}; E/R value derived from fit to measured value of k.

(f) Recommended in Hampson and Garvin, 1978 [6].

Preferred Value

$k = 1.4 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

$k_1/k = 1$

Reliability

$\Delta \log k = \pm 0.2$ at 298 K

Comments on Preferred Value

Preferred value is that reported by Clyne and McDermid, 1975 [2]. This recommendation also accepts the mechanism given in that reference, i.e. the only reaction channel is that yielding $N_2O + O$ as products. Confirmation of this mechanism in a separate study is desirable. Temperature dependent data on this rate constant are needed.

References

[1] Phillips, L. F. and Schiff, H. I., J. Chem. Phys. 42, 3171 (1965).

[2] Clyne, M. A. A. and McDermid, I. S., J. Chem. Soc. Faraday Trans. 1 71, 2189 (1975).

[3] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System" Butterworths, London (1973).

[4] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[5] NASA Reference Publication 1010, R. D. Hudson, editor Chapter 1 (1977).

[6] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + NO_2 \rightarrow O_2 + NO$

$\Delta H^\circ = -192.1$ kJ mol^{-1}

Rate coefficient data

$k/cm^3\ molecule^{-1}s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.12 \pm 0.44) \times 10^{-12}$	230-339	Davis, Herron and Huie, 1973 [1]	(a)
9.3×10^{-12} 10.5×10^{-12}	296 240	Slanger, Wood and Black, 1973 [2]	(b)
$1.85 \times 10^{-10} \times T^{-0.53}$ $(9.5 \pm 1.1) \times 10^{-12}$	298-1055 298	Bemand, Clyne and Watson, 1974 [3]	(c)
Reviews and Evaluations			
9.1×10^{-12}	220-500	Huie and Herron, 1973 [4]	(d)
$1.7 \times 10^{-11} \exp(-300/T)$	300-550	Baulch, et al, 1973 [5]	(e)
9.1×10^{-12}	200-300	NASA, 1977 [6]	(f)

Comments

(a) Flash photolysis, [O] monitored by resonance fluorescence. Recommended in Huie and Herron, 1973 [4]; Hampson and Garvin, 1975 [7]; NASA, 1977 [6]; and in Hampson and Garvin, 1978 [8].

(b) Flash photolysis, [O] monitored by chemiluminescent reaction with NO.

(c) Discharge flow system. At 298 K results obtained by two independent techniques: [O] monitored by resonance fluorescence and [NO_2] monitored by mass spectrometry. Results are in good agreement. High temperature results obtained by the resonance fluorescence technique show appreciable scatter.

(d) Evaluation, based on all previously reported data. Only newer results are those in reference [3]. Accepted results reported by Davis, et al 1973 [1] as most extensive data set.

(e) This recommendation is now outdated due to newer results in references [1], [2] and [3].

(f) Accepted results reported in reference [1]. Accompanying note cautioned that there might be a slight negative temperature dependence.

Preferred Value

$k = 9.3 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ over range 230-340 K

Reliability

$\Delta \log k = \pm 0.06$ at 298 K

$\Delta E/R = {}^{+\,0}_{-\,150}$

Comments on Preferred Value

Room temperature preferred value is average of values reported in reference [1-3]. There may be a slight negative temperature dependence as indicated by the high temperature results in reference [3], but a temperature-independent value is recommended for temperatures below 340 K.

References

[1] Davis, D. D., Herron, J. T. and Huie, R. E., J. Chem. Phys. <u>58</u>, 530 (1973).

[2] Slanger, T. G., Wood, B. J. and Black, G., Int. J. Chem. Kinet. <u>5</u>, 615 (1973).

[3] Bemand, P. P., Clyne, M. A. and Watson, R. T., J. Chem. Soc. Faraday Trans. 2 <u>70</u>, 564 (1974).

[4] Huie, R. E. and Herron, J. T., Data sheet published in R. F. Hampson, Ed., Nat. Bur. Stand. (U.S.), NBSIR 73-207 (1973).

[5] Baulch, D. L., Drysdale, D. D. and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System", Butterworths, London (1973).

[6] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

[7] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[8] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + NO_3 \rightarrow O_2 + NO_2$

$\Delta H° = -287$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
<u>Relative Rate Coefficients</u>			
$(1.0 \pm 0.4) \times 10^{-11}$	298-329	Graham and Johnston, 1978 [1]	(a)
<u>Reviews and Evaluations</u>			
1.0×10^{-11}	300	Hampson and Garvin, 1978 [2]	(b)

Comments

(a) Value derived by computer simulation of complex system (N_2O_5 catalyzed decomposition of O_3 with photolysis of NO_3 and molecular modulation experiments) with 15 step mechanism.

(b) Quoting result reported in reference [1].

Preferred Value

$k = 1 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K

Reliability

$\Delta \log k = \pm 0.5$ at 298 K

Comments on Preferred Value

Preferred value is the only reported value for this rate constant. Since this value is derived from the analysis of a very complex system and is not confirmed by separate study, it must be used with caution. The temperature dependence is expected to be small.

References

[1] Graham, R. A. and Johnston, H. S., J. Phys. Chem. 82, 254 (1978).

[2] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O + N_2O_5 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule$^{-1}s^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 3 \times 10^{-16}$	223-300	Kaiser and Japar, 1978 [1]	(a)
Relative Rate Coefficients			
$< 2 \times 10^{-14}$	298	Graham and Johnston, 1978 [2]	(b,d)
Reviews and Evaluations			
$< 2 \times 10^{-13}$	300	Hampson and Garvin, 1975 [3]	(c,d)

Comments

(a) Discharge flow, $[N_2O_5]$ monitored by mass spectrometry. Upper limit only.

(b) Value derived by computer simulation of complex system. Value depends on identify of products.

(c) Quoting a preliminary value.

(d) Also quoted in Hampson and Garvin, 1978 [4].

Preferred Value

$k \leq 3 \times 10^{-16}$ cm^{3}molecule^{-1}s^{-1} over range 220-300 K

Comments on Preferred Value

Preferred value is that given by the only published direct study of this reaction. On the basis of the upper limiting value of the rate constant, this reaction can not be of any importance.

References

[1] Kaiser, E. W. and Japar, S. M., Chem. Phys. Lett. 54, 265 (1978).

[2] Graham, R. A. and Johnston, H. S., J. Phys. Chem. 82, 254 (1978).

[3] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[4] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+) \quad (1)$$
$$\rightarrow O(^3P) + O_2(^3\Sigma_g^-) \quad (2)$$

$\Delta H°(1) = - \ 33$ kJ mol^{-1}

$\Delta H°(2) = - \ 190$ kJ mol^{-1}

Rate coefficient data $k = k_1 + k_2$

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.0 \pm 0.5) \times 10^{-11}$	300	Heidner, Husain and Wiesenfeld, 1973 [1]	(a)
$(5.3 \pm 0.6) \times 10^{-11}$	300	Fletcher and Husain, 1976 [2]	(b)
$2.9 \times 10^{-11} \exp((67 \pm 10)/T)$	104-354	Streit, et al, 1976 [3]	(c,i)
$(3.7 \pm 0.7) \times 10^{-11}$	300		
$(4.0 \pm 0.6) \times 10^{-11}$	300	Lee and Slanger, 1978 [4]	(d)
Branching Ratios			
$k_1/k = 0.77 \pm 0.2$	300	Lee and Slanger, 1978 [4]	(d)
$k_1/k = 0.8 \ (+0.2, -0.3)$	300	Schofield, 1978 [5]	(e)
Reviews and Evaluations			
7.4×10^{-11}	300	Cvetanovic, 1974 [6]	(f)
7.4×10^{-11}	300	Hampson and Garvin, 1975 [7]	(g)

3.7×10^{-11}	298	Schofield, 1978 [5]	(e)
$2.9 \times 10^{-11} \exp(67/T)$	200-300	NASA, 1977 [8]	(h,i)

Comments

(a) Flow system. $[O(^1D)]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm $O(3D_2 \rightarrow 2D_2)$. Analysis of data uses modified Beer-Lambert law: $I_t/I_o = \exp(-\varepsilon(cl)^\gamma)$ with $\gamma = 0.41$.

(b) Same system as described in (a) with modified detection circuitry. Apparently supersedes result reported in [1].

(c) Flow system. $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.

(d) $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. $O_2(^1\Sigma_g^+)$ monitored by time resolved build-up of the $O_2(^1\Sigma_g^+) \rightarrow (^3\Sigma_g^-)$ (1-1) and (0-0) band emissions.

(e) Evaluation. Recommended value of electronic energy transfer efficiency to give $O_2(^1\Sigma_g^+)$ based on all previously reported results. Only newer measurement of this efficiency is that of Lee and Slanger, 1978 [4].

(f) Recommended value based on analysis of complete set of $O(^1D)$ rate data - both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [7].

(g) Accepted recommendation of Cvetanovic, 1974 [6].

(h) Accepted results in Streit, et al, 1976 [3].

(i) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k = 4.6 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K

$k = 3.7 \times 10^{-11} \exp(67/T)$ cm^{3}molecule^{-1}s^{-1} over range 200-350 K

$k_1/k = 0.8$

Reliability

$\Delta \log k = \pm 0.15$

$\Delta E/R = \pm 100$ K

$\Delta \log (k_1/k) = \pm 0.1$

Comments on Preferred Value

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio $k/k(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [6]. These values are the following: 0.37 (NOAA Laboratories [3]); 0.31 (Cambridge Laboratory [2]); 0.35 (Cvetanovic's review [6]); 0.34 (mean value). The preferred value of the rate constant for the reference reaction of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} $cm^3 molecule^{-1} s^{-1}$, ref. [3]) and that reported from the Cambridge Laboratory (1.7×10^{-10} $cm^3 molecule^{-1} s^{-1}$, ref. [2]). The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 0.34$ and $k(O(^1D) + CO_2 = 1.35 \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$. The temperature dependence in reference [3] is accepted.

The preferred value for k has been derived in this way for consistency with the method used to derive the other $O(^1D)$ rate coefficient values recommended in this evaluation. Inclusion of the recent data of Lee and Slanger, 1978 [4] with equal weighting would result in lowering the preferred value of k at 298 K to 4.4×10^{-11} $cm^3 molecule^{-1} s^{-1}$.

The value recommended in Schofield, 1978 [5] for the efficiency of transfer of the $O(^1D)$ electronic energy to give O_2 in the $^1\Sigma_g{}^+$ electronic state has been adopted here. It is based on a number of studies referenced therein and is confirmed by the recent results of Lee and Slanger, 1978 [4].

The predominant fate of the $O_2(^1\Sigma_g{}^+)$ in the atmosphere would appear to be quenching to the ground state (see reference [9] for values of rate coefficients).

For further comments on $O(^1D)$ values see Introduction.

References

[1] Heidner, R. F. III, Husain, D. and Wiesenfeld, J. R., J. Chem. Soc. Faraday Trans. 2, 69, 927 (1973).

[2] Fletcher, I. S. and Husain, D., Can. J. Chem. 54, 1765 (1976).

[3] Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A. and Schiff, H. I., J. Chem. Phys. 65, 4761 (1976).

[4] Lee, L. C. and Slanger, T., J. Chem. Phys. 69, 4053 (1978).

[5] Schofield, K., J. Photochem. 9, 55 (1978).

[6] Cvetanovic, R. J., Can. J. Chem. 52, 1452 (1974).

[7] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[8] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

[9] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

$O(^1D) + N_2 \rightarrow O(^3P) + N_2$

$\Delta H° = - 190$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.9 \pm 0.6) \times 10^{-11}$	300	Heidner, Husain and Wiesenfeld, 1973 [1]	(a)
$2.0 \times 10^{-11} \exp((107 \pm 8)/T)$ $(2.8 \pm 0.6) \times 10^{-11}$	104-354 300	Streit, et al, 1976 [2]	(b,g)
Reviews and Evaluations			
5.4×10^{-11}	300	Cvetanovic, 1974 [3]	(c)
5.4×10^{-11}	300	Hampson and Garvin, 1975 [4]	(d)
2.8×10^{-11}	298	Schofield, 1978 [5]	(e)
$2.0 \times 10^{-11} \exp(107/T)$	200-300	NASA, 1977 [6]	(f,g)

Comments

(a) Flow system. $[O(^1D)]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm $O(3D_2 \leftarrow 2D_2)$. Analysis of data uses modified Beer-Lambert law: $I_t/I_o = \exp(-\varepsilon(cl)^\gamma)$ with $\gamma = 0.41$.

(b) Flow system. $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.

(c) Recommended value based on analysis of complete set of $O(^1D)$ rate data - both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [4].

(d) Accepted recommendation of Cvetanovic, 1974 [3].

(e) Evaluation - details not given.

(f) Accepted results in Streit, et al, 1976 [2].

(g) Recommended in Hampson and Garvin, 1978 [7].

Preferred Value

$k = 4.5 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1} at 298 K

$k = 3.2 \times 10^{-11} \exp(107/T)$ cm^{3}molecule^{-1}s^{-1} over range 200-350 K

Reliability

$\Delta \log k = \pm 0.15$

$\Delta E/R = \pm 100$ K

Comments on Preferred Value

Preferred value is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio $k/k(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [3]. These values are the following: 0.28 (NOAA Laboratories [2]); 0.40 (Cambridge Laboratory [1], [8]); 0.30 (Cvetanovic's review [3]; 0.33 (mean value). The preferred value of the rate constant for the reference of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} $cm^3 molecule^{-1} s^{-1}$, ref. [2]) and that reported from the Cambridge Laboratory (1.7×10^{-10} $cm^3 molecule^{-1} s^{-1}$, ref. [8]). The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 0.33$ and $k(O(^1D) + CO_2) = 1.35 \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$. The temperature dependence in reference [2] is accepted. For further comments on $O(^1D)$ values see Introduction.

References

[1] Heidner, R. F. III, Husain, D. and Wiesenfeld, J. R., J. Chem. Soc. Faraday Trans. 2 69, 927 (1973).

[2] Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A. and Schiff, H. I., J. Chem. Phys. 65, 4761 (1976).

[3] Cvetanovic, R. J., Can. J. Chem. 52, 1452 (1974).

[4] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[5] Schofield, K., J. Photochem. 9, 55 (1978).

[6] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

[7] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Spec. Publ. 513 (1978).

[8] Fletcher, I. S. and Husain, D., Can. J. Chem. <u>54</u>, 1765 (1976).

<u>Note</u>: This reference is the source of the value quoted in this review for the $O(^1D) + CO_2$ rate constant as measured at the University of Cambridge Laboratory. The value given in this reference ($(1.7 \pm 0.2) \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$) apparently supersedes the value ($(2.1 \pm 0.2) \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$) given in reference [1].

$$\begin{aligned} O(^1D) + N_2O &\rightarrow N_2 + O_2 \quad &(1)\\ &\rightarrow 2NO \quad &(2)\\ &\rightarrow O(^3P) + N_2O \quad &(3) \end{aligned}$$

$\Delta H°(1) = - 520$ kJ mol^{-1}

$\Delta H°(2) = - 340$ kJ mol^{-1}

$\Delta H°(3) = - 190$ kJ mol^{-1}

Rate coefficient data. $k = k_1 + k_2 + k_3$

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.2) \times 10^{-10}$	300	Heidner and Husain, 1973 [1]	(a)
$(1.1 \pm 0.2) \times 10^{-10}$	204-359	Davidson, et al, 1977 [2]	(b,i)
Branching Ratios			
$k_1/k_2 = 0.92 \pm 0.10$	290	Pirkle, et al, 1977 [3]	(c)
$k_1/k_2 = (0.72 \pm 0.11) + (21.6 \pm 7.0)/T$	170-434	Davidson, et al, 1979 [4]	(d)
$k_1/k_2 = 0.80 \pm 0.11$	300		
$k_3/k \leq 0.038$	300		

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2.2×10^{-10}	300	Cvetanovic, 1974 [5]	(e)
2.2×10^{-10}	300	Hampson and Garvin, 1975 [6]	(f)
1.2×10^{-10}	298	Schofield, 1978 [7]	(g)
1.1×10^{-10}	200-300	NASA, 1977 [8]	(h,i)

Comments

(a) Flow system. $[O(^1D)]$ monitored in absorption by time resolved attenuation of resonance radiation at 115.2 nm. $O(3D_2 \leftarrow 2D_2)$. Analysis of data uses modified Beer-Lambert law: $I_t/I_o = \exp(-\varepsilon(cl)^{\gamma})$ with $\gamma = 0.41$.

(b) Flow system. $[O(^1D)]$ monitored by time resolved decay of the $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.

(c) Branching ratio measurements. Product N_2 measured by gas chromatography. NO and its oxidation product NO_2 measured by chemiluminescence analyzer. Value quoted for ratio k_1/k_2 is that measured in excess helium. Lower value (0.73 ± 0.11) measured in absence of helium.

(d) Branching ratio measurements using chemical-ionization mass spectrometry to measure products. Value quoted for ratio k_1/k_2 is that measured in excess helium. Lower value (0.68 ± 0.11) measured in pure N_2O. Reaction channels (1) and (2) are the only significant reaction channels.

(e) Recommended value based on analysis of complete set of $O(^1D)$ rate data - both large body of relative rate data and the existing absolute rate data. Recommended in Hampson and Garvin, 1975 [6]. Reviewed branching ratio data and recommended value of $k_1/k_2 = 1$.

(f) Accepted recomendation of Cvetanovic, 1974 [5].

(g) Evaluation - details not given.

(h) Accepted results in Davidson, et al, 1977 [2] and the branching ratio of unity recommended in Cvetanovic, 1974 [5].

(i) Recommended in Hampson and Garvin, 1978 [9].

Preferred Value

$k_1 = 7.4 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}

$k_2 = 8.6 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}

Independent of temperature over range 200-350

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.15$

$\Delta (E/R)_1 = \Delta (E/R)_2 = \pm 100$ K

Comments on Preferred Value

Preferred value for k is derived from a consideration of the rate data for this reaction relative to that for the reference reaction: $O(^1D) + CO_2$. The ratio $k/k(O(^1D) + CO_2)$ is derived from the absolute values reported from the NOAA Laboratories and from the University of Cambridge. The preferred value for this ratio is the mean value of these two derived ratios and that given in reference [5]. These values are the following: 1.10 (NOAA Laboratories [2], [10]; 1.29 (Cambridge Laboratory [1], [11]; 1.31 (Cvetanovic's review [5]; 1.2 (mean value). The preferred value of the rate constant for the reference reaction of $O(^1D)$ with CO_2 is taken as the simple average of the value reported from the NOAA Laboratories (1.0×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [10] and that reported from the Cambridge Laboratory (1.7×10^{-10} cm^{3}molecule^{-1}s^{-1}, ref. [11]. The preferred value for k is then derived from the values $k/k(O(^1D) + CO_2) = 1.2$ and $k(O(^1D) + CO_2) = 1.35 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}. The temperature independence of k reported in reference [2] is accepted.

The conclusion stated in reference [4] that reaction channels (1) and (2) are the only significant reaction channels is accepted. This is equivalent to setting $k = k_1 + k_2$.

The branching ratio $R = k_1/k_2$ reported in reference [4] has only a very slight temperature dependence decreasing from 0.83 at 200 K to 0.78 at 350 K. These results can be approximated by a value of 0.80 independent of temperature. The value of the branching ratio recommended in this review (0.85 ± 0.1) is the simple average of the results in references [3] and [4].

The recommendation given here can be stated in the equivalent form: $k = 1.6 \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$ and $k_1/k_2 = 0.85 \pm 0.1$. For further comments on $O(^1D)$ values see Introduction.

References

[1] Heidner, R. F. III and Husain, D., Int. J. Chem. Kinet. 5, 819 (1973).

[2] Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L. and Howard, C. J., J. Chem. Phys. 67, 5021 (1977).

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[9] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. Spec. Publ. 513 (1978).

[10] Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A. and Schiff, H. I., J. Chem. Phys. 65, 4761 (1976).

[11] Fletcher, I. S. and Husain, D., Can. J. Chem. 54, 1765 (1976).

Note: This reference is the source of the value quoted in this review for the $O(^1D) + CO_2$ rate constant as measured at the University of Cambridge Laboratory. The value given in this reference ($(1.7 \pm 0.2) \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$) apparently supersedes the value ($(2.1 \pm 0.2) \times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$) reported in Heidner, R. F. III, Husain, D. and Wiesenfeld, J. R., J. Chem. Soc. Faraday Trans. 2 69, 927 (1973).

$HO + HNO_3 \rightarrow H_2O + NO_3$

$\Delta H° = -75$ kJ mol^{-1}

Rate coefficient data

$k/cm^3\ molecule^{-1}s^{-1}$	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(8 \pm 2) \times 10^{-14}$	240-406	Smith and Zellner, 1975 [1]	(a,f)
$(8.9 \pm 1.3) \times 10^{-14}$	270-470	Margitan, Kaufman and Anderson, 1975 [2]	(b)
$(1.6 \pm 0.3) \times 10^{-13}$	1000-1100	Glanzer and Troe, 1974 [3]	(c)
<u>Reviews and Evaluations</u>			
$6 \times 10^{-13} \exp(-400/T)$	300-650	Tsang, 1973 [4]	(d)
1.3×10^{-13}	300	Baulch, et al, 1973 [5]	(d)
1.3×10^{-13}	220-270	Hampson and Garvin, 1975 [6]	(d)
8×10^{-14}	200-300	NASA, 1977 [7]	(e,f)

Comments

(a) Flash photolysis of HNO_3. [OH] monitored by resonance absorption. Experiments with pure HNO_3 (< 0.4% NO_2) over range 240-300 K. Other experiments over range 240-406 K with correction made for effect of 1.4% NO_2 impurity. Value given is that recommended by author for room temperature and below. Within the stated error limits it encompasses all data over entire temperature range. Recommended in NASA, 1977 [7] and in Hampson and Garvin, 1978 [8].

(b) Discharge flow system. Hydroxyl radicals produced by reaction of H atoms with NO_2. [OH] monitored by resonance fluorescence. Value given is mean of values measured at 295, 420 and 465 K. Slightly higher value at 272 K considered by authors to be less reliable.

(c) Thermal decomposition of HNO_3 in shock wave. [NO_3] monitored by absorption.

(d) Evaluation - outdated by newer data in references [1], [2] and [3].

(e) Accepted results of Smith and Zellner, 1975 [1].

(f) Recommended in Hampson and Garvin, 1978 [8].

Preferred Value

$k = 8.5 \times 10^{-14}$ $cm^3 molecule^{-1} s^{-1}$ over range 240-470 K

Reliability

$\Delta \log k = \pm 0.10$

$\Delta E/R = \pm 300$ K

Comments on Preferred Value

Preferred value is mean of values reported in references [1] and [2]. It should be noted that this is an unusually low A-factor for a simple H atom abstraction and together with the fact that the indicated products are unconfirmed suggests the need for mechanistic studies. Although the high temperature results in reference [3] have not been used in the derivation of the preferred value, they support the low A-factor. They have been used in the calculation of Δ E/R.

References

[1] Smith, I. W. M. and Zellner, R., Int. J. Chem. Kinet. Symposium No. 1, p. 341 (1975).

[2] Margitan, J. J., Kaufman, F. and Anderson, J. G., Int. J. Chem. Kinet. Symposium No. 1, p. 281 (1975).

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[6] Hampson, R. F. and Garvin, D., Nat. Bur. Stand. (U.S.), Tech. Note 866 (1975).

[7] NASA Reference Publication 1010, R. D. Hudson, editor, Chapter 1 (1977).

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HO + HO_2NO_2 → products

Rate coefficient data: no data on this reaction exist

Preferred Value

No preferred value.

Comments on Preferred Value

No study of this reaction has been reported. The rate constant can only be very roughly estimated from consideration of similar reactions. Presumably the reaction proceeds by H-atom abstraction. The rate coefficient for H-atom abstraction by the HO radical from the related molecule $HONO_2$ is 8.5×10^{-14} $cm^3 molecule^{-1} s^{-1}$, this evaluation. Based on this a value of approximately 1×10^{-13} $cm^3 molecule^{-1} s^{-1}$ is suggested for this rate coefficient. This value must be considered to be very uncertain (to at least an order of magnitude). Clearly studies of this reaction are needed.

$$HO_2 + NO \rightarrow HO + NO_2 \qquad (1)$$

$\Delta H° = - 20$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977 [1]	(a,o)
$(3.3 \pm 0.7) \times 10^{-12} \exp((254 \pm 50)/T)$	230-400	Howard, 1978 [2]	(b)
$(8 \pm 2) \times 10^{-12}$	298	Margitan and Anderson, 1978 [3]	(c)
$(7.9 \pm 1.0) \times 10^{-12}$	298	Reimann and Kaufman, 1978 [4]	(d)
$5.7 \times 10^{-12} \exp((130 \pm 270)/T)$	270-425	Leu, 1979 [5]	(e)
$(9.8 \pm 1.6) \times 10^{-12}$	298		
<u>Relative Rate Coefficients</u>			
1.2×10^{-12}	296	Cox and Derwent, 1975 [6]	(f)
$(7.5 \pm 1.7) \times 10^{-12}$	1350-1700	Glanzer and Troe, 1975 [7]	(g)
$(1.9 \pm 0.5) \times 10^{-11} \exp(-(1200 \pm 150)/T)$	298-670	Hack, Hoyermann and Wagner, 1975 [8]	(h)
2.5×10^{-13}	298		
0.8×10^{-12}	296	Simonaitis and Heicklen, 1976 [9]	(i)
$1.0 \times 10^{-11} \exp(-(700 \pm 250)/T)$	245-328	Simonaitis and Heicklen, 1978 [10]	(j)
1.0×10^{-12}	296		

$(8.3 \pm 1.4) \times 10^{-12}$	298	Burrows, et al, 1978 [11]	(k)
4.1×10^{-12}	283	Cox and Patrick, 1979 [12]	(l)

Reviews and Evaluations

2×10^{-13}	300	Hampson and Garvin, 1975 [13]	(m)
8×10^{-12}	200-300	NASA, 1977 [14]	(n,o)

Comments

(a) Discharge flow system. $[HO_2]$ monitored by laser magnetic resonance. From observation of HO_2 decay in steady-state experiments, an upper limit of 4.5×10^{-30} $cm^6 molecule^{-2} s^{-1}$ for the third order rate constant for a potential addition reaction channel was established. If the value of this rate constant is as much as one tenth of this upper limit, then the addition channel becomes important under atmospheric conditions.

(b) Same system as described in (a).

(c) Discharge flow system. [HO] monitored by resonance fluorescence.

(d) Discharge flow system. [HO] monitored with tunable dye laser.

(e) Discharge flow system. [HO] monitored by resonance fluorescence.

(f) Steady photolysis of HONO in NO_2 and CO at 1 atm $N_2 + O_2$. Observed effect of added NO and NO_2 on rate of formation of nitrogen oxides. Rate constant values derived from computer fit to nine step reaction mechanism. Reaction (2) at a rate of 0.12 times rate of reaction (1) included in mechanism but adduct not observed.

(g) Shock wave pyrolysis of HNO_3. $[HO_2]$ measured by UV absorption. Rate constant values derived from computer fit. Value of k calculated from measured rate of reverse reaction and equilibrium constant.

(h) Discharge flow system. [OH] monitored by ESR technique. Steady-state [HO] and $[HO_2]$ reached in chemical system described by reaction (1) and the reference reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$
$k/k(HO + H_2O_2) = 2.5 \exp(-530/T)$; $k(HO + H_2O_2) = 7.6 \times 10^{-12} \exp(-670/T)$ $cm^3 molecule^{-1} s^{-1}$, this evaluation.

(i) Steady photolysis of $N_2O-H_2-O_2-NO$ mixtures at 214 nm. Initial quantum yield for NO disappearance monitored by chemiluminescent reaction with O_3. $k/k^{1/2}(HO_2 + HO_2) = 5.1 \times 10^{-7}$; $k(HO_2 + HO_2) = 2.3 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$, this evaluation. $k_2/k_1 \leq 2 \times 10^{-3}$ at 1 atm H_2.

(j) Same system as described in (i), $k/k^{1/2}(HO_2 + HO_2) = 6.4 \times 10^{-6} \exp(-700/T)$.

(k) Discharge flow system. [HO] and $[HO_2]$ measured by laser magnetic resonance. Steady-state [HO] and $[HO_2]$ reached in chemical system described by reaction (1) and the reference reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$. $k/k(HO + H_2O_2) = 10.4 \pm 0.5$; $k(HO + H_2O_2) = 8.0 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$, this evaluation.

(l) Periodic photolysis of Cl_2 in excess H_2 and O_2 with NO_2 present. $[HO_2]$ monitored by molecular modulation ultraviolet spectrometry. $k(HO_2 + NO_2 \rightarrow HO_2NO_2) = 9 \times 10^{-13}$ $cm^3 molecule^{-1} s^{-1}$. Study of HONO-CO photolysis system gave $k/k(HO_2 + NO_2) = 4.5 \pm 0.6$. Authors combined these results to derive value of k shown in table.

(m) Evaluation based on indirect studies. Outdated by results of newer, direct studies.

(n) Accepted results of Howard and Evenson, 1977 [1]. Assumed k to be temperature - independent.

(o) Recommended in Hampson and Garvin, 1978 [15].

Preferred Value

$k = 8.4 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

$k = 4.3 \times 10^{-12} \exp(200/T)$ $cm^3 molecule^{-1} s^{-1}$ over range 230-425 K

Reliability

$\Delta \log k = \pm 0.08$ at 298 K

$\Delta (E/R) = \pm 200$ K

Comments on Preferred Value

Preferred value at 298 K is the average of the measured values reported in references [1-5 and 11]. The temperature dependence is derived from a least squares fit to the data of Howard, 1978 [2] and Leu, 1979 [5]. The direct studies have all been made at low pressures, and it is possible that this rate constant may exhibit a pressure dependence. Studies at atmospheric pressures are needed.

References

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$NO + O_3 \rightarrow NO_2 + O_2$

$\Delta H° = -200$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1}s^{-1}	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(1.73 \pm 0.1) \times 10^{-14}$	298	Stedman and Niki, 1973 [1]	(a)
1.41×10^{-14}	298	Ghormley, Ellsworth and Hochanadel, 1973 [2]	(b)
$(1.81 \pm 0.13) \times 10^{-14}$	298	Bemand, Clyne and Watson, 1974 [3]	(c)
1.70×10^{-14}	290	Becker, Schurath and Seitz, 1974 [4]	(d)
$(2.34 \pm 0.23) \times 10^{-12} \exp(-(1450 \pm 50)/T)$	203-361	Birks, et al, 1976 [5]	(e)
$(1.73 \pm 0.09) \times 10^{-14}$	297		
<u>Reviews and Evaluations</u>			
$9 \times 10^{-13} \exp(-1200/T)$	198-330	Herron and Huie, 1973 [6]	(f,h)
$1.5 \times 10^{-12} \exp(-1330/T)$	200-350	Baulch, Drysdale and Horne, 1973 [7]	(f)
$2.1 \times 10^{-12} \exp(-1450/T)$	200-300	NASA, 1977 [8]	(g,i)

Comments

(a) Photolysis of NO_2 in air. In separate experiments monitored $[O_3]$ and [NO] by chemiluminescence detectors.

(b) Flash photolysis system. Monitored $[O_3]$ and $[NO_2]$ by optical absorption.

(c) Flow system. Monitored $[O_3]$ by mass spectrometry.

(d) Large static reactor. Monitored [NO] by monitoring $NO_2{}^*$ chemiluminescence. No details of measurement given.

(e) Fast flow system. Monitored $[O_3]$ by mass spectrometry.

(f) Evaluation based on all previously reported data. Newer results reported in references [1] - [5].

(g) Evaluation based on results reported in Birks, et al, 1976 [5] with lower "A factor" based on reconsideration of primary data.

(h) Recommended in Hampson and Garvin, 1975 [9].

(i) Recommended in Hampson and Garvin, 1978 [10].

Preferred Value

$k = 1.8 \times 10^{-14}\ cm^3 molecule^{-1} s^{-1}$ at 298 K

$k = 2.3 \times 10^{-12} \exp(-1450/T)\ cm^3 molecule^{-1} s^{-1}$ over range 200-360 K

Reliability

$\Delta \log k = \pm 0.06$ at 298 K

$\Delta (E/R) = \pm 200$ K

Comments on Preferred Value

Preferred value at room temperature based on results reported in references [1], [3] and [5]. Result in reference [2] is definitely low in comparison with these results. Earlier results are summarized in references [6] and [7]. Temperature dependence reported in reference [5] accepted as being determined in the most complete study covering an extensive temperature range.

References

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$NO + NO_3 \rightarrow 2NO_2$

$\Delta H^\circ = -95\ kJ\ mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}s^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients			
8.7×10^{-12}	297	Harker and Johnston, 1973 [1]	(a)
$(1.3 \pm 0.7) \times 10^{-11}$	1000-1100	Glanzer and Troe, 1974 [2]	(b)
$(1.9 \pm 0.4) \times 10^{-11}$	297	Graham and Johnston, 1978 [3]	(c)
Reviews and Evaluations			
2×10^{-11} (estimate)	300	Baulch, et al, 1973 [5]	(d)
8.7×10^{-12}	300	Hampson and Garvin, 1975 [6]	(e)
1.9×10^{-11}	300	Hampson and Garvin, 1978 [7]	(f)

Comments

(a) Photolysis of NO_2 in long-path infrared cell. $[NO_2]$ and $[N_2O_5]$ monitored as function of time and molecular modulation spectrum of NO_2 obtained in steady flow system. Derived value of $k/K_{eq} = 0.71 \pm 0.05\ s^{-1}$ where K_{eq} is for system: $NO_2 + NO_3 = N_2O_5$. Authors combined this value with value of $K_{eq} = 1.24 \times 10^{-11}\ cm^3 molecule^{-1}$ from reference [4] to give value of k listed in table.

(b) Thermal decomposition of HNO_3 in shock wave. Value of k varied to give best fit to observed NO_2 and NO_3 profiles.

(c) Studied kinetics of N_2O_5 catalyzed decomposition of O_3. From analysis of complex system, derived expression for equilibrium constant for system: $NO_2 + NO_3 = N_2O_5$. Authors combined value of K_{eq} at 297 K (2.7×10^{-11} $cm^3 molecule^{-1}$) with value of k/K_{eq} reported in Harker and Johnston, 1973 [1] to give value of k listed in table.

(d) No recommendation given; only order of magnitude estimate.

(e) Accepted results of Harker and Johnston, 1973 [1].

(f) Accepted results of Graham and Johnston, 1978 [3].

Preferred Value

$k = 2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

Reliability

$\Delta \log k = \pm 0.5$

Comments on Preferred Value

Preferred value is that given in reference [3]. This value could be subject to large systematic error because it is derived from analyzing results of two complex systems.

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$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H° = -105\ kJ\ mol^{-1}$

Rate coefficient data

$k/cm^3\ molecule^{-1}s^{-1}$	Temp./K	Reference	Comments
<u>Absolute Rate Coefficients</u>			
$(6.5 \pm 0.8) \times 10^{-17}$	298	Stedman and Niki, 1973 [1]	(a)
$(4.4 \pm 0.6) \times 10^{-17}$	299	Wu, Morris and Niki, 1973 [2]	(b)
$(3.2 \pm 0.5) \times 10^{-17}$	298	Ghormley, Ellsworth and Hochanadel, 1973 [3]	(c)
$(9.76 \pm 0.54) \times 10^{-14} \exp(-(2427 \pm 140)/T)$	260-343	Davis, et al, 1974 [4]	(d)
$(3.42 \pm 0.27) \times 10^{-17}$	303		
$(1.34 \pm 0.11) \times 10^{-13} \exp(-(2466 \pm 30)/T)$	231-298	Graham and Johnston, 1974 [5]	(e)
$(3.49 \pm 0.23) \times 10^{-17}$	298		
$(1.57 \pm 0.41) \times 10^{-13} \exp(-(2509 \pm 76)/T)$	259-362	Huie and Herron, 1974 [6]	(f)
$(3.78 \pm 0.07) \times 10^{-17}$	297		
3.24×10^{-17}	289	Becker, Schurath and Seitz, 1974 [7]	(g)
<u>Reviews and Evaluations</u>			
5×10^{-17}	298	Huie and Herron, 1973 [8]	(h)
$9.8 \times 10^{-12} \exp(-3500/T)$	286-302	Baulch, Drysdale and Horne, 1973 [9]	(h)

$1.2 \times 10^{-13} \exp(-2450/T)$	220-340	Hampson and Garvin, 1975 [10]	(i)
$1.2 \times 10^{-13} \exp(-2450/T)$	200-300	NASA 1977, [11]	(j,k)

Comments

(a) Static reactor, reactants at ppm concentration level. [O_3] monitored by chemiluminescence detector.

(b) Same system as in reference [1]. In separate experiments using long-path infrared spectrometry, the stoichiometric ratio ($\Delta NO_2/\Delta O_3$) was measured in O_3 excess (1.88 ± 0.15) and in NO_2 excess (1.68 ± 0.15).

(c) Flash photolysis system. Monitored [O_3] and [NO_2] by optical absorption.

(d) Stop-flow time-of-flight mass spectrometry. [O_3] monitored. "A factor" stated in abstract and text is incorrect; correct value given in table (D. D. Davis, private communication).

(e) Long path static cell. [O_3] and [NO_2] monitored in separate experiments by UV absorption spectrometry. Stoichiometric ratio ($\Delta NO_2/\Delta O_3$) measured to be 1.89 ± 0.08.

(f) Stopped-flow system. [O_3] monitored by molecular beam sampling mass spectrometry.

(g) Large static reactor. [O_3] monitored by optical absorption at 253.7 nm. No details of measurement given.

(h) Evaluation - outdated by newer data in references [4-6].

(i) Recommended value derived from a least squares fit of the data points in the three recent temperature dependent studies, references [4-6], to an Arrhenius expression.

(j) Accepted the recommendation in Hampson and Garvin, 1975 [10].

(k) Recommended in Hampson and Garvin, 1978 [12].

Preferred Value

$k = 3.2 \times 10^{-17}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K

$k = 1.2 \times 10^{-13} \exp(-2450/T)$ $cm^3 molecule^{-1} s^{-1}$ over range 230-360 K

Reliability

$\Delta \log k = \pm 0.06$ at 298 K

$\Delta (E/R) = \pm 150$ K

Comments on Preferred Value

Preferred value derived from a least squares fit of the data points in the three recent temperature dependent studies, references [4-6], to an Arrhenius expression.

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$NO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH^0_0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$NO + h\nu \rightarrow N(^4S) + O(^3P)$	627.9	190.5
$\rightarrow N(^4S) + O(^1D)$	817.7	146.3
$\rightarrow N(^2D) + O(^3P)$	857.8	139.5
$\rightarrow N(^4S) + O(^1S)$	1032.1	115.9
$\rightarrow N(^2D) + O(^1D)$	1047.6	114.2
$\rightarrow N(^2D) + O(^1S)$	1262.1	94.8

Electronic energy levels of NO and transitions

State	T_0/cm^{-1}	λ(vac)/nm	Transition
$X(^2\pi_{1/2})$	0		
$A(^2\Sigma)$	44199	226.2	A-X (γ)
$B(^2\pi)$	45505	219.8	B-X (β)
$C(^2\pi)$	52372	190.9	C-X (δ)
$D(^2\pi)$	53291	187.6	D-X (ε)

Energy levels are from [1].

Calculation of the rate of dissocation of nitric oxide in the stratosphere and mesosphere.

Dissociation of nitric oxide in the atmosphere occurs by absorption from the v" = 0 level of the $X^2\pi$ ground state to the v' = 0 and 1 levels of the $C(^2\pi)$ state in the $\delta(0\text{-}0)$ and $\delta(1\text{-}0)$ absorption bands followed by predissociation of these states in competition with emission and quenching. This absorption occurs in the same spectral region as the Schumann-Runge absorption bands of O_2. A line by line analysis must be made to determine the overlap between the solar radiation transmitted through the Schumann-Runge bands and the NO absorption lines in order to calculate the effective rate of predissociation of nitric oxide in the atmosphere. Results of such a detailed analysis have been reported by Cieslik and Nicolet, 1973 [2] and by Frederick and Hudson, 1979 [3]. Because of their detail these results are not repeated here. Instead it is recommended that the reader use the values of the dissociation rate given as a function of altitude and solar zenith angle in Table 4 of Frederick and Hudson, 1979 [3].

References

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$NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0^0/kJ mol^{-1}	$\lambda_{threshold}$/nm
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	398
$\rightarrow NO + O(^1D)$ (2)	490	244

Absorption cross section data

Wavelength range/nm	Reference	Comments
190-420	Johnston and Graham, 1974 [1]	(a)
185-410	Bass, Ledford and Laufer, 1976 [2]	(b)
375-420	Harker, Ho and Ratto, 1977 [3]	(c)
390-420	Davenport, 1978 [4]	(d)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1	295-445	Jones and Bayes, 1973 [5]	(e)
ϕ_1	313-416	Gaedtke and Troe, 1975 [6]	(f)
ϕ_1	375-420	Harker, Ho and Ratto, 1977 [3]	(g)
ϕ_1	390-420	Davenport, 1978 [4]	(h)
ϕ_2	214-252	Uselman and Lee, 1976 [7]	(i)

Comments

(a) Measured at 294K with resolution of 1.3 nm. Values tabulated at 5 nm intervals; results of same study tabulated at 1 nm intervals in Graham, 1975 [8].

(b) Measured at 298K and also at 235K for 290-410 nm. Resolution < 0.04 nm. Values tabulated at 0.125 nm intervals. Also reports results for N_2O_4.

(c) Measured at 296K at 0.5 nm intervals with resolution of 0.1 nm.

(d) Measured at 297, 277, 247, 226 and 204K. Resolution of 0.04 nm at 297K. Values tabulated at 1 nm intervals.

(e) Relative quantum yields for NO production measured and normalized to literature values at 313 and 366 nm.

(f) Quantum yield for disappearance of NO_2 measured for mixtures containing up to 1000 atm N_2.

(g) Quantum yield for NO_2 photodissociation by pulsed dye laser measured at 1 nm intervals. Values given here are taken from tabulated results provided by the authors.

(h) Quantum yield for NO production measured relative to NO production from NOCl photolysis at six wavelengths for T = 300 and 223K.

(i) Quantum yield for $O(^1D)$ determined in presence of neopentane from measured yield of neopentanol.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
185	26.0	245	4.3	305	16.6	365	57.8
190	29.3	250	2.8	310	17.6	370	54.2
195	24.2	255	1.4	315	22.5	375	53.5
200	25.0	260	1.9	320	25.4	380	59.9
205	37.5	265	2.0	325	27.9	385	59.4
210	38.5	270	3.1	330	29.9	390	60.0
215	40.2	275	4.0	335	34.5	395	58.9
220	39.6	280	5.5	340	38.8	400	67.6
225	32.4	285	7.0	345	40.7	405	63.2
230	24.3	290	8.2	350	41.0	410	57.7
235	14.8	295	9.7	355	51.3		
240	6.7	300	11.7	360	45.1		

Quantum yields

λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1	λ/nm	ϕ_1
376	0.75	386	0.74	396	0.78	406	0.30
378	0.74	388	0.76	398	0.72	408	0.18
380	0.81	390	0.74	400	0.65	410	0.14
382	0.65	392	0.73	402	0.57	415	0.067
384	0.66	394	0.83	404	0.40	420	0.023

Preferred values for quantum yields (continued)

The above table gives values of ϕ_1 at closely spaced wavelength values in the neighborhood of the thermodynamic threshold for photodissociation. For shorter wavelengths (295-365 nm) use the formula:
$\phi_1(\lambda) = 1.0-0.0008\ (\lambda-275)$.

Comments on preferred values

The preferred absorption cross section values are those of Bass, Ledford and Laufer, 1976 [2]. The absorption spectrum is highly structured; for greater detail the reader should consult reference [2] where values are tabulated every 1/8th nanometer. They are in extremely good agreement with the results of reference [4] and agree with results of reference [1] and [3] to within 15%.

The preferred quantum yield values for 375-420 nm are those reported by Harker et al, 1977 [3]. This is the most extensive investigation of quantum yields in this wavelength range. The results of Davenport, 1978 [4] are in extremely good agreement at the six wavelengths studied. Reference [4] gives quantum yield data at 223K which show that values of ϕ_1 at low temperature are reduced for wavelengths greater than the thermodynamic threshold for photodissociation but are independent of temperature for shorter wavelengths. In agreement with these observations, Pitts, Sharp and Chan, 1964 [9] observed an increase of ϕ_1 with increasing temperature at 405 and 436 nm. The preferred values of ϕ_1 at shorter wavelengths are the values recommended in Jones and Bayes, 1973 [5] which are based on their own relative values normalized to literature values at 313 and 366 nm. The observation by Uselman and Lee, 1976 [7] that $\phi_2 = 0.5 \pm 0.1$, independent of wavelength, for the range 214-242 nm indicates that process (1) is competitive with process (2) at energies above the threshold for process (2).

A recent discussion of the photochemistry of NO_2 is given in Okabe, 1978 [10].

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$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH_0^o/kJ mol^{-1}	$\lambda_{threshold}$/nm
$NO_3 + h\nu \rightarrow NO + O_2(^3\Sigma_g^-)$ (1a)	13	9000
$\rightarrow NO + O_2(^1\Delta_g)$ (1b)	107	1100
$\rightarrow NO + O_2(^1\Sigma_g^+)$ (1c)	170	700
$\rightarrow NO_2 + O$ (2)	206	580

Absorption cross section data

Wavelength range/nm	Reference	Comments
400-704	Graham and Johnston, 1978 [1]	(a)
500-670	Wayne, et al, 1978 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1, ϕ_2 ($\phi_1 = \phi_{1a} + \phi_{1b} + \phi_{1c}$)	470-700	Graham and Johnston, 1978 [1]	(c)

Comments

(a) Measured at 298K with resolution of 0.83 nm. Values tabulated at 1 nm intervals, NO_3 was produced in the N_2O_5 catalyzed decomposition of O_3. These results supersede results reported in Johnston and Graham, 1974 [3].

(b) Measured at 298K with resolution of 0.5 to 0.8 nm. NO_3 was produced by addition of NO_2 to a flow of O_3. Relative values reported. Preliminary results.

(c) Measured at 298 and 329K. Modulation experiments were performed with three broad-band fluorescent lamps with overlapping spectral distributions. Primary quantum yield estimated from product quantum yield, lamp emission spectra and NO_3 absorption spectrum. Only values averaged over specified wavelength ranges are given: λ = 470-610 nm, $\phi_1 = 0.23$, $\phi_2 = 0.77$; λ = 610-700 nm, $\phi_1 = 0.07$, where $\phi_1 = \phi_{1a} + \phi_{1b} + \phi_{1c}$

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
470	51	580	305
475	60	585	277
480	64	590	514
485	69	595	408
490	88	600	283
495	97	605	345
500	99	610	148
505	110	615	196
510	132	620	358
515	140	625	925
520	145	630	566
525	148	635	145
530	194	640	111
535	204	645	62
540	183	650	38
545	181	655	76
550	236	660	736
555	268	665	875
560	307	670	95
565	253	675	37
570	254	680	44
575	274	685	7

Quantum yields

No recommendation

Comments on preferred values

The preferred absorption cross section values have been derived from the tabulated results in Graham and Johnston, 1978 [1] by averaging the values over 5 nm intervals. For greater detail see the original reference. These are the only published final results.

The only published quantum yield data are reported in Graham and Johnston, 1978 [1]. In this study using three broad band light sources, only values of ϕ_1 and ϕ_2 averaged over specified wavelength ranges are given (see Comment (c) above). Because of the lack of good spectral resolution in the determination of primary quantum yields, no recommendation is given. However calculated photodissociation rates are not very sensitive to the spectral resolution, and it is therefore recommended that modelers use simply the photodissociation rates for NO_3 in the lower atmosphere calculated in reference [1]: $j_1 = 0.04 \pm 0.02\ \mathrm{sec}^{-1}$ and $j_2 = 0.10 \pm 0.02\ \mathrm{sec}^{-1}$.

Note the extremely low value of $\phi_1 = 0.07$ averaged over the strong 610-700 nm absorption region. This means that absorption in the strong bands centered at 662 and 627 nm does not lead to dissociation under the experimental condition of one atmosphere total pressure.

Also these results indicate a substantial contribution of channel (2) at wavelengths longer than the threshold wavelength (580 nm). Calculations by the authors suggest that only 40% of this effect can be accounted for by internal energy.

More experimental work on primary quantum yield values is needed; in particular, studies with good spectral resolution are needed. Also pressure and temperature effects should be investigated.

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$N_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0^o/kJ mol^{-1}	$\lambda_{threshold}$/nm
$N_2O + h\nu \rightarrow N_2 + O(^3P)$	(1)	161	742
$\rightarrow N_2 + O(^1D)$	(2)	351	341
$\rightarrow N + NO$	(3)	475	252
$\rightarrow N_2 + O(^1S)$	(4)	565	212

Absorption cross section data

Wavelength range/nm	Reference	Comments
210-328	Johnston and Selwyn, 1975 [1]	(a)
173-240	Selwyn, Podolske and Johnston, 1977 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 \leq 0.03$	214	Paraskevopoulos and Cvetanovic, 1969 [3]	(c)
$\phi_3 \leq 0.01$	185-230	Preston and Barr, 1971 [4]	(d)

Comments

(a) Measured at 298K. Results shown in two figures. Good agreement with previous results (Bates and Hayes, 1967 [5]) in the range 210 to 235 nm. However, no absorption detected for $\lambda > 260$ nm ($\sigma < 2 \times 10^{-25}$ cm^2), in contrast with results in reference [5].

(b) Measured at five temperatures from 194 to 302K with resolution of 0.7 nm. Values tabulated at 1 nm intervals. Also, a nine parameter fit expressing σ as a function of λ and T is given.

(c) Photolysis of N_2O at 298K in presence of neopentane, butene-1 and added gases. Yield of $O(^3P)$ atoms determined from yield of addition products with butene-1.

(d) Photolysis of N_2O containing 1% ^{15}NO at 296K and λ = 185, 214 and 229 nm. Isotopic composition of product N_2 measured.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

$$\ell n\ \sigma(\lambda,T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4$$
$$+ (T-300)\ \exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$A_1 = 68.21023$

$A_2 = -4.071805$

$A_3 = 4.301146 \times 10^{-2}$

$A_4 = -1.777846 \times 10^{-4}$

$A_5 = 2.520672 \times 10^{-7}$

$B_1 = 123.4014$

$B_2 = -2.116255$

$B_3 = 1.111572 \times 10^{-2}$

$B_4 = 1.881058 \times 10^{-5}$

Quantum yields

$\phi_2 = 1.0$ for $\lambda = 185\text{-}230$ nm.

Comments on preferred values

The preferred absorption cross section values are from Selwyn, Podolske and Johnston, 1977 [2]. The tabulated values are room temperature values. For values tabulated at 1 nm intervals and five temperatures from 194 to 302K, consult the original reference. The nine parameter expression for $\ell n\ \sigma(\lambda,T)$ is also from reference [2]. It fits the 310 reported data with a standard deviation of about four percent. For a discussion of earlier data see the review by Hudson, 1974 [6].

The preferred value of the quantum yield (ϕ_2 equal to unity) is based on the results reported in Paraskevopoulos and Cvetanovic, 1969 [3], Preston and Barr, 1971 [4], and Greiner, 1967 [7].

A recent discussion of the photochemistry of N_2O is given in Okabe, 1978 [8].

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$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0^o/kJ mol^{-1}	$\lambda_{threshold}$/nm
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	(1)	89	1340
$\rightarrow N_2O_4 + O(^3P)$	(2)	242	495
$\rightarrow N_2O_4 + O(^1D)$	(3)	432	275

Absorption cross section data

Wavelength range/nm	Reference	Comments
285-380	Jones and Wulf, 1937 [1]	(a)
205-310	Graham and Johnston, 1978 [2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\Phi(-N_2O_5) = 0.6$	280,265	Holmes and Daniels, 1934 [3]	(c)
$\Phi(-N_2O_5) = 0.62$	280	Murphy, 1969 [4]	(d)

Comments

(a) Spectrograms taken at 298K.

(b) Measured at 298K with resolution of 0.83 nm. Corrections were made for absorption by O_3, HNO_3 and NO_2. Values tabulated at 5 nm intervals; results of same study tabulated at 1 nm intervals in Graham, 1975 [5].

(c) Overall quantum yield for disappearance of N_2O_5 measured at 273K.

(d) Overall quantum yield for disappearance of N_2O_5 measured at 273K. Measurements also made in presence of 100-600 torr SF_6, CO_2, N_2 and O_2. Overall quantum yield observed to decrease with increasing pressure of added gas.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
205	690	280	10.7
210	520	285	8.3
215	330	290	6.3
220	206	295	4.6
225	131	300	3.2
230	93	305	2.2
235	72	310	1.5
240	57	320	0.75
245	45	330	0.40
250	35	340	0.27
255	26.3	350	0.18
260	21.2	360	0.10
265	17.7	370	0.05
270	15.2	380	0.01
275	12.5		

Quantum yields

No recommendation

Comments on preferred values

The preferred absorption cross section values are those reported in Graham and Johnston, 1978 [2] for 205-310 nm and in Jones and Wulf, 1937 [1] for 320-380 nm. Although over the wavelength range common to both studies the values reported in reference [2] are higher than those reported in reference [1], since the disagreement decreases steadily towards the long wavelength end of this common range no adjustment has been made to the values from reference [1] in the statement of preferred values at longer wavelengths.

No recommendation is made for primary quantum yields because the primary photodissociation products have not been identified, and the only quantum yield data reported are for the overall disappearance of N_2O_5. The derivation of primary quantum yield values from these data requires the identification of the primary products and knowledge of the extent of their reaction with N_2O_5. Clearly primary quantum yield data are needed.

References

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$HONO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_o^o/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HONO + h\nu \rightarrow HO + NO$	(1)	202	591
$\rightarrow H + NO_2$	(2)	326	367
$\rightarrow HNC + O$	(3)	423	283

Absorption cross section data

Wavelength range/nm	Reference	Comments
300-400	Johnston and Graham, 1974 [1]	(a)
200-400	Cox and Derwent, 1976 [2]	(b)
310-396	Stockwell and Calvert, 1978 [3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 0.92 \pm 0.16$	365 ± 5	Cox and Derwent, 1976 [2]	(d)

Comments

(a) HONO prepared from mixtures of NO, NO_2 and H_2O. [HONO] calculated assuming equilibrium conditions. Later these same authors found that the actual concentration of HONO was much less than the calculated equilibrium concentration, and therefore the values reported in refe[illegible] [1] were much too low. (Graham and Johnston, 1977 [4]). Slightly modified values given in Gran[illegible], 1975 [5].

(b) HONO prepared from reaction of sulphuric acid with sodium nitrite. Resolution < 0.1 nm. Correction was made for absorption by NO_2. Values are tabulated at 5 nm intervals from 200-310 nm and at 1 nm intervals from 310-400 nm.

(c) HONO prepared from mixtures of NO, NO_2 and H_2O. It was shown that equilibrium conditions were established. Resolution < 1 nm from 325-400 nm. Corrections were made from absorption by NO_2, N_2O_3 and N_2O_4. Values are tabulated at 1 nm intervals.

(d) Value estimated by comparison of rates of photon absorption by NO_2 and HONO with their measured rates of decomposition in the same photolysis cell. This result supersedes earlier estimate by same method in Cox, 1974 [6] owing to use here of more reliable absorption cross section data.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/\text{cm}^2$
310	0
315	0.4
320	4.0
325	3.8
330	8.8
335	5.7
340	17.6
345	11.1
350	10.0
355	26.5
360	7.2
365	18.2
370	20.9
375	3.7
380	8.2
385	14.7
390	1.4
395	0

Quantum yields

ϕ_1 = 1.0 throughout this wavelength region

Comments on preferred values

The preferred absorption cross section values have been derived from the tabulated results in Stockwell and Calvert, 1978 [3] by averaging the values over 5 nm intervals. For greater detail see the original reference. These values are preferred over those reported by Cox and Derwent, 1976 [2] because of the use of higher resolution cross section data in correcting for absorption by NO_2. These two studies are in reasonably good agreement. For values at shorter wavelengths, use values tabulated in Cox and Derwent, 1976 [2].

Based on the results of Cox and Derwent, 1976 [2], the preferred value of ϕ_1 is set equal to unity throughout this wavelength range. It should be emphasized that quantum yield data exist for only one wavelength - clearly more data are needed.

References

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$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH_0^o/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	418	286
$\rightarrow HONO + O(^1D)$	(4)	488	245

Absorption cross section data

Wavelength range/nm	Reference	Comments
190-370	Johnston and Graham, 1973 [1]	(a)
185-325	Biaume, 1973 [2]	(b)
120-170	Beddard, Giachardi and Wayne, 1974 [3]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 1.0$	200-315	Johnston, Chang and Whitten, 1974 [4]	(d)

Comments

(a) Continuous absorption spectrum. Values are tabulated at 5 nm intervals from 190-325 nm. Also, it is reported that $\sigma << 10^{-22}$ cm^2 from 330-370 nm.

(b) Measurements made and values tabulated for discrete emission lines of selected lamps. Photodissociation rate for HNO_3 in the stratosphere calculated assuming $\phi_1 = 1.0$.

(c) Results given in figure of molar decadic extinction coefficient as a function of wavelength.

(d) Photolysis of HNO_3 in presence of excess CO and excess O_2 to prevent complications due to secondary reactions. Results interpreted by complex reaction scheme.

Preferred Values

Absorption cross sections

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
190	1320	260	1.90
195	910	265	1.80
200	550	270	1.63
205	255	275	1.40
210	97	280	1.14
215	32.8	285	0.88
220	14.4	290	0.63
225	8.51	295	0.43
230	5.63	300	0.28
235	3.74	305	0.17
240	2.60	310	0.09
245	2.10	315	0.05
250	1.95	320	0.02
255	1.94	325	0.00

Quantum yields

ϕ_1 = 1.0 throughout this wavelength region

Comments on preferred values

The preferred absorption cross section values are those of Johnston and Graham, 1973 [1]. The results of Biaume, 1973, [2] are in excellent agreement. For discussion of earlier results see review by Okabe, 1973 [5].

The preferred value of the quantum yield (ϕ_1 equal to unity) is based on the results of Johnston, et al, 1974 [4]. Ealier results of Berces and Forgeteg, 1970 [6] are discussed in review by Okabe, 1973 [5].

References

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$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH^o_{298}/kJ mol^{-1}	$\lambda_{threshold}$/nm
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	89	1340
$\rightarrow HO + NO_3$ (2)	164	730

Note: ΔH^o_{298} values are given since the heat of formation of HO_2NO_2 at 0 K is not known.

Absorption cross section data

Wavelength range/nm	Reference	Comments
190-330	Graham, Winer and Pitts, 1978 [1]	(a)
195-265	Cox and Patrick, 1979 [2]	(b)

Comments

(a) Measured at 289K. HO_2NO_2 prepared from NO_2 and H_2O_2. Corrections were made for absorption by H_2O_2, HNO_3 and NO_2.

(b) Measured at 283K. HO_2NO_2 prepared by photolysis of Cl_2 in excess H_2 with NO_2 present in a mixture of N_2 and O_2 at 1 atmosphere pressure. Correction was made for absorption by O_3, assuming that all the absorption at 265 nm was due to O_3.

Absorption cross section data

	$10^{20}\ \sigma/\mathrm{cm}^2$	
λ/nm	[1]	[2]
190	1610	
195	960	404
200	640	434
205	430	420
210	290	378
215	200	298
220	154	220
225	123	163
230	99	120
235	82	93
240	68	76
245	58	65
250	51	54
255	45	44
260	40	30
265	35	< 10
270	28	
275	23	
280	18	
285	14	
290	10.9	
295	8.4	
300	6.2	
305	5.0	
310	4.2	
315	3.6	
320	3.0	
325	2.6	
330	2.2	

Quantum yield data

No data

Preferred Values

Absorption cross sections

No recommendation - see comments.

Quantum yields

No recommendation can be made for the values of ϕ_1 and ϕ_2, since there are no data to provide a basis for a recommendation.

Comments on preferred values

No recommendation is made for absorption cross section values. The wavelength region of importance for photodissociation in the atmosphere is for λ > 290 nm. While the two sets of data are in reasonable agreement from 205 to 255 nm, the fall off in values reported in [2] from 255 to 265 nm suggests negligible absorption beyond 270 nm in contrast to the data reported in [1]. This fall off could possibly be accounted for by an overcompensation for absorption by ozone. Alternatively the absorption at long wavelengths reported in [1] could possibly be accounted for by the presence of an absorbing impurity. Additional studies in the important atmospheric photodissociation region (λ > 290 nm) are needed to resolve the apparent discrepancy between the reported results.

Clearly, data are needed on the identification of primary products and quantum yields.

References

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