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Chemical Kinetics Data Survey VI: Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Atmospheric Chemistry

R. F. Hampson, Editor

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Physical Chemistry Division
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National Bureau of Standards
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August 1973

Interim Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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Chemical Kinetics Data Survey

VI. Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Atmospheric Chemistry

Abstract

Photochemical and rate data have been evaluated for twelve gas phase reactions of interest for the chemistry of the stratosphere. The results are presented in data sheets, one for each reaction. For each reaction the data are summarized. A preferred value is given for the rate constant or the primary quantum yield and photoabsorption cross section.

Key words: atmospheric chemistry; chemical kinetics; data evaluation; gas phase reaction; optical absorption cross section; photochemistry; quantum yield; rate constants.

Introduction

This report presents evaluations of chemical kinetic and photochemical data for twelve gas phase reactions. It is the sixth in a series. The objective of the work and a description of the general format of a data sheet including explanatory material regarding general conventions for the presentation of data have been given in the introductory sections of two previous reports: NBS Report 10692 (January 1972) and NBS Report 10828 (April 1972).

The evaluations in these two reports have been updated recently and will be published in "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry", R. F. Hampson, editor. J. Phys. Chem. Ref. Data 2, #2(1973). For some reactions, a change was made in the recommended value of the rate constant, quantum yield or absorption cross section. These changes are summarized in the following tables.

Table 1. Revised Recommended Values for Reactions Evaluated in NBS Reports 10692 and 10828

RATE CONSTANTS

Reaction	$k/\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$	T/K	Δlog k
$H + HNO \rightarrow H_2 + NO$	7×10^{-12}	2000	±0.3
$HNO + HO \rightarrow H_2O + NO$	7×10^{-11}	1600-2100	±0.7
$HNO_2 + HO \rightarrow H_2O + NO_2$	No recommendation		
$HNO_3 + HO \rightarrow H_2O + NO_3$	$6 \times 10^{-13} \exp(-400/T)$	300-650	±0.5
$HO + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-1000/T)$	220-450	±0.3
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$3 \times 10^{-11} \exp(-500/T)$ (a)	300-1000	±0.3(b)
$H_2O + NO + NO_2 \rightarrow 2HNO_2$	$< 1.1 \times 10^{-55}$ (c)	300	
$H_2O + N_2O_5 \rightarrow 2HNO_3$	$< 1 \times 10^{-20}$	300	
$H_2O + O(^1D) \rightarrow 2HO$	3.5×10^{-10}	300	±0.1
$H_2O_2 + NO \rightarrow HO + HNO_2$	$\sim 5 \times 10^{-20}$	300	
$NO_2 + O_3 \rightarrow NO_3 + O_2$	5×10^{-17}	298	±0.2
$N_2O + O(^1D) \rightarrow N_2 + O_2$	1.1×10^{-10}	300	±0.1
$\rightarrow 2NO$	1.1×10^{-10}	300	±0.1
$O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} \exp(-2300/T)$	200-1000	±0.1
$O_2(^1\Delta) + M \rightarrow O_2 + M$	$< 2 \times 10^{-20}$ $(M{=}N_2)$	300	

(a) $-d[HO_2]/dt = 2k[HO_2]^2$

(b) Uncertainty in log k increases to ±1 at 1000 K.

(c) $-d[NO_2]/dt = k[NO][NO_2][H_2O]^2$. The experimental data show a <u>second order</u> dependence of rate on $[H_2O]$. Value for k is for a surface reaction. This is adopted as the upper limit for the gas phase rate constant.

Table 1 (Continued)

PHOTOCHEMICAL DATA

Reaction	Quantum yield, $\phi(\lambda)$	Wavelength λ, nm
$HNO_3 + h\nu \rightarrow HO + NO_2$	no recommendation	
$O_3 + h\nu(uv) \rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	0	< 350
$\rightarrow O(^3P) + O_2(\text{singlet})$	∿1	310-350
	0	< 310
$\rightarrow O(^1D) + O_2(^1\Delta)$	1	250-310
	0	>310

Also, the newer values of the absorption cross section for nitric acid by Johnston and Graham (J. Phys. Chem. 77, 62 (1973)) are now the recommended values.

Note concerning the O_3 quantum yields

The behavior of $\phi(O^1D)$ near λ = 310 nm is currently under study in several laboratories. These should provide a better definition of $\phi(O(^1D)$ in the critical region near the thermochemical threshold. A reanalysis of the matter will appear in a later publication in this series.

Chemical Kinetics Data Survey

The Reaction of H with H_2O_2

1. Two channels are possible for this reaction; they are

$$H + H_2O_2 \rightarrow H_2 + HO_2 \qquad k_1$$

$$H + H_2O_2 \rightarrow H_2O + HO \qquad k_2$$

2. ΔH°_{298} (1) = -61 ± 8 kJ/mol (-14.5 ± 2 kcal/mol) (a)

ΔH°_{298} (2) = -284 kJ/mol (-68.0 kcal/mol) (a)

$\log_{10} K_{eq.}$ (1) = 0.342 + 3.26 (1000/T) (b)

$\log_{10} K_{eq.}$ (2) = 0.877 + 14.98 (1000/T) (b)

3. Data

The available rate data have been presented and evaluated by Baulch, Drysdale, Horne and Lloyd (c). In their 1972 review, they recommended the expression $k_1 = 2.8 \times 10^{-12} \exp(-1900/T)$ cm^3 $molecule^{-1} s^{-1}$ from 300 to 800 K and made no recommendation for k_2. There have been no more recent measurements.

Albers et al (d) measured the total rate of removal of D atoms in a discharge-flow reactor from 294 to 464 K with 5-8 torr H_2O_2 and added O atoms to suppress the chain decomposition initiated by OH. D atoms were monitored by ESR and mass spectrometry. They estimate that $k_1/k_2 \approx 10$ for D atoms at 421 K. Also they find $k_1^{(H)}/k_1^{(D)} = 0.43$ at 375 K. They give the result that $k_1^{(D)} + k_2^{(D)} = 1.2 \times 10^{-11} \exp(-4200/RT)$ cm^3 $molecule^{-1} s^{-1}$. (294-464 K).

Baldwin et al (e) studied the decomposition of H_2O_2 in the presence of H_2 from 713-773 K. They report k_1/k_2 to have the value 0.143 over this temperature range (note: in their abstract this is incorrectly given as 0.125). Also they measure the ratio k_2/k_3 where (3) is $H + O_2 + M \rightarrow HO_2 + M$. From this ratio and their previously measured values of k_3/k_4 where (4) is $H + O_2 \rightarrow HO + O$ they derive values of k_2/k_4. Baulch et al (c) use the values k_1/k_2 and k_2/k_4 in (e) with their own recommended expression for k_4 to obtain values of k_1. (Note: Because Baulch et al used the value of k_1/k_2 in Baldwin's abstract, the calculated values of k_1 given on p. 212 of (c) should be increased by 14%; however this will not seriously affect their evaluation).

4. Preferred value

$k_1 = 2.8 \times 10^{-12} \exp(-1900/T)$ cm^3 molecule^{-1}s^{-1} (300-800 K)

uncertainty: factor of two

no value is recommended for k_2

5. Remarks

The recommendations of Baulch et al have been adopted. The value derived there for $k_2 = 3.7 \times 10^{-9} \exp(-5900/T)$ cm^3 molecule^{-1}s^{-1} as noted there can not be recommended with any confidence because of the unreasonably high value of the pre-exponential factor. By extrapolation, k_1 at stratospheric temperatures (220 K) is estimated to be 5×10^{-16} cm^3 molecule^{-1}s^{-1}. From these expressions k_2/k_1 at 220K is estimated to be 10^{-5}, subject to a large uncertainty.

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M. D. Scheer
September, 1972

PHOTOCHEMISTRY OF HNO_2

1. Primary Photochemical Transitions

Reaction	ΔH^o_0 kJ/mol	ΔH^o_0 kcal/mol	λ threshold (nm)
$HNO_2 \rightarrow OH + NO$	202	(48)	590
$\rightarrow H + NO_2$	326	(78)	370
$\rightarrow HNO + O$	423	(101)	280

(ΔH^o_0 values from [a] except ΔH^o_0 (HNO) from [b])

2. Data

The absorption spectrum of HNO_2 vapor in the region 300-400 nm, has been reported and partly analyzed (ref [c] and references cited therein). It consists of a series of diffuse absorption bands which showed no fine structure when photographed on a 20-foot grating spectrograph with a resolving power of 150,000. Fig. 1 (from [c]) shows the absorption spectrum of HNO_2 at 25°C.

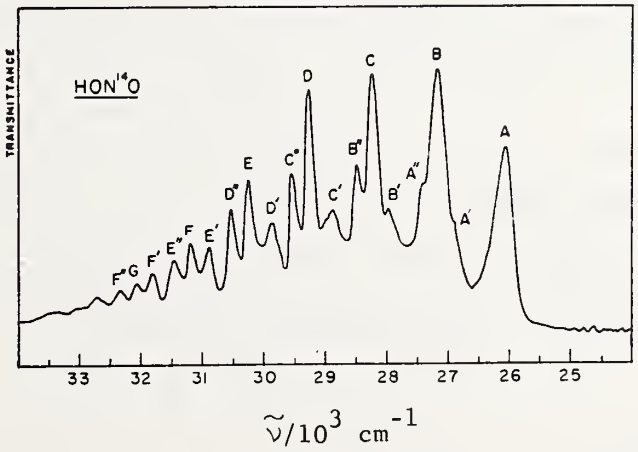

Fig. 1 The absorption spectrum of HONO at 25 C.

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No absorption coefficients nor quantum yields have been published. Preliminary measurements (H. Johnston, private communication) on $NO + NO_2 + H_2O \rightleftarrows 2\ HNO_2$ equilibrium mixtures provide a scale for figure 1, good to a factor of 1.5 to 2. The absorption cross sections for peaks B and E, averaged over a 1 nm wavelength interval were 10.7×10^{-20} and 3.8×10^{-20} cm^2 $molecule^{-1}$ respectively.

The only related data on absorption coefficients are for HNO_2 in aqueous solution [d]. For HNO_2 in 0.05 normal HCl, there are a series of bands from 380 to 320 nm, with the maximum value of the decadic molar extinction coefficient equal to 50 liter mol^{-1} cm^{-1} at approximately 371 and 358 nm. (abs. cross section = 1.9×10^{-19} cm^2). These values obtained in a polar solvent are not recommended for use in calculating the absorption of HNO_2 in the gas phase.

3. Preferred values

No values are recommended for the absorption coefficient or the quantum yield.

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R. Hampson
November 1972

Chemical Kinetics Data Survey

The Reaction of HO with H_2O_2

1. Reaction

$HO + H_2O_2 \rightarrow HO_2 + H_2O$ $\qquad k_1$

2. $\Delta H°$ (298) = -124.3 kJ mol^{-1} (-29.7 kcal mol^{-1}) (a)

$\log_{10} K_{eq} = -0.329 + 6.612\ (1000/T)$ (j)

3. Data

a. The available data prior to 1972 have been described and evaluated by Baulch et al [h] and by Drysdale and Lloyd [i]. In these reviews in 1972 and 1970, they recommended the expression $k_1 = 1.7 \times 10^{-11} \exp(-910/T)$ cm^3 $molecule^{-1} s^{-1}$ from 300 to 800 K.

Upper and lower limits for k_1 at 298 K have been derived from studies employing flash photolysis [b] and electric discharge [c] of H_2O_2.

Absolute values of k_1 over the temperature range 307 - 462 K have been determined in flash photolysis studies by following the OH decay by kinetic spectroscopy.

Rate ratio data at higher temperatures extends the range. A k_1/k_2 ratio was determined at 798 K using the thermal decomposition of H_2O_2 in the presence CO [d].

$$CO + HO \rightarrow CO_2 + H \qquad (2)$$

The rate relative to reaction 3,

$$HO + H_2 \rightarrow H + H_2O \qquad (3)$$

has been determined between 700 and 800 K by examination of the inhibition of the second explosion limit of the H_2/O_2 system by H_2O_2 [e], in studies of the decomposition of H_2O_2 in the presence of H_2 in boric acid coated vessels [f] and from studies of the $H_2/O_2/N_2$ system [g].

b. Recent measurements

There has been only one measurement involving the rate of this reaction since the 1972 review by Baulch et al (h).

Quantity Measured	System
$k_1/k_2 = 8.13 \pm 0.56$ where k_2: $HO + CO \rightarrow CO_2 + H$	Photolysis of H_2O_2 (0.94 torr) at 254 nm. in presence of O_2 (5.4 torr) and CO (3-32 torr). Measured initial rate of formation of CO_2. GORSE, VOLMAN 1972 (k)

4. Preferred Value

$k_1 = 1.7 \times 10^{-11} \exp(-910/T)$ cm^3 molecule^{-1}s^{-1} for $300 < T < 800$.

k_1 (300 K) $= 8.2 \times 10^{-13}$ cm^3 molecule^{-1}s^{-1}. This is the evaluation given in refs [h, i]. It fits the measured data within 50%.

5. Remarks

Reaction 1 is a simple H atom abstraction

$$HO + H\text{-}O_2H \rightarrow H_2O + HO_2$$

and is the only interaction expected in this system.

The evaluation relies heavily on the data of Greiner which are the only absolute rate measurements available. The flash photolysis study is subject to some uncertainty due to the method of temperature measurement. The temperature was varied by changing inert gas pressures thereby lowering the effect of flash heating. This coupled with the normal experimental uncertainties gives a reliabity factor of approximately 2 to the data. Thus, the expression given above probably predicts the value for k_1 within a factor of 2 over the temperature range 298 to 800 K. At stratospheric temperatures 200-240 K the uncertainty is considerably larger (probably at least a factor of 4). Thus a number of lower temperature measurements are in order.

A value of k_1 can be derived from the recent relative rate measurement in ref. (k) by selecting a value for k_2: $HO + CO \rightarrow CO_2 + H$. For the room temperature value of k_2 we select the recent direct measurement of Stuhl and Niki (ℓ): $k_2 = 1.35 \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$. This result has been confirmed quite recently in a study using a completely different technique (m). Using this value, we derive the value $k_1 = (11 \pm 3) \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$ from the ratio measured in (k). We consider this to be in substantial agreement with the value k_1 (300 K) $= 8.2 \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$ recommended in Section 4. The combined uncertainties in the measured values of (k_1/k_2) and k_2 and the complexity of the mechanism used in (k) do not justify changing the recommended value of k_1. Alternatively, one can use for k_2 the expression $k_2 = 5.1 \times 10^{-13} \exp(-300/T)$ cm^3 $molecule^{-1} s^{-1}$ recommended by Wilson in his recent lengthy review of hydroxyl radical reaction kinetics (n). This expression gives $k_2 = 1.88 \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$, which value, when combined with the ratio measured in (k) gives $k_1 = 15 \times 10^{-13}$ cm^3 $molecule^{-1} s^{-1}$.

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July, 1972
Revised July, 1973
M. J. Kurylo

Chemical Kinetics Data Survey

The Combination of HO with NO

1. Reaction evaluated

	ΔH°_{298} kJ/mol	kcal/mol	(a)
$HO + NO + M \rightarrow HNO_2 + M$	-209.32	(-50.03)	k_1

2. Related reactions

$HNO_2 + M \rightarrow HO + NO + M$	209.32	(50.03)	k_2
$HO + CO \rightarrow CO_2 + H$	-103.97	(-24.85)	k_3
$HO + H_2 \rightarrow H_2O + H$	- 62.81	(-15.01)	k_4

3. Data

Results $k_1 \times 10^{31}$ / $cm^6 molecule^{-2} s^{-1}$	P(M)/torr
4 ± 2	5
2.5 ± 1	8

System

Fast flow experiments with excess NO_2 added to H atoms in Ar, T = 297 K. OH detected by resonance fluorescence

ANDERSON, KAUFMAN, 1972 (b)

$k_1 \times 10^{31}$ / $cm^6 molecule^{-2} s^{-1}$	T/K
4.1 ± 0.6	300
1.9 ± 0.3	416

$k_1(H_2)/k_1(He) = 2.3 \pm 0.9$

Flash photolysis of NO_2 in presence of H_2 (2.5 or 15 torr) and NO (<0.4 torr). He added to bring total pressure to 30 torr. OH detected by U.V. absorption.

MORLEY, SMITH, 1972 (c)

$k' \times 10^{31}$ / $cm^{6} molecule^{-2} s^{-1}$	T/K
13	273
8.0	298
3.6	398

$k_1(Ar)/k_1(He) = 0.45$ at 298 K

Flow experiment with OH (from H + NO_2) and excess NO. OH detected by e.s.r. M = He (0.5 to 5 torr).

WESTENBERG, DeHAAS, 1972 (d)

$k' \times 10^{13}$ / $cm^{3} molecule^{-1} s^{-1}$	P(M)/torr
0.8	5
1.4	10
2.2	20
5	82

Pulsed vacuum u.v. photolysis of H_2O in presence of NO and excess He(5 - 82 torr). OH detected by resonance fluorescence

STUHL, NIKI, 1972 (e)

$k' = 34k_3 + 234k_4$

(expression derived from data)

value reported:

$k' = 6 \times 10^{-12}$ $cm^{3} molecule^{-1} s^{-1}$

Photolysis of N_2O (47 torr) in presence of H_2 (760 torr), O_2 (50 torr), CO (110 torr), and NO (60 or 120 mtorr). $\Phi(NO_2)$ measured. T = 300 K.

SIMONAITIS, HEICKLEN, 1973 (f)

---

*k' is the pressure dependent rate constant defined by the expression:

$$d[HNO_2]/dt = k'[HO][NO]$$

4. Preferred values

Preferred values of k_1 are given in Figure 1.

$\Delta \log k = \pm 0.5$

Values of k based on a N_2 efficiency of 0.5

5. Remarks

Experimental results are in satisfactory agreement in the sense that all the data can be fitted with a maximum deviation of ±40% (see Table 1). At the present time this is probably all that can be expected. The present fit is based on RRKM calculations (g,h) assuming a loose complex [transition state frequencies 3600, 1600, 60(2), and 40 yielding $k_{1\infty}$ (300) = 2×10^{-11} $cm^3 molecule^{-1} s^{-1}$] and with all overall rotations active. The last ignores angular momentum conservation. The justification is that in other cases when this is combined with the two adjustable parameters $k_{1\infty}$ and λ (collision efficiency) a satisfactory fit can be made over large temperature ranges (h). The symbol $k_{1\infty}$ denotes the limiting high pressure second order rate constant for reaction 1. The approach is thus largely empirical. In this study λ is .8 and the collision diameter 6.5Å. Third body efficiencies are He(.42), Ar(.21), and H_2(1.0). All calculations are based on the more stable trans-HNO_2 form. Values of k_1 calculated for the cis form are about 20% slower. Conversion to values of k_2 can be effected through the equilibrium constant $\log_{10} K_P$ (atm) = 7.7516 - 10976/T (derived from thermochemical data in ref. j.).

6. Comments on measurements

ref f. The value reported for $k_1[M]$ is based on the values $k_3 = 1.35 \times 10^{-13}$ and $k_4 = 7.1 \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$ (i).

Table 1. Comparison between Experimental and Calculated Values of k_1

Ref	M	P(M)/torr	T/K	$k_1 \times 10^{31}$ / $cm^6 molecule^{-2} s^{-1}$ Exptl.	Calc.
(b)	Ar	5	297	4	3.8
		8		2.5	3.3
(c)	He	30	300	4.1	4.1
			416	1.9	2.4
(d)	He	3	273	13	8.7
			298	8	6.9
			398	3.6	3.8
	Ar	3	298	3.6	3.5
(e)	He	5	298	5.2	6.2
		10		4.4	5.5
		20		3.4	4.3
		82		1.9	2.9
(f)	H_2,CO,O_2,N_2O $X(H_2)=0.78$	970	300	1.9	1.5

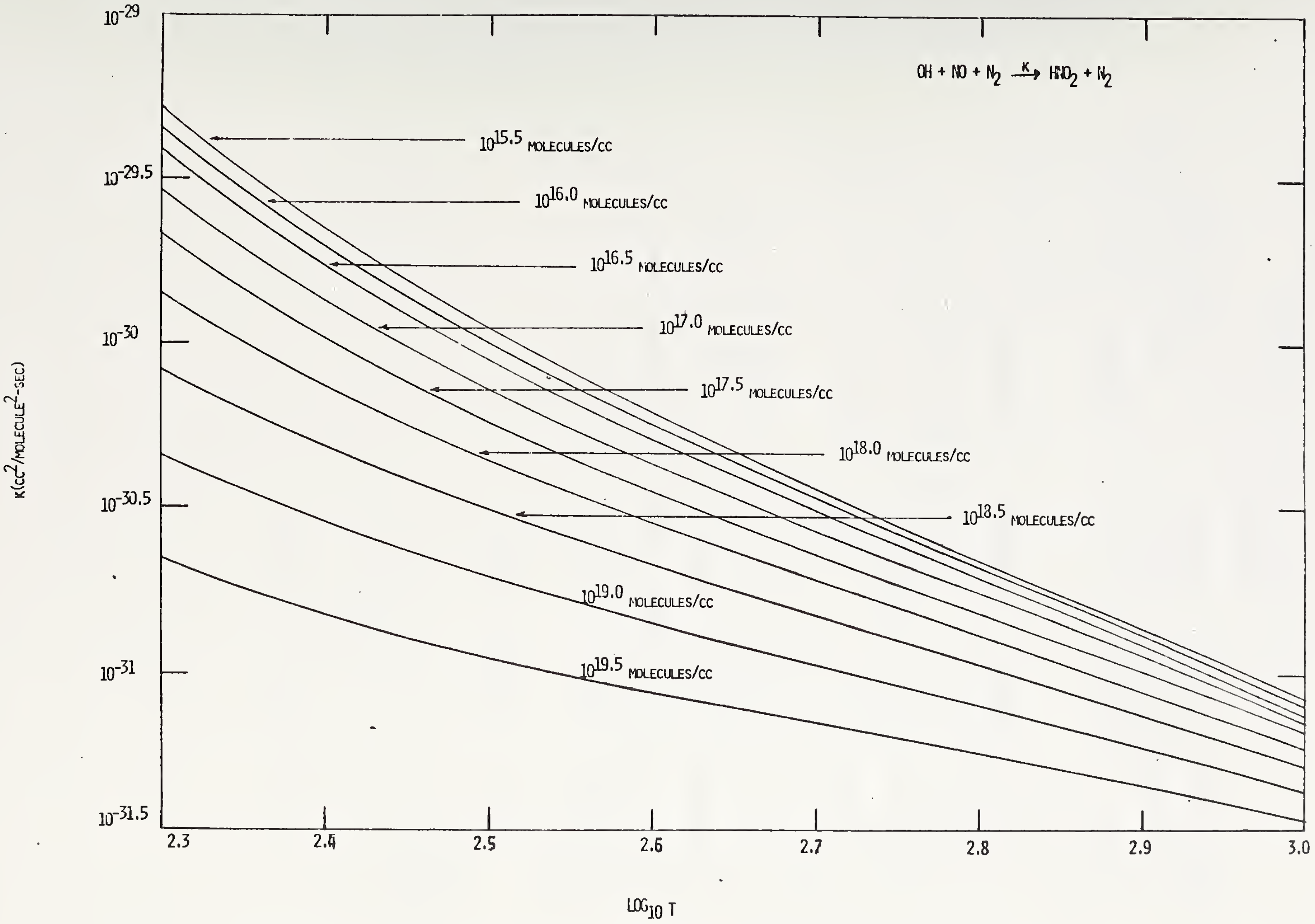

Fig. 1. The third order rate constant for the reaction $HO + NO + M \rightarrow HNO_2 + M$ as a function of temperature and concentration (for $M = N_2$)

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W. Tsang
May 1973

Chemical Kinetics Data Survey

The Combination of HO with NO_2

1. **Reaction evaluated**

	ΔH°_{298} kJ/mol	kcal/mol	(a,b)
$HO + NO_2 + M \rightarrow HNO_3 + M$	-207.2	(-49.52)	k_1

2. **Related reactions**

$HNO_3 + M \rightarrow HO + NO_2 + M$	207.2	(49.52)	k_2
$HO + HNO_3 \rightarrow H_2O + NO_3$	-76	(-18)	k_3
$HO + CO \rightarrow CO_2 + H$	-103.97	(-24.85)	k_4

3. **Data**

a. **Direct Studies**

Results	System
$k_1/k_3 = 2.2 \times 10^{-20}$ cm^3 $molecule^{-1}$	Nitric acid photolysis at 300 K and 150-750 torr Kr. Measured change in Φ (NO_2) as function of [Kr]. BERCES, FORGETEG, 1970 (c)
$k_1 = 1.6 \times 10^{-29}$ cm^6 $molecule^{-2} s^{-1}$	Mass spectrometric study of $H + NO_2 \rightarrow HO + NO$ at 0.2 to 1 torr total pressure. Measure Δ [NO_2] MULCAHY, WILLIAMS, 1971 (d)

$k' \times 10^{12}$* $cm^3\ molecule^{-1} s^{-1}$ T = 300 K	$k' \times 10^{12}$* $cm^3\ molecule^{-1} s^{-1}$ T = 416 K	P(M)/torr
1	0.4	30
2.0	0.75	100
3.3	1.6	300

Flash photolysis of NO_2 in presence of H_2 at 300 and 416 K, 20-300 torr He, Followed disappearance of OH by resonance absorption.

$k_1(SF_6)/k_1\ (He) = 4.8 \pm 0.8$

$k_1(H_2)/k_1\ (He) = 4 \pm 1$

MORLEY, SMITH, 1972 (e)

$k_\infty/k_4 = 15 \exp(380/T)$

where k_∞ = limiting high pressure 2nd order value for k_1

$k_1/k_4 = 2 \times 10^{-18} \exp(550/T)$

cm^3/molecule M = He

$k_1(H_2O)/k_1\ (He) \sim 8$

$k_1(CO)/k_1\ (He) \sim 1.5$

Photolysis of NO_2 at 228.8 nm in presence of 3-20 torr H_2O, 0-1000 torr He, 1-350 torr CO, and 3-30 torr NO_2 at 300 and 423 K. Measured $\Phi(CO_2)$.

SIMONAITIS, HEICKLEN, 1972 (f)

$k_1 \times 10^{30}$ $cm^6\ molecule^{-2} s^{-1}$	P(Ar)/torr
1 ± 0.3	0.5-3
0.8	6
0.6	10
2	P = 8 torr $X(N_2) = 0.8$ $X(Ar) = 0.2$

Fast flow experiments with excess NO_2 added to flowing H atoms in Ar at 297K. OH detected by resonance fluorescence.

ANDERSON, KAUFMAN, 1972 (g)

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*k' is the pressure dependent rate constant defined by the expression $d[HNO_3]/dt = k'[HO][NO_2]$.

$k_1 \times 10^{30}$ $cm^6 molecule^{-2} s^{-1}$	M	T/K
2.01	He	273
1.57	He	298
0.58	He	398
0.83	Ar	298

Similar experiments as in ref. (g), except that OH was detected by e.s.r. P = 0.5 to 5 torr.

WESTENBERG, DEHAAS, 1972 (h)

b. Indirect Studies

$k_2[M] = 0.16\ s^{-1}$

$[M] = 1$ atm N_2, $T = 670$ K

Decomposition of HNO_3 in 1 atm N_2 in static system. $[HNO_3]$ and $[NO_2]$ determined by absorption.

JOHNSTON et al, 1953 (i)

$k_2 \times 10^{19}$ $cm^3 molecule^{-1} s^{-1}$	T/K
0.53	648
1.7	673
4.8	698

$P(HNO_3) \sim 3$ torr

Decomposition of HNO_3 in static system. $P(HNO_3)$ was 0.5-20 torr. $[NO_2]$ determined by absorption.

$k_2(M)/k_2(HNO_3)$	M
1	H_2O
0.25	CO_2
0.15	O_2
0.1	Ar

(T = 673 K)

JOHNSTON et al, 1955 (j)

$k_2 = 2.6 \times 10^{-9} \exp(-15{,}400/T)$ $cm^3\ molecule^{-1} s^{-1}$	Shock tube study of HNO_3 decomposition in 500 torr Ar (2-4% HNO_3) at 800-1200 K. Rate determined from NO_2 appearance. HARRISON et al, 1962 (k)
$k_2[M] = 0.012\ s^{-1}$	Decomposition of HNO_3 at 622 K in N_2; $P(HNO_3) \sim 30$ torr, total pressure 680 and 230 torr. Rate determined from $\triangle [HNO_3]$ and agrees with that determined from $\triangle [NO_2]$. GODFREY, et al, 1965 (ℓ)

4. Preferred value

Preferred values of k_1 are given in Figure 1.

$\triangle \log k = \pm 0.3$

Values of k based on a N_2 efficiency of 0.26

5. Remarks

The fit of the data is based on RRKM calculations (o,p) a loose complex and overall rotations active. The transition state structure is 3600, 1600(2), 760, 40(2) and 2 free internal rotors (1.6×10^{-40} g-cm^2). This yields $k_{1\infty}$ (300 K) = 1.0×10^{-11} cm^3 molecule^{-1}s^{-1}. The collision diameter is 6.5A and the collision efficiency is 1. The third body efficiencies are $HNO_3 = 1.00$, He = .26, Ar = .12, and $N_2 = .26$. A summary of the data on third body effects can be found in Table 3. A satisfactory fit can also be obtained with a transition-state model with an elongated central bond (factor of 3) and with the overall rotation about this bond as active. (p). Except for ref. c and d, results can be fitted to within a factor of 2. This is summarized in Tables 1 and 2. Note that the data range from .5 torr to an atmosphere and 273-1100 K and involves the forward and reverse reactions. The larger discrepancies of ref. c and d (compared to the other results) can be attributed to errors in specification of the reaction mechanism.

6. Comments on measurements

ref c. From the measured k_1/k_3, taking the value of $k_3 = 1.4 \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$ (ref m), the value k_1 = 3×10^{-33} cm^6 $molecule^{-2}s^{-1}$ is derived. Note that in nitric acid systems at low temperatures, reactions are often subject to surface effects.

ref. d. This is basically a qualitative study with respect to the process of interest.

ref. f. The value of k_3 used in the present analysis to get the values of k_1 in Table 1 is 1.33×10^{-13} cm^3 $molecule^{-1}s^{-1}$ (n).

ref. i and ℓ. This fit does not substantiate the claims that the measured rates are in the limiting high pressure region. The present results indicate that $k_2[M]/k_2^{\infty} \sim 0.1$.

Table 1 Comparison between Experimental and Calculated Values of k_1

Ref	M	P(M)/torr	T/K	$k_1 \times 10^{31}$ / $cm^6 molecule^{-2} s^{-1}$ Exptl.	Calc.
(h)	He	3	273	20	22
		3	298	16	18
		3	398	6	11
	Ar	3	298	8	10
(e)	He	30	300	10.4	8.6
		100		6.2	5.3
		300		3.5	2.9
	He	30	416	5.8	6.1
		100		3.3	4.3
		300		2.2	2.7
(f)	He	30	300	13.6	8.6
		100		9.5	5.3
		300		5.2	2.9
		1000		1.9	1.4
	He	30	423	8.6	5.8
		100		6.7	4.1
		300		4.1	2.6
		1000		1.8	1.5

7

				$k_1 \times 10^{31}$ / $cm^6\,molecule^{-2}\,s^{-1}$	
Ref.	M	P(M)/torr	T/K	Exptl	Calc.
(g)	Ar	.5-3	297	10	12
		6		8	8
		10		6	7.5
	N_2,Ar	8	297	20	19
(c)	Kr	300	300	.03	2
(d)	Ar	1	300	170	10

Table 2 Comparison between Experimental and Calculated Values for k_2

Ref	M	P(M)/torr	T/K	$k_2 \times 10^{19}$ / $cm^3 molecule^{-1} s^{-1}$ Exptl.	Calc.
(k)	Ar	500	900	980	800
			1000	5000	9000
			1100	25000	50000
(j)	HNO_3	3	648	.53	.63
			673	1.7	2.3
			698	4.8	8.0
(ℓ)	N_2	760	622	.012	.014
(i)	N_2	760	670	.15	.22

Table 3. Summary of Experimental Data on Third Body Effects

M	Ref. j	Ref. e	Ref. f	Ref. h	Ref. g
HNO_3	1				
He		1	1	1	
Ar	~ 0.1			0.5	1
H_2O	~ 1		8		
SF_6		4.8			
CO_2	~ 0.25				
N_2					2.2
H_2		4.0			
O_2	~ 0.15				
CO			1.5		

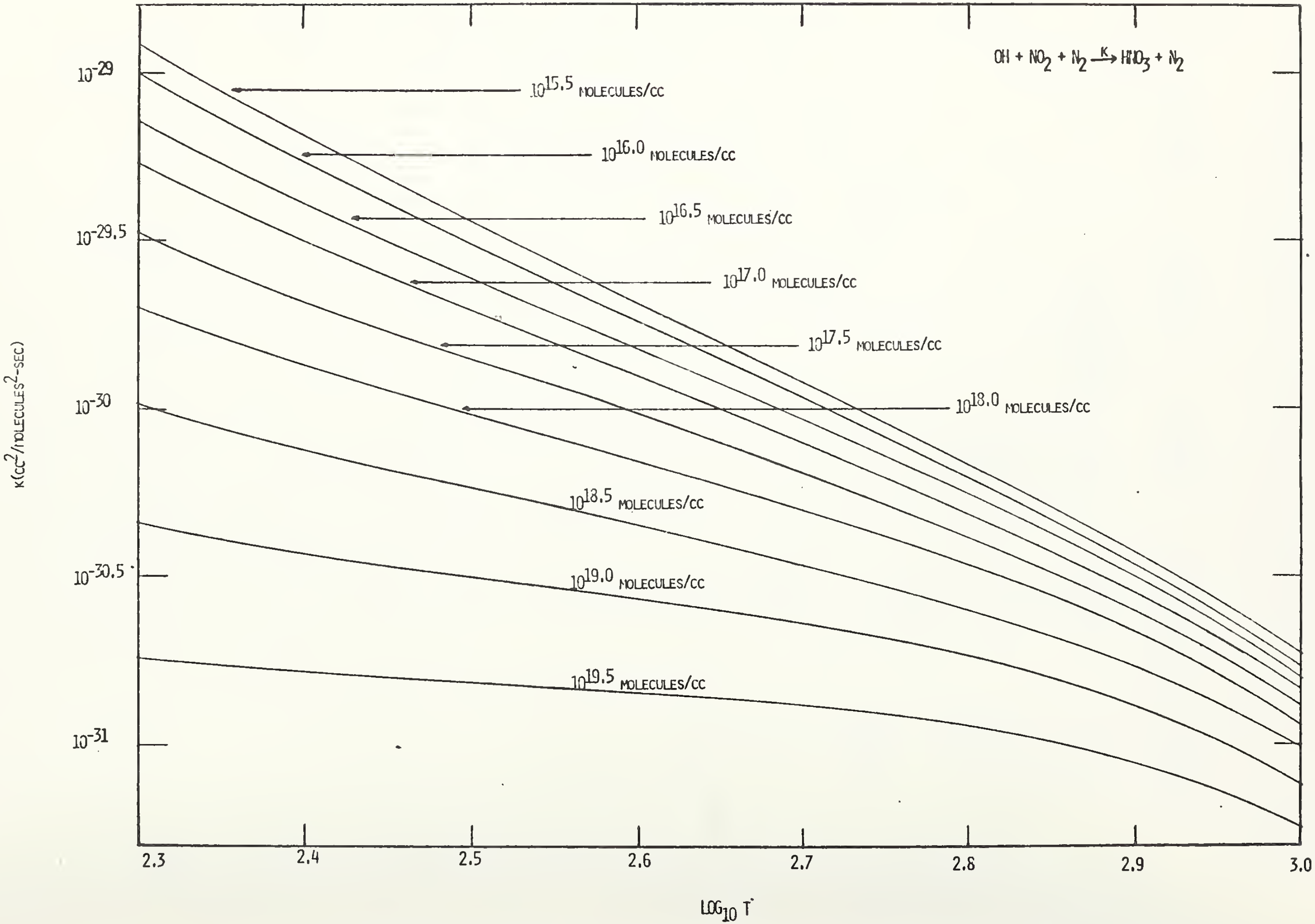

Fig. 1. The third order rate constant for the reaction $HO + NO_2 + M \rightarrow HNO_3 + M$ as a function of temperature and concentration (for $M = N_2$)

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W. Tsang
May, 1973

Chemical Kinetics Data Survey

Photochemistry of NO

1. Primary Photochemical Transitions

a. Dissociation

Reaction	ΔH_0^o kJ/mol	ΔH_0^o kcal/mol	λ threshold (nm)
NO → $N(^4S) + O(^3P)$	627.9	(150.07)	190.5
→ $N(^4S) + O(^1D)$	817.7	(195.43)	146.3
→ $N(^4S) + O(^1S)$	1032.1	(246.68)	115.9
→ $N(^2D) + O(^3P)$	857.8	(205.03)	139.5
→ $N(^2D) + O(^1D)$	1047.6	(250.38)	114.2
→ $N(^2D) + O(^1S)$	1262.1	(301.64)	94.8

ΔH_0^o values calculated from ΔH_f^o (0) in (a) and energies of excitation of $O(^1D)$, $O(^1S)$, and $N(^2D)$ in (b).

The bond dissociation energy has been determined to be 52400 ± 10 cm^{-1} or 626.84 ± 0.12 kJ/mol (149.82 ± 0.03 kcal/mol) (c). This energy corresponds to a threshold wavelength of 190.8 nm.

b. Electronic Energy Levels of NO and Transitions

State	T_0/cm^{-1}	λ(vac)/nm	Transitions
$D(^2\Sigma^+)$	53291 (a)	187.65	D → X (ε)
$C(^2\Pi)$	52372 (a)	190.94	C → X (δ)
$B(^2\Pi_r)$	45505 (a)	219.76	B → X (β)
$A(^2\Sigma^+)$	44199.2 (a)	226.25	A → X (γ)
$a(^4\Pi)$	37965 ± 25 (b)	263	-
$X(^2\Pi_{1/2})$	0	-	-

a. From ref. (x)
b. From ref. (y)

2. Absorption Coefficient Data

The spectroscopy of NO absorption bands has been studied in detail. It is summarized in reference (x). See also references (f, z) for examples of the complexities that occur.

Hudson (h) in 1971 reviewed the u.v. absorption coefficient measurements on NO, with emphasis on data for $\lambda < 160$ nm. Marmo (d) and Thompson, Harteck and Reeves (e) reported absorption coefficients covering the range $110 < \lambda < 230$ nm. These coefficients are not independent of the resolution of their instruments except possibly for $\lambda < 130$ nm. See Figures 1 and 2 for a qualitative view of the spectrum.

a. $\lambda < 130$ nm Watanabe, Matsuga and Sakai, 1967, (g) presented extensive tables of absorption coefficients and photoionization yields. For the range $106 < \lambda < 135$ nm these are based on measurements in a 10 cm long cell with 0.02 nm band pass. There is reasonable agreement with (d).

b. Banded absorption Integrated absorption coefficients and oscillator strengths have been measured for the β, γ, δ and ϵ band systems. These are summarized below as oscillator strengths, f (v', v") for individual bands. v' is the vibrational quantum number in the upper state, v" is that in the ground state. This oscillator strength is related to the integrated absorption coefficient for the same band via

$$f(v', v'') = (mc^2/\Pi e^2 N_o)\ (K_o/F(v''))$$
$$= 4.203 \times 10^{-8}\ (K_o/F(v''))$$

where c is the velocity of light, m and e are the mass and charge of the electron, N_o is the number of molecules per cm^3 at 1 atm. and 273.15 K, and F(v") is the fraction of these molecules in the lower vibrational state (under the conditions of the experiment). K_o is in cm^{-2} atm^{-1}.

Methods of measurement. Bethke 1959 (aa), measured integrated absorption coefficients photometrically for NO pressurized with argon. Callear and Pilling, 1970 (bb), used a similar spectrographic studies and analysis of fluorescence intensities. Farmer et al, 1972 (cc) and Pery-Thorne and Banfield, 1970 (dd) measured refractive index dispersion near absorption lines. Marr, 1964 (ee), reanalyzed the earlier data and presented smoothed values for many transitions in the γ and β bands.

Oscillator Strengths

β bands (B-X), ref(aa) *

v', v"	$10^4 f(v' v")$	v', v"	$10^4 f(v', v")$
2, 0	0.0155 ± 10%	9, 0	3.58 ± 10%
3, 0	0.0461 ± 10%	11, 0	3.62 ± 20%
4, 0	0.138 ± 20%	12, 0	23.1 ± 10%
5, 0	0.264 ± 10%	14, 0	2.006 ± 10%
6, 0	0.462 ± 20%		

γ bands (A-X)

v', v"	$10^4 f(v', v")$		
	Ref (aa)	Ref (cc) *	Ref (dd)
0, 0	3.99 ± 10%	4.0 ± 5%	3.64 ± 0.05
1, 0	7.88 ± 10%	8.09 ± 5%	-
2, 0	6.73 ± 10%	7.00 ± 5%	-
3, 0	3.60 ± 10%	2.4 ± 25%	-

δ bands (C-X)

v', v"	$10^4 f(v', v")$	
	Ref (aa)	Ref (bb) *
0, 0	24.9 ± 10%	56 ± 18%
1, 0	57.8 ± 10%	-
2, 0	27.4 ± 10%	-

ϵ bands (D-X)

v', v"	$10^4 f(v', v")$	
	Ref (aa) *	Ref (bb)
0, 0	25.4 ± 10%	same as for (aa)
1, 0	46.0 ± 10%	-
2, 0	33.2 ± 10%	-

* Preferred values

3. Photochemical data

There have been two recent reviews of the photochemistry of NO: 1) Heicklen and Cohen, 1968, (ref. i), and 2) Preston and Cvetanovic, 1972, (ref j).

a. $\lambda > 191$ nm

Table I summarizes the results of studies of the photochemistry of NO at photon energies less than the dissociation energy.

Absorption produces an excited NO. Products are formed exclusively from reactions of this excited molecular species.

MECHANISM:

$NO + h\nu \rightarrow NO^*$

$NO^* \rightarrow NO + h\nu$

$NO^* + NO \rightarrow 2NO$

$NO^* + NO \rightarrow N_2 + O_2$

$NO^* + NO \rightarrow N_2O + O$

$2NO + O_2 \rightarrow 2NO_2$

b. $\lambda < 191$ nm

Table II summarizes the results of studies of the photochemistry of NO at photon energies greater than the dissociation energy. $\Phi(N_2)$ is always < 1, indicating that absorption produces bound excited states which can fluoresce or be collisionally quenched or dissociate. Products are formed by atom-molecule reactions.

MECHANISM:

$NO + h\nu \rightarrow NO^*$

$NO^* \rightarrow NO + h\nu$

$NO^* + M \rightarrow NO + M$

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

$N + NO \rightarrow N_2 + O$

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

Table I. Summary of data on photochemistry of NO at energies less than the dissociation energy (i.e. at $\lambda > 191$ nm).

λ (nm)	P(NO) (torr)	Products	Quantum Yields	Excited State
214, 226 (Cd(II))	20-600	N_2, NO_2 N_2O	$\Phi(N_2)=0.19$ $\Phi(N_2O)=0.096$ $\Phi(-NO)$(calc) $= 1.05^{(1)}$	$v = 1$ and $v' = 0$ of $A^2\Sigma$
HEICKLEN, 1966 (k)				
199, 193, 186 (Al spark)	50-650	N_2, NO_2, N_2O	$\Phi(-NO) =$ $1.45^{(2)}$	probably $v = 5$ of $B^2\Pi$ by λ=199 nm.
Absorption of 186 nm line probably not important.				
MacDONALD, 1928 (ℓ)				

Note 1. Obtained indirectly; based on mechanism assuming $\Phi(N_2O) = 2$ in presence of large conc. of CH_4.

Note 2. Obtained directly; incident light intensity measured by irradiation of thermocouple.

Table II. Summary of data on photochemistry of NO at energies greater than the dissociation energy (i.e. at $\lambda < 191$ nm).

λ (nm)	P(NO) (torr)	Products	Quantum Yields(1)	Excited State
~160 (H_2 discharge)	2-500	N_2, NO_2	$\Phi(N_2)=.2-.4$ $\Phi(NO_2)=.3-.7$ $\Phi(-NO)$ = 0.8-1.8	$A^2\Sigma$, $B^2\Pi$ $C^2\Pi$, $D^2\Sigma$
147	10-700	N_2, NO_2 N_2O(2)	$\Phi(N_2)=.3-.5$ $\Phi(NO_2)=.6-1.1$ $\Phi(N_2O)=.02-.1$ $\Phi(-NO)$ = 1.3-2.7	v = 7 of $D^2\Sigma$ v = 3 of $E^2\Sigma$
123.6, 116.5	10-950	N_2, NO_2	$\Phi(N_2)=.2-.5$ $\Phi(NO_2)=.4-1.0$ $\Phi(-NO)$ = 1.0-2.3	NO^+ (3)
LEIGA, TAYLOR, 1965 (m)				
~183.2 (Hg arc) and metal spark sources	0.07-7	N_2, NO_2	only dcmp. rate of NO meas.	v = 1 of $C^2\Pi$ with perhaps some abs. to v = 9 of $B^2\Pi$
FLORY, JOHNSTON, 1935 (n)				

Note 1. Φ values in ref (ℓ) based on $\Phi(O_3) = 2$ in photolysis of 1 atm. O_2 flowing through reaction vessel.

Note 2. Secondary product from N + NO_2 (see ref. o).

Note 3. Ionization potential of NO = 9.25 eV (corresponds to λ = 134 nm; at 123.6 nm the ionization yield is 0.77 (g).

In addition to these studies giving values of quantum yields of product formation, the wavelength dependence of the formation of oxygen atoms from photolysis of NO has been studied by Stuhl and Niki (u). They detected O atoms (by NO_2^* emission) when NO was photolyzed at $\lambda > 160$ nm and at $\lambda > 180$ nm but not at $\lambda > 210$ nm. These observations are consistent with the value of the thermochemical threshold for photodissociation (191 nm).

4. Excited States of NO

a. Lifetimes

(1) Mean lifetimes (1/e) of low-lying excited states of NO with respect to spontaneous radiation and predissociation.

State	Lifetime τ_o/s	Reference
$A^2\Sigma$	2×10^{-7}	(p)
$B^2\Pi$	3×10^{-6}	(q)
$C^2\Pi$	6×10^{-10}(a)	(c)
$D^2\Sigma$	2×10^{-8}	(r)

Note (a): predissociation at limiting high [Ar].

(2) Specific rate constants for spontaneous radiation and predissociation (all paths). From reference (c).

Rate constant, k/s^{-1}

State	emission to $X^2\Pi$	emission to $A^2\Sigma$	predissociation
$A^2\Sigma$	0.51×10^7	--	--
$C^2\Pi$	5.1×10^7	3.5×10^7	1.65×10^9 (a)
$D^2\Sigma$	4.1×10^7	0.95×10^7	$<0.8 \times 10^7$

Note (a): k (predissociation) at limiting high [Ar].

b. Quenching of excited states

The table below gives ratios of total quenching coefficients, k_Q, in cm^3 molecule^{-1}s^{-1}, to total spontaneous decay rates, i.e. predissociation plus radiative transitions, $1/\tau_o$ (or $k_p + \Sigma k_r$), in reciprocal seconds. These are based on the quenching half pressure, i.e. that pressure of added gas which reduces the intensity of fluorescence to one-half its value in the absence of added gas. Data from reference (c) and at 298 K except as indicated.

The following formula relates the quenching coefficient, k_Q in cm^3 molecule^{-1}s^{-1}, the radiative lifetime, τ_o in s, and the half pressure, $P_{0.5}$ in kN m^{-2}.

$$k_Q \cdot \tau_o = 4.1 \times 10^{-18}/P_{0.5}$$

$10^{18}\ k_Q \cdot \tau_o/\mathrm{cm}^3\ \mathrm{molecule}^{-1}$

State	NO	N_2	Ar	CO_2	O_2
$A(^2\Sigma)$	47	.0164	< 0.016	79	34 (a)
$C(^2\Sigma)$	2.34	0.91	< 0.008	2.0	
$D(^2\Sigma)$	71	5.6	3.08	22.8	

State	N_2O	H_2	H_2O	CO_2
$B(^2\Pi)$	140 (b,c)	60 (b,c)	$<$ 1500 (b,c)	30 (b,c)

(a) Reference (s), data on O_2

(b) Reference (t)

(c) T = 196 K

(Use values of τ_o in section 4a to obtain k_Q from the table)

5. Preferred values

a. Absorption coefficients

i) Banded spectra (data in section 2b)

β bands. Use data from (aa)

γ bands. Use data from (cc)

δ bands. Use data from (bb) See remarks

ϵ bands. Use data from (aa)

ii) $\lambda < 130$ nm. Use data from (g)

b. Quantum yields

No general recommendations. Product yields depend upon the composition of the mixture being photolyzed and the wavelength of the exciting light. See remarks for some estimates pertinent to absorption in the atmosphere.

6. Remarks

a. Absorption coefficients

(i) $\lambda > 130$ nm. The spectrum is highly structured. The apparent absorption coefficients that have been measured depend strongly upon instrumental resolution. Figure 1 may be used only to locate the wavelengths where absorption occurs but not to obtain the magnitude of the absorption coefficient.

Values for absorption coefficients, either for bands or lines, should be developed from oscillator strengths, $f(v', v'')$, populations of absorbers and line strength formulae. See (w) for application of the technique to NO.

The oscillator strength for δ (0,0) measured by Callear and Piling (bb) is preferred to Bethke's (aa) because it is based on two methods-integrated absorption and fluorescence lifetimes-that agree. This agreement is an argument that large systematic biases are absent from the spectrographic measurements. The value from (bb) is 2.25 times that from (aa).

Oscillator strengths for δ (1,0 and δ (2,0) are available only from (aa). Should they be used as is, or increased, i.e., normalized to the δ (0,0) reported in (bb)? Two arguments suggest that they should be increased. First, the reported oscillator strengths vary approximately as do the Franck-Condon factors. Secondly, Callear and Pilling show that collisional (pressure) broadening is much weaker for the δ (0,0) than the ε (0,0) band. This suggests that the δ bands were insufficiently broadened in Bethke's experiments. The argument is weak because of the high pressures (100 psia) of argon used by Bethke.

Arbitrarily we suggest that the δ (1,0) and δ (2,0) oscillator strengths from (aa) given in section 2b should be multiplied by 2.25. When these new values are used in aeronomic calculations they should be considered to be upper limits.

(ii) $\underline{\lambda < 130 \text{ nm}}$. Absorption into a continuum is the most important element here. The higher resolution study (g) has been selected. The data in Figure 2 are in reasonable agreement.

6.b. Quantum Yields

Product formation following absorption of light by NO. Bound excited states of NO, $a^4\Pi$, $A^2\Sigma^+$, $B^2\Pi$, $C^2\Pi$ and $D^2\Sigma^+$ are formed in the photon absorption by NO in the wavelength range $230 > \lambda > 150$ nm. Other observed products are due to reactions of NO^*. Pertinent processes are reaction of NO^* with NO, predissociation (atom formation), reactive quenching and physical quenching. The first is important in laboratory studies but need not be considered for the photolysis of trace amounts of NO in air. (Mechanisms applicable to laboratory photolyses are given in Section 3 a,b.)

The other processes are important for atmospheric photolysis of NO. Cieslik and Nicolet (w) have developed an overall photodissociation rate. The remarks that follow rely heavily on their discussion and on two recent reviews (i, j) and the summary in (c).

Each state is considered separately. An estimate is made for an "effective initial quantum yield" of products (e.g. O, N, NO_2). More precisely, these estimates are ratios: Products formed per NO^* disappearing by all paths. For each excited electronic state a vibrational-rotational level is reached that is strongly predissociated. (The evidence is either absence of higher levels in emission spectra or line broadening). All higher levels are assumed to dissociate to atoms either directly or via another electronic state. The main discussion is about the fate of lower levels.

NO $(A^2\Sigma^+)$

This is the upper state for the γ bands $(X \rightarrow A)$. Vibrational levels $v' > 4$ are predissociated. $\phi(0) = \phi(N) = 1$, $v' > 4$. For lower levels the only important atmospheric reaction partner is O_2(s). (N_2 is 2000 fold less efficient and is ignored here). Quenching by O_2 may be a chemical reaction, in analogy to NO and CO_2 (s, k, v). The level $A(v = 0)$ is 1.017 ev below the dissociation limit for the ground state (forming ground state atoms)

The minimum required steps are

$$NO + h\nu \rightarrow NO(A^2\Sigma^+, v = 0) \qquad 1$$

$$NO(A^2\Sigma^+) \rightarrow NO + h\nu \qquad 2$$

$$NO(A^2\Sigma^+) + O_2 \rightarrow NO + O_2 \qquad 3$$

$$\rightarrow NO_2 + O \qquad 4$$

$$\phi(O) = \phi(NO_2) \sim k_4[O_2]/((k_3 + k_4)[O_2] + k_2)$$

Reaction (4) is speculative. It has not been observed. ϕ can vary from zero to near 1 depending upon the value of k_4/k_3. We guess that $k_4/k_3 > 1$.

Rate constants are $k_2 = 5 \times 10^6 s^{-1}$ (c) and $(k_3 + k_4) = 1.6 \times 10^{-10}$ cm^3 $molecule^{-1} s^{-1}$ (s). At 20 km radiative loss would be about 8% of the total but would increase in importance with increasing altitude.

NO($B^2\Pi$)

This is the upper state for the β bands ($X \rightarrow B$). Emission has not been observed for $v' > 7$ (which lies close to the dissociation limit of NO), $\phi(O) = \phi(N) = 1$, $v' > 7$. Our knowledge of the photochemistry of this state is sketchy. We follow Preston and Cvetanovic (j) and suggest a behavior similar to that of $A^2\Sigma^+$.

NO($C^2\Pi$)

This is the upper state of the δ bands ($X \rightarrow C$). Emission from $v' > 0$ has not been observed. $\phi(O) = \phi(N) = 1$, $v' > 0$. Emission has been observed from $v' = 0$, but even here some levels are predissociated. This state has its minimum energy at approximately the dissociation limit for the X state. Cieslik and Nicolet (w) consider the C state to be the most important contributor to the photodissociation process in the upper atmosphere.

A mechanism for photolysis in air that can be used to estimate a lower limit for the quantum yield is

$$NO + h\nu \rightarrow NO(C^2\Pi,\ v = 0) \qquad 1$$

$$NO\ (C^2\Pi) \rightarrow NO + h\nu \text{ (to } X^2\Pi \text{ and } A^2\Sigma^+) \qquad 2$$

$$NO(C^2\Pi) \rightarrow N + O \qquad 3$$

$$NO(C^2\Pi) + M \rightarrow \text{loss of } NO(C^2\Pi) \qquad 4$$

$$\emptyset(N) = \emptyset(0) \geq k_3/(k_3 + k_2 + k_4[M])$$

$$\geq 17 \times 10^8/(17 \times 10^8 + 9 \times 10^7 + 15 \times 10^{-10}[M])$$

$$\geq 1/(1 + 0.8 \times 10^{-18}[M])$$

Rate constants given in reference [c] have been used. These apply to NO($C^2\Pi$, v = 0) the level least likely to predissociate. The value for k_4 is for nitrogen. It is used here as an upper limit for physical quenching.

At 20 km, [M] ~ 2×10^{18} molecules cm^{-3} and $\emptyset \geq 0.4$. This lower limit will increase with altitude. Reactive quenching by O_2 (see remarks on NO($A^2\Sigma^+$)) would also increase $\emptyset(0)$.

NO($D^2\Sigma^+$)

This is the upperstate of the ε bands (X → D). It has approximately the same energy as $C^2\Sigma^+$. However, the rate of predissociation is less than 1/5 that of spontaneous emission:

$$NO + h\nu \rightarrow NO(D^2\Sigma^+) \quad 1$$

$$NO(D^2\Sigma^+) \rightarrow NO + h\nu \text{ (to X and A))} \quad 2$$

$$NO(D^2\Sigma^+) \rightarrow N + O \quad 3$$

$$NO(D^2\Sigma^+) + N_2 \rightarrow NO\ (X) \quad 4$$

$$NO(D^2\Sigma^+) + O_2 \rightarrow ?\ ? \quad 5$$

Ignoring reaction 5

$$\phi(0) = \phi(N) = k_3/(k_3 + k_2 + k_4\,[N_2])$$

$$= (< 8 \times 10^6)/((< 8 \times 10^6) + 5 \times 10^7 + 3 \times 10^{-10}[N_2])$$

$$< 1/(1 + 60 + 3.8 \times 10^{-17}[N_2])$$

Thus radiative loss and quenching are controlling. If, however, reaction 5 is efficient and is a chemical reaction, the quantum yields would be larger. See discussion of $NO(A^2\Sigma^+)$.

$NO(a^4\Pi)$

Unimportant. Gas phase absorption to this state is not observed. Excitation to this state probably is followed only by quenching to the ground state.

Summary of estimates of quantum yields for photolysis of traces of NO in air

Electronic State formed	Vibrational level	Reactions Products	Products/ΔNO^*
$NO(A^2\Sigma^+)$	$v > 4$	N + O	~ 1
	$v = 0$	$NO_2 + O$? reactive quenching	0 - 1
$NO(B^2\Pi)$	$v > 7$	N + O	~ 1
	$v \leq 7$		? possibly similar to $A^2\Sigma^+$
$NO(C^2\Pi)$	$v > 0$	N + O	~ 1
	$v = 0$	N + O	pressure dependent, > 0.4 at 20 km.
$NO(D^2\Sigma^+)$	-	-	~ 0, radiative loss and quenching dominate
$NO(a^4\Pi)$	-	-	Unimportant

6.b. Photodissociation of NO in the stratosphere

The discussion of the photochemistry of NO given in earlier sections is not sufficient to define the stratospheric photodissociation of NO. A major fraction of the photodissociation occurs in the same wavelength region as that for the Schumann-Runge absorption bands of O_2.

A line by line analysis must be made to determine the overlap between the radiation transmitted through the S-R bands and the NO absorption lines. From this analysis the effective absorption by NO can be obtained. Only then can the photochemical discussion be applied. See Cieslik and Nicolet (w) for a detailed study of the problem.

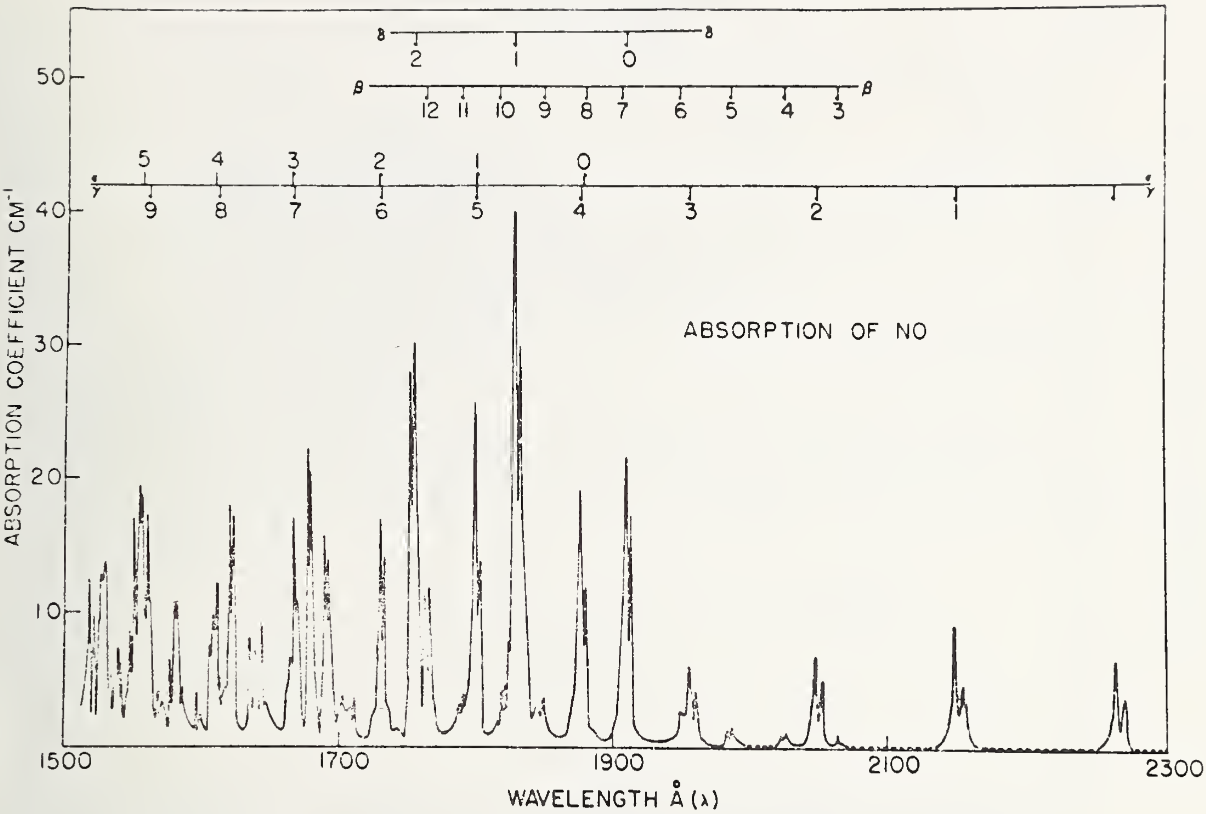

Fig. 1 Apparent absorption coefficient of NO in the wavelength region 150 - 230 nm in units of cm^{-1} (atm at 273 K)$^{-1}$ base e. The positions of the band heads for the δ, β, ε, and γ bands are indicated at the top. Band pass: 0.085 nm. Data of F. Marmo. From Watanabe, Zelikoff, Inn, Geophysical Research Paper No. 21, AFCRL, June 1953.

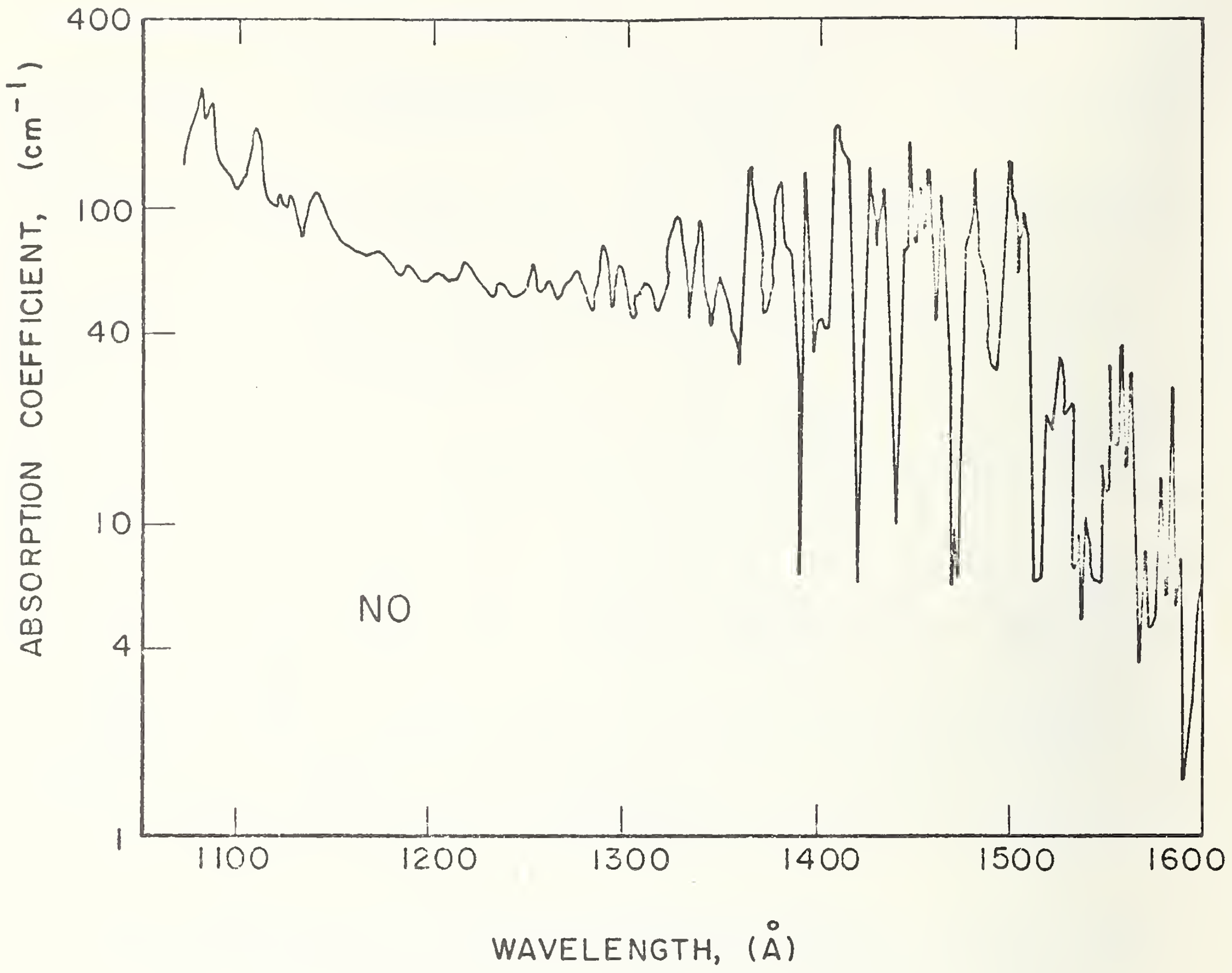

Fig. 2 Apparent absorption coefficient of NO in the wavelength region 110 - 160 nm in units of cm^{-1} (atm at 273 K)$^{-1}$ base e.

Data of F. Marmo. From Watanabe, Zelikoff, Inn, Geophysical Research Paper No 21. AFCRL. June 1953

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Chemical Kinetics Data Survey

The Combination Reaction of NO and O

1. $NO + O(^3P) + M \rightarrow NO_2 + M$ k_1

2. $\Delta H^\circ_{298} = -306.2$ kJ mol^{-1} (-73.2 kcal mol^{-1}) (a)

3. Data

a. The rate measurements on this reaction prior to July 1970 were compiled and reviewed by Baulch, Drysdale, and Horne (b). The major investigations of the temperature dependence of the reaction were performed using discharge flow systems by Clyne and Thrush (c) over the range 212-293 K, and by Klein and Herron (d) over the range 300-505 K. The third body effect was studied extensively by Kaufman and Kelso (e) at room temperature also using a discharge flow system.

b. Recent measurements

k_1 ($cm^6 molecule^{-2} s^{-1}$)	M	T	System
6.65×10^{-32}	He	300 K	Pulsed vacuum-uv photolysis of NO (1-3.5 torr) or of O_2(0.1 torr) in presence of NO (< 0.3 torr) and He (< 31 torr). O atom decay rate monitored by chemiluminescent reaction $O + NO \rightarrow NO_2 + h\nu$ STUHL, NIKI 1971 (f)
15×10^{-32}	NO	300 K	

k_1(cm^6 molecule^{-2}s^{-1})	M	T	System
13.5×10^{-32}	Ar	300 K	Pulsed photolysis of O_2 (0.1 torr) at 147 nm in presence of NO (1-8 mtorr) and Ar (6 or 10 torr). O atom decay rate detected by resonance fluorescence. SLANGER, BLACK 1970 (g)
6.0×10^{-32}	Ar	296	Pulsed photolysis of O_2 (0.1 torr) at 147 nm. in the presence of 0.1 torr NO and 10 torr Ar. Experiments primarily performed to measure rate constant for $O + NO_2 \rightarrow NO + O_2$. SLANGER, WOOD, BLACK 1973 (h)
13.0×10^{-32}	Ar	241	

4. Preferred values

$k = 2.9 \times 10^{-33} \exp(940/T)$ cm^6 molecule^{-2}s^{-1}, M = O_2

Temperature range: 200-500 K.

Estimated error limit: ± 20% at 298 K, ± 50% at other temperatures.

$k(298\ K) = 6.8 \times 10^{-32}$ cm^6 molecule^{-2}s^{-1} M = O_2

$k(220\ K) = 2.1 \times 10^{-31}$ cm^6 molecule^{-2}s^{-1} M = O_2

Relative efficiencies for M:

N_2 (1.4); O_2 (1); Ar (1)

5. Remarks

The recommended rate expression is that given by Baulch et al (b). The relative efficiency values are also from (b). This expression for k (T) has been confirmed by the recent measurements of Stuhl and Niki at 300 K (f) and those of Slanger, Wood, and Black at room temperature and at 241 K (h). The earlier measurement by Slanger and Black (g) is apparently a factor of two high. The authors speculated that a fast secondary reaction between atomic oxygen and vibrationally excited nitrogen dioxide produced in reaction (1) was the cause of the higher measured rate constant.

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January, 1973

PHOTOCHEMISTRY OF NO_2

1. Primary Photochemical Transitions

Reaction	ΔH_0^o kJ/mol	ΔH_0^o (kcal/mol)	λ threshold (nm)
$NO_2 \rightarrow NO(X^2\Pi) + O(^3P)$	300	(71.8)	398
$NO_2 \rightarrow NO(X^2\Pi) + O(^1D)$	490	(117.2)	244
$NO_2 \rightarrow NO(X^2\Pi) + O(^1S)$	705	(168.4)	170
$NO_2 \rightarrow N(^4S) + O_2(X^3\Sigma_g^-)$	435	(103.9)	275
$NO_2 \rightarrow N(^4S) + O_2(a^1\Delta_g)$	529	(126.5)	226
$NO_2 \rightarrow N(^4S) + O_2\ (b^1\Sigma_g^+)$	592	(141.4)	202
$NO_2 \rightarrow NO(A^2\Sigma^+) + O(^3P)$	829	(198.2)	144
$NO_2 \rightarrow NO(A^2\Sigma^+) + O(^1D)$	1019	(243.6)	117
$NO_2 \rightarrow NO(A^2\Sigma^+) + O(^1S)$	1234	(294.8)	97

ΔH_0^o values calculated using ΔHf_0^o values in (a), excitation energies of $O(^1D)$ and $O(^1S)$ in (b), and excitation energies of $NO(A^2\Sigma^+)$, $O_2(a^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$ in (c).

2. Data

2a. Absorption Coefficient

240-500 nm	See Figure 1. HALL, BLACET, 1952 (d)
400-700 nm	DIXON, 1940 (e)
108-270 nm	See Figures 2a, 2b, 2c, 2d NAKAYAMA, KITAMURA, WATANABE, 1959 (f)
405-515 nm	WILKERSON, ERCOLI, TOMPKINS, 1973 (y)

See Appendix for conversion factors for units of absorption coefficients.

2b. Overall Quantum yield for O_2 production, $\Phi(O_2)$:

$$NO_2 + h\nu \rightarrow NO + O\ (^3P)$$

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

λ(nm)	$\Phi(O_2)^*$
313	0.97
366	0.92
380	0.82
405	0.36
436	0.005

$\Phi(O_2)$ measured. Equal to $\phi(O)$ at low pressures. $P(NO_2)$ = 10 torr. Values also given at 344, 406, 496, and 566 K for λ = 405 nm. Non-zero value at 436 nm believed due to trace component of 405 nm.

*at T = 296 K

PITTS, SHARP, CHAN, 1964 (h)

λ(nm)	$\Phi(O_2)$	
270	1.0	Weighted average of results of four studies (1928-53).
313	0.97	
366	0.92	
405	0.36	
436	0.00	LEIGHTON, 1961 (i)

λ(nm)	$\Phi(O_2)$	
313	0.99	Reassessment of data considered in (i) and those reported in (h).
366	0.96	
380	0.82	
405	0.36	
436	<0.005	DEMERJIAN, KERR, CALVERT, 1974 (u)

2c. Overall quantum yield for NO production, $\Phi(NO)$:

λ(nm)	$\Phi(NO)$	
295-398	2.0	Relative overall quantum yield for production of NO, $\Phi(NO)$, measured. Values normalized to values at 313 and 366 nm in (i). $P(NO_2) = 3$ torr.
400	1.35	
405	0.64	
410	0.32	
415	0.10	
420	0.07	Also, see Figure 3
425	0.06	NOTE: Preliminary data
435	0.05	
490	0.03	
580	0.02	JONES, BAYES 1972 (g)

3. Preferred values

a. Absorption coefficients

240-500 nm	Use data in ref (d). See Fig. 1. (See also special note under remarks)
108-270 nm	Use data in ref (f). See Figures 2a, 2b, 2c, and 2d.

NOTE: Units of absorption coefficients

In Fig. 1, k is in units of (mm Hg at 298 K)$^{-1}$cm^{-1} (base 10)

In Fig. 2a-d, k is in units of (atm at 273 K)$^{-1}$cm^{-1} (base e)

See Appendix for table of conversion factors for units.

Absorption cross-sections averaged over 10 nm intervals:

λ(nm)	$\sigma(NO_2)$	λ(nm)	$\sigma(NO_2)$
290	$0.99 \times 10^{-19} cm^2$	400	$6.53 \times 10^{-19} cm^2$
300	1.41	410	6.38
310	2.18	420	6.23
320	2.98	430	5.88
330	3.74	440	5.54
340	4.54	450	5.20
350	5.20	460	4.47
360	5.69	470	4.05
370	6.04	480	3.51
380	6.23	490	3.06
390	6.38	500	2.64

$\sigma = (1/n\ell) \log_e (I_o/I)$ where n is the concentration of NO_2 in molecules cm^{-3} and ℓ is the path length in cm.

b. Primary quantum yields for O atom formation, $\phi(O(^3P))$

λ(nm)	$\phi(O(^3P))$
295-398	1.0
400	0.70
405	0.29
410	0.12
415	0.05
420	0.02
425	0.01
435	0.002
440	0.001
>440	ZERO

4. Remarks

a. Absorption coefficient

Ref. (d) Figure 1 also includes absorption coefficient data for N_2O_4. Resolution in spectrum that data are based on was 0.4 nm. It is not possible to assess the reproducibility of these absorption coefficients. Values for NO_2 and N_2O_4 were calculated from measured optical densities of two mixtures of NO_2 and N_2O_4 having mole fractions of N_2O_4 equal to 0.20 and 0.57. A third mixture, $X_{N_2O_4} = 0.41$ gave good agreement. These measurements agree with those in (e) and (f) over the regions of wavelength overlap.

The absorption coefficient data averaged over 10 nm intervals centered on the wavelength shown are derived from Table 14 of (i). They are based on data in (d). The entire table covers the wavelength range 290-700 nm and is based on (d) and (e).

The selection of the data in (d) is a tentative selection; work is in progress to measure the absorption coefficient over the photochemically active region $\lambda \lesssim 400$ nm (aa).

Ref. (f) These are the only data for $\lambda < 240$ nm. They have been critically reviewed in (x).

Ref. (y) Measurements made on a 1.13% NO_2 in N_2 mixture at 745 torr total pressure, 23.9°C, 10 cm path length. High resolution (0.003 nm). Results are consistent with the low-resolution data in (d) within the probable errors of the two studies.

Special Note Recent experiments (S. E. Novick, B. J. Howard, and W. Klemperer, J. Chem. Phys. 57, 5619 (1972) indicate the existence of the trimer N_3O_6 and possibly higher polymers in the gas phase. However, N_3O_6 will not be important in the atmosphere: the total $[NO_2]$ is to small. If these recent experiments are verified, the experimental measurements of equilibrium constants and optical absorption coefficients must be reanalyzed. Any effects of polymers will be more pronounced at low temperatures and at high pressures of NO_2. The spectrum of N_3O_6 is not known.

It is our conjecture that the present absorption coefficients for NO_2 are good ($\sim$ 15%) for $\lambda > 300$ nm but that the data for shorter wavelength regions may require revision.

b. Primary quantum yield for O atom production, $\phi(O)$

Ref. (g) In order to deduce the value of $\phi(O)$ from the measured value of $\Phi(NO)$, it is necessary to assume a mechanism of photolysis of NO_2. It is well established (h, ℓ) that for $\lambda < 398$ nm and at low conversions and low pressures, the mechanism is:

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

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

Isotopic scrambling experiments with $^{36}O_2$ showed the production of a free oxygen atom at $\lambda \leq 410$ nm. Similar results have been found by other workers (h, k-l). This confirms the above two-step mechanism for this wavelength range. For regions where this simple mechanism is applicable, $\phi(O) = (1/2) \times \Phi(NO)$. The preferred values of $\phi(O)$ were derived from the values of $\Phi(NO)$ in (g) according to the following scheme:

$\lambda < 415$ nm $\qquad \phi(O) = (1/2) \times \Phi(NO)$

$\lambda > 415$ nm $\qquad \phi(O) = \exp[(\epsilon_\lambda - 3.115)/0.043]$

where $\epsilon_\lambda = 1239.8/\lambda(\text{nm})$ is the photon energy in ev, 3.115eV corresponds to 398 nm, and 0.043eV is the e-folding parameter in region B in Figure 3.

The small non-zero values of $\Phi(NO)$ at $\lambda \gtrsim 440$ nm are suggested by the authors to result from reactions of NO_2^* to produce NO but not free O atoms. At this wavelength the photon energy is 0.3 eV (*i.e.* approximately 12 kT) less than the energy required to dissociate NO_2 into NO and O.

5. Discussion

This section summarizes interpretations of the photochemistry of NO_2 and describes related work on excited states and fluorescence.

I. Primary Photochemical Processes in Various Wavelength Regions.

a) $\lambda < 250$ nm

Wavelength threshold for $O(^1D)$ production is 244.1 nm. Lines are sharp in band at 249.1 nm and broadened in band at 245.9 nm, while the bands at 244.7 nm and beyond are diffuse. Broadening of lines for $\lambda >$ threshold wavelength used as argument against correlation of absorption in this region with $O(^1D)$ formation (j).

Chemical evidence from photolysis at $\lambda = 228.8$ nm shows that of oxygen atoms produced, 40% are $O(^1D)$ (k2). Photo-oxidation of butene-1 shows a change in mechanism between 228.1 and 253.7 nm, suggesting $O(^1D)$ formation at 228.8 nm (k3).

If the broadened bands at 245.9 nm do correlate with formation of $O(^1D)$ then absorption from internally excited NO_2 may be involved.

b) $250 < \lambda < 398$ nm

$NO_2 \rightarrow NO\ (X^2\pi) + O(^3P)$ throughout this region. For discussion of complex mechanisms of photolysis see (h) and (ℓ).

Addition of high pressures of N_2 reduces the total quantum yield in this wavelength region. This effect is partly due to changed rates of secondary reactions and partly due to quenching of the upper state formed in the photoabsorption act (cc). The latter (quenching) has a negligible effect on the primary process for pressures less than 1 atm. The former is significant at 1 atmosphere of N_2, $\Phi(P=0)/\Phi(P) \sim 1.27$, due to the process:

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

$$NO_3 + NO \rightarrow 2NO_2$$

competing with $O + NO_2 \rightarrow O_2 + NO$

c) $\lambda > 398$ nm

Threshold for $O(^3P)$ production is 398 nm. Some residual oxygen atom production at longer wavelengths by absorption from internally excited NO_2 (h) or by collisionally induced dissociation of NO_2^* (g). Otherwise absorption in this region results in formation of NO_2^* the dominant fate of which is fluorescence or collisional quenching. In presence of O_2, NO_2^* can undergo energy transfer to give $O_2(^1\Delta g)$ (z).

Under high resolution, lines in the absorption spectrum are sharp for $\lambda > 397.9$ nm and diffuse at shorter wavelength (m). This onset of diffuseness is in excellent agreement with the calculated wavelength threshold for $O(^3P)$ production. This line spectrum of NO_2 is very rich. Only a few bands have been analyzed (m). A. E. Douglas (private communication) has estimated that there may be

100,000 lines in the visible region that may be observed with the high resolution available with a 10m grating spectrograph. Even with this resolution many of the lines are blends.

The plot of absorption coefficient versus wavelength, Figure 1, has the appearance of lines superimposed on a "continuum". This background is not a true continuum but is due to absorption in the wings of many lines. It is an intrinsic part of the spectrum and is not due to limitations of instrumental resolution.

A recent discussion of the photochemistry of NO_2 is given in (dd).

II. Excited States of NO_2

a. Lifetime measurements from fluorescence.

Wavelength Region (nm)	State	τ, μs	Note	Ref.
400-600	$^2B_2$?	40-90	1,3	n,o
458-521	$^2B_2$, continuum	?	2,3	p
451-460	$^2B_1$, $^2B_2$	62-75	4	(bb)

Notes:

1. Excitation primarily by Hg lines. Lifetime dependence upon exciting λ both found (n) and not found (o).

2. Excitation by laser lines. Fluorescence spectrum shows vibrational and rotational structure and continuum (p).

3. The number of upper electronic states is in question. One mechanism is in (o3). A recent theoretical treatment of the potential energy diagram is in (q).

Discussions of the transitions in the absorption spectrum of NO_2 are in (r) and (s).

4. This detailed study using a tunable dye laser shows a structure of lifetimes as a function of wavelength. The conclusion is that the shorter life times (τ = 40-60 μs) reported in the literature are due to geometrical effects. Earlier experiments are discussed in detail.

b. Quenching of $NO_2^*(^2B_2)$ fluorescence by various gases

NO_2: λ_E = 436 nm (exciting wavelength)

NO_2^*: λ_F = 470 nm (fluorescence wavelength)

M	a_M(cm^3 molecule^{-1})	$k_{Q,M}$(cm^{3}molecule^{-1}s^{-1})
N_2	3.4×10^{-15}	0.62×10^{-10}
O_2	3.7	0.67
NO	6.2	1.1
NO_2	7.7	1.4
CO_2	8.1	1.5
H_2O	21	3.8

Notes:

The quenching constant a_m is defined by the equation:

1. $a_M = k_{Q,M} \times \tau_{rad}$ for the mechanism:

$NO_2^* \rightarrow NO_2 + h\nu$ $k_{rad} = 1/\tau_{rad}$

$NO_2^* + M \rightarrow NO_2 + M$ $k_{Q,M}$

2. $a(NO_2)$ from Table I of ref. (o3). Other values of a_M based on this value and ratios of a_M (λ_E = 436 nm) in Table II of ref. t and arguments therein that $a(M)/a(NO_2)$ is independent of λ_F and λ_E.

3. $k_{Q,M}$ calc. from a_M with $\tau_{rad} = 5.5 \times 10^{-5}$ s. (o3).

c. Fluorescence of NO_2 in the atmosphere

Based on mechanism in note 1 of section b above, the fraction of NO_2^* fluorescing in the presence of quenching gas, M, at concentration [M] is given by:

$$f_{fluorescing} = (1 + \sum_M a_M [M])^{-1}$$

In one atmosphere of N_2 $f \sim 1.2 \times 10^{-5}$ for excitation at 436.0 nm and fluorescence at 470.0 nm.

Total fluorescence per unit volume in sunlight depends upon incident light flux, absorption coefficient, and a_M all of which are functions of wavelengths. Data for the calculation not available.

d. Photochemistry of NO_2 in Air

To a good first approximation the following mechanism controls the relative concentrations of NO_2, NO, O, and O_3 in a polluted atmosphere (i):

$$NO_2 + h\nu \rightarrow NO + O \qquad k_a = 8.0 \times 10^{-3} s^{-1} \quad (u)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad k_2 = 5.6 \times 10^{-34} cm^{-6} molecule^{-2} s^{-1} \quad (v)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad k_3 = 1.6 \times 10^{-14} cm^{-3} molecule^{-1} s^{-1} \quad (w)$$

The specific rate of photodissociation of NO_2 to give O atoms by absorption of solar radiation is denoted by k_a after the notation in ref. (i).

These reactions are controlling because they are much faster than any other reactions and involving these species in the polluted atmosphere. They establish the following stationary-state concentration or intermediates:

$$[O]_{ss} = k_a[NO_2]/k_2[O_2][M] = 1.1 \times 10^{-7}[NO_2]$$

$$[O_3]_{ss} = k_a[NO_2]/k_3[NO]$$

$$= 5 \times 10^{11} \times [NO_2]/[NO] \quad molecule/cm^3$$

These formulae may be used, as a first approximation, to estimate [O] and $[O_3]$ at any instant for which measurements of $[NO_2]$ and [NO] are available.

The lifetime of an oxygen atom in air at one atmosphere, $\tau(O) = 1/k_2[O_2][M]$, is 12 μsec. This mechanism conserves the sum $[NO_2] + [NO]$. It does not give the rate of input or of destruction of nitrogen oxides in the atmosphere.

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January, 1973

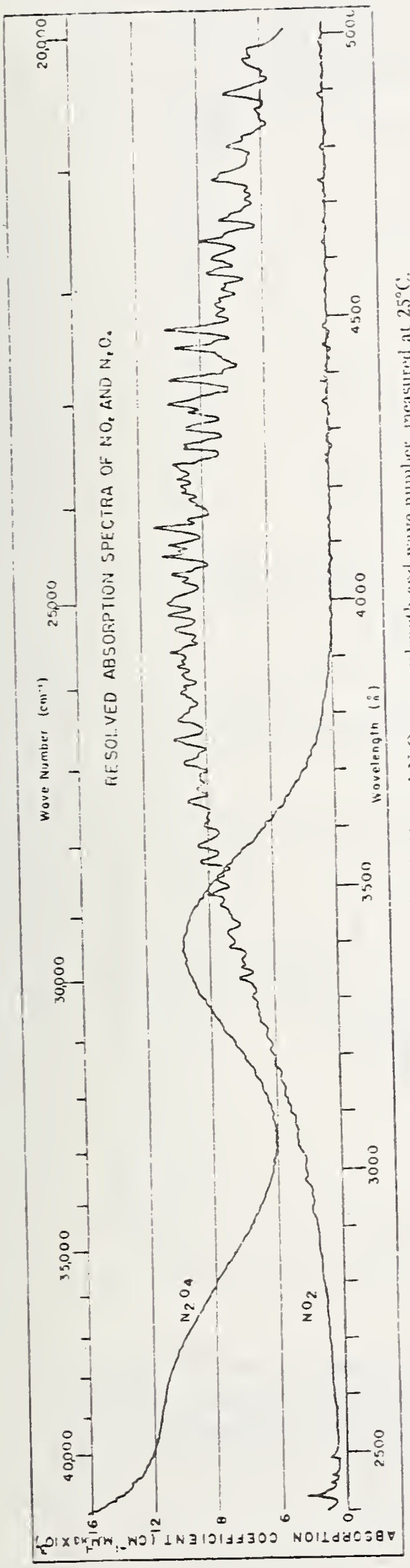

FIG. 1. Absorption coefficients ($1/pl \log_{10} I_0/I$) of NO_2 and N_2O_4 as wavelength and wave number, measured at 25°C.

Figure 1.
Absorption coefficients
$k = (1/p\ell) \log_{10} (Io/I)$
NO_2 and N_2O_4 at 25 C. where
p is the pressure in torr
at 25 C and ℓ is the path
length in cm.
HALL, BLACET, 1952 (d)

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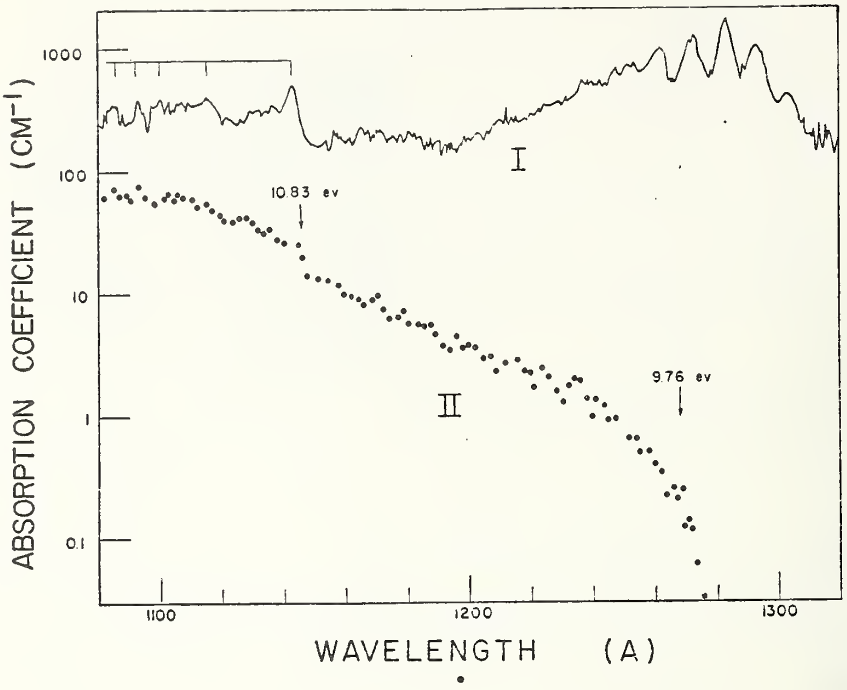

Fig. 2a. Absorption coefficient (I) and ionization coefficient (II) of NO_2 in the region 108-130 nm.

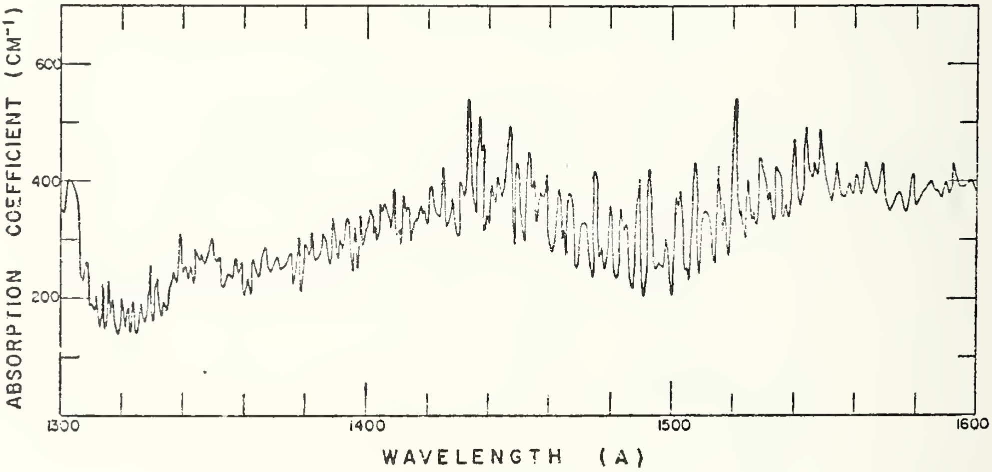

Fig. 2b. Absorption coefficient of NO_2 in the region 130-160 nm.

NOTE: In Fig. 2a-d, the absorption coefficient, k, is defined as: $k = (1/\ell) \log_e (I_o/I)$ where ℓ, in cm., is the layer thickness of the absorbing gas reduced to 273 K and 1 atm pressure.

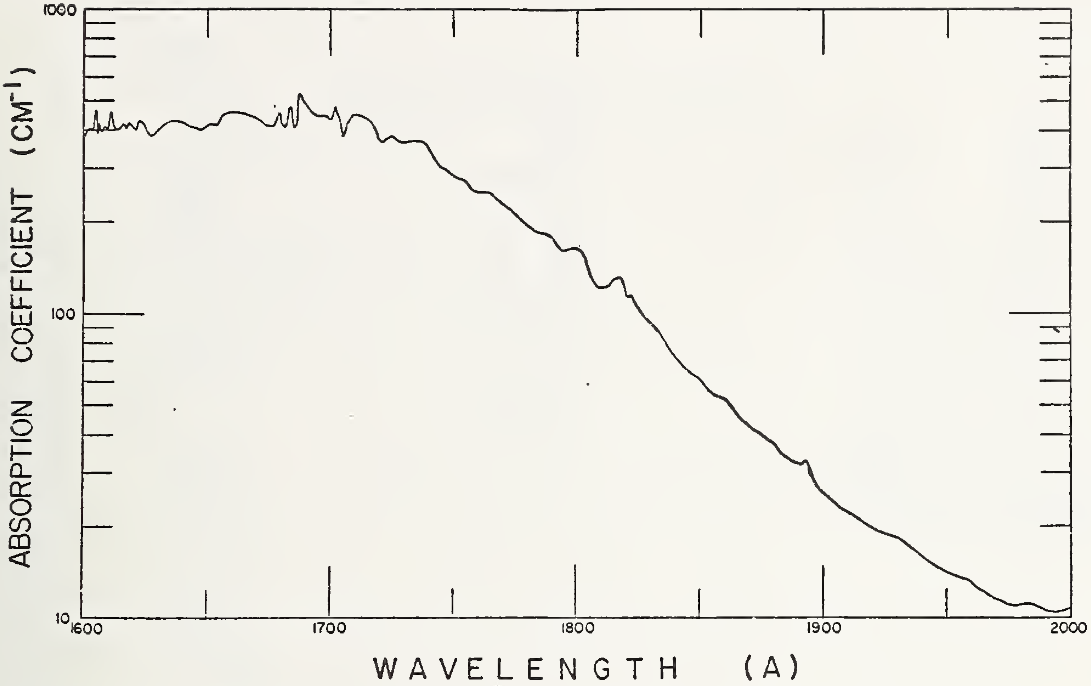

Fig. 2c. Absorption coefficient of NO_2 in the region 160-200 nm.

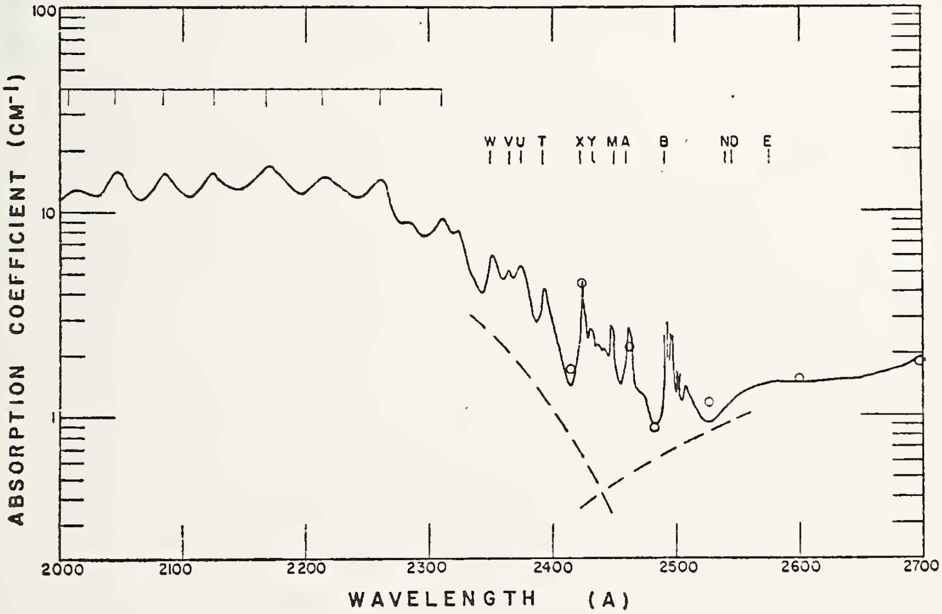

Fig. 2d. Absorption coefficient of NO_2 in the region 200-270 nm. Dashed curves are suggested continua, and circles are some values by Hall and Blacet.

NAKAYAMA, KITAMURA, WATANABE, 1959 (f)

NOTE: In Fig. 2a-d, the absorption coefficient, k, is defined as: $k = (1/\ell) \log_e (I_o/I)$ where ℓ, in cm., is the layer thickness of the absorbing gas reduced to 273 K and 1 atm pressure.

(Figures 2a-d reprinted with permission of American Institute of Physics)

Figure 3.

Wavelength dependence of the quantum yield for NO formation during NO_2 photolysis.

JONES, BAYES 1972 (g)

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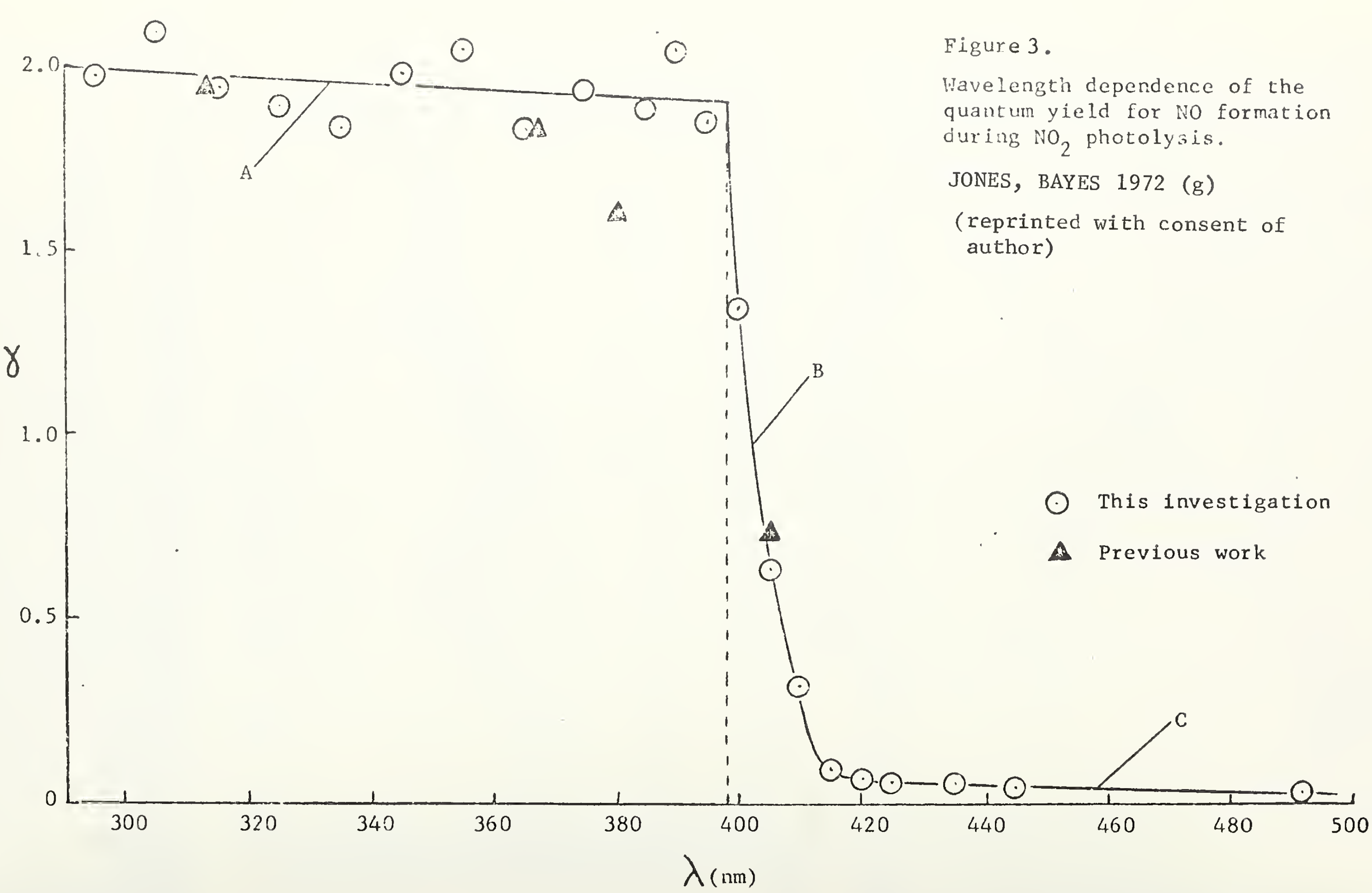

Chemical Kinetics Data Survey

The Bimolecular Reaction between NO_2 and $O(^3P)$

1. $NO_2 + O(^3P) \rightarrow NO + O_2$ k_1

2. $\Delta H^\circ_{298} = -192$ kJ mol^{-1} (-45.9 kcal mol^{-1}) (a)

3. Data

a. Prior to the review of Baulch, Drysdale, and Horne (b), dated July, 1970, this reaction had been studied over the temperature range 278-543 K in discharge flow systems, at 300 K in flash photolysis-flow systems, and at 298 and 410 K in a static flash photolysis system. Details are given in (b). Baulch *et*. *al*. recommended the expression $k_1 = 1.7 \times 10^{-11} \exp(-300/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280-550 K.

b. Recent measurements:

k_1(cm^3 molecule^{-1} s^{-1})	T(K)	System
4.4×10^{-12}	300	Flash photolysis of NO (0.15 torr) in presence of NO_2 (1-6 mtorr) and He (10torr). O atom decay monitored by chemiluminescent reaction $O + NO \rightarrow NO_2 + h\nu$. STUHL, NIKI 1970 (c).

6.1×10^{-12}	298	Discharge flow system. O atoms formed from N + NO reaction. $[NO_2]$ = 0.1-1.3 mtorr. [O] followed by resonance fluorescence. Total pressure = 1.3 torr. CLYNE, CRUSE 1972 (d).
9.12×10^{-12}	230-339	Flash photolysis of O_2 (1 torr) in presence of NO_2 (1-7 mtorr) and 5 torr diluent (N_2,Ar). [O] followed by resonance fluorescence. DAVIS, HERRON, HUIE 1973 (e).
9.3×10^{-12} 10.5×10^{-12}	296 240	Flash photolysis of O_2 (0.1 torr) in presence of NO (0.1 torr), Ar (10 torr) and NO_2 (0.2-2 mtorr). O atom decay monitored by chemiluminescent reaction $O + NO \rightarrow NO_2 + h\nu$. Flow system. SLANGER, WOOD, BLACK 1973 (f).
$k_1/k_2\ [M] = 5.5$ where k_2: $NO + O + M \rightarrow NO_2 + M$ and [M] = 1 atm N_2, 297 K.		Photolysis of NO_2. $[NO_2]$ and $[N_2O_5]$ followed by long path I. R. absorption. Molecular modulation spectrum of NO_2 measured. HARKER, JOHNSTON, 1973 (g).

k_1/k_3 [M] = 9.2×10^2 where k_3: $O + O_2 + M \rightarrow$ $O_3 + M$ and [M] = 1 atm air 298 K	Photolysis of NO_2 (1-100 ppm) in air studied using NO/O_3 chemiluminescence detectors. STEDMAN, NIKI, 1972 (h).

4. Recommended rate:

$k = 9.1 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}

Temperature range 220-500 K

Estimated error limits: ±20%

5. Remarks:

The rate expression recommended by Baulch, et al (b) was based on the data of Westenberg and de Haas (k), Klein and Herron (l), and Smith (m). In the flash photolysis experiments of Smith (m), k_1 and k_4 (O + 1-butene → products) were each measured relative to k_5 ($O + CS_2 \rightarrow CO + SO$). The absolute value of k_5 was also measured. The value of k_1 reported was equal to $(k_1/k_5) \times k_5$. Alternatively, one can derive the value of (k_1/k_4) from the reported values of (k_1/k_5) and (k_4/k_5) and then combine this ratio with the value of k_4 in ref (n) to give the value of k_1 to be 7.2×10^{-12} cm^3 molecule^{-1}s^{-1} at 298 K and 9.2×10^{-12} cm^3 molecule^{-1}s^{-1} at 410 K. These values agree with the present recommended rate within the stated experimental uncertainty (±30%) in ref (m). In the experiments of Klein and Herron (l), performed using a discharge flow system coupled to a mass spectrometer, a sudden decrease in the measured rate constant was observed at temperatures below 260 K, indicating that some phenomenon was complicating the system. If this complication existed unrecognized at the high temperatures used in the kinetic analysis, this could explain the reported lower values of the rate constant.

The data of Westenberg and de Haas scatter considerably, but show little apparent temperature dependence. A simple average of the data gives $k_1 = 8.1 \times 10^{-12}$ cm^3 $molecule^{-1}s^{-1}$, which is within 15% of the recommended value.

Since the review by Baulch, <u>et</u> <u>al</u> (b) there have been several investigations of reaction (1). Stuhl and Niki (c) and Clyne and Cruse (d) obtained values in reasonable agreement with the recommended value of Baulch <u>et</u> <u>al</u> (b). Davis, Herron, and Huie (e), however, obtained a higher rate constant which also showed no temperature dependence. Slanger, Wood, and Black (f) confirmed this value using an experimental technique similar to that of Stuhl and Niki (c). The ratio k_1/k_2 (M) in (g) when combined with the value 9.5×10^{-32} cm^6 $molecule^{-2}s^{-1}$ recommended in this report for k_2 ($NO + O + N_2 \rightarrow NO_2 + N_2$) (see separate data sheet on $NO + O + M$) gives a value of $k_1 = 12.8 \times 10^{-12}$ cm^3 $molecule^{-1}s^{-1}$. The ratio k_1/k_3 [M] in (h) when combined with the values for k_3 ($O + O_2 + M \rightarrow O_3 + M$) in (i) and (j) gives a value of $k_1 = 13.1 \times 10^{-12}$ cm^3 $molecule^{-1}s^{-1}$. These recent results from NO_2 photolytic systems (g, h) confirm earlier results on similar systems (o, p).

Since the measurements of Davis, et al form the most extensive data set, and since these data seem to be supported by the most recent work, we have chosen the rate constant reported in that work as the recommended value.

A theoretical calculation using the bond energy-bond order (BEBO) method has been made for reaction 1 (g). An activation energy of about 12.5 kJ/mol is predicted - at variance with the zero temperature dependence preferred here.

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January, 1973

The Termolecular Association of NO_2 and $O(^3P)$

1. $NO_2 + O(^3P) + M \rightarrow NO_3 + M$ (1)

2. $\Delta H^\circ_{298} = -205 \pm 20$ kJ mol^{-1} (-49 ± 5 kcal mol^{-1}) (a)

3. Data

a. Measurements of the rate of Reaction (1) in competition with the bimolecular reaction between NO_2 and O:

$$NO_2 + O \rightarrow NO + O_2 \qquad k_2$$

in the steady u.v. photolysis of NO_2 at room temperature.

$(k_1/k_2) \times 10^{20}$ (cm^3/molecule)	M	System
7.7	N_2	Stirred-flow photolysis reactor. $[NO_2] = 8\text{-}130 \times 10^{12}$ molecule/cm^3; total pressure = 1 atm; λ = 366 nm. Value of k_1/k_2 obtained from intercept of plot of $1/\Phi\ (NO_2)$ vs. $[NO]/[NO_2]$. FORD, ENDOW 1957 (b)
1.12	N_2	Static photolysis system.
1.09	CO_2	Effect of total pressure (up to 1.5 atm) on $\Phi\ (NO_2)$ studied. $[NO_2] = 2 \times 10^{17}$ molecule/cm^3; λ = 366 nm.

		Values of k_1/k_2 are equal to slopes of $1/\Phi$ (NO_2) vs. [M] plots although not identified as such in paper. FORD, JAFFE 1963 (c)
1.34	N_2	Effect of addition of 1 atm N_2 on Φ (NO_2) measured. Black light fluorescent tube used; peak output at 350 nm. $[NO_2] = 4 \times 10^{14}$ molecule/cm^3. SHUCK, STEPHENS, SCHROCK 1966 (d)
1.10	N_2	Effect of $P(N_2)$ on Φ (NO_2) measured. $[NO_2] = 2 \times 10^{17}$ molecule/cm^3; λ = 366 nm. Pressure range: 0.3 to 200 atm. k_1 found to be 3rd order up to 10 atm and reached limiting 2nd order value at ~ 100 atm. TROE, 1969 (e)
1.36 16.6	CO_2 CF_2Cl_2	Effect of total pressure up to 2.2 atm on Φ (O_2) from photolysis of NO_2 at 313 nm measured. $[NO_2] = 2 \times 10^{17}$ molecule/cm^3. Data for C_2H_4, C_3H_8, and i-C_4H_{10} as third bodies not quoted here; values are suspect because of reactivity with atomic oxygen. BLACET, HALL, LEIGHTON 1962 (f)

1.18	AIR	Photolysis of NO_2 in 1 atm. air with black-light fluorescent lamps. $[NO_2] \sim 3 \times 10^{13}$ molecule/cm^3. NO produced monitored by its chemiluminescent reaction with O_3. Value of k_1/k_2 calculated from expression: $-d \ell n [NO_2]/dt = 2I_a/[1 + k_1 [M]/k_2]$ Absorbed light intensity, I_a, determined separately from initial rate of photolysis of NO_2 in O_2. STEDMAN, NIKI 1972 (g)
0.89	N_2	Photolysis of NO_2 (10^{15} molecules/cm^3) in N_2 (1 atm) with black light in 67 liter quartz tube. $[NO_2]$ and $[N_2O_5]$ measured by i.r. absorption. Value of k_1/k_2 derived from $d[NO_2]/dt$; values agreeing within 10% derived separately from $d[N_2O_5]/dt$. HARKER, JOHNSTON 1973 (h)

b. Flash photolysis studies of reaction (1):

$(k_1 [M] + k_2)/k_3$	P(M)/torr	System
1.8	100	O atoms from flash photolysis of NO_2 ($\lambda > 300$ nm). M = Ar. $[NO_2] \sim 10^{15} - 10^{16}$ molecule/cm^3. Total reaction of O atoms with NO_2 by both channels ((1) + (2)) competes with reaction with CS_2 (3). [CS] monitored by absorption at 257.6 nm. Data also given for T = 410 K. SMITH 1968 (i)
4.2	700	
(T = 298 K)		
(k_3: $O + CS_2 \rightarrow CS + SO$)		

$k_1 [M] + k_2$ (cm^3 $molecule^{-1} s^{-1}$)	P(M) (torr)	
10.6×10^{-12}	200	O atoms from flash photolysis of O_2. Resonance fluorescence used to monitor atom decay by overall reaction with NO_2 in both channels ((1) + (2)). M = Ar. $[NO_2] \sim 10^{14}$ molecule/cm^3. Data also given for T = 263 K and 230 K. HUIE 1972 (j)
11.7×10^{-12}	400	
$k_2 = 9.1 \times 10^{-12}$		
(T = 298 K)		

4. Preferred Value

$\frac{k_1}{k_2}$ $(M = N_2) = 1.1 \pm 0.4 \times 10^{-20}$ cm^3/molecule at 298 K

$k_1 = 1.0 \pm 0.5 \times 10^{-31}$ cm^6 $molecule^{-2}s^{-1}$

based on $k_2 = 9.1 \times 10^{-12}$ cm^3 $molecule^{-1}s^{-1}$ (value recommended in separate data sheet on $O + NO_2 \rightarrow NO + O_2$).

5. Remarks

In the experiments involving the ultraviolet photolysis of nitrogen dioxide, the relative rate constant for reaction (1) was derived from the experimental quantum yields using the mechanism for the photolysis of NO_2:

$NO_2 + h\nu \rightarrow NO + O\ (^3P)$

$O + NO_2 \rightarrow NO + O_2$

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

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

$NO_3 + NO \rightarrow 2NO_2$

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

$O_3 + NO \rightarrow NO_2 + O_2$

$NO_3 + NO_2 \rightarrow N_2O_5$

and assuming steady state values for O, NO_3, and O_3. Depending on the species being monitored and on the experimental conditions, various expressions leading to the ratio k_1/k_2 may be derived.

The recommended value for k_1/k_2 is the simple average of the values (for $M = N_2$) from references c, d, e, g, and h. These values all lie within about 20% (one standard deviation) of the average value. The only value which deviates significantly is from reference (b). The data from which this value was obtained, however, show considerable scatter, and the derived value of the ratio is quite sensitive to small changes in the intercept of the plot, so that this value is rejected.

Comments on measurements

Ref (i). In this work, consistent results were unobtainable without the addition of NO, presumably to remove NO_3. The derived value of k_1/k_2 at 298 K given there is a factor of eight higher than that recommended here. It is possible to derive the relationship: $k_1/k_3 = 1.2 \times 10^{-19}$ cm^3/molecule from the data at [M] = 100 and 700 torr. With the absolute value of k_3 measured in the same study ($k_3 = 4.0 \times 10^{-12}$ cm^3 $molecule^{-1}s^{-1}$), one can derive a value of $k_1 = 5 \times 10^{-31}$ cm^6 $molecule^{-2}s^{-1}$, almost a factor of five higher than the value of k_1 recommended here. In view of the complications in this system, these results are rejected.

Ref (j). The only direct measurement of k_1 reported is from reference (j). Although there were no apparent complications in the system, the procedure involved measuring a small (20-30%) change, due to the contribution of reaction (1) in a large second order rate constant. At room temperature, the reported value of k_1 was about a factor of two higher than that recommended here. The temperature dependence of the reaction derived from these data is about T^{-5}, which is far steeper than would be expected ($\sim T^{-3/2}$) based on RRKM calculations on other atom-molecule addition reactions (k). These calculations also indicate that the observed pressure effect reported in (j) at 230 K is too sharp.

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March, 1973

N_2O_5 PHOTOCHEMISTRY

Reaction	ΔH_0^o kJ/mol	ΔH_0^o (Kcal/mol)	λ threshold (nm)
$N_2O_5 \rightarrow N_2O_4 + O\ (^3P)$	242	57.8	495
$N_2O_5 \rightarrow N_2O_4 + O\ (^1D)$	432	103.2	276
$N_2O_5 \rightarrow N_2O_3 + O_2$	66	15.9	1800
$N_2O_5 \rightarrow NO_3 + NO_2$	90	21.4	1300

ΔH_0^o calculated using ΔH_f° values in ref [a] (except for ΔH_f° (NO_3) which is from JANAF tables but consistent with ref [a]) and excitation energy of $O(^1D)$ from ref [b].

2. Data:

2a. Absorption Spectrum

Wavelength Range	Observation
ultraviolet	continuous absorption beginning at about 305 nm extending into the Schumann region UREY, DAWSEY, RICE, 1929 [c]
450-250 nm	continuous absorption 450-320nm transparent 320-280 nm. continuous absorption λ<280 nm. NOTE: NO_2 always present DUTTA, SEN GUPTA, 1933 [d]

2b. Absorption Coefficient

Wavelength Range	Data		Unit
265-436 nm	λ(nm)	k	1 cm^{-1}(atm at 273 K)$^{-1}$ base 10
(selected H_g lines)	265	2.1	
	280	0.96	
	302,313,334	ZERO	
	366,405,436	ZERO	
	HOLMES, DANIELS, 1934 [e]		
285-380 nm.	Value of k rises steadily from k=0.002 at 380 nm to k=0.52 at 285 nm. See FIG. 1 JONES, WULF, 1937 [f]		1 cm^{-1}(atm at 273 K)$^{-1}$ base 10

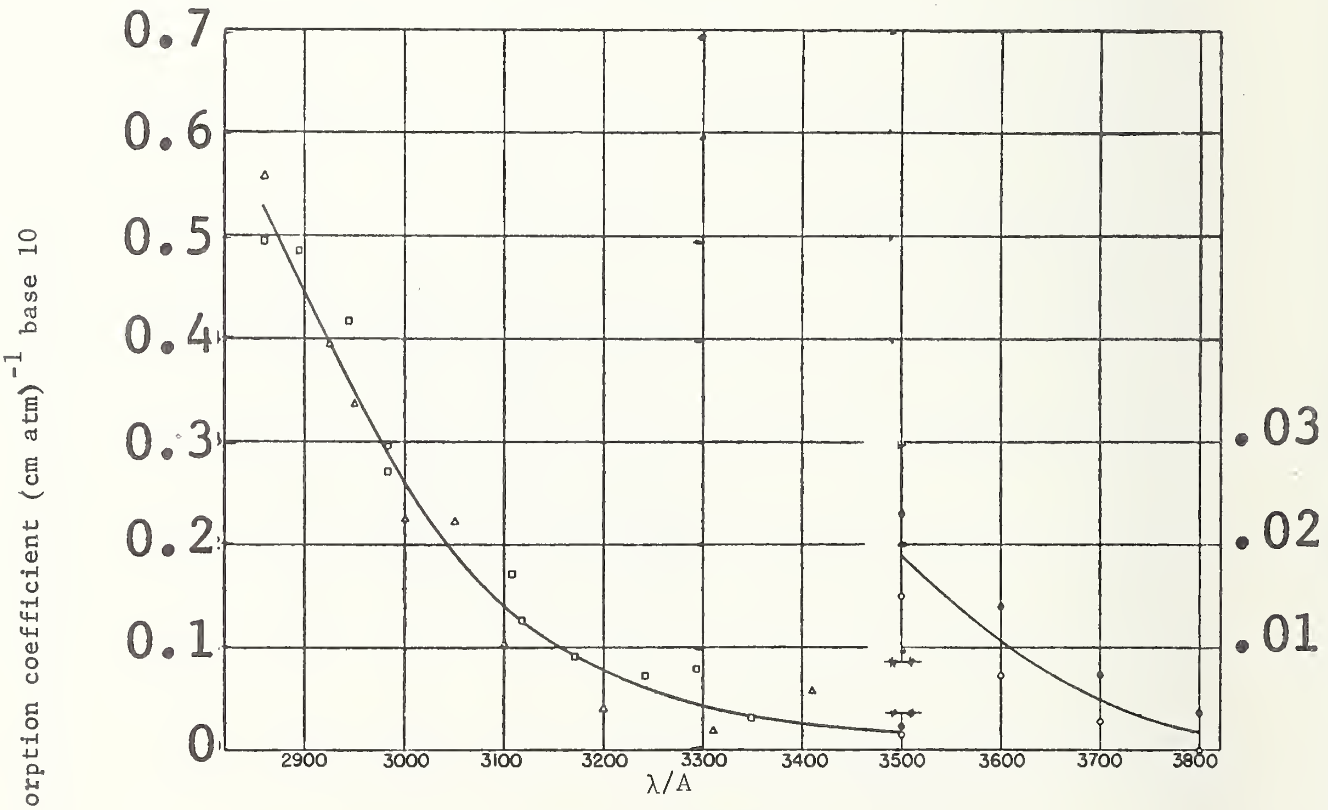

Fig. 1. Absorption coefficient of N_2O_5, 285-380 nm in units of cm^{-1}(atm at 273 K)$^{-1}$ base 10 (From E. J. Jones and O. R. Wulf, J. Chem. Phys. 5, 873 (1937), reprinted with consent of authors)

2c. Quantum yields

$\Phi(-N_2O_5)$ = net quantum yield for disappearance of N_2O_5

λ (nm)	$\Phi(-N_2O_5)$	$P_{N_2O_5}$
280	0.6	51 torr, 0°C
280	0.6	eq. v.p., 10°C
265	0.6	51 torr, 0°C

HOLMES, DANIELS, 1934 [e]

280	0.62	14-51 torr, 0.2°C.

MURPHY, 1969 [g]

Effect of added inert gas on value of $\Phi(-N_2O_5)$

M	P_M (torr)	$\Phi(-N_2O_5)$	$P_{N_2O_5}$ (torr)	
SF_6	110-620	0.50-0.32	25-30	
CO_2	110-600	0.59-0.36	35-40	λ=280nm
N_2	100-600	0.62-0.55	18-25	t=0.2°C
O_2	100-600	0.53-0.29	≈ 30	

MURPHY, 1969 [g]

Because $\Phi(-N_2O_5) < 1$ and decreases with increasing pressure of inert gas the photoabsorption act is believed to form an excited molecular state that can either dissociate or be quenched upon collision. The initial photodissociation products are unknown. The relationship between the overall Φ and the effective ϕ for photodissociation depends upon the extent of reaction of products of photolysis with N_2O_5. See section 4 for one mechanism.

3. Recommended values.

3a. Absorption coefficients.

380-285 nm. Values shown in Fig. 1 (from [f])

280 and 265 nm. Values in section 2b (derived from [e])

To convert values given in 2b into cross sections in cm^2 $molecule^{-1}$ (base e) multiply by 8.57×10^{-20}

3b. Quantum yields

According to mechanism of N_2O_5 photolysis given in section 4, the primary quantum yield for production of O atoms, $\phi_O = 0.5 \times \Phi(-N_2O_5)$

From the data of ref. [g]:

$$\phi_O = (3.12 + 0.00084\ P_{N_2} + 0.0058\ P_{O_2})^{-1}$$

where P_{N_2} and P_{O_2} are expressed in torr.

4. Remarks

The mechanism proposed for the photochemistry of pure N_2O_5 is:

$$N_2O_5\ (S_o) + h\nu \rightarrow N_2O_5^*\ (S_1)$$

$$N_2O_5^*\ (S_1) \rightarrow N_2O_5^*\ (T_1)$$

$$N_2O_5^*\ (T_1) \rightarrow N_2O_4 + O$$

$$N_2O_5^*\ (T_1) + M \rightarrow N_2O_5 + M$$

$$O + N_2O_5 \rightarrow N_2O_4 + O_2\ (\text{or } 2NO_2 + O_2).$$

By this mechanism, the limiting low pressure primary quantum yield for the production of O atoms is one-half the value of $\Phi(-N_2O_5)$ obtained in the absence of inert gas, i.e. $0.5 \times 0.62 = 0.31$.

References

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R. Hampson
Nov. 1972

Photolysis of O_2

1. Primary Photochemical Transitions

Reaction	ΔH_0^o kJ/mol	(kcal/mol)	λ threshold (nm)
$O_2 \rightarrow O(^3P) + O(^3P)$	493.57	(117.97)	242.4
$\rightarrow O(^3P) + O(^1D)$	683.39	(163.33)	175.0
$\rightarrow O(^3P) + O(^1S)$	897.81	(214.58)	133.2

(ΔH_0^o values calculated from ΔH_f^o (0) in (a) and energies of excitation of $O(^1D)$ and $O(^1S)$ in (b)).

2. Absorption Coefficient Data

Wavelength range	System
< 300 nm	Critical review of u.v. absorption cross section data. HUDSON, 1971 (c)
175-205 nm	Computed absorption cross section at high resolution of the Schumann-Runge bands from (0,0) band at 205 nm to dissociation limit at 175 nm. ACKERMAN, BIAUMÉ, KOCKARTS, 1970 (d)

178-205 nm	High-resolution study of structure of Schumann-Runge bands from (0,0) to (13,0) band. ACKERMAN, BIAUMÉ, 1970 (e)
116-244 nm	Table of adopted values of absorption cross section averaged over 500 cm^{-1} intervals. ACKERMAN, 1971 (f)
181-235 nm	Absorption cross section of the O_2 continuum and its pressure dependence measured. OGAWA, 1971 (g)
243-264 nm	Absorption measured for eight bands of the Herzberg I ($A^3\Sigma_u^+ - X^3\Sigma_g^-$) system. HASSON, NICHOLLS, 1971 (h1)
192-243 nm	Absorption cross section of weak photodissociation continuum adjoining the Herzberg I system measured over 109 ft. path length. HASSON, NICHOLLS 1971 (h2).

175-203 nm	Band oscillator strengths and predissociation line widths of Schumann-Runge band system derived. Continuum cross section calculated from 176-210 nm for T = 150, 200, 250, and 300 K. HUDSON, MAHLE 1972 (i)

3. Photochemical Data

A recent review and compilation of spectroscopic data (including the u.v. spectrum) of O_2 is given in ref (j).

a) $\lambda > 175$ nm

a1. Spectroscopy (c,k,ℓ,m)

λ range	Transition	Name
185-260 nm	$A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$	Herzberg Continuum
175-200 nm	$B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$	Schumann-Runge Band System

The $B^3\Sigma_u^-$ predissociates by crossing at about the v' = 2 level to the $^3\Pi_u$ state.

a2. Photochemistry

At λ = 184.9 nm $\phi(O) = 2$ based on $\Phi(O_3) = 2.0$ for $P(O_2) > 100$ torr (ref n) ($\Phi(O_3)$ measured relative to $\Phi(N_2)$ from N_2O which was taken to be 1.44). At $P(O_2) < 100$ torr $\Phi(O_3)$ decreases presumably due to O atom wall losses. Such a decrease is apparently an experimental artifact and not indicative of primary photochemical processes. The same study at 193.1 nm reports $\Phi(O_3) = 0.3$ independent of $P(O_2)$ from 300 to 1300 torr. The explanation requires direct excitation and subsequent quenching of a rotational line of the S-R continuum. This is contrary to spectroscopic evidence (c) which indicates that all of the rotational lines near 193 nm are strongly predissociated.

b) $175 > \lambda > 133.2$ nm

b1. Spectroscopy (c)

Absorption consists of the Schumann-Runge (B → X) dissociation continuum ($O(^3P) + O(^1D)$) with two superimposed continua bands centered at 135.2 and 133.2 nm. The former has been suggested to correspond to the spin-forbidden dissociation of O_2 into two $O(^1D)$ atoms. The low wavelength boundary of this region corresponds to the thermochemical onset for the dissociation into $O(^3P) + O(^1S)$.

b2. Photochemistry

Emission from $O(^1D)$ at 630 nm ($O(^1D) \rightarrow O(^3P)$) has been observed by Noxon (o) in the 147 nm photolysis of O_2. Emission from O_2 ($b^1\Sigma_g^+$) at 760 nm ($b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$) was also observed. The O_2 ($b^1\Sigma_g^+$) is presumed to be produced in the reaction:

$$O(^1D) + O_2(X^3\Sigma_g^-) \rightarrow O(^3P) + O_2(b^1\Sigma_g^+)$$

on the basis of the intensity of the 760 nm emission and assuming that $O_2(b^1\Sigma_g^+)$ is produced in the above reaction with 100% efficiency, an "order of magnitude" calculation indicated that $O(^1D)$ and $O(^3P)$ are formed in equal amounts in the primary photolysis of O_2 at 147 nm. The 147 nm photolysis of O_2 in the presence of H_2 and NO was studied by Young (p). Assuming that $O(^1D)$ reacts with but is not quenched to $O(^3P)$ by H_2, and that $O(^3P)$ reacts with NO to form NO_2^* which fluoresces, he found that the $O(^1D)$ and $O(^3P)$ productions are equal. Other investigators (q, r) have monitored O_3 formation to deduce thereby total O atom quantum yields of 2 but were unable to distinguish between $O(^3P)$ and $O(^1D)$. The fall-off in $\Phi(O_3)$ at low pressure was also observed in these systems and has been inadequately explained on the basis of $O(^1D)$ reactions.

c) $133.2 > \lambda > 100$ nm

c1. Spectroscopy (c)

A continuum in the Schumann-Runge system centered at 133.2 nm is presumedly due to the onset of the dissociation of O_2 into $O(^3P)$ and $O(^1S)$. The region between 102.7 nm, corresponding to the ionization potential of O_2, and 130 nm consists of a large number of strong absorption bands. A narrow window at Lyman-α, 121.56 nm has been observed repeatedly.

c2. Photochemistry

Emission from $O(^1S)$ at 557.7 nm ($O(^1S) \rightarrow O(^1D)$) has been observed in the flash photolysis of O_2 between 134 and 105 nm (s). This emission is enhanced in the presence of Ar, Kr, or Xe. The quantum yield for production of $O(^1S)$ has not been determined.

4. Preferred values

a. Absorption Coefficients

243-195 nm	Use data of HASSON and NICHOLLS (h2).
210-176 nm	a) Continuum cross sections: use data Table 4 of HUDSON & MAHLE (i). b) Schumann-Runge bands: use data in ACKERMAN, BIAUMÉ, AND KOCKARTS (d).

175-135 nm	See Figures 13, 14, and 15 of HUDSON (c).
244-116 nm	The most conveniently tabulated data is that given by ACKERMAN in Table 1 of ref (f). These are average adopted values not significantly different from values recommended above. They are given here in Table 1.

b. <u>Quantum yields</u>

b1. $O_2 + h\nu \rightarrow O(^3P) + O(^3P)$

$200 > \lambda > 175$ nm $\phi = 1$

b2. $O_2 + h\nu \rightarrow O(^3P) + O(^1D)$

$175 > \lambda > 133$ nm $\phi = 1$

b3. $O_2 + h\nu \rightarrow O + O$

$200 > \lambda > 106$ nm $\phi = 1$

5. Remarks

No photolytic system studied to date has used wavelengths corresponding to thresholds indicated in Section 1. Quantum yields for production of oxygen atoms in specific electronic states are needed.

TABLE 1. Averaged absorption cross section values (from Ackerman, reference f)

Δλ(Å)	Δν (cm^{-1})	$\sigma(O_2)(cm^2)$
Lyα 1.215,67	82.259	1.00×10^{-20}
1.170-1.163	85.500-86.000	2.00×10^{-20}
1.176-1.170	85.000-85.500	1.25×10^{-18}
1.183-1.176	84.500-85.000	2.55×10^{-19}
1.190-1.183	84.000-84.500	3.00×10^{-20}
1.198-1.190	83.500-84.000	3.75×10^{-19}
1.205-1.198	83.000-83.500	4.45×10^{-18}
1.212-1.205	82.500-83.000	8.35
1.220-1.212	82.000-82.500	6.00×10^{-19}
1.227-1.220	81.500-82.000	2.35
1.235-1.227	81.000-81.500	4.50
1.242-1.235	80.500-81.000	3.35
1.250-1.242	80.000-80.500	1.75×10^{-17}
1.258-1.250	79.500-80.000	8.95×10^{-19}
1.266-1.258	79.000-79.500	4.30
1.274-1.266	78.500-79.000	1.10
1.282-1.274	78.000-78.500	2.05
1.290-1.282	77.500-78.000	4.43
1.299-1.290	77.000-77.500	5.55
1.307-1.299	76.500-77.000	4.20
1.316-1.307	76.000-76.500	6.85
1.324-1.316	75.500-76.000	1.45×10^{-18}
1.333-1.324	75.000-75.500	2.25
1.342-1.333	74.500-75.000	2.30
1.351-1.342	74.000-74.500	4.55
1.360-1.351	73.500-74.000	7.23
1.370-1.360	73.000-73.500	9.50
1.379-1.370	72.500-73.000	1.23×10^{-17} ,
1.389-1.379	72.000-72.500	1.32
1.408-1.389	71.000-72.000	1.36
1.428-1.408	70.000-71.000	1.40
1.449-1.428	69.000-70.000	1.48

TABLE 1 (Continued)

Δλ (Å)	Δν (cm^{-1})	$\sigma(O_2)(cm^2)$
1.470-1.449	68.000-69.000	1.41×10^{-17}
1.492-1.470	67.000-68.000	1.29
1.515-1.492	66.000-67.000	1.15
1.538-1.515	65.000-66.000	9.91×10^{-18}
1.562-1.538	64.000-65.000	8.24
1.587-1.562	63.000-64.000	6.58
1.613-1.587	62.000-63.000	4.97
1.639-1.613	61.000-62.000	3.45
1.667-1.639	60.000-61.000	2.08
1.695-1.667	59.000-60.000	1.23
1.724-1.695	58.000-59.000	7.22×10^{-19}
1.739-1.724	57.500-58.000	4.58
1.754-1.739	57.000-57.500	2.74
2.020-1.754	49.500-57.000	*
2.041-2.020	49.000-49.500	1.14×10^{-23}
2.062-2.041	48.500-49.000	1.05
2.083-2.062	48.000-48.500	1.00
2.105-2.083	47.500-48.000	9.55×10^{-24}
2.128-2.105	47.000-47.500	8.93
2.150-2.128	46.500-47.000	8.28
2.174-2.150	46.000-46.500	7.60
2.198-2.174	45.500-46.000	6.92
2.222-2.198	45.000-45.500	6.28
2.247-2.222	44.500-45.000	5.65
2.273-2.247	44.000-44.500	5.03
2.299-2.273	43.500-44.000	4.40
2.326-2.299	43.000-43.500	3.76
2.353-2.326	42.500-43.000	3.09
2.381-2.353	42.000-42.500	2.44
2.410-2.381	41.500-42.000	1.75
2.439-2.410	41.000-41.500	6.74×10^{-25}

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A. H. Laufer
May 1973

Appendix A

Reactions of Potential Interest for the Chemistry of the Stratosphere

(Revised May 1973)

This list of reactions is based on several sources. It includes those used in models by P. J. Crutzen, J. Geophys. Res. 76, 7311 (1971), Univ. of Stockholm Meteorology Report AP-6 (1971); by H. S. Johnston, Science 173, 517 (1971), UCRL Report 20568 (1971), MS. "Formation and Stability of Nitric Oxide in the Stratosphere" (July 1971), and mentioned in discussions; those considered important by J. London and H. U. Dutsch, letter from J. L. to D. G., Oct. 19, 1971; and other reactions considered in studies at NBS.

The reactions are arranged in alphabetical order by first reactant.

Notes on entries in the Table:

1. Importance in Stratosphere. An asterisk in this column indicates that a student of the atmospheric modelling problems considers this reaction to be important. Absence of a mark does not imply the opposite.

2. Status of Data. An asterisk in this column indicates that an evaluator or modeller considers that better measurements are needed. Other remarks indicate the reliability of the data as assessed by an evaluator. Absence of a mark or comment has no significance.

3. Evaluation. References to recent evaluations are given here. The listing may not be complete. The notations are identified below.

a. R. F. Hampson et al, "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). (Updated versions of evaluations in NBS Reports 10692 and 10828).

b. R. F. Hampson et al, NBSIR 73-207, May 1973, (this report).

c. D. Garvin, editor, NBSIR 73-203 (May 1973).

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e. D.L. Baulch, D. D. Drysdale, D. G. Horne, A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions, Volume 1, Homogeneous gas phase reactions of the H_2-O_2 system", Butterworth and Co., London (1972).

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Reaction	Import. in Strat.	Status of Data Δ log k	Evaluation
$CH_4 + O(^1D) \rightarrow CH_3 + HO$	*	±0.1	d
$CO + HO \rightarrow CO_2 + H$		±0.1	c
$H + HNO \rightarrow H_2 + NO$		upper limit only	a, d
$H + HNO_2 \rightarrow$ Products		no data	a
$H + HNO_3 \rightarrow$ Products		upper limit only	a
$H + H_2O_2 \rightarrow H_2 + HO_2$		±0.3	e, d
$H + NO_2 \rightarrow HO + NO$		±0.1	a, d
$H + O_2 + M \rightarrow HO_2 + M$	*	±0.07	c
$H + O_3 \rightarrow HO + O_2$	*	±0.1	a
$HNO + HO \rightarrow H_2O + NO$		±0.7(T>1600K)	a, d
$HNO_2 + HO \rightarrow H_2O + NO_2$		no data	a
$HNO_2 + O \rightarrow HO + NO_2$		no data	a
$HNO_2 + h\nu \rightarrow$ Products		no data	b
$HNO_3 + HO \rightarrow H_2O + NO_3$	*	±0.5	a
$HNO_3 + O \rightarrow HO + NO_3$	*	upper limit only	a
$HNO_3 + h\nu \rightarrow HO + NO_2$	*	σ data only	a
$HO + HO \rightarrow H_2O + O$	*	±0.2	e
$HO + HO_2 \rightarrow H_2O + O_2$	*	±1	g,e,c
$HO + H_2O_2 \rightarrow H_2O + HO_2$	*	±0.1	b, e

Reaction	Import. in Strat.	Status of Data Δ log k	Evaluation
$HO + NO + M \rightarrow HNO_2 + M$	*	±0.5	b
$HO + NO_2 + M \rightarrow HNO_3 + M$	*	±0.3	b
$HO + O \rightarrow H + O_2$	*	±0.3	e,i
$HO + O_3 \rightarrow HO_2 + O_2$	*	±0.3	a
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	*	±0.3	a,e
$HO_2 + NO \rightarrow HO + NO_2$	*	±0.5	c
$HO_2 + NO + M \rightarrow HNO_3 + M$	*		
$HO_2 + O \rightarrow HO + O_2$	*	±1	g
$HO_2 + O_3 \rightarrow HO + 2O_2$	*	±0.3	c
$HO_2 + h\nu \rightarrow HO + O$	*	σ ± 30% some ϕ data	d
$H_2O + NO + NO_2 \rightarrow 2HNO_2$		upper limit only	a
$H_2O + N_2O_5 \rightarrow 2HNO_3$	*	upper limit only	a
$H_2O + O(^1D) \rightarrow 2HO$	*	±0.1	d,a
$H_2O + h\nu \rightarrow HO + O$	*		
$H_2O_2 + NO \rightarrow HO + HNO_2$		upper limit only	a
$H_2O_2 + h\nu \rightarrow 2HO$	*	σ, ϕ	a
$NO + NO + O_2 \rightarrow 2NO_2$	*	±0.2	c
$NO + NO_2 \rightarrow N_2O_3$			
$NO + NO_3 \rightarrow 2NO_2$	*	±0.7	d

Reaction	Import. in Strat.	Status of Data Δ log k	Evaluation
$NO + O + M \rightarrow NO_2 + M$	*	±0.2	b,d
$NO + O_3 \rightarrow NO_2 + O_2$	*	±0.11	a,d
$NO + h\nu \rightarrow N + O$		fragmentary data	b
$NO + M \rightarrow N + O + M$		questionable data	d
$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	*	±0.2	h
$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$		±0.4	d
$NO_2 + NO_3 \rightarrow N_2O_5^*$	*		c
$NO_2 + O \rightarrow NO + O_2$	*	±0.1	b
$NO_2 + O + M \rightarrow NO_3 + M$	*	±0.3	b,d
$NO_2 + O_3 \rightarrow NO_3 + O_2$	*	±0.2(T=298 K)	a,d
$NO_2 + h\nu \rightarrow NO + O$	*		b
$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	*	±0.5	d
$NO_3 + h\nu \rightarrow NO_2 + O$	*	±1	c
$NO_3^* \rightarrow NO_2 + O$			
$N_2O + O(^1D) \rightarrow N_2 + O_2$	*	±0.1	d,a
$\rightarrow NO + NO$	*		
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	*		
$N_2O_5 + O \rightarrow 2NO_2 + O$	*	upper limit only	
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$		±0.3	d,c

Reaction	Import. in Strat.	Status of Data Δ log k	Evaluation
$N_2O_5 + h\nu \rightarrow ?$	*	fragmentary data	b
$N_2O_5^* \rightarrow NO_2 + NO_3$	*		
$N_2O_5^* + M \rightleftarrows N_2O_5 + M$	*		
$O + O + M \rightarrow O_2 + M$	*	±0.3	f
$O + O_2 + M \rightarrow O_3 + M$	*	±0.07	c
$O + O_3 \rightarrow 2O_2$	*	±0.1	a,c
$O(^1D) + O_2 \rightarrow O + O_2\ (^1\Sigma_g^+)$		±0.1	d
$O(^1D) + O_3 \rightarrow 2O + O_2$		±0.3	d
$O(^1D) + O_3 \rightarrow 2O_2$			
$O(^1D) + M \rightarrow O + M$	*	±0.1 (except $M=O_3$)	d
$O_2 + h\nu \rightarrow O + O$	*	σ, ϕ	b
$O_2 + M \rightarrow O + O + M$		±0.3	f
$O_2(^1\Delta) + O_3 \rightarrow O + 2O_2$		±0.05	
$O_2(^1\Delta) + M \rightarrow O_2 + M$		±0.1 ($M = O_2$) upper limit only ($M=N_2$)	a
$O_2(^1\Sigma_g^+) + O_3 \rightarrow O + 2O_2 + M$			
$O_2(^1\Sigma_g^+) + M \rightarrow O_2 + M$		±0.1	a
$O_3 + h\nu \rightarrow O + O_2$	*	σ, ϕ	a

Appendix Conversion Tables

Equivalent Second Order Rate Constants

Equivalent Third Order Rate Constants

Conversion Factors for Units of Molecular Energy

Units of Optical Absorption Coefficients (Discussion)

Conversion Factors for Units of Optical Absorption Coefficients

EQUIVALENT SECOND ORDER RATE CONSTANTS

A \ B	$cm^3 mol^{-1} s^{-1}$	$dm^3 mol^{-1} s^{-1}$	$m^3 mol^{-1} s^{-1}$	$cm^3 molecule^{-1} s^{-1}$	$(mm\ Hg)^{-1} s^{-1}$	$atm^{-1} s^{-1}$	$ppm^{-1} min^{-1}$	$m^2 kN^{-1} s^{-1}$
1 $cm^3 mol^{-1} s^{-1}$ =	1	10^{-3}	10^{-6}	1.66×10^{-24}	$1.604 \times 10^{-5} T^{-1}$	$1.219 \times 10^{-2} T^{-1}$	2.453×10^{-9}	$1.203 \times 10^{-4} T^{-1}$
1 $dm^3 mol^{-1} s^{-1}$ =	10^3	1	10^{-3}	1.66×10^{-21}	$1.604 \times 10^{-2} T^{-1}$	$12.19\ T^{-1}$	2.453×10^{-6}	$1.203 \times 10^{-1} T^{-1}$
1 $m^3 mol^{-1} s^{-1}$ =	10^6	10^3	1	1.66×10^{-18}	$16.04\ T^{-1}$	$1.219 \times 10^4 T^{-1}$	2.453×10^{-3}	$120.3\ T^{-1}$
1 $cm^3 molecule^{-1} s^{-1}$ =	6.023×10^{23}	6.023×10^{20}	6.023×10^{17}	1	$9.658 \times 10^{18} T^{-1}$	$7.34 \times 10^{21} T^{-1}$	1.478×10^{15}	$7.244 \times 10^{19} T^{-1}$
1 $(mm\ Hg)^{-1} s^{-1}$ =	$6.236 \times 10^4 T$	$62.36\ T$	$6.236 \times 10^{-2} T$	$1.035 \times 10^{-19} T$	1	760	4.56×10^{-2}	7.500
1 $atm^{-1} s^{-1}$ =	$82.06\ T$	$8.206 \times 10^{-2} T$	$8.206 \times 10^{-5} T$	$1.362 \times 10^{-22} T$	1.316×10^{-3}	1	6×10^{-5}	9.869×10^{-3}
1 $ppm^{-1} min^{-1}$ = at 298K, 1 atm. total pressure	4.077×10^8	4.077×10^5	407.7	6.76×10^{-16}	21.93	1.667×10^4	1	164.5
1 $m^2 kN^{-1} s^{-1}$ =	$8314\ T$	$8.314\ T$	$8.314 \times 10^{-3} T$	$1.38 \times 10^{-20} T$	0.1333	101.325	6.079×10^{-3}	1

To convert a rate constant from one set of units A to a new set B find the conversion factor for the row A under Column B and multiply the old value by it, e.g. to convert $cm^3 molecule^{-1} s^{-1}$ to $m^3 mol^{-1} s^{-1}$ multiply by 6.023×10^{17}.

Table adapted from High Temperature Reaction Rate Data No. 5, The University, Leeds (1970)

EQUIVALENT THIRD ORDER RATE CONSTANTS

A \ B	$cm^6 mol^{-2} s^{-1}$	$dm^6 mol^{-2} s^{-1}$	$m^6 mol^{-2} s^{-1}$	$cm^6 molecule^{-2} s^{-1}$	$(mm Hg)^{-2} s^{-1}$	$atm^{-2} s^{-1}$	$ppm^{-2} min^{-1}$	$m^4 kN^{-2} s^{-1}$
1 $cm^6 mol^{-2} s^{-1}$ =	1	10^{-6}	10^{-12}	2.76×10^{-48}	$2.57 \times 10^{-10} T^{-2}$	$1.48 \times 10^{-4} T^{-2}$	1.003×10^{-19}	$1.447 \times 10^{-8} T^{-2}$
1 $dm^6 mol^{-2} s^{-1}$ =	10^6	1	10^{-6}	2.76×10^{-42}	$2.57 \times 10^{-4} T^{-2}$	$148\ T^{-2}$	1.003×10^{-13}	$1.447 \times 10^{-2} T^{-2}$
1 $m^6 mol^{-2} s^{-1}$ =	10^{12}	10^6	1	2.76×10^{-36}	$257\ T^{-2}$	$1.48 \times 10^{8} T^{-2}$	1.003×10^{-7}	$1.447 \times 10^{4} T^{-2}$
1 $cm^6 molecule^{-2} s^{-1}$ =	3.628×10^{47}	3.628×10^{41}	3.628×10^{35}	1	$9.328 \times 10^{37} T^{-2}$	$5.388 \times 10^{43} T^{-2}$	3.64×10^{28}	$5.248 \times 10^{39} T^{-2}$
1 $(mm Hg)^{-2} s^{-1}$ =	$3.89 \times 10^{9} T^{2}$	$3.89 \times 10^{3} T^{2}$	$3.89 \times 10^{-3} T^{2}$	$1.07 \times 10^{-38} T^{2}$	1	5.776×10^{5}	3.46×10^{-5}	56.25
1 $atm^{-2} s^{-1}$ =	$6.733 \times 10^{3} T^{2}$	$6.733 \times 10^{-3} T^{2}$	$6.733 \times 10^{-9} T^{2}$	$1.86 \times 10^{-44} T^{2}$	1.73×10^{-6}	1	6×10^{-11}	9.74×10^{-5}
1 $ppm^{-2} min^{-1}$ = at 298K, 1 atm. total pressure	9.97×10^{18}	9.97×10^{12}	9.97×10^{6}	2.75×10^{-29}	2.89×10^{4}	1.667×10^{10}	1	1.623×10^{6}
1 $m^4 kN^{-2} s^{-1}$ =	$6.91 \times 10^{7} T^{2}$	$69.1\ T^{2}$	$6.91 \times 10^{-5} T^{2}$	$1.904 \times 10^{-40} T^{2}$	0.0178	1.027×10^{4}	6.16×10^{-7}	1

See note to Table for Second Order Rate Constants

CONVERSION FACTORS FOR UNITS OF MOLECULAR ENERGY

	J/mol	cal/mol	cm^3 atm/mol	kWh/mol	Btu/lb-mol	cm^{-1}/molecule	eV/molecule
1 J/mol =	1	2.390057×10^{-1}	9.86923	2.77778×10^{-7}	0.429923	8.35940×10^{-2}	1.036409×10^{-5}
1 cal/mol =	4.18400	1	41.2929	1.162222×10^{-6}	1.798796	3.49757×10^{-1}	4.33634×10^{-5}
1 cm^3 atm/mol =	0.1013250	2.42173×10^{-2}	1	2.81458×10^{-8}	4.35619×10^{-2}	8.47016×10^{-3}	1.050141×10^{-6}
1 kWh/mol =	3,600,000	860,421	3.55292×10^{7}	1	1,547,721	300,938	37.3107
1 Btu/lb-mol =	2.32600	5.55927×10^{-1}	22.9558	6.46111×10^{-7}	1	1.944396×10^{-1}	2.41069×10^{-5}
1 cm^{-1}/molecule =	11.96258	2.85912	118.0614	3.32294×10^{-6}	5.14299	1	1.239812×10^{-4}
1 eV/molecule =	96487.0	23060.9	952,252	2.68019×10^{-2}	41482.0	8065.73	1

The underlined numbers represent the fundamental values used in deriving this table. The remaining factors were obtained by applying the relationships:

$n_{ij} = n_{ik} \cdot n_{kj}$ $\qquad$ $n_{ii} = n_{ik} \cdot n_{ki} = 1$

Gas constant. $R = 8.3143 \pm 0.0012$ J/K mol = 1.98717 cal/K mol = 82.056 cm^3atm/K mol
= 0.69502 cm^{-1}/K molecule = 8.6170×10^{-5} ev/K molecule

(From NBS Technical Note 270-3)

UNITS OF OPTICAL ABSORPTION COEFFICIENTS

The molar (linear) absorption coefficient ϵ is defined by the Lambert-Beer equation: $\epsilon = (1/\ell c) \log_{10} (I_o/I_t)$ where I_o and I_t are incident and transmitted intensity, ℓ is the path length, and c is the concentration*. The units for ϵ are (concentration^{-1} length^{-1}).

A variety of equivalent forms of this equation have been used to define reported values of ϵ. Both logarithmic bases e and 10 have been used. Length has invariably been expressed in cm. Concentration has usually been expressed in (mol/liter). Often a pressure unit has been used instead of a concentration unit, in which case the temperature to which the value of the pressure is referred must be specified. When pressure units are used the absorption coefficient is usually denoted by k (or α) with units of [(pressure (T))$^{-1}$ (length)$^{-1}$]. When the pressure unit used is (1 atmosphere at 273 K), the value of k is expressed in any of the numerically equivalent forms: [atm at 273 K^{-1}cm^{-1}]; [(NTP)$^{-1}$ cm^{-1}]; or cm^{-1}. This last form is equivalent to converting the measured value of ℓ at T and P to its corresponding value ℓ_o at the reference state $T_o = 273$ K and $P_o = 1$ atm ($\ell_o = \ell \times (P/P_o) \times T_o/T$)) and using the eqn: $k = (1/\ell_o) \log (I_o/I_t)$.

Alternatively the molecular concentration, n, expressed in (molecules/cm^3) may be used. Then the molecular "cross-section", σ, is defined as $\sigma = (1/n\ell) \log_e (I_o/I_t)$.

Because of the diversity of units, when using reported values in numerical calculations one must always determine what defining equation was used. When reporting absorption coefficients it is recommended that the units be given explicitly and that the defining equation appear in table and figure captions.

A table of conversion factors is attached.

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[*] Commission on Symbols, Terminology, and Units, I.U.P.A.C., M. L. McGlashan chairman, Pure and Applied Chemistry, 21, 1 (1970).

CONVERSION FACTORS FOR UNITS OF OPTICAL ABSORPTION COEFFICIENTS

A \ B	(cross section σ) $cm^2 molecule^{-1}$ base e	$(atm\ at\ 273)^{-1} cm^{-1}$ base e	$dm^3 mol^{-1} cm^{-1}$ base 10	$cm^2 mol^{-1}$ base 10
1 $(atm\ at\ 298)^{-1} cm^{-1}$ base e =	4.06×10^{-20}	1.09	10.6	1.06×10^4
1 $(atm\ at\ 298)^{-1} cm^{-1}$ base 10 =	9.35×10^{-20}	2.51	24.4	2.44×10^4
1 $(mm\ Hg\ at\ 298)^{-1} cm^{-1}$ base 10 =	7.11×10^{-17}	1.91×10^3	1.86×10^4	1.86×10^7
1 $(atm\ at\ 273)^{-1} cm^{-1}$ base e =	3.72×10^{-20}	1	9.73	9.73×10^3
1 $(atm\ at\ 273)^{-1} cm^{-1}$ base 10 =	8.57×10^{-20}	2.303	22.4	2.24×10^4
1 $dm^3\ mol^{-1} cm^{-1}$ base 10 =	3.82×10^{-21}	0.103	1	10^3
1 $cm^2\ mol^{-1}$ base 10 =	3.82×10^{-24}	1.03×10^{-4}	10^{-3}	1
1 $cm^2\ molecule^{-1}$ base e =	1	2.69×10^{19}	2.62×10^{20}	2.62×10^{23}

To convert an absorption coefficient from one set of units A to a new set B, multiply by the value tabulated for row A under column B, e.g. to convert the value of the absorption coefficient expressed in $dm^3\ mol^{-1} cm^{-1}$ base 10 to $(atm\ at\ 273)^{-1} cm^{-1}$ base e, multiply by 0.103.

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

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

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

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

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

Page No.	Reaction/Reference * = Preferred Value	Temp. Range/K	Reaction Rate Constant k/cm^3 molecule^{-1}s^{-1}	Notes and Reliability of log k
49	$HO_2 + CH_3O \rightarrow CH_3O_2H + O_2$ Change reaction to read: $HO_2 + \underline{CH_3O_2} \rightarrow CH_3O_2H + O_2$			
49	$CH_3O_2 + NO \rightarrow CH_3O_2NO$ (a) $\rightarrow CH_2O + HONO$ (b) $\rightarrow CH_3O + NO_2$ (c)			
	Demerjian, et al (1972) review	300	$\underline{k_c \doteq 3.3 \times 10^{-12} \exp(-500/T)}$	estimate
50	$O_3 + C_2H_4 \rightarrow$ products			
	Demerjian, et al (1972) review	300	$\underline{2.7 \times 10^{-18}}$	
51	$O_3 + C_3H_6 \rightarrow$ products			
	DeMore (1969)	183, 193, 300	$\underline{1.65 \times 10^{-15} \exp(-1600/T)}$	(b)
	*This survey (D.G.)	200-300	$\underline{2 \times 10^{-15} \exp(-1600/T)}$	(a)

Add the following references:

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

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

7 Aug 73

ERRATA-NBSIR 73-206, second printing

page 13 Reaction Mechanism, 5th line: delete 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 $\varepsilon(T \leqq 300\ K)$ for $\lambda = 230$, 240, 250, 260, and 270 nm are in units of 10^5 cm^2/mol

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

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Photochemical and rate data have been evaluated for twelve gas phase reactions of interest for the chemistry of the stratosphere. The results are presented in data sheets, one for each reaction. For each reaction the data are summarized. A preferred value is given for the rate constant or the primary quantum yield and photoabsorption cross section.

17. KEY WORDS (Alphabetical order, separated by semicolons) Atmospheric chemistry; chemical kinetics; data evaluation; gas phase reaction; optical absorption cross section; photochemistry; quantum yield; rate constants.

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