Temperature and Pressure Dependence of the Rate Coefficient for the Reaction $NO_3 + NO_2 + N_2 \rightarrow N_2O_5 + N_2$

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A discharge flow tube experiment has been conducted to determine the rate coefficient, k_2 , for reaction (2): NO₃ + NO₂ + N₂ \rightarrow N₂O₅ + N₂ from 236 to 358 K and 0.5 to 8 Torr. This represents the first study of the temperature dependence of k_2 at low pressures, *i.e.* under conditions relevant to the middle and upper stratosphere. The data obtained here have been combined with other measurements of k_2 and the following fall-off parameters are recommended: $k_0 = (2.8 \pm 0.4) \times 10^{-30} (T/300)^{(-3.5 \pm 0.5)} \text{ cm}^6 \text{ s}^{-1}$, $k_{\infty} = (1.66 \pm 0.25) \times 10^{-12} (T/300)^{(-0.2 \pm 0.2)} \text{ cm}^3 \text{ s}^{-1}$, for $F_c = 2.5 \exp(-1950/T) + 0.9 \exp(-T/430)$.

The nitrate radical, NO_3 , is an important constituent of both the troposphere and the stratosphere. Although it is formed continuously in the atmosphere *via* the reaction of NO_2 with O_3 , reaction (1),

$$NO_2 + O_3 \xrightarrow{\kappa_1} NO_3 + O_2$$
 (1)

it exists only at low concentrations during the daytime because of its rapid photolysis rate. Its concentration builds up at night, however, and NO_3 has been observed by visible absorption spectroscopy in both the troposphere¹ and the stratosphere.²

In the stratosphere, night-time $[NO_3]$ is controlled by a fairly simple mechanism involving its formation, reaction (1), its reaction with NO₂,

$$NO_3 + NO_2 + M \xrightarrow{k_2} N_2O_5 + M$$
 (2)

and the thermal decomposition of N_2O_5 ,

$$N_2O_5 + M \xrightarrow{k_{-2}} NO_3 + NO_2 + M$$
 (-2)

This simple analysis leads to an expected night-time steady state NO_3 concentration given by:

$$[NO_3]_{ss} = \frac{k_1[O_3]}{k_2} + \frac{k_{-2}[N_2O_5]}{k_2[NO_2]}$$
(A)

In the lower stratosphere (below *ca.* 35 km), k_{-2} is slow and [NO₃] is determined solely from its formation *via* reaction (1) and its loss *via* reaction (2). Measured stratospheric [NO₃] altitude profiles are in broad agreement with those predicted by the above mechanism, but quantitative discrepancies of *ca.* 40% exist.²

In the lower troposphere, k_{-2} is rapid and the equilibrium, (B),

$$K_2 = \frac{[NO_3][NO_2]}{[N_2O_5]} = \frac{k_{-2}}{k_2}$$
(B)

is rapidly established. Tropospheric NO_3 mixing ratios can be high enough for NO_3 to become an important oxidant, reacting at a significant rate with such species as aldehydes, alkenes, dimethyl sulphide, and terpenes.³

In addition to its atmospheric significance, reaction (2) is also an ideal case for the study of association reactions, because a large portion of the fall-off region is accessible in the laboratory. Hence, obtaining rate constant data for reaction (2) over a wide variety of temperatures and pressures can provide a test of our theoretical understanding of this type of reaction. Whilst a number of studies of k_2 ,⁴ ⁸ k_{-2} ,^{9.10} and K_2 ¹¹⁻¹⁵ have been reported in the literature, a quantitative understanding of this equilibrium system has not yet been obtained. Recent direct measurements of K_2 ^{11,12} disagree by as much as a factor of 1.8 at room temperature. In addition, discrepancies of at least a factor of three between directly measured K_2 and those determined kinetically (from ratios of k_{-2} to k_2) have been noted for certain conditions of temperature and pressure.^{5,12}

Whilst the association reaction, k_2 , has been studied at room temperature by numerous investigators^{4–8} over a wide range of pressure (0.5–150000 Torr†), only one temperature dependent study⁴ has been conducted, covering the centre portion of the fall-off curve. Hence, to date the temperature dependence of k_2 either at low pressures (<20 Torr) or high pressures (>1 atm‡) has only been inferred.

As part of a continuing effort in this laboratory to obtain a quantitative understanding of the $NO_3-NO_2-N_2O_5$ system, we report the rate coefficient for reaction (2) over the pressure range 0.5-8 Torr and the temperature range 236-358 K. These data are combined with previous investigations of k_2 and fit to the Troe expression to determine the fall-off parameters, as a function of temperature, for this reaction.

Experimental

The experiments were carried out using the discharge flow technique, with laser-induced fluorescence (LIF) detection of NO_3 . The detailed description of the experimental apparatus is presented in a previous publication,¹⁶ so only a summary will be given here. The flow tube had an internal diameter of 20.2 mm and was surrounded by two coaxial jackets. The inner jacket was used for the circulation of temperature-regulating fluid and the outer jacket was evacuated to thermally insulate the system.

Experiments were carried out over the pressure range 0.5-8Torr (with N₂ as the main carrier gas) and over the temperature range 236-358 K. Pressure measurements were made at both ends of the flow tube. For experiments below ambient temperature, ethanol was circulated through the temperature-regulating jacket using a Neslab ULT-80DD circulating bath. Above ambient temperature, water was circulated by a Neslab RTE-110 circulating bath.

 NO_3 detection was accomplished by LIF. NO_3 was excited at right angles to the direction of flow by radiation from an Ar⁺-pumped ring dye laser (Coherent CR-699). The dye laser

^{† 1} Torr = 133.322 Pa.

 $^{+ 1 \}text{ atm} = 101 325 \text{ Pa.}$

was operated broad band using Kiton Red dye. A birefringent filter was used for intracavity tuning and NO₃ fluorescence was excited near 623 nm. Laser power, as monitored by a Coherent model 212 power meter, was typically 300-500 mW and was constant within a few percent over the course of a rate coefficient measurement. Fluorescence was detected perpendicular to both the direction of flow and to the direction of laser propagation with a cooled photomultiplier tube (Hamamatsu R374). A 640 nm long-pass filter was used to reduce room light and scattered laser light. Fluorescence from NO₂ was also obtained under these conditions. However, because NO₂ fluoresces largely in the IR, the use of a 750 nm short-wave-pass filter greatly reduced the interference from NO₂ fluorescence. Also, because the NO₂ absorption spectrum near 623 nm is very structured it was found that tuning the laser to a minimum in the NO₂ absorption spectrum helped limit the magnitude of the NO₂ fluorescence. The sensitivity of NO₃ fluorescence relative to that of NO_2 was estimated to be ca. 150:1 after optimization of the laser frequency. Photons detected by the photomultiplier tube were counted using a preamplifier/pulse counter and ratemeter (MIT Instruments). Counts were acquired and averaged using an IBM-PC for two to four 32 s time periods at each reaction distance.

 NO_3 was formed via the reaction of F atoms with HNO_3 ,

$$F + HNO_3 \xrightarrow{k_3} NO_3 + HF$$
 (3)

where $k_3 = 2.4 \times 10^{-11}$ cm³ s⁻¹.¹⁷ The fluorine atoms were generated by a microwave discharge of a dilute F₂-He mixture (*ca.* 5% F₂). The discharge was excited in an alumina sidearm attached to the main flow tube. HNO₃ flows, generated by bubbling N₂ through a mixture of conc. HNO₃ in conc. H₂SO₄ (initially 1 : 2 by volume) were introduced into the flow tube, along with the main N₂ flow, through another sidearm located *ca.* 60 cm upstream of the discharge sidearm. The concentration of HNO₃ was calculated assuming saturation of the N₂ carrier gas at an HNO₃ vapour pressure of *ca.* 20 Torr at room temperature. [HNO₃] was always maintained at least 10 times [F] to minimize the occurrence of a secondary source reaction between F and NO₃ :

$$F + NO_3 \xrightarrow{\kappa_4} FO + NO_2$$
 (4)

If FO radicals were indeed present, their most likely fate would be self-reaction leading to the production of F atoms and hence to NO₃ regeneration. Modelling of a worst case scenario in which [FO] was 0.1 [F] showed that the presence of [FO] could lead to a maximum underestimation of k_2 of *ca.* 6%. Tests in which the [F]/[HNO₃] ratio was changed by a factor of two in back to back measurements led to no change in the measured rate coefficient within experimental uncertainty, indicating that problems due to FO formation were minimal.

NO₂ was added through a 9 mm o.d. movable injector which was concentric with the main flow tube. The injector allowed for a maximum reaction distance of 65 cm, the entire length of which was in the temperature controlled region. For the majority of measurements, a 4.47% NO₂ in N₂ mixture was used. Calibration of the mixture was accomplished by measuring the visible absorption of NO₂ with a photodiode array spectrometer. An absorption cross-section of 6.2×10^{-19} cm² molecule⁻¹ at 400 nm for a spectral resolution of 0.1 nm was used for quantitative analysis.^{18,19} For some rate-coefficient measurements at low pressure (1 Torr or less), pure NO₂ was used. In these cases, NO₂ flows were determined by measuring the rate of change of pressure with time into a calibrated volume. At 236 K, an additional

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flow of N₂ (100 to 200 cm³ min⁻¹) was added down the injector to speed up the rate of flow of the NO₂ in the cooled region of the injector and reduce the rate of N₂O₄ formation. It was calculated that in all cases the amount of NO₂ present as N₂O₄ was <2%, based on the rate-coefficient data for N₂O₄ formation reported by Borrell *et al.*²⁰

All gas flows, except the pure $NO_2 dP/dt$ measurements discussed above, were determined using mass flow controllers which were calibrated with a dry test meter. Pressures were measured using MKS Model 227 Baratron capacitance manometers. NO_2 was purified before use by a number of freeze-pump-thaw cycles. Both N_2 and He diluent gases were of UHP grade.

Results and Discussion

Data Analysis

All experiments were conducted under conditions of excess NO_2 over NO_3 , $[NO_2] > 10[NO_3]$. Hence, pseudo-first order conditions were obtained:

$$-d \ln[NO_3]/dt = k_2[NO_2] = k'$$
(C)

As in all flow-tube experiments, the reaction distance (z) is the actual measured parameter and is related to time from a knowledge of the flow velocity (v) through the flow tube:

$$-d \ln[NO_3] = (k_2/v)[NO_2] dz$$
 (D)

Because we had the capability of measuring the pressure at both ends of the flow tube, changes in velocity along the length of the flow tube due to the pressure drop could be accounted for explicitly, using the Poiseuille equation.¹⁶

Data analysis was conducted using a standard spreadsheet on an IBM-PC. Gas flow rates, the pressure at the detection end of the flow tube, and the temperature were entered and concentrations were automatically calculated. Values of the NO₃ fluorescence (minus the background signal) were entered at each z. After correction of the reaction time at each z for the pressure drop, the natural log of NO₃ fluorescence was fitted vs. time by an unweighted linear leastsquares method to obtain the pseudo-first-order rate coefficient, k'. The process was repeated for at least seven different [NO₂] at each pressure and temperature studied. The measured values of k' were corrected for the measured loss of NO₃ on the injector. Corrections for axial and radial diffusion were also made, using the expressions given by Keyser.²¹ The diffusion coefficient, D_c , for NO₃ in N₂ was estimated as $(120/P)(T/300)^{1.5}$ cm² s⁻¹, ca. three times smaller than the value of D_c in He employed by Hammer et al.²² Typical axial diffusion corrections were ca. 1-2%, while radial diffusion corrections ranged from <1% at low pressure to as high as 9% for the higher pressure studies. For all combinations of flow velocity, diffusion coefficient and wall loss employed in our study, Keyser²¹ has shown that the corrections for radial and axial diffusion lead to values for k' which are accurate to better than $\pm 5\%$. The bimolecular rate coefficient, k_2 , was then obtained as the slope of an unweighted linear leastsquares fit of the corrected k' against [NO₂]. Plots of k' vs. $[NO_2]$ for selected pressures at 333 K are shown in Fig. 1.

Before obtaining the final values of k_2 , corrections had to be made for the occurrence of other reactions consuming NO₃. The reaction of NO₃ and NO₂ is believed to have a bimolecular component,

$$NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$$
 (5)

The ratio of k_5 to k_6 , the rate coefficient for the reaction of NO₃ with NO,

$$NO_3 + NO \rightarrow 2NO_2$$
 (6)



Fig. 1 $k' vs. [NO_2]$ for reaction (2) for selected pressures at 333 K : •, 1 Torr; ∇ , 2 Torr; ∇ , 5 Torr

has recently been measured²³ as a function of temperature. Using the temperature-dependent value for k_6 measured by Sander and Kircher,²⁴ the following expression for k_5 is obtained,²³ $k_5 = 4.11 \times 10^{-14} \exp(-1253/T)$ cm³ s⁻¹. Because the NO produced in reaction (5) reacts rapidly with NO₃ via reaction (6), our measured rate coefficient data were corrected by subtracting twice the value of this expression at each temperature and pressure. The correction is largest at high T and low P, and was ca. 8% at 1 Torr, 358 K.

In addition, corrections had to be made for the contribution of NO_2 as a third body:

$$NO_3 + NO_2 + NO_2 \rightarrow N_2O_5 + NO_2$$
(7)

The method used to correct the data was analogous to that of Smith *et al.*⁵

$$k'/[NO_2] = k_2[N_2] + k_7[NO_2]$$
 (E)

Hence, a plot of $k'/[NO_2]$ vs. $[NO_2]$ yields as its slope k_7 and as its intercept $k_2[N_2]$. The contribution of reaction (7) was found to be measurable only at and below 1 Torr, where the ratio of $[NO_2]$ to $[N_2]$ is highest. An average value of $(6 \pm 3) \times 10^{-30}$ cm⁶ s⁻¹ was measured for k_7 independent of temperature, ca. a factor of three smaller than that estimated by Smith *et al.*⁵ The maximum contribution of reaction (7) to the measured rate coefficient was ca. 8% for the highest $[NO_2]$ at 0.5 Torr and 298 K.

In all, 23 rate coefficients, $k_2(T, P)$, were obtained as summarized in Table 1. Precision errors in plots of k' vs. [NO₂] were typically 5–10%, and an overall uncertainty of $\pm 15\%$ (2σ) is reported after the inclusion of potential systematic errors (uncertainties in NO₂ mixture calibrations, pressure and temperature measurements, and corrections for diffusion and secondary chemistry). The data point at 0.5 Torr and 298

Table 1 Measured rate coefficients, k_2 , for NO₃ + NO₂ + N₂ \rightarrow N₂O₅ + N₂

P/Torr	$k_2/10^{-13} \text{ cm}^3 \text{ s}^{-1}$						
	236 K	267 K	298 K	333 K	358 K		
0.5			0.42				
1	1.56	1.05	0.59	0.31			
2	2.35	1.39	1.14	0.61	0.44		
3	3.10	2.00	1.47	0.85	0.59		
4		2.25	1.69	1.06	0.74		
5				1.24	0.88		
6			1.84				
8			2.35				

K is quoted with an uncertainty of $\pm 30\%$, due to the poten-

tially large contribution of reaction (7).

Determination of Fall-off Parameters

Troe and co-workers^{25,26} have shown that the pressure and temperature dependence of rate coefficient data for association reactions can be described as follows:

$$k = \frac{k_{\infty} k_0[\mathbf{M}]}{k_{\infty} + k_0[\mathbf{M}]} F_{c}^{(1 + (N^{-1} \log(k_0[\mathbf{M}]/k_{\infty}))^2)^{-1}}$$
(F)

where $N = 0.75 - 1.27 \log(F_c)$ and k_0 , k_{∞} and F_c are all functions of temperature. Because reaction (2) has been studied most thoroughly at room temperature, fall-off parameters at 298 K were determined first by using the available data. Measurements at low pressure, similar to ours, were conducted at 298 K by Smith et al.⁵ Their values were in agreement with our measurements within the combined uncertainty of the two studies at each pressure common to the two studies. Measurements of k_2 at room temperature at mid-range pressures (20-700 Torr) have been made by Kircher et al.,⁴ Burrows et al.,⁷ and Wallington et al.⁸ and these data have also been included in our room-temperature fits. The analysis of the very high pressure data (2–200 atm) for k_2 of Croce de Cobos et al.⁶ was based on a rather large correction for the interfering reaction of NO_3 with NO, reaction (6). At the time of their measurements, the accepted value for k_6 was 2×10^{-11} cm³ s⁻¹. However, more recent studies^{16,22,24,27} have shown that k_6 is somewhat higher. Re-analysis of the Croce de Cobos data using a revised value of 2.7×10^{-11} $cm^3 s^{-1}$ for k_6 (the mean of the four recent determinations) leads to a lowering of their higher pressure data (>25 atm) for k_2 by ca. 10%. Correction of their lower pressure data (<25 atm) led to a negative value for k_2 , indicating a severe problem with these data. It is apparent from a simulation of their reaction conditions that in these rate-coefficient determinations the formation of NO₃ (from the third-body association of O atoms with NO₂) was incomplete. It is also possible that uncertainties in the rate-coefficient data employed in their model led to an over-estimation of the amount of NO present in their system. In some determinations of the fall-off parameters for k_2 we have used the corrected data above 25 atm, as summarized in Table 2. In other cases, where fall-off parameters for atmospheric conditions were desired, the entire Croce de Cobos et al. data set was excluded from the fit.

The data set described above was used in an unweighted non-linear least-squares fit to the Troe expression to determine room-temperature fall-off parameters. The fit was conducted in three different ways—the first with F_c treated as a fit parameter using the entire data set, the second with F_c fixed to the value calculated by Malko and Troe²⁸ ($F_c =$ 0.35) again using the full data set, and the third with F_c fixed at 0.6 as recommended by JPL-90²⁹ excluding the data of Croce de Cobos *et al.*⁶ The results of the room temperature fall-off parameter determinations are summarized in Table 3

Table 2 Re-analysis of the high-pressure data for k_2 of ref. 6

P/atm	$k^{a}/10^{12} \text{ cm}^{3} \text{ s}^{-1}$	$k(\text{corrected})/10^{12} \text{ cm}^3 \text{ s}^{-1}$		
25	1.8	1.6		
50	2.0	1.8		
100	2.0	1.9		
150	2.1	2.0		
200	2.0	1.9		

" Ref. 6.

Table 3 Summary of fall-off parameters for k

	F _c	$k_0/10^{-30} \text{ cm}^6 \text{ s}^{-1}$	n	$k_{\infty}/10^{-12} \text{ cm}^3 \text{ s}^{-1}$	т		
ref. 5 ^e	0.47 (fit)	2.12		1.85			
ref. 5^{b}	0.4 (fit)	2.32		1.84			
ref. 5 ^c	0.6 (fit)	1.97		1.4			
ref. 4	ref. 28	4.5	3.4	1.65	0.4		
ref. 4	0.6 (fixed)	2.0	4.3	1.4	0.5		
ref. 29	0.6 (fixed)	2.2	4.3	1.5	0.5		
ref. 30	ref. 28	2.7	3.4	2.0	-0.2		
this work ^d	0.41 (fit)	2.7		1.85			
this work ^d	ref. 28	3.3	4.3 ± 0.5	2.1	-0.3 ± 0.2		
this work ^d	0.6 (fixed)	2.2	3.8 ± 0.5	1.3	0.8 ± 0.3		
this work ^d	(e) ´´	2.8	3.5 ± 0.5	1.66	0.2 ± 0.2		

" Using data of ref. 4, 5, 6. " Using data of ref. 5 and 6. " Using data of ref. 4 and 5. " Data sets for various fits as described in text. ^e Temperature dependence as ref. 28, absolute magnitude scaled to obtain best fit to data.

and are shown in Fig. 2. The fit with F_{c} fixed to the value of Malko and Troe, shown as the solid line in Fig. 2, yields essentially the same parameters as those obtained with F_{c} allowed to float (which gave $F_c = 0.41$). However, the parameters obtained using $F_{\rm c} = 0.6$ also yield a very good fit to the data for atmospheric conditions. The room-temperature parameters determined here with $F_c = 0.6$ are essentially identical to those currently recommended by JPL-90.29

The temperature dependence of the fall-off parameters was then determined. The data set employed included the average of the 298 K measurements of this study and Smith et al., the temperature dependent data of this study and Kircher et al.4 and, in some instances, the corrected 298 K data of Croce de Cobos et al.⁶ The data were fit in three ways. In the first treatment, the value of F_{e} was determined from the theoretical treatment of Malko and Troe.²⁸ A bi-exponential fit to their F_{c} calculations at different temperatures yielded the following expression:

$$F_{\rm c} = 0.7 \exp(-T/430) + 2.0 \exp(-1950/T)$$
 (G)

This expression provides a better fit to the data of Malko and Troe than their originally reported biexponential function. Both k_0 and k_{∞} were constrained to the room-temperature values determined above using the Malko and Troe F_c s. Their temperature dependence was represented as follows,

$$k_0(T) = k_0(298 \text{ K})(T/298)^{-n}$$
 (H)

$$k_{\infty}(T) = k_{\infty}(298 \text{ K})(T/298)^{-m}$$
 (I)

and n and m were determined from an unweighted non-linear least-squares fit to the data. Treatment of the data by this method yielded a value of (4.3 ± 0.5) for n and (-0.3 ± 0.2) for m. Fig. 3 shows the results of this fit (as solid lines) and the individual data points employed in the fit. The values of nand *m* reported here agree within reported uncertainties with those of Kircher et al.,⁴ indicating the consistency of the two sets of temperature-dependent data.

The second treatment of the data consisted of fixing F_c to 0.6 independent of temperature (as recommended by JPL-90) and again constraining the values of k_0 and k_∞ to their previously determined room-temperature values. Using this method, the values of n and m were determined to be 3.8 ± 0.5 and 0.8 ± 0.3 , respectively. These n and m are in agreement within uncertainty with the currently recommended parameters of JPL-90,²⁹ $n = 4.3 \pm 1.3$ and $m = 0.5 \pm 0.5$.

The third method of obtaining temperature-dependent falloff parameters involved fixing the temperature dependence of $F_{\rm c}$ to the form recommended by Malko and Troe, but allowing the absolute magnitude of F_c to float. The parameters k_0 , k_{∞} , n and m were also allowed to float. This procedure yielded best fit F_{c} s that were 30% higher than those of Malko and Troe, $F_c = 2.5 \exp(-1950/T) + 0.9 \exp(-T/430)$, with $k_0 = (2.8 \pm 0.4) \times 10^{-30} (T/300)^{(-3.5 \pm 0.5)} \text{ cm}^6 \text{ s}^{-1}$, and $k_{\infty} = (1.66 \pm 0.25) \times 10^{-12} (T/300)^{(-0.2 \pm 0.2)} \text{ cm}^3 \text{ s}^{-1}$. The results of this fit are shown in Fig. 4, and provide the best fit to the data set. The k_2 values determined by this fit, in general, are within 10% of those currently recommended by JPL-90.²⁹ The k_2 values recommended by CODATA³⁰ also agree (within 10%) with those determined here at higher pressures (>100 Torr). However the CODATA values are ca. 20% lower in the 1-5 Torr range owing to the lower F_c recommended by CODATA. It is particularly interesting



Fig. 2 Fall-off curve for reaction (2) at 298 K. Solid line-fit obtained with F_c as ref. 28; dotted line—fit obtained with $F_c = 0.6$. ●, This work; □, ref. 5; △, ref. 4; ○, ref. 6; ■, ref. 7; ▲, ref. 8



Fig. 3 Fall-off curves for reaction (2) as a function of temperature. ●, 236 K; ▽, 267 K; O, 298 K; V, 358 K. Solid lines—fit obtained with F_c as ref. 28



Fig. 4 Fall-off curves for reaction (2) as a function of temperature. Solid lines—fit obtained with temperature dependence of F_c as ref. 28, and absolute magnitude scaled to obtain best fit. Symbols as Fig. 3

that, even though the data of Croce de Cobos⁶ were not employed in this fit, the fitted fall-off curves come quite close to reproducing the Croce de Cobos data. The results of our fall-off parameter determinations for reaction (2) as a function of temperature, together with previous determinations, are summarized in Table 3.

The largest remaining uncertainty in the shape of the falloff curve for reaction (2) appears to be in the high pressure region. Measurements of k_2 above 1 atm have only been carried out in one study⁶ and the accuracy of these data, as pointed out earlier, is in question. Using the F_c values of Malko and Troe²⁸ yields an opposite temperature dependence for k_{∞} to that obtained using an F_{c} of 0.6. Clearly, a more definitive study is required at high pressures to yield the temperature dependence of $F_{\rm c}$ and k_{∞} . From an experimental standpoint, it is probably a simpler approach to study the rate coefficient for N₂O₅ dissociation, k_{-2} , at high pressure. Because F_c must be the same for both k_2 and k_{-2} , such measurements of k_{-2} can aid in the determination of the shape of the fall-off curve for k_2 . Measurements of k_{-2} from 253 K to 323 K and 0.5 to 3000 Torr have recently been made in our laboratory and higher pressure measurements (up to ca. 20 atm) are currently in progress.³¹ It is hoped that the measurements for k_{-2} above 1 atm will aid in the determination of the shape of the fall-off curves for this atmospherically and theoretically important reaction pair. A comprehensive evaluation of the entire data set $(k_2, k_{-2} \text{ and } K_2)$ will be included when these above results are published.

Conclusions

We have reported rate coefficients, k_2 , for the association of NO₃ and NO₂ to form N₂O₅ over the temperature range 236 K-358 K, and the pressure range 0.5-8 Torr. This represents the first measurement of k_2 as a function of temperature in the low pressure regime (<20 Torr), and provides the first measurement of k_2 at the temperatures and pressures relevant to the middle and upper stratosphere.

The data obtained here have been combined with previous measurements of k_2 to obtain a refined set of temperaturedependent fall-off parameters for reaction (2). The recommended parameters are: $F_c = 2.5 \exp(-1950/T)$ + 0.9 $\exp(-T/430)$, $k_0 = (2.8 \pm 0.4) \times 10^{-30}$ (T/ $300)^{(-3.5\pm0.5)}$ cm⁶ s⁻¹, and $k_{\infty} = (1.66 \pm 0.25) \times 10^{-12}$ (T/ $300)^{(-0.2\pm0.2)}$ cm³ s⁻¹.

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References

- 1 U. Platt, D. Perner, A. M. Winer, G. W. Harris and J. N. Pitts, Jr., Geophys. Res. Lett., 1980, 7, 89.
- 2 J. P. Smith and S. Solomon, J. Geophys. Res., 1990, 95, 13819.
- 3 A. M. Winer, R. Atkinson and J. N. Pitts Jr., Science, 1984, 224, 156.
- 4 C. C. Kircher, J. J. Margitan and S. P. Sander, J. Phys. Chem., 1984, 88, 4370.
- 5 C. A. Smith, A. R. Ravishankara and P. H. Wine, J. Phys. Chem., 1985, 89, 1423.
- 6 A. E. Croce de Cobos, H. Hippler and J. Troe, J. Phys. Chem., 1984, 88, 5083.
- 7 J. P. Burrows, G. S. Tyndall, G. K. Moortgat, J. Phys. Chem., 1985, 89, 4848.
- 8 T. J. Wallington, R. Atkinson, A. M. Winer and J. N. Pitts Jr., Int. J. Chem. Kinet., 1987, 19, 243.
- P. Connell and H. S. Johnston, Geophys. Res. Lett., 1979, 6, 553.
 A. A. Viggiano, J. A. Davidson, F. C. Fehsenfeld and E. E. Fer-
- guson, J. Chem. Phys., 1981, 74, 6113.
- 11 J. P. Burrows, G. S. Tyndall and G. K. Moortgat, Chem. Phys. Lett., 1985, 119, 193.
- 12 C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter and J. G. Calvert, J. Chem. Phys., 1988, 88, 4997.
- 13 E. C. Tuazon, E. Sanhueza, R. Atkinson, W. P. L. Carter, A. M. Winer and J. N. Pitts Jr., J. Phys. Chem., 1984, 88, 3095.
- 14 D. Perner, A. Schmeltekopf, R. H. Winkler, H. S. Johnston, J. G. Calvert, C. A. Cantrell and W. R. Stockwell, J. Geophys. Res., 1985, 90, 3807.
- 15 R. A. Graham and H. S. Johnston, J. Phys. Chem., 1978, 82, 254.
- 16 G. S. Tyndall, J. J. Orlando, C. A. Cantrell, R. E. Shetter and J. G. Calvert, J. Phys. Chem., in the press.
- 17 A. Mellouki, G. LeBras and G. Poulet, J. Phys. Chem., 1987, 91, 5760.
- 18 J. A. Davidson, C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich and J. G. Calvert, J. Geophys. Res., 1988, 93, 7105.
- 19 W. Schneider, G. K. Moortgat, G. S. Tyndall and J. P. Burrows, J. Photochem. Photobiol., 1987, 40, 195.
- 20 P. Borrell, C. J. Cobos and K. Luther, J. Phys. Chem., 1988, 92, 4377.
- 21 L. F. Keyser, J. Phys. Chem., 1984, 88, 4750.
- 22 P. D. Hammer, E. J. Dlugokencky and C. J. Howard, J. Phys. Chem., 1986, 90, 1491.
- 23 C. A. Cantrell, R. E. Shetter, A. H. McDaniel and J. G. Calvert, J. Geophys. Res., 1990, 95, 20531.
- 24 S. P. Sander and C. C. Kircher, Chem. Phys. Lett., 1986, 126, 149.
- 25 J. Troe, J. Phys. Chem., 1979, 83, 114.
- 26 R. G. Gilbert, K. Luther and J. Troe, Ber. Bunsenges. Phys. Chem., 1983, 87, 169.
- 27 A. Torabi and A. R. Ravishankara, XVI Informal Conference on Photochemistry, Cambridge, MA., 1984.
- 28 M. W. Malko and J. Troe, Int. J. Chem. Kinet., 1982, 14, 399.
- 29 W. B. DeMore, M. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard and A. R. Ravishankara, JPL Publication 90-1, 1990.
- 30 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr and J. Troe, J. Phys. Chem. Ref. Data, 1989, 18, 881.
- 31 C. A. Cantrell, R. E. Shetter, J. G. Calvert, G. S. Tyndall and J. J. Orlando, J. Phys. Chem., to be submitted.

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