TEMPERATURE DEPENDENCE OF THE REACTION NO + $NO_3 \rightarrow 2NO_2$

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The flash photolysis-visible absorption technique has been used to measure rate constants for the reaction NO+NO₃ \rightarrow 2NO₂ (1) over the temperature range 224-328 K. The temperature dependence of the rate constant is given by the expression $k_1(T) = (1.59 \pm 0.32) \times 10^{-11} \exp(122/T)$ cm³ molecule⁻¹ s⁻¹ where the stated uncertainties refer to the $\pm 2\sigma$ limits from both random and systematic errors.

1. Introduction

The nitrate radical, NO_3 , plays an important part in the chemistry of the troposphere and lower stratosphere. The reaction

$$NO_3 + NO \rightarrow 2NO_2 \tag{1}$$

has a role in the partitioning among species in the NO_x family particularly at sunset and at night in the vicinity of local NO sources. Rate constants for reaction (1) have been determined by a number of different techniques with the measured values at 298 K spread over a wide range between 7.5×10^{-13} and 2.0×10^{-10} cm³ molecule s⁻¹ [1-10]. Recently, however, detection techniques for NO3 using longpath absorption and laser-induced fluorescence have become sufficiently sensitive to permit rate constants for rapid NO₃ reactions to be measured under conditions relatively free of interfering secondary processes. These techniques have been applied successfully to several key NO₃ reaction rate studies, with rate constants for the reactions of NO_3 with NO_2 , O, Cl and several other species being measured [11,12]. In this study, the flash photolysis-visible absorption technique was used to measure the temperature dependence of k_1 over the range 224–328 K.

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2. Experimental

The experimental apparatus has been described in detail previously [12,13] with the approach being virtually identical to our previous study [14] of the reaction $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$. Briefly, NO_3 radicals were produced by flash photolysis using a Pyrex flash lamp/reaction cell and were monitored spectrophotometrically in the (0,0) band at 661.8 nm with a resolution of about 0.4 nm. Absorption signals from 25–50 flashes were averaged to obtain firstorder kinetic decay plots which could be followed over 3–4 1/e times. The chemical source of NO_3 was the photolysis of Cl_2 – $ClONO_2$ mixtures at wavelengths longer than 300 nm:

$$Cl_{2} + h\nu \rightarrow 2Cl,$$

$$Cl + ClONO_{2} \rightarrow Cl_{2} + NO_{3},$$

$$k_{2} = 6.3 \times 10^{-12} \exp(150/T)$$

$$cm^{3} \text{ molecule}^{-1} \text{ s}^{-1} [15].$$
(2)

Sufficient ClONO₂ ((1.5–4) × 10¹⁵ molecule cm⁻³) was used to ensure that NO₃ was always formed on a time scale at least ten times faster than its loss by reaction with NO, and that Cl atoms were scavenged completely by ClONO₂. Cl₂ and NO concentrations were varied over the ranges (0.6–3) × 10¹⁵ and (0.2–2) × 10¹⁴ molecule cm⁻³, respectively. Initial NO₃ concentrations varied from (1–3) × 10¹² mole-

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cule cm^{-3} , ensuring that NO was always present in large excess over NO₃.

Reagents entered the reaction cell pre-mixed through calibrated flowmeters. The preparation and handling of $ClONO_2$ was carried out in an identical manner to our previous study [14]. Cl_2 and NO were used as received without additional purification. He and N₂ were passed through molecular sieve traps at 77 and 195 K, respectively.

3. Results and discussion

The reaction between NO₃ and NO was studied as a function of temperature (224-328 K), total pressure (50-700 Torr) and diluent gas (M = He, N₂). For each kinetic run, the pseudo-first-order rate constant, k'_1 , was obtained from the slope of the plot of ln(NO₃ absorbance) versus time. Fig. 1 shows a plot of k'_1 versus [NO] at 298 K. The bimolecular rate constant, k_1 , at each temperature was obtained from the slope of the corresponding plot of k'_1 versus [NO]. Values of k_1 are listed in table 1 and plotted in fig. 2 in the form ln k_1 versus 1/T. The Arrhenius expression obtained from this plot is

$$k_1(T) = (1.59 \pm 0.32) \times 10^{-11} \exp(122/T)$$

 cm^3 molecule⁻¹ s⁻¹,

where the stated uncertainty refers to the $\pm 2\sigma$ limits from both random and systematic errors. The derived values of k_1 were independent of pressure and bath



Fig. 1. Plot of k'_1 versus [NO] at 298 K for the reaction NO + NO₃ \rightarrow 2NO₂.

Table 1				
Summary of	kinetic data	for NO +	$NO_3 \rightarrow$	$2NO_2$

T (K)	Number of experiments	$10^{11} k_1^{a}$ (cm ³ molecule ⁻¹ s ⁻¹)		
224	10	2.72 ± 0.54		
242	10	2.66 ± 0.53		
269	10	2.48 ± 0.50		
298	22	2.41 ± 0.48		
315	10	2.36 ± 0.47		
328	10	2.28 ± 0.46		

a) Error limits are ±20, random plus systematic uncertainty.

gas (He/N_2) within the above error limits.

Several possibilities concerning interfering secondary reactions were investigated. Cl_2O can be formed by the reaction of $ClONO_2$ on moist surfaces in the reactor and gas-handling system,

 $2\text{ClONO}_2 + \text{H}_2\text{O}_{adsorbed} \rightarrow 2\text{HNO}_3 + \text{Cl}_2\text{O},$

and may be present as an impurity arising from the $CIONO_2$ synthesis. The presence of Cl_2O would result in the regeneration of atomic chlorine, and



Fig. 2. Plot of k_1 versus 1/T. (\diamond) Data from this study. (\diamond) Data from the discharge flow/laser-induced fluorescence study of Hammer et al. [10].

therefore NO₃, through the following mechanism:

Cl + Cl₂O → Cl₂ + ClO,

$$k_3 = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [11], (3)$$

 $ClO + NO \rightarrow Cl + NO_2$,

$$k_4 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [11], \quad (4)$$

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3.$$
 (2)

To test this possibility, an effort was made to observe ClO in absorption from the photolysis of Cl₂-ClONO₂ mixtures. The CIO detection sensitivity was first optimized by observing its formation in a Cl_2-O_3 system (excess O₃) at 277.4 nm (peak of the (11,0) band of the A ²II \leftarrow X ²II transition, $\sigma_{CIO} \approx 5 \times 10^{-18} \text{ cm}^2$ molecule $^{-1}$ [16]. Efforts to detect CIO in the Cl₂-ClONO₂ system were unsuccessful, suggesting an upper limit of ≈ 0.01 for the ratio [Cl₂O]/[ClONO₂]. This is consistent with previous observations [12,14] that careful purification can reduce the Cl₂O impurity in the synthesis of $CIONO_2$ to less than 0.1% and that precautions in the handling of ClONO₂, such as adequate preconditioning of the reaction cell, can minimize the heterogeneous formation of Cl₂O. Because atomic chlorine reacts about ten times faster with Cl₂O than with ClONO₂ at room temperature, a relatively small Cl₂O impurity can still perturb the kinetics of the NO + NO3 system. Computer simulations of reactions (1)-(4) indicate that, under reac-

Table 2

Summary of experimental results for NO + NO₃ \rightarrow 2NO₂

tion conditions similar to those carried out in this study, a 1% Cl₂O impurity will result in a first-order regeneration term for NO_3 that is indistinguishable from the first-order decay term due to the NO + NO_2 reaction and will cause the rate constant to be underestimated by 13%. This value can therefore be considered an upper limit to the error caused by the presence of Cl_2O in this system.

The system was also tested for the presence of atomic oxygen which might be formed from the photolysis of $ClONO_2$ or impurity NO_2 at wavelengths longer than 300 nm. This was accomplished by adding 100 Torr of O_2 to Cl_2 -ClONO₂ mixtures and testing for the formation of O_3 by UV absorption at 254 nm. No O_3 could be detected which implies an upper limit of 0.01 for the ratio $[O]_0/[NO_3]_0$.

The results of previous determinations of k_1 are summarized in table 2. Early studies of reaction (1) were generally carried out in static reactors with a large number of competing reactions under conditions where direct NO₃ detection was not possible [2,4,5]. Husain and Norrish used the flash photolysis/absorption technique to monitor the production and removal of NO₂ following the photolysis of NO₂ [3]. This study was complicated, however, by the relatively poor sensitivity afforded by plate photometry and a short optical path length. Graham and Johnston were able to improve on previous measurements of k_1 by using molecular modulation combined with long-path

Ref.	$\frac{10^{11} k}{(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})}$	<i>T</i> (K)	Technique ^{a)}
[1] ^{b)}	1.0	300	ST/VIS
[2]	0.45	300	SSP
[3]	20	298	FP/VIS
[4]	0.075	298	SSP
[5]	0.87	29 7	MM/IR
[6]	1.3 ± 0.7	1000-1100	ST/VIS
[7]	1.9 ± 0.4	297	MM/IR-VIS
[8]	2.0 ± 1.0	292-298	FP/VIS
[9]	3.24 ± 0.32	298	DF/LIF
	2.93 ± 0.09	298	FP/VIS
[10]	$(1.55 \pm 0.23) \exp[(195 \pm 39)/7]$	209-299	DF/LIF
	2.95 ± 0.16	296-414	
this work	$(1.59 \pm 0.32) \exp(122/T)$	224-328	FP/VIS

a) SSP - steady-state photolysis, MM - molecular modulation, ST - shock tube, DF - discharge flow, FP - flash photolysis,

IR - infrared absorption, VIS - visible absorption, LIF - laser-induced fluorescence.
 b) Data from this study used to reinterpret room temperature results of Hisatsune et al. [17].

absorption to detect NO_3 and several other species. Croce de Cobos et al. [8] used a flash photolysis system to derive a value for k_1 at 298 K in the pressure range 2-200 atm in good agreement with the value obtained by Graham and Johnston. Unlike the previous investigations, recent studies by Torabi and Ravishankara [9] and Hammer et al. [10] used both flash photolysis/absorption and discharge flow/laserinduced fluorescence methods to measure the rate constant under conditions where only reaction (1)controlled the NO₃ decay profile. The studies are in good agreement concerning k_1 at 298 K, obtaining a value about 50% higher than the recommendations of recent rate constant reviews [11,12] which are based primarily on the results of Graham and Johnston [7]. The only other study of the temperature dependence of k_1 is that of Hammer et al. [10] who obtained a temperature-independent value of k_1 above 298 K and a temperature dependence in good agreement with this study below 298 K.

A number of different explanations can be invoked to explain the small, negative temperature dependence observed in both this study and that of Hammer et al. According to the latter study, elementary transition state theory cannot simultaneously account for both the magnitude and temperature dependence of the A factor, and also does not predict the curvature observed in their Arrhenius plot. An alternative explanation that qualitatively accounts for negative temperature dependences in other radical-radical and radicalmolecule reactions involves the passage of the reaction intermediate over a bound potential energy surface. Several groups have reported the observation of an asymmetric NO₂ dimer, ON-ONO₂, which would presumably have the same geometry as the $NO + NO_3$ transition state [18-22]. This species, however, has only been observed in matrices at temperatures not much higher than 4 K. In an experiment involving the supersonic expansion of NO₂ with electrostatic deflection, Novick et al. [23] were unable to observe a polar component to the mass spectrum of $(NO_2)_2$. This component would have suggested the presence of the ON-ONO₂ isomer. However, the formation of even a weakly bound isomer in the NO + NO₃ reaction could conceivably explain the small negative temperature dependence observed in this study and that of Hammer et al.

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