some basic points of the previous suggestions¹³⁻¹⁵ for the mechanism of the reaction.

It is worth comparing the results presented here with those obtained in the acidic nitrate-ferroin system. The main difference between the two systems is that Fe^{2+} ions react with the autocatalyst (HNO₂) but ferroin does not.¹⁷ Thus, the formula of

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the wave velocity¹¹ in the acidic nitrate-ferroin system does not contain the term corresponding to $k_3[Fe^{2+}]_0$, that is, the wave velocity is independent of the initial concentration of ferroin and the curve of the nitrate dependence starts from the origin.

The fact that the differences between the reactions of similar substrates can be so markedly reflected in the velocity formulas, presents additional perspectives for the investigation of chemical waves.

Registry No. NO₃⁻, 14797-55-8; Fe²⁺, 15438-31-0.

Rate Coefficient for the Reaction NO + NO₃ \rightarrow 2NO₂ between 223 and 400 K

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The rate coefficient for the reaction NO + NO₃ \rightarrow 2NO₂ (1) has been measured in a discharge flow system between 223 and 400 K. Measurements were made by laser-induced fluorescence detection of NO_3 in the presence of excess NO or by chemiluminescent detection of NO in the presence of excess NO₃. Analysis of the kinetics was made using a modified form of the usual flow equations, which explicitly accounts for the viscous pressure drop. The rate coefficients are in excellent agreement with the determination of Sander and Kircher (Chem. Phys. Lett. 1986, 126, 149). The recommended rate coefficient from this study and that of Sander and Kircher can be adequately described by the expression $k_1 = (1.65 \pm 0.35) \times$ $10^{-11}e^{[(110\pm50)/T]}$ cm³ molecule⁻¹ s⁻¹. The possible effects of secondary chemistry on the rate coefficients determined are discussed.

Introduction

The reaction between NO and NO_3 (1) ties together three members of the odd nitrogen family (NO, NO₂, and NO₃). The

$$NO + NO_3 \rightarrow 2NO_2$$
 (1)

reaction has been implicated in controlling the NO₃ chemistry when a large local source of NO is present, e.g., in the urban troposphere, and its rate becomes competitive with NO₃ photolysis for NO mixing ratios approaching 0.3 ppb (\sim 7.5 × 10⁹ molecules cm⁻³).^{1,2} In the laboratory, reaction 1 is important as a titration reaction in flow tube studies when the absolute NO3 concentration is required for cross-section determinations³⁻⁶ or kinetics measurements.⁷⁻⁹ Reaction 1 has also been utilized to remove NO₃ irreversibly in experiments to measure the thermal decay of N_2O_5 in order to prevent regeneration of N_2O_5 , ^{10,11} The rate coefficient for reaction 1 also appears in expressions describing the decomposition of N_2O_5 -containing mixtures.¹²⁻¹⁴

The reaction has been the subject of three previous direct studies, two of which involved measurement of the temperature dependence. Hammer et al. presented the most extensive data set on the reaction, measuring k_1 between 209 and 414 K in a flow tube system.¹⁵ They found a weak negative temperature dependence below 300 K and a virtually temperature-independent rate coefficient above 300 K. Sander and Kircher covered a smaller temperature range (224-328 K) in their flash photolysis experiments.¹⁶ Their rate coefficients were 20-25% lower than those of Hammer et al. and showed a weaker temperature dependence. Torabi and Ravishankara measured k_1 at 296 K using both flow tube and pulsed photolysis experiments.¹⁷ Values of k_1 derived by using the two methods agreed with each other, within 10%, and also supported the higher values found by Hammer et al.

We have measured k_1 as a function of temperature using a flow tube, with laser-induced fluorescence (LIF) detection of NO₃ or chemiluminescent detection of NO. The goals of the study were to reconcile the differences between the absolute magnitudes of the Hammer et al. and Sander and Kircher measurements, to use a wide enough temperature range to be able to investigate the discontinuous temperature dependence reported by Hammer et al., and to perform the reaction using either excess NO or excess NO₃ to evaluate the possible effects of secondary chemistry.

Experimental Section

The experiments were carried out using the flow tube technique with detection of NO₃ by laser-induced fluorescence or NO detection by chemiluminescence. The flow tube (20.2-mm i.d.) was surrounded by two coaxial jackets; the inner one allowed circulation of fluid for temperature regulation, and the outer one could be evacuated to thermally insulate the system against heat loss or frosting. The reaction was studied between 223 and 400 K over a pressure range 0.4-1.5 Torr with helium as the carrier gas. For experiments below ambient temperature, ethanol was circulated

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by a Neslab ULT-80DD bath; above ambient temperature, ethylene glycol was circulated by a Neslab RTE-110 bath. The free radicals from the source (fluorine atoms from discharge, NO₃ from thermal source) entered the flow tube through a side arm. while the NO was introduced down a movable injector, external diameter 9 mm, concentric with the flow tube. The reaction distance could be varied up to 65 cm, the entire length of which was contained within the temperature-controlled region. Since wall losses for NO_3 are usually small, the main flow tube was uncoated, while the outside of the injector was coated with a fluorocarbon wax. Due to the jackets of the flow tube, it was impractical to measure the pressure at the center of the flow region. Instead, pressure ports were installed at each end of the measurement region. This enabled the variation of pressure with reaction distance to be taken into account explicitly in the analysis (see Results section).

The detection cell was machined out of a cube of stainless steel (7.5-cm sides). Tubular extensions held matt-black circular baffles (4-6-mm diameter) machined to a knife-edge finish and quartz windows mounted at Brewster's angle on a length of glass tubing. A blackened cylindrical insert extended from the end of the flow tube past the detection region to eliminate scattered light from the cell. The insert had a 180° 4-mm slit cut into it perpendicular to the cylinder axis to allow the laser light to pass and to restrict the field of view of the detector to approximately the same volume as that occupied by the laser beam.

Laser-induced fluorescence of NO₃ was excited by radiation from an argon ion pumped dye laser (Coherent CR-699 ring dye laser 01-configuration, pumped by Coherent Innova 100 ion laser). The dye laser was operated broad band with Kiton Red dye, using only a birefringent filter for intracavity tuning. In this way output powers of 300-500 mW could be obtained to excite the fluorescence. The wavelength used to excite NO₃ was 623 nm. Although the NO₃ cross section at 662 nm is larger than at 623 nm,¹⁸ it has been shown that the majority of NO₃ fluorescence occurs at \geq 662 nm, regardless of the excitation wavelength.^{19,20} Hence, by exciting at 623 nm and detecting $\lambda > 650$ nm, it was possible to separate the incident exciting light at 623 nm from the fluorescence and to measure NO₃ with good sensitivity. The fluorescence was detected perpendicular to the directions of gas flow and laser propagation by a Hamamatsu R374 photomultiplier tube held at 243 K in a thermoelectrically cooled housing (Pacific Instruments Model 3470). The fluorescence passed through a series of matt-black knife-edge slits and a 640-nm long-wave-pass filter which served to reduce both ambient light and scattered laser light. Photons detected at the photomultiplier were counted with a preamplifier/pulse counter (Pacific Instruments or MIT Instruments) and MIT Instruments PRM-100 rate meter. Counts were acquired and averaged for two or three 32-s periods at each reaction distance (depending on the signal-to-noise ratio for a given experiment) with a PC computer. The laser power was monitored behind the cell by a Coherent 212 power meter. The power did not vary by more than a few percent during the course of a rate coefficient determination, so it was not necessary to normalize the signal to the laser power. From titration experiments we estimate that $\sim 10^{10}$ molecules cm⁻³ could be detected with a signal-to-noise ratio of ~ 10 and with a signal-to-background ratio of ~ 0.02 at a pressure of 1 Torr for 350-mW laser power. The fluorescence intensity was found to behave linearly with [NO₃] and laser power over a wide range of conditions (40-500-mW laser power, $(1-100) \times 10^{11}$ molecules cm⁻³ NO₃). The initial [NO₃] in experiments with excess NO was in the range $(4-10) \times 10^{11}$ molecules cm⁻³, and a ratio of $[NO]/[NO_3]_0 > 10$ was usually obtained, in order to maintain pseudo-first-order conditions. In some experiments using low [NO], the [NO]/[NO₃] ratio dropped

below 10; in these cases, the effective NO was calculated from the reduction in NO₃ fluorescence at the shortest reaction time. assuming that the loss of NO₃ equaled the loss of NO to that point. These points did not affect the regression analysis particularly, since they were at very low [NO].

For the experiments in which NO was detected by chemiluminescence the combination of filters and baffles used was not changed, but a black cloth was placed over the whole of the detection chamber and side arms. A flow of 240 sccm ozonized O_2 (4% O_3) was added 7 cm upstream of the detection region to excite the $NO-O_3$ chemiluminescence.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2a}$$

$$\rightarrow NO_2^* + O_2$$
 (2b)

$$NO_2^* \rightarrow NO_2 + h\nu$$

The pressure was approximately 1 Torr for these measurements. Two methods were used for the production of NO₃ radicals. The first was the reaction of NO_2 with O_3 .²¹ A mixture of NO (0.2% in He) was mixed with a flow of O₃ in He and allowed to react slowly in a reactor of approximately 1-L volume at a temperature around 430 K and a total pressure of 5-50 Torr. The

following reactions occur:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{3}$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \tag{4}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \tag{5}$$

At 430 K approximately 80% of the NO was converted to NO₃, as verified by titration of the NO_3 in the main flow tube by NO_3 The remaining NO_x presumably remained as NO_2 or N_2O_5 . The resulting mixture then entered the flow tube through a side arm. In the reactor, the NO, concentration was $\sim 5 \times 10^{13}$ molecules cm⁻³, while the O₃ concentration was $\sim 1 \times 10^{16}$ molecules cm⁻³. In the main flow tube, the NO_x concentration was $<10^{12}$ molecules cm⁻³, while the O₃ concentration was $\sim 1 \times 10^{14}$ molecules cm⁻³. The resultant cooling and dilution prevented regeneration of NO₃ by reaction 3. Also, any N_2O_5 produced in the side arm will not dissociate at the lower pressures and temperatures encountered in the flow tube, thus minimizing regeneration of NO₃ by reaction 5. We estimate from computer simulation of the reactions given above that decomposition of N_2O_5 at the highest temperature (296) K) and pressure (1.5 Torr) used would affect the NO₃ decays by less than 0.1%.

In the second method, fluorine atoms generated by a microwave discharge in a dilute F_2 -He mixture were reacted with excess HNO₃ to generate NO₃ ($k_6 = (2.4 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).^{7,9,22}

$$F + HNO_3 \rightarrow HF + NO_3$$
 (6)

The microwave discharge was excited in an alumina tube, and the free radicals entered the main flow tube via a short Pyrex side-arm reactor (10 cm long, 1 cm diameter) at 90° to the alumina tube. This configuration reduced the amount of light from the discharge reaching the detection area. The side-arm reactor could also be used to carry out reactions before reaching the main flow tube (see below). The source reaction (6) was carried out in the main flow tube, allowing enough time for the reaction to go to completion before the NO was added. Initial experiments showed regeneration of NO₃ at long reaction times, which was thought to be due to the presence of FO radicals, formed by the reaction of F atoms at the surface of the glass tube

$$F + glass \rightarrow FO$$
 (7)

or, if the concentration of HNO₃ was too low, by reaction with NO33,5,7,9

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^{2223.}

Rate Coefficient for NO + NO₃ \rightarrow 2NO₂

$$F + NO_3 \rightarrow FO + NO_2$$
 (8)

followed by

$$FO + NO \rightarrow F + NO_2$$
 (9)

$$F + HNO_3 \rightarrow HF + NO_3$$
 (6)

A large apparent injector loss of the NO₃ (typically 10 s^{-1}) was found in the preliminary experiments where FO was thought to be present. Production of FO was minimized by the use of low microwave power and the addition of a large flow of He to the F_2 -He mix, which reduced the residence time in the discharge tube. However, some regeneration of NO₃ still occurred, so a small flow of NO was added to the side arm, sufficient to react away at least 80% of the remaining FO before it reached the main flow tube. In this way, a clear maximum was observed in the detected NO_3 as a function of the added NO. The injector loss of NO_3 was found to be very low $(0 \pm 4 \text{ s}^{-1})$ for conditions of low FO. It is probable that the large apparent injector loss of NO₃ was actually due to FO being removed on the clean surfaces of the injector. This would lead to an apparent increase in the NO_3 as the injector was retracted. In a few experiments the nitric acid was allowed to react with the F atoms in the side-arm reactor. This generally resulted in a lower NO₃ signal than when the reaction took place in the flow tube. This is indicative of unidentified nonlinear processes removing NO₃ at the elevated concentrations encountered in the side arm. The reaction between FO and NO₃⁹ could be a possible candidate (but it would have to be considerably faster than $ClO + NO_3^{18}$):

$$FO + NO_3 \rightarrow FO_2 + NO_2$$
 (10)

At the low pressures used here, FO₂ should have a lifetime of the order of seconds, and its formation should not lead to regeneration of NO₃ in the main flow tube.¹⁸

Regular titrations were carried out to determine the efficiency of NO₃ production and to ensure that pseudo-first-order conditions were met. The reaction between NO₃ and NO was used for this purpose. The ratio of initial NO_3 to F_2 was usually found to be 1.6 ± 0.2 . Although this represents less than unity conversion of F_2 to NO₃, we feel it is likely that the fluorine is essentially completely dissociated in the discharge and that either some F atom recombination occurs after the discharge region or some NO₃ is destroyed by secondary reactions, as described above. The concentration of HNO₃ in the main flow tube was kept in excess of 1.2×10^{14} molecules cm⁻³, giving a ratio [HNO₃]/[F]₀ > 120, to ensure that the occurrence of reaction 8 was negligible.

All gases were introduced into the flow tube using mass flow controllers (MKS or Tylan) which were calibrated against a dry test meter or a bubble flow meter. Pressure was measured with MKS Model 227 Baratron capacitance manometers. The helium used for the main carrier gas and for making gas mixtures was chromatographic grade (U.S. Welding). Mixtures of NO in He or N_2 were made up from pure NO (Linde) and high-purity diluent gas. The majority of experiments were carried out using a 2.10% (±0.06%, 2σ) mixture of NO in N₂. The concentration of the mixtures was checked periodically in a 20-cm cell by FTIR spectrometry. No statistically significant difference in the NO content of the mixture was found between determinations carried out over the course of 6 months. The level of NO_2 impurity in the NO was found to be $\sim 2\%$ of the NO. No other reactive impurities were detected in the infrared region (only a little N₂O).

Flows of nitric acid were generated by bubbling He through a mixture of concentrated HNO₃ (70 wt %) in concentrated H₂SO₄ (initially 1:2 by volume) held in a wash bottle at ambient tem-perature.^{6,9,22} The flow of nitric acid was estimated assuming saturation of the carrier gas at a nitric acid vapor pressure of ~ 20 Torr at 296 K.²³ Infrared analysis showed the concentration of H_2O in the vapor to be less than 1% of the HNO₃.

Ozone was produced by the action of a corona discharge into pure O_2 . For the thermal NO₃ source the O_3 was trapped on silica gel at 196 K and introduced to the reactor by flowing He over it at approximately 40 Torr. For the experiments using excess NO₃ and chemiluminescent detection of NO, the O₃ was prepared continuously. Fluorine was obtained as a 5% mixture in He from Spectra Gases and normally used directly from the cylinder. For experiments using low NO concentrations, the F₂ mixture was further diluted by a factor of 10 in chromatographic grade helium.

Results

The reaction of NO with NO₃ was studied by using three different chemical systems: excess NO, using a thermal source of NO₃; excess NO, using a discharge source of NO₃; and excess NO_3 , also using a discharge source of NO_3 . Each system will be discussed separately.

The analysis was based on a standard first-order analysis, modified to include the viscous pressure drop down the tube. The viscous pressure drop down the flow tube is given in cgs units by Poiseuille's law^{24,25}

$$P_z^2 - P_0^2 = \frac{16RT\eta z(dn/dt)}{\pi a^4}$$
(1)

where η is the viscosity, subscript zero represents the value of a quantity as measured at the lower pressure port, z is the distance upstream measured from the lower pressure port, a is the radius of the flow tube, and dn/dt is the molar flow rate past a given point in the tube.

By expressing both the concentrations of NO and NO₃ as functions of P (and hence of z), the standard first-order equation can be integrated explicitly to include the pressure drop. The resulting equation has the form

$$\ln [NO_3]_z - \ln [NO_3]_0 = -k_1 [NO]_0 t_c$$

where

$$t_{\rm c} = \frac{z}{\nu_0} \left(1 + \frac{(P_l^2 - P_0^2)z}{2lP_0^2} \right)$$

The fixed distance between the two pressure ports (65 cm) is referred to as l. The term t_c has the dimensions of time and can be thought of as a corrected reaction time. It actually corrects both the reaction time and [NO]; this enables P_0 and [NO]₀ to be used. In practice, the term $(P_1^2 - P_0^2)$ was evaluated from the known physical properties of the flow tube and the carrier gas²⁶ by using the Poiseuille equation (I). This leads to the following working form of the expression for t_c for helium as carrier gas:

$$t_{\rm c} = \frac{z}{\nu_0} \left(1 + \frac{2.64 \times 10^{-7} F T^{0.5} z}{a^4 P_0^2} \right)$$

Here, F is the total flow rate in standard $\text{cm}^3 \text{ s}^{-1}$ and P_0 is measured in Torr. For moderate pressure drops the expression reduces to the form normally used in kinetics experiments, in which the pressure is measured at the midpoint of the flow tube (z =l/2), and mean values of the flow parameters are used. However, the analytical solution given here takes explicit account of the nonlinear variation of reaction time with z, caused by the viscous pressure drop. Note that the correction applies to the region of the flow tube actually used in a particular experiment. For most circumstances the correction is small. It is useful in our case because of the high rate coefficient of the reaction being studied, which necessitates a high flow velocity, and the rather narrow radius of the flow tube. Note also that the correction enters as a quadratic term in P_0 , since it affects both the [NO] and the velocity. In the most extreme case, for the fastest flows at 400 K, the values of $[NO]_0$ and ν_0 differed by about 9% from those that would be calculated by using the mean pressure in the tube.

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TABLE I: Summa	ry of Ex	perimental	Conditions fo	r Measurement	of .	k 1
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temp, K	conditions	range of NO, ^a 10 ¹² molecules cm ⁻³	no. of expts	press. range, Torr	$k_1, 10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹
223	F ₂ -HNO ₃	3.9-10.4	8	0.7-0.9	2.72 ± 0.10^{b}
243	F,-HNO	3.6-12.1	11	0.7-1.2	2.61 ± 0.07
296	F ₂ -HNO ₃	1.8-7.3	19	0.7-1.2	2.23 ± 0.10
323	F ₂ -HNO ₃	1.6-8.9	10	0.7-1.3	2.32 ± 0.11
353	F ₂ -HNO ₃	1.6-8.8	11	0.7-1.4	2.23 ± 0.08
400	F ₂ -HNO ₃	2.1-10.3	10	0.6-1.1	2.27 ± 0.11
243	NO2-01	1.5-5.5	21	0.5-1.0	2.87 ± 0.24
273	NO ₂ -O ₁	1.5-4.3	9	0.5-0.8	2.78 ± 0.19
296	NO ₂ -O ₁	0.9-5.3	15	0.4-0.8	2.61 ± 0.17
223	excess NO ₃ ^c	5.8-16.3	3	1.0	2.43 ± 0.08
296	excess NO ₃ ^c	8.6-12.3	3	1.0	2.17 ± 0.08
353	excess NO ₃ ^c	6.6-11.2	3	1.0	2.10 ± 0.08

^a For excess NO₃ experiments, range of NO₃. ^b Precision at 1σ level. ^c Carried out using F₂-HNO₃ source of NO₃.

The calculated second-order rate coefficients obtained by using the two different approaches differed by less than 1%, but the relative standard deviation was reduced from 6.9% to 3.2% by using the "corrected" time base.

In practice, the flow rates of the various constituents were entered into a spread sheet, along with P_0 and the temperature, to obtain the concentrations. Then, values of the NO3 fluorescence at different values of z and finally the background signal were entered. The program automatically applied the pressure correction and fitted the values of ln ([NO₃] - background) against t_c by the nonweighted linear least-squares method. Second-order rate coefficients $k_1(T)$ were obtained from an unweighted linear least-squares fit of k' against [NO], after correcting for axial and radial diffusion.^{27,28} The radial correction was the simple analytical form (eq 23 in Keyser's paper), which is valid for conditions of low wall loss of NO₃ and moderate pressure range (diffusion coefficient >30 cm² s⁻¹). The diffusion coefficient D_c for NO₃ in He was taken from Hammer et al.,¹⁵ $D_c = (310/P)(T/273)^{1.5}$ cm² s⁻¹. For conditions encountered here, the diffusion coefficient was always greater than 100 cm² s⁻¹. By performing titrations at various positions along the flow tube, it was possible to show that the loss of NO3 on the wall of the main flow tube was less than 5 s^{-1} .

The Reaction NO + NO₃: Discharge Flow Source Using *Excess NO.* The most extensive set of results was obtained by using the reaction of F atoms with HNO3 to produce NO3. Some problems were encountered with regeneration of NO3 due to formation of FO, but these were eliminated satisfactorily, as described in the Experimental Section. The loss of NO₃ on the surface of the injector was measured each day by performing an experiment in the absence of NO. This decay rate was subtracted from all the runs on a given day, to ensure that experiments from different days had consistent intercepts. Due to the low wall reactivity of NO₃ ($< 5 s^{-1}$), it was not necessary to measure the injector loss more than once per day.

It was observed that the fluorescence did not decay completely to baseline (scattered light + dark counts), even at long reaction times. This was found to be due to LIF of the product NO₂. Even though the absorption cross section of NO₂ is approximately 1000 times lower than that of NO3 at 623 nm,²⁹ the radiative lifetime is sufficiently short that it is not quenched as efficiently as NO₃, giving a detection sensitivity for NO2 about 100 times less than for NO_3 for the conditions of this study. This can lead to substantial curvature at high NO concentrations, since two NO₂ molecules are produced for each NO₃ reacted. The relative sensitivities for NO₂ and NO₃ were demonstrated by introducing NO₂ directly into the flow tube down the movable injector. Since the NO₂ is formed as a direct product of the reaction being studied,³ the correct baseline to use is that measured at long reaction time, when all the NO₃ has been converted to NO₂.³⁰



Figure 1. Second-order plot for NO + NO₃ \rightarrow 2NO₂ at 296 K for experiments with excess NO. Data are shown for experiments using both NO₃ sources: \bullet , discharge flow; ∇ , thermal source.



Figure 2. Arrhenius plot showing all directly measured rate coefficients for $NO + NO_3$. Solid lines are described in the text. Symbols: (III) this work, discharge flow; (\bullet) this work, thermal source; (∇) this work, excess NO₃; (Δ) Sander and Kircher;¹⁶ (O) Hammer et al.;¹⁵ (\Box) Torabi and Ravishankara.¹⁷ Error bars shown are representative of combined uncertainties as reported by respective authors.

This interference was discovered after the room-temperature data had been taken, so the 296 K decays were "linearized" by adjusting the baseline (within reasonable limits based on observed sensitivities for NO₂ relative to NO₃) until the decays were logarithmic.

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For all the determinations at other temperatures, the baseline was measured at long reaction time, with a high flow of NO. The contribution to the total fluorescence from NO₂ contained in the NO ($\sim 2\%$) was negligible.

The data obtained at 296 K are shown in Figure 1. The rate coefficients obtained, at temperatures between 223 and 400 K, are summarized in Table I and shown in Figure 2. A weak, but distinctly negative, temperature dependence was obtained. The data are well described by the Arrhenius-type expression, $k = Ae^{(B/T)}$

$$k_1 = (1.68 \pm 0.14) \times 10^{-11} e^{[(103 \pm 50)/T]}$$

where the errors are 2σ (precision) and $\sigma(A) = A\sigma(\ln A)$. We estimate potential systematic uncertainties to be on the order of 6%. The measured rate coefficients did not show any systematic dependence on the flow rate or pressure (varied by a factor of ~ 3) or the initial NO₃ concentration. The data above room temperature could be interpreted as showing a discontinuity in the slope, similar to that seen by Hammer et al. However, since our temperature dependence is less, the effect is less pronounced. We prefer, though, to describe the data by a simple two-parameter fit, which represents our data within the uncertainty limits.

The Reaction $NO + NO_3$: Thermal Source Using Excess NO. The second source used for NO₃ production was the thermal reaction of NO₂ with O₃.²¹ The source reactor was held at 430 K and operated at a pressure between 5 and 50 Torr, depending on the flows of NO and O₃ used. The source did not allow a large range of NO₃ to be produced. If the residence time in the reactor was too short, the formation reaction (3) did not go to completion.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{3}$$

At slower flows, the yield of NO₃ dropped, probably due to N_2O_5 formation in the cooler region between the reactor and the flow tube. Measurements of k_1 were carried out between 296 and 243 K. Below this temperature the NO₃ behavior was irreproducible, and it took a long time to obtain a steady signal after moving the injector. This could be due to some heterogeneous reaction involving O₃ which led to production of NO₃ or NO₂ (which would have caused a background shift). At 243 K the signal changes were instantaneous and quite reproducible, and we assume that the kinetics data for $T \ge 243$ K are not influenced by the uncharacterized interference seen below 243 K. Also, experiments were carried out in which a stable signal was obtained at room temperature, and then the flow tube was cooled stepwise to 243 K. In these cases, the NO₃ fluorescence at 243 K was within a few percent of that measured at 296 K, after correcting for the change in density of the gas. This suggests that no unidentified reactions were removing NO₃ between these two temperatures. Attempts were made to measure the injector loss of NO₃ using this source; this was always found to be equal to 0 s^{-1} within experimental error.

The presence of O_3 in the flow tube led to one complication in the analysis: the observation of NO-O₃ chemiluminescence from the excess NO, which manifested itself as a constant baseline shift. The background (chemiluminescence + scattered light) was measured separately for each NO concentration without the source NO turned on. Experiments with and without the laser showed that NO₃ production from reaction between the added NO and O₃ was negligible. Correction was also made for the LIF of product NO₂ molecules, but in general the correction was less critical than for the experiments using the F₂ source, since the NO concentrations used here were lower (and hence, the NO₃ decay did not approach baseline).

The O_3 concentration in the main flow tube was calculated to be of the order 10^{14} molecules cm⁻³ for these experiments based on a vapor pressure of 6 Torr at 196 K. This is probably an upper limit for what was actually obtained in the flow tube, since the residence time for the carrier gas in the ozone trap was usually kept quite short. It was noted that, immediately after the ozone trap was loaded, a very large and unstable chemiluminescence background was observed, and the flow had to be reduced sub-



Figure 3. Second-order plot for NO + NO₃ at 243 K. Data are obtained by using a thermal source of NO₃. Solid line is an unweighted linear least-squares fit to data, constrained to pass through origin. Symbols: \bullet , included in fit; Δ , not included in fit.

stantially before stable kinetics measurements could be made.

A second systematic error is that associated with the reaction of NO with O₃. This could lead to depletion of the NO on a time scale comparable to the NO₃ decay. Computer simulation of the reaction system shows that this would lead to an underestimation of the rate coefficient of the order 5% at the highest O₃ concentration and lowest flow velocities used. As discussed above, the ozone concentration was probably overestimated, so that the figure of 5% must be considered an upper limit for the systematic error.

Representative data obtained at 296 K are included in Figure 1 for comparison with experiments using the other source, and data obtained at 243 K are shown in Figure 3. The rate coefficients obtained by using this source are included in Figure 2 and summarized in Table I. Two different NO mixtures were used to obtain the data at 296 and 273 K, with no systematic differences found. The results obtained with this source are systematically about 10% higher than those obtained with the discharge source, but overlap within the experimental uncertainty. The data obtained by using the thermal source were more scattered than those using the discharge source, and this is reflected in the error bars of the derived rate coefficients. The scatter comes partly from fluctuations in the signal, possibly due to instabilities in the ozone flow and partly from thermal instabilities in our laboratory, which led to drifts in the detection stability. These were minimized before the work using the discharge flow source. Figure 3 shows the data points measured at 243 K and an unweighted linear least-squares fit to the data. The three points lying well below the line were excluded from the fit, since they clearly made the fit skew away from the origin. If the fit to the remaining points was not constrained to pass through the origin, a rate coefficient of $(2.81 \pm$ $(0.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ was obtained, with an intercept}$ of 7 s⁻¹. If the fit was constrained to pass through the origin, a rate coefficient of $(3.00 \pm 0.06) \times 10^{-11}$ was obtained. The skewing of the fit away from the origin reflects the uncertainty in fitting some of the data. The rate coefficient given, $(2.89 \pm$ $(0.24) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is the mean of these two values, as an attempt to remove the skewing of the data. At the other temperatures the fit was found to pass through the origin. The temperature dependence of the data is also in good agreement with that obtained from the discharge source $(E/R \sim 110 \text{ K})$.

The Reaction $NO + NO_3$: Discharge Flow Source Using Excess NO_3 . Some experiments were also carried out using an excess of NO_3 with NO being detected by chemiluminescence.

A flow of ozonized oxygen was added to the flow tube just before the detection region. For these experiments, the F₂ source was used, since this could generate large concentrations of NO_3 (>10¹³ molecules cm⁻³). The procedure was first to carry out a titration of NO₃ by NO, to determine the NO₃ concentration. The NO₃ flow was set up, and then small flows of the NO mix (2.10%) were added down the movable injector. The decrease in NO₃ fluorescence was measured for three or four flows of NO, from which the total NO₃ could be calculated.^{3,6} Canosa-Mas et al.⁶ have examined potential causes of systematic error in this titration, and for the conditions of our experiments (1 Torr of He, flow velocity 2000 cm s⁻¹, $[NO_3] < 1.2 \times 10^{13}$ molecules cm⁻³) the observed stoichiometry factor should be unity. The laser beam was then blocked, and the detection region was covered with a black cloth to eliminate room light. A small flow of NO was added down the movable injector, and chemiluminescence from the reaction NO + O_3 used to monitor the NO decay as the injector was pulled out. The entire titration was carried out with the ozonized O₂ flowing. Under these conditions the NO sensitivity was $\sim 2 \times 10^{10}$ molecules cm⁻³. The background was very stable, and very fast NO decays could be measured with good precision.

Three NO decays were measured at each of three temperatures. The rate coefficients obtained are included in Table I with uncertainties at the 1σ level. We estimate an overall uncertainty (95% confidence) of $\pm 20\%$ since the use of the titration to determine the NO₃ concentration introduces a larger uncertainty for these measurements than for those using excess NO, where the NO concentration could be determined solely from flow rates. The results obtained agree within experimental error with those obtained by using the F-HNO₃ source and excess NO at corresponding temperatures.

Discussion

Absolute Value of the Rate Coefficient k_1 . The most extensive data set, obtained with the discharge flow source and excess NO, agree almost identically with the data of Sander and Kircher (see Figure 2). Within the uncertainties of the two studies the results cannot be distinguished. Our experiments using the O₃ source and those using excess NO₃ also support lower values for the rate coefficient at each temperature than those found by Hammer et al. The lower line shown in Figure 2 is an unweighted least-squares regression through our data obtained using excess NO and that of Sander and Kircher.¹⁶ Also shown are the results of Hammer et al.¹⁵ and Torabi and Ravishankara.¹⁷ The upper regression line shown is a fit to these two data sets below 350 K.

As described in the Experimental and Results sections, some evidence was found for production of FO in the radical production region. Measures were taken to reduce this, by titrating the FO by NO. Simulations of the chemistry in the main flow tube and the side arm were carried out using the ACUCHEM program.³¹ We estimate that an initial FO concentration equal to 0.1 of the NO₃ would give a measured rate coefficient approximately 10% too low. The decays would actually look reasonably well behaved, since the most acute curvature takes place in the first 10 ms, past the travel of the injector. Therefore, a significant FO concentration would lead to erroneous measurements. However, the simulations show that the NO added to the side arm would reduce the FO to less than 20% of its initial value (for reasonably low FO). Since the NO₃ never increased by more than 5% when NO was added to the side arm, the remaining FO could not have been more than a few percent of the NO₃. Hammer et al. also used the $F + HNO_3$ reaction as a source of NO₃ but found good agreement between the results obtained with different sources. The main difference between our experiments and theirs is that our F atom concentrations were roughly an order of magnitude higher than theirs, due to a larger scattered laser light contribution which reduced

our sensitivity. Therefore, any uncertainties due to radical-radical reactions may have been magnified in our study. However, we feel that all necessary measures were taken to reduce or account for these uncertainties.

To test whether regeneration of NO_3 was a problem, the reaction was studied by using excess NO_3 . The experiments carried out using excess NO_3 are not significantly different from those using excess NO. If the above regeneration mechanism were operative, it would have led to an overestimation of the NO removal rate. However, as pointed out by Sander⁵ and by Mellouki et al.,⁸ the NO_3 would also have been overestimated in the titration. The overall effect would be an underestimation of the rate coefficient. Again, this would be comparable to the ratio of FO to NO_3 . For the reasons described above, the effect should be much less than 10%. Regeneration of NO_3 via FO is not the only interference which could be occurring; however, it is difficult to conceive of a mechanism that would simultaneously regenerate both NO and NO_3 .

The precision of the rate coefficients obtained by using the discharge source lay between 4 and 5% (1 σ). More scatter was evident in the experiments done using the thermal source, ~8%. Some of this was due to uncontrolled environmental effects in the laboratory at that time, which led to drifts in the stability of the detection system over the time scale of an experiment. We estimate an additional systematic uncertainty of 5-6% from flow calibrations, pressure measurement, etc., leading to overall uncertainties (95% confidence) of ~15% for the discharge flow experiments and ~20% for the experiments using NO₂-O₃. Temperature Dependence of the Rate Coefficient k_1 . The

Temperature Dependence of the Rate Coefficient k_1 . The temperature dependence measured here is very similar to that measured by Sander and Kircher.¹⁶ There is slight evidence for curvature at higher temperature, possibly even a temperatureindependent rate coefficient, but within the uncertainties of the measurements this is not unambiguously determined. Hammer et al. were unable to account for their temperature dependence theoretically, and we therefore prefer to express the dependence in the simplest and most useful form, i.e., a two-parameter, Arrhenius fit. Combining all of our data with those of Kircher and Sander we obtain

$$k_1 = (1.65 \pm 0.35) \times 10^{-11} e^{[(110\pm 25)/T]}$$
 cm³ molecule⁻¹ s⁻¹

where the error in the A factor includes precision (2σ) and an estimated 10% from systematic sources, while the error in the exponential term represents statistical uncertainty only. This final value should be adequate to describe the reaction for most applications near ambient temperature. Experiments at much higher temperatures (600-800 K) would be useful to confirm the temperature dependence for incorporation into future theory.

Conclusions

We have remeasured the rate coefficient for NO + NO₃ between 223 and 400 K. The data support the lower values of the rate coefficient obtained by Sander and Kircher. Data obtained with different NO₃ sources show small but systematic differences, outside the precision of the individual measurements. It should be pointed out, of course, that the total spread in the measurements obtained by all investigators is only $\sim \pm 25\%$ (at the lowest temperature) and $\pm 15\%$ at 400 K, which is not a large uncertainty. However, since the individual data sets are so self-consistent, the differences must be due to systematic errors associated with unidentified chemical reactions occurring in the different systems. We have been unable to verify the discontinuous Arrhenius behavior observed by Hammer et al.

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