interactions (A), electron transfer (B), or proton transfer (C). Naturally, the reaction may proceed by an intermediate between these extreme forms that is controlled by the ability of the system to develop charge at the carbon and oxygen atoms.

The reaction of a triplet carbene with methanol to give benzhydryl methyl ether necessarily involves intersystem crossing. Intersystem crossing will occur at a set of nuclear coordinates common to both the singlet and triplet surfaces. We propose that the data for alkyl- and halo-substituted diphenylcarbenes and diphenylcarbene itself is best interpreted as involving a tripletsinglet crossing point which resembles an intermediate such as C (on the singlet surface). Thus, donating substituents will facilitate reaction of the triplet with methanol allowing it to more easily intersystem cross to a structure such as C on the singlet surface. This higher crossing probability is reflected as an increase in the preexponential factor (see effect of dimethyl substitution in Table III). We also note that in this interpretation the effect of a second methyl substituent (see Table III) is expected to enhance the substituent effect observed on monosubstitution rather than offset the effect of the first methyl group as one would anticipate in a mechanism controlled solely by the energy gap. On the other hand, electron-withdrawing substituents (such as -CN or $-CO_2CH_3$) will lower the energy of the singlet carbene relative to the triplet carbene but will raise the energy of that part of the singlet reaction surface resembling species C. The two effects of an electron-withdrawing substituent on different portions of the singlet surface may now favor the preequilibrium mechanism as in the case of the last three entries in Table III.

The proton-transfer transition structure interpretation of the data for unsubstituted diphenylcarbene also explains the small but finite CH₃OH/CH₃OD isotope effects on the reaction, and why Bethell¹⁰ found that more acidic alcohols react more rapidly than less acidic ones with diphenylcarbene. Neither of these two facts can be readily explained by a mechanism involving a preequilibrium followed by diffusion-controlled singlet carbene reaction with alcohol.

It is important to note that our data does not indicate which mechanism is actually preferred for reaction of singlet diphenylcarbene with methanol. Our data indicates only that triplet diphenylcarbene can most easily cross to that portion of the singlet reaction surface which resembles proton transfer. A surface crossing as pictured above would involve the coupling of a covalent triplet to a zwitterionic singlet state. This is, in general, the most favorable type of structure for spin-orbit-assisted intersystem crossing according to the theory of Salem and Rowland.¹⁸



Registry No. Diphenyldiazomethane, 883-40-9; (4-bromophenyl)phenyldiazomethane, 1140-32-5; bis(4-bromophenyl)diazomethane, 20359-77-7; (4-chlorophenyl)phenyldiazomethane, 1140-33-6; bis(4chlorophenyl)diazomethane, 1143-92-6; bis(4-methylphenyl)diazomethane, 1143-91-5; (4-cyanophenyl)(4-methylphenyl)diazomethane, 100813-36-3; (4-cyanophenyl)phenyldiazomethane, 838-14-2; (4-carbomethoxyphenyl)phenyldiazomethane, 100813-37-4; 4-phenyldiphenyldiazomethane, 30905-13-6; 4-methyldiphenyldiazomethane, 20359-75-5; diphenylcarbene, 3129-17-7; (4-bromophenyl)phenylmethylene, 14845-79-5; bis(4-bromophenyl)methylene, 61242-60-2; (4-chlorophenyl)phenylmethylene, 14845-78-4; bis(4-chlorophenyl)methylene, 24436-61-1; bis(4-methylphenyl)methylene, 32076-77-0; (4-cyanophenyl)(4methylphenyl)methylene, 100813-38-5; (4-cyanophenyl)phenylmethylene, 64568-30-5; (4-carbomethoxyphenyl)phenylmethylene, 100813-39-6; 4-biphenylphenylcarbene, 14845-83-1; (4-methylphenyl)phenylmethylene, 14845-80-8; cyclohexane, 110-82-7; isooctane, 26635-64-3; methanol, 67-56-1.

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Kinetics of the Gas-Phase Reaction NO + NO₃ \rightarrow 2NO₂

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The rate constant for the reaction NO + NO₃ \rightarrow 2NO₂ was measured over the temperature range of 209-414 K by using laser-induced fluorescence detection of NO₃ in a flow tube reactor. Our recommended results are $k(T) = (1.55 \pm 0.23)$ × $10^{-11} \exp[(195 \pm 39)/T]$ cm³ molecule⁻¹ s⁻¹ for $T \le 300$ K and $k(T) = (2.95 \pm 0.27) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for T> 300 K. These two expressions were required to describe the observed non-Arrhenius behavior of k(T).

Introduction

The role of the nitrate free radical (NO_3) in the chemistry of the earth's atmosphere has been recognized for some time.¹⁻³ NO_3 has been measured in the stratosphere^{4,5} and the troposphere,⁶⁻¹¹ and its atmospheric behavior has been modeled.¹²⁻¹⁶ There are compounds¹² and many such reactions have been studied in the laboratory.¹⁷⁻²³

The kinetics and photochemistry of the $NO_{x}-O_{3}-N_{2}O_{5}$ system of which NO_3 is an important constituent have been studied by several investigators.²⁴⁻³⁰ However, little data has been available on the kinetics of the fundamental reaction

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

and until very recently the accepted rate constant was k(297 K)= $(1.9 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ which was inferred from

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Figure 1. Apparatus, viewed from above. The entrance and exit beams of the multipass cell were actually separated vertically.

indirect measurements by Graham and Johnston.²⁴ No measurements of the temperature dependence of the reaction have been reported. The reaction enthalpy of (1) is $\Delta H^{\circ}_{298} = -23.0$ kcal mol⁻¹ from $\Delta H_{\rm f}^{\circ}$ (298) = 17.3 kcal mol⁻¹ for NO₃ as determined by Kircher et al.³¹

In this work we have directly measured this rate constant over the temperature range 209-414 K at low pressures. Such a direct determination was made possible by the quantitative detection of NO₃ using laser-induced fluorescence.

Experimental Section

Measurements of the kinetics of reaction 1 were made using a flow tube reactor.³² The NO₃ concentration was measured by means of laser-induced fluorescence (LIF). Experiments were done with NO added in excess over NO_3 and thus the reaction was pseudo-first-order in NO₃. LIF was also used to detect NO₂

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Figure 2. Side view of LIF cell. The flexible seal permitted movement of the PMT assembly for signal optimization. The mask eliminated stray laser light at the edges of the field of view.

for diagnostic purposes. A small-volume multipass absorption cell could be installed just downstream from the LIF cell to verify the detection calibration and also to perform diagnostics. Figure 1 provides an overview of the experimental apparatus.

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Quantitative detection of NO3 was achieved primarily by measuring the fluorescence from excitation of the 0-0 ${}^{2}E' \leftarrow {}^{2}A_{2}'$ transition which has a peak absorption cross section at 662 nm. Details of NO₃ LIF detection were recently described by Ishiwata et al.³³ and Nelson et al.,^{34,35} and it is clear that when NO₃ is excited at 662 nm most of the fluorescence intensity occurs at wavelengths longer than 710 nm, excluding fluorescence of the 662-nm band. The collision-free lifetime of the excited state has been measured³⁵ and is anomalously long: 340 µs, roughly 2 orders of magnitude longer than that expected on the basis of a simple polyatomic system with the observed absorption cross section. Marinelli et al.³⁶ have demonstrated that the 662-nm band lacks fine structure. Magnotta and Johnston²⁶ showed that no photodissociation occurs at this wavelength, thus eliminating this as a cause of the absence of structure. The mechanism proposed to explain these observations involves multilevel mixing effects and is quite complex.^{35,37} From the standpoint of NO₃ kinetics, it is important to determine the consequences of the above considerations in regard to the sensitivity, linearity, and reliability of NO₃ concentration measurements. These matters were explored by empirical methods as discussed below and no complications were found for the LIF method.

The LIF cell and detection system are illustrated in Figure 2. The side arms for the laser beam entrance and exit were optically isolated from the main cell body by O-ring seals and opaque masks to prevent light pipe effects. This, together with high-grade brewster angle windows, baffles, and a Wood's horn, served to minimize scattered laser light. A lens was used to collimate the fluorescence image on the detector so that the collection efficiency was optimized with respect to signal-to-noise. The estimated effective field of view was a volume of radius 2 mm and length 1.5 cm, and a solid angle of 0.08 sr. Optical filters could be inserted just above the lens. A long-pass filter with a 695-nm cutoff was used for the kinetics measurements. The detector was a Hamamatsu R943-02 PMT which has a long wavelength cutoff at about 900 nm and a photocathode area of 1 cm². The PMT was cooled to below 268 K. Under typical conditions of 1 torr of He buffer gas, a laser power of 400 mW, and a signal integration time of 15 s, the NO₃ detection threshold was better than 10^8 molecule cm⁻³.

The multipass absorption cell (Figure 1) had a mirror separation of 30 cm and an envelope inner diameter of 2.3 cm. It was constructed following the basic design of White.³⁸ Dielectric mirrors with a reflectance >99% between 450 and 700 nm were mounted inside the cell and adjusted for 60 passes, giving a total path length of 18 m. Absorption measurements were made using a quartz halogen lamp light source and a grating spectrometer with a liquid nitrogen cooled diode array detector.³⁹ The absorption detection threshold for the 662-nm band of NO₃ was roughly 10¹⁰ molecule cm⁻³. The estimated accuracy of [NO₃] measurements was 20%. This was determined by using σ (662 nm) = 1.7 × 10⁻¹⁷ cm² for the NO₃ absorption cross section.⁴⁰

The laser system (Figure 1) consisted of a passively stabilized ring dye laser pumped by an argon ion laser. To attain lasing at 662 nm, DCM dye⁴¹ was used as described by Marason⁴² and

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Figure 3. NO₃ source using F + HNO₃ reaction.

Johnston et al.⁴³ The dye laser was operated with all wavelength-selective optics removed from the cavity except the birefringent filter, since single-mode operation was not required considering the absence of structure in NO₃ absorption as previously mentioned. Typically, 400-mW output at 662 nm was obtained when pumping with 6.5 W from the argon ion laser operating on all lines. Operating with greater pumping powers caused complications due to the onset of thermal lensing effects within the dye jet.⁴³ An interferometric lambdameter described by Hall and Lee⁴⁴ was constructed for the purpose of making wavelength calibration measurements. Using the lambdameter, the effective laser line width was estimated to be a few gigahertz on the basis of an observed coherence length of about 10 cm.

The flow tube shown in Figure 1 was constructed with 2.54cm-i.d. precision-bore Pyrex and had a total length of about 100 cm. The Pyrex moveable inlet of 0.8-cm o.d. and 0.5-cm i.d. permitted NO reactant addition over a range of 10-60 cm from the detection region. Thermal regulation of the reaction zone was achieved by circulating fluid from a constant temperature bath through a Pyrex outer jacket on the flow tube. Ethanol was used for temperatures below 303 K and dibutyl phthalate or silicone oil (20 cSt) for higher temperatures. Chromel-alumel thermocouples were used to monitor the fluid temperature. Temperature calibration for the reaction zone was achieved by inserting a thermocouple supported at the end of the moveable inlet and comparing such measurements with those made in the fluid. This discrepancy did not exceed 2 K and the measurements were easily adjusted. All active surfaces of the radical sources and the flow tube were periodically cleaned with a dilute HF/HNO3 solution to minimize wall losses of radical species.

Pressure measurements were made with two capacitance manometers having ranges of 1000 and 10 torr full scale. Calibration was done with a water manometer to an accuracy exceeding 1% of full scale at pressures less than 18 torr. The 10-torr gauge was used to directly measure the pressure at the center of the reaction zone. Flow rates of the stable gases were measured with thermal mass flow meters calibrated either with a wet test meter (3–150 STP cm³ s⁻¹, where STP = 273 K and 1 atm) or by determining the rate of pressure change in a calibrated volume (0.001–5 STP cm³ s⁻¹).

The manifold for gas handling and pressure measurement, including the valves, was constructed mainly from stainless steel. The stable gases were prepared and handled as follows. The He carrier gas was UHP certified to ≥99.999% purity and was further purified by directing its flow through a molecular sieve trap at liquid nitrogen temperature. An NO/He mixture was prepared by flowing NO (>99.0% purity) through a silica gel trap at 196 K and then diluting it with UHP He. NO_2 was prepared from purified NO by reaction with O2 at a pressure of about 800 torr followed by successive distillations in excess O_2 . The liquid NO_2 was stored in a stainless steel reservoir and during use was maintained at 273 K by an ice bath. O3 was synthesized by flowing O₂ through an electrical discharge and was trapped on silica gel at 163 K. Purification to about 95% (major impurity O₂) was achieved by pumping for several hours on the reservoir. The O₃ was stored at 196 K. N₂O₅ was prepared by the reaction of purified NO with excess O₃ and was stored at about 196 K.

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TABLE I: Summary of Rate Coefficient Data^a

no. of expts	source	NO mixture ^b	P, torr	\bar{v} range, 10 ³ cm s ⁻¹	[NO] range, 10 ¹² molecule cm ⁻³	k ^I range, s ⁻¹	$k^{\text{II}} \pm \sigma$, 10^{-11} cm^3 molecule s ⁻¹	<i>T</i> , K	Figure 5 symbol
40	N ₂ O ₅	1	1.10-2.20	1.4-1.6	0.71-6.1	30.0-256.2	3.97 ± 0.36	209	
18	F atom	3	1.06	1.4	0.80-5.7	29.1-211.9	3.76 ± 0.34	213	
20	N_2O_5	1	1.07	1.5-1.7	0.93-6.2	34.9-270.0	3.76 ± 0.34	230	
44	N_2O_5	1	1.10	1.7	0.90-7.0	30.3-234.2	3.21 ± 0.29	258	
18	F atom	1	0.99-2.06	2.0-2.3	1.9-6.0	53.6-177.5	2.97 ± 0.27	296	Δ
17	N ₂ O ₅	3	1.05	0.91-1.9	0.73-5.9	21.7-176.9	3.02 ± 0.27	297	\diamond
52	N_2O_5	1	1.07-2.60	1.8-2.4	2.0-6.8	57.8-195.2	2.90 ± 0.26	297	$\mathbf{\nabla}$
38	N ₂ O ₅	1	0.71-2.40	1.7-2.3	0.60-6.3	16.9-181.5	2.95 ± 0.27	298	×
24	N_2O_5	2	1.10-2.26	2.0-2.3	1.3-6.0	39.2-178.6	3.09 ± 0.28	299	0
15	N ₂ O ₅	3	1.05	1.3-2.2	0.56-5.9	16.7-168.2	2.87 ± 0.26	343	
25	F atom	3	1.05	0.96-2.6	0.73-5.3	20.7-159.7	2.97 ± 0.27	414	
22	N_2O_5	3	1.04	1.2-2.5	0.52-5.4	13.9-154.2	2.86 ± 0.26	410	

^aSets of experiments are identified according to the NO₃ source, NO mixture, and temperature. $\sigma = 95\%$ confidence limit of $\pm 9\%$ as discussed in text. ^bNO/He mixture identification (f = P(NO)/P(total)): f(1) = 0.0333, f(2) = 0.0314, f(3) = 0.0357.

 HNO_3 was synthesized by the reaction of KNO_3 with concentrated reagent H_2SO_4 in a molar ratio of about 1:3, respectively. The resulting HNO_3 vapor was then passed over anhydrous $CaSO_4$ and collected at 196 K as a white solid. The HNO_3 was used as a 4% mixture in helium and was stored in a light-tight reservoir at room temperature.

 NO_3 radicals were made in various continuous flow reactors connected directly to the flow tube. Three methods were used to produce NO_3 , although only the first two described below were used for the kinetics measurements. (1) Fluorine compounds mixed in helium (2% CF_4 or 5% F_2) were passed through a microwave discharge to produce fluorine atoms in the first stage of the reactor shown in Figure 3. These were then reacted with the 4% HNO₃ mixture described above:

$$F + HNO_3 \rightarrow HF + NO_3$$
 (2)

A Woods's horn and a right angle flow path served to minimize interference with LIF detection caused by stray light from the discharge. Typical flow rates into the discharge were 0.2–0.3 STP cm³ s⁻¹ for helium and 0.001 STP cm³ s⁻¹ for the fluorine compound mixtures. The flow rate for the HNO₃ mixture ranged from 0.05 to 1.0 STP cm³ s⁻¹. The latter was adjusted to give an excess HNO₃ concentration sufficient to extinguish a chemiluminescence signal observed with the PMT. This signal was present even in the absence of NO in the flow tube and may have been due to secondary reactions of the source reactants. (2) The second NO₃ source was the thermal decomposition of N₂O₅

$$N_2O_5 + He \rightarrow NO_2 + NO_3 + He$$
 (3)

in a glass reactor 10-cm long and 10-cm i.d. heated to 400 K. A Teflon stopcock at its exit served to control the pressure in the reactor which was typically 3–10 torr. Conditions were chosen so that the reaction went to completion, as calculated from the rate constant for (3) which was estimated to be $34-85 \text{ s}^{-1}$ for this range of pressures. This estimate was based on the rate coefficient for the reverse of reaction 3 and the equilibrium constant⁴⁰ and was further corroborated by the measurements of Viggiano et al.⁴⁵ (3) The third NO₃ source, which was used only for detection diagnostics, was the reaction of NO with excess O₃ in helium at elevated temperatures in a reaction vessel similar to that described for method 2. This produces NO₃ stoichiometrically:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{4}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{5}$$

Note that for the first two methods, the NO₃ concentration could be determined by quantitative conversion with excess NO and measuring the amount of NO₂ formed. Such measurements were made by observing LIF at $\lambda > 540$ nm from excitation of NO₂ by the argon ion laser with multiline optics. The stoichiometry of this titration was verified by the measured absence of NO₃ fluorescence under these conditions. Experiments were also done using the diode array spectrometer and the white cell mentioned previously to measure $[NO_2]$ and $[NO_3]$ simultaneously by absorption. These measurements permitted the verification of the stoichiometry to within an estimated error of 15%. Although the NO₂ detection sensitivity was comparable to that for NO₃ in ~1 torr of He, the use of direct optical absorption measurements of NO₃ proved to be more accurate for calibration purposes.

Several test measurements were made to verify the validity of the LIF detection method. A Stern-Volmer plot of inverse LIF fluorescence intensity, 1/I, vs. total pressure was linear within experimental error over the pressure range of 1.1-10 torr of helium, indicating that the collisional quenching mechanism was empirically simple. Thus the fluorescence signals were easily calibrated with respect to pressure differences between different decay measurements. A plot of fluorescence signal vs. laser power was linear with zero intercept over the range of 30-400 mW, showing that saturation effects were not apparent. The absence of saturation was essential since all NO3 fluorescence signals were normalized to the laser power at the fluorescence cell during the kinetics measurements. The linearity of the fluorescence signal vs. [NO₃] was checked by verifying the simultaneous proportionality of the NO₃ absorption measurements with the fluorescence measurements. The above tests were done with both the $F + HNO_3$ reactor and the N₂O₅ thermolysis sources of NO₃.

Ranges for total pressure, flow velocity (\bar{v}), and [NO] are indicated in Table I. The [NO₃] measurement range was $3 \times 10^{8}-5 \times 10^{10}$ molecule cm⁻³. The NO₃ wall loss rate was determined from [NO₃] decays measured with the NO₃ source connected to the moveable inlet. This rate was less than 1 s⁻¹ over the temperature range of 207-415 K. This surface loss is also revealed by the positive slope of the [NO] = 0 decay plot in Figure 4. Here NO₃ was removed by the injector surface. A small correction was made for this effect.

The experimental conditions were chosen in such a way that the basic premises and approximations for the flow tube method were valid.³² An estimated expression for the diffusion coefficient of NO₃ in a helium buffer was used:

$$D = 3.1 \times 10^2 \left(\frac{T}{273 \text{ K}}\right)^{3/2} \left(\frac{1 \text{ torr}}{P}\right) \text{ cm}^2 \text{ s}^{-1}$$

This was derived by semiempirical methods using a hard-sphere approximation and the measured diffusion coefficient of CO_2 in helium.⁴⁶ From this it was possible to calculate corrections for the effect of axial concentration gradients on the transport velocity of NO₃ along the flow tube.³² This axial diffusion correction generally did not exceed +2% of the measured k^1 and was applied to all the data. An estimate of the effects of radial concentration gradients was also made and found to be small. This error would be largest for decay measurements made at the lowest temperatures, highest total pressures, and greatest [NO]. The effect would appear as curvature in the k^1 vs. [NO] plots and as systematic

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Figure 4. Typical decay plots. The experimental conditions for the data shown are T = 297 K, flow velocity $\bar{v} = 1900$ cm s⁻¹, and [He] = 3.39 $\times 10^{16}$ molecule cm⁻³. NO concentrations in molecule cm⁻³ are [NO] = 0 for \times , [NO] = 2.58 $\times 10^{12}$ for Δ , [NO] = 4.09 $\times 10^{12}$ for O, and [NO] = 5.92 $\times 10^{12}$ for \Box . Extrapolation of all four plots gives an excellent intersection.

discrepancies between data points taken at comparable temperatures and k^{I} but different total pressures. No evidence for such discrepancies was observed. The small magnitude of corrections for axial diffusion and the negligible NO₃ wall loss rates as discussed above also served to verify the reliability of the flow tube measurements.

Results

The NO + NO₃ kinetic measurements are summarized in Table I. Sets of data obtained with different NO₃ sources and different NO mixtures are listed separately. Also listed for each data set are the ranges of several important parameters: total pressure, flow velocity, [NO], and the first-order rate constant k^{I} . Some typical NO₃ decay plots are shown in Figure 4. Figure 5 shows a plot of k^{I} vs. [NO]. The rate coefficients for the five independent sets of room temperature data agree within 6%.

Figure 6 is a semilog plot of the bimolecular rate constant k^{II} vs. T^{-1} for the data in Table I. Note that there is a statistically significant curvature. Two Arrhenius expressions were determined to represent the behavior of the k^{II} data for different temperature regions. These are given below in units of cm³ molecule⁻¹ s⁻¹ with 95% confidence limits:

$$k^{11}(T) =$$

(1.55 ± 0.23) × 10⁻¹¹ exp[(195 ± 39)/T] T ≤ 300 K
= (2.95 ± 0.16) × 10⁻¹¹ T > 300 K

The error analysis was carried out as follows. For a 95% confidence limit an estimate for the error of the results of each decay plot (or each k^{II} determination for a particular T and [NO]) is 9%, using uncertainties for the gas flow rates (±3%), temperature (±1%), pressure (±1%), flow tube radius (±1%), and the slope of the decay plots (±4%). The formalism of the error analysis is given by Cvetanovič et al.⁴⁷ In practice a particular point for k^{II} in Figure 6 was obtained as the slope of a two-parameter linear least-squares fit to a set of data (k^{I} vs. [NO]) at a given temperature. The uncertainty in the slope was typically less than ±2% (95% confidence limit). However, this does not



Figure 5. Plot of k^1 vs. [NO] for data at 296-299 K. The symbols O, \times , and \diamond correspond to results from the jacketed flow tube of Figure 1 and the N₂O₅ thermal decomposition for NO₃ and three different NO mixtures. The symbols ∇ and Δ correspond to data from the same NO mixture and a nonjacketed flow tube but from the N₂O₅ and F + HNO₃ sources, respectively. The slope of the linear fit to all of the data gives a rate coefficient of $k^{II} = (2.90 \pm 0.05) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The uncertainty is derived from the fit for one standard deviation and does not include an estimate for systematic errors. The data are described further in Table I with the symbols indicated in the last column.



Figure 6. Arrhenius plot for k^{II} . The solid lines are fits to our data (\diamond) above and below room temperature as discussed in the text. The error bars correspond to $\pm 9\%$, and only one is shown for data points that are clustered. The (×) are data of Sander (ref 49). The error bar shown corresponds to $\pm 20\%$, which applies to all of his data.

reveal systematic errors which might affect all the data points of the set in the same way. For this reason the minimum error estimate of $\pm 9\%$ for k^{II} was used regardless of the number of k^{I} data points available for determining k^{II} . The statistical errors shown in the above Arrhenius parameters were determined by

TABLE II: Summary of Results for Reaction 1^a

$A, 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹	E_{a}/R , K	$k(T), 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹	<i>T</i> , K	method	ref	
 1.55 ± 0.23	-195 ± 39		209-299	FT, LIF	this work	
2.95 ± 0.16	0		296-414			
		2.98 ± 0.27	298			
		3.24 ± 0.32	298	FT, LIF	Torabi ⁴⁸	
		2.93 ± 0.09	298	LP, A		
1.59 ± 0.10	-122 ± 17		224-328	FP, A	Sander ⁴⁹	
		2.39 ± 0.48	298			
		2.0 ± 1.0	292-298	FP, A, CRS	Croce de Cobos et al. ³⁰	
		1.9 ± 0.4	297	CRS, A	Graham and Johnston ²⁴	
		1.3 ± 0.7	1000-1100	ST, A	Glänzer and Troe ²⁹	

^a FP = flash photolysis, FT = flow tube, ST = shock tube, CRS = complex reaction system, LP = laser photolysis, A = absorption.

nonlinear least-squares fitting. The minimum error for any calculated value of k^{II} should be taken as $\pm 9\%$. This adjustment has been made for the error values of the recommended results given in the abstract although strictly speaking the $\pm 9\%$ error should be applied after calculating k^{II} for a specific T.

Discussion

Previous and concurrent results for the rate coefficient of reaction 1 are listed in Table II. The room temperature value given by Graham and Johnston²⁴ was derived from a study of the kinetics of a complex reaction system involving the N_2O_5 catalyzed decomposition of O_3 . They used their measured value of the equilibrium constant of the reaction

$$N_2O_5 \rightleftharpoons NO_3 + NO_2$$
 $K_{eq} = 3.8 \times 10^{10}$ molecule cm⁻³
(6)

together with other results obtained from the literature. The high-temperature value of Glänzer and Troe²⁹ was obtained by the analysis of HNO₃ thermal decomposition in a shock tube. Their rate constant corresponded to the best fit of their model to the observed NO₂ and NO₃ profiles. Croce de Cobos et al.³⁰ derived their value from the analysis of secondary reactions in their high-pressure (up to 200 atm) flash photolysis study of reaction (8) below. Torabi⁴⁸ measured the room temperature rate constant directly using both a flow system and a laser photolysis system. He observed no system dependence and no pressure dependence in the pressure range of 1-500 torr. Sander et al.49 used flash photolysis methods to obtain their rate constant expression. Curvature in their Arrhenius plot was not apparent, possibly as a consequence of their restricted range of temperatures. They observed no conclusive evidence for pressure dependence of reaction 1 in the range of 20-700 torr of helium.

The analysis of our results was considerably simplified by the absence of significant secondary reactions. The two most notable of these, with rate coefficients given in units of cm^3 molecule⁻¹ s⁻¹, are

$$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2 \tag{7}$$

$$k^{II}(T) = (8.5 \pm 2.8) \times 10^{-13} \exp[-(2450 \pm 100)/T]$$

and

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$
 (8)
 $k^{II}\{209 \text{ K}, P(\text{He})=3 \text{ torr}\} = 2.8 \times 10^{-13}$

Reaction 7 (measured by Graham and Johnston²⁴) would become significant only at very large NO₃ concentrations, e.g., when [NO₃] $\geq 5 \times 10^{14}$ molecule cm⁻³ for the worst case of T = 414 K and an initial [NO] of 6×10^{11} molecule cm⁻³. The effects of the breakdown of pseudo-first-order kinetics would appear well before such NO₃ concentrations could be attained. Reaction 8,⁴⁰ for which the worst case rate coefficient is given, would contribute



Figure 7. Assumed transition state for reaction 1.

significantly only at much higher helium concentrations. Thus it is clear that the radical concentration in our experiment was far too low for either reaction 7 or 8 to contribute a significant error.

An attempt was made to apply elementary transition-state theory to explain the temperature dependence of k^{II} . Partition functions were estimated for a bent transition state with two free internal rotations, as shown in Figure 7. Molecular constants from the literature were used to calculate the partition functions for NO (Huber and Herzberg⁵⁰) and NO₃ (Ishiwata et al.⁵¹). The activation energy was taken as zero, typical for many radicalradical reactions. A temperature dependence for the rate coefficient of T^n with n < -0.5 could be obtained by choosing a tight transition state with minimal thermal excitation of the rocking modes about the bonds being broken and formed. This compares with a value of $n \approx -0.8$ obtained from a T^n fit to our data for T < 300 K. However, this model gave an estimated rate coefficient which was too small by more than an order of magnitude. Choosing a looser transition state with very low frequency rocking modes gave the proper magnitude for the rate coefficient but also gave the wrong temperature dependence, i.e., n > 0. This situation is unavoidable since increasing the effective density of energy levels available to the transition state as required to increase the rate coefficient also increases the power of the temperature dependence by virtue of the partition function. In any case these simple models do not account for the observed curvature of the Arrhenius plot. The curvature might possibly be explained by the contribution of another reaction channel with a positive activation energy which would become important at higher temperatures. However, the Glänzer and Troe data²⁹ do not indicate that $k > 3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 1100 K. A more complex transition-state scheme such as that proposed by Mozurkewich and Benson⁵² is currently being explored.

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