species, formate on the support, and adsorbed O on Rh; (2) the removal of adsorbed O by H_2 and H to form $H_2O(g)$ and OH on the support; (3) dissociation of the C-O bond in the Rh carbonyl hydride, to form active C on Rh; and (4) reaction of the active surface C on Rh with H_2 and H(a) to form $CH_4(g)$. This proposed mechanistic scheme is very similar to one suggested earlier by Solymosi and co-workers.²² Its most novel feature is the proposed carbonyl hydride intermediate.

The reason for CO_2 hydrogenation proceeding at an apparent faster rate than does CO hydrogenation, even though the mechanisms are thought to be similar, is that the reactions are negative order in CO; there is a lower steady-state concentration of CO for the CO_2 methanation process.¹ We agree with Goodman and co-workers that, for CO_2 and CO methanation, there must be a delicate balance of the C(a) formation step and the C(a) surface hydrogenation step,¹ such that either the dissociation of the carbonyl hydride or the hydrogenation of active C may be rate limiting, dependent upon reaction conditions. As for which step was rate determining for our catalyst films, we can only propose that, for the impurity boron work, the rate-determining step was hydrogenation of active C (see last section).

Conclusions

The following conclusions can be made from this work:

Methane was the only hydrocarbon reaction product observed in these studies.

There is a support effect for CO_2 hydrogenation over supported Rh catalyst films. The turnover frequencies at a given temperature

The activation energy for hydrogenation of CO_2 is higher for Rh/TiO_2 than for Rh/Al_2O_3 for sample films containing low weight percent Rh.

A formate species is formed upon heating for catalyst films containing low Rh loading on Al_2O_3 indicating the possibility of location on the support well removed from the Rh-support interface. The formate species was not observed for catalyst films containing high Rh loading or on blank supports.

A Rh-carbonyl hydride species is formed during CO_2 hydrogenation which is a key observable intermediate in catalytic methanation. This intermediate has been observed for CO hydrogenation over supported Rh films also.²⁶ The carbonyl hydride can be formed as a result of hydrogen migration from the support in the absence of gas-phase H₂.

The presence of H_2 , H(a), and impurity boron all enhance the dissociation of CO_2 over supported Rh. However, impurity boron poisons the methanation reaction.

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Registry No. CO₂, 124-38-9; CH₄, 74-82-8; Rh, 7440-16-6; H₂, 1333-74-0.

Kinetics of the Reaction $NO_2 + NO_3 + M$ at Low Pressures and 298 K

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A discharge flow-long path laser absorption apparatus has been utilized to measure absolute rate constants for the recombination reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ at 298 K over the pressure ranges of 0.5-6.0 torr of N_2 and 1.0-8.0 torr of He. The title reaction is found to be in the falloff regime between third- and second-order kinetics over this pressure range. Falloff parameters were obtained by fitting the kinetic data to the falloff equation of Troe and co-workers. A fitted falloff expression of our data in conjunction with recently published rate coefficients for N_2O_5 decomposition was employed to calculate K_{eq} (298) and $\Delta H_f^{\circ}(298)$ for NO₃.

Introduction

The oxides of nitrogen have been recognized as major constituents of both the stratosphere and the troposphere. In these parts of the atmosphere they engage in various reactions that control the concentrations of important species such as O_3 , OH, and HO₂. Since NO₃ is one of these nitrogen species, a thorough understanding of its chemistry is of importance. NO₃ is produced mainly via the reaction of O₃ with NO₂ and is photochemically destroyed during sunlight hours. At night, however, it reacts with NO₂ to produce N₂O₅, a temporary reservoir. In the troposphere, the ambient temperature can be high enough for the thermal decomposition of N₂O₅ to be competitive with this formation such that an equilibrium is set up.

$$NO_3 + NO_2 + M \xrightarrow[k_{-1}]{k_1} N_2O_5 + M$$
(1)

To evaluate the concentration of N_2O_5 that is produced and the rate at which it is produced, the rate coefficient k_1 for reaction 1 is needed. However, until now it has been calculated from the thermochemical data in conjunction with the rate coefficient for

 N_2O_5 decomposition, k_{-1} . k_{-1} has been measured by Mills and Johnston, ^{la} Johnston and Perrine, ^{lb} Johnston, ^{lc} Wilson and Johnston, ^{ld} Hisatsune, ^{le} and Schott and Davidson^{lf} at various temperatures and pressures. The most recent measurements were those of Viggiano et al.^{2a} and Connell and Johnston.^{2b}

In addition to the above-mentioned need for atmospheric chemistry, reaction 1, forward and reverse, and has been considered for a long time as an example of classic association reactions. All the species involved in this reaction are well identified. Both forward and reverse reactions are pressure and temperature dependent in regimes that are easily accessible in the laboratory. Therefore, a complete set of rate data on this system will provide a proving ground for association reaction theories.

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^{(1) (}a) Mills, R. L.; Johnston, H. S. J. Am. Chem. Soc. 1951, 73, 938. (b) Johnston, H. S.; Perrine, R. L. J. Am. Chem. Soc. 1951, 73, 4782. (c) Johnston, H. S. J. Am. Chem. Soc. 1953, 75, 1567. (d) Wilson, D. J.; Johnston, H. S. J. Am. Chem. Soc. 1953, 75, 5763. (e) Hisatsune, I. C.; Crawford, B.; Ogg, R. A. J. Am. Chem. Soc. 1957, 79, 4648. (f) Schott, G.; Davidson, N. J. Am. Chem. Soc. 1958, 80, 1841.

^{(2) (}a) Viggiano, A. A.; Davidson, J. J.; Fehsenfeld, F. C.; Ferguson, E. F. J. Chem. Phys. **1981**, 74, 6113. (b) Connell, P.; Johnston, H. S. Geophys. Res. Lett. **1979**, 6, 553.



Figure 1. Schematic diagram of discharge flow-long path absorption apparatus

Since the initiation of this study, two other groups have measured k_1 using the pulsed photolysis absorption technique. In the first of these studies, Kircher et al.³ measured k_1 in the pressure regime of 20–700 torr between 236 and 358 K. The study by Croce de Cobos et al.⁴ has been aimed at extracting the high-pressure limiting rate coefficient by measuring k_1 between 2 and 200 atm at 298 K.

In the present study a discharge flow-long path laser absorption apparatus has been employed to directly determine the absoute rate constants for reaction 1 at 298 K over the pressure range of 0.5-8 torr of He and N₂. In addition, semiempirical calculations such as those described by Malko and Troe⁵ have been carried out for estimating the rate constant for reaction 1 as a function of pressure in the falloff regime.

Experimental Section

The experimental apparatus used in this investigation is shown schematically in Figure 1. The discharge flow-long path absorption apparatus consisted of a conventional 2.5-cm-i.d. discharge flow tube connected to a 4.8 cm by 3.5 cm absorption cell.

A characterization of the NO₃ production method used in this study has been discussed in detail previously.⁶ Briefly, a constant source of NO₃ radicals was produced by passing a 1% mixture of F_2 in He through a microwave discharge to produce F atoms that subsequently reacted with an excess of HNO₃.

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

HNO₃ was introduced into the flow tube 5 cm upstream of the microwave discharge inlet port by passing He through a bubbler containing several milliliters of the pure acid. The HNO₃ concentration was at least 10 times larger than that of F atoms in all experiments. Excess HNO₃ prevents the secondary reaction $F + NO_3 \rightarrow FO + NO_2$ from consuming NO₃. Microwave power to the discharge tube was always kept below 5 W to minimize the production of O(³P) atoms. The presence of O(³P) atoms in the flow system results in a background source of NO₂ due to the reaction of O(³P) atoms with NO₃.

$$O(^{3}P) + NO_{3} \rightarrow NO_{2} + O_{2}$$
(3)

However, the amount of NO_2 produced through reaction 3 was negligible compared to the concentration of NO_2 added during these studies.⁶ A minimum time of 27 ms (i.e., a minimum distance of 40 cm) was provided to ensure the reactions 2 and 3 went to completion before the introduction of NO_2 .

NO₃ radical concentrations were monitored as a function of injector displacement along the flow tube by measuring the absorption at 662 nm. The NO₃ absorption cell was equipped with 1/2-in.-thick antireflection-coated windows and was positioned near the focal point of a modified "white cell" that consisted of three concave dielectric coated mirrors as shown in Figure 1. The CW

662-nm probe beam was provided by a Spectra-Physics 380 C tunable ring dye laser that was pumped by the all-lines output of a 4-W Lexel argon ion laser. In order to generate a wavelength in the region where NO_3 has its strongest absorption feature, the ring dye laser was run using DCM dye. The wavelength of the probe beam was periodically checked by employing a calibrated 0.75-m Spex monochromator. The probe beam was multipassed through the absorption cell between 140 and 170 times providing path lengths between 670 and 820 cm. By utilizing this multipassing configuration, we could reduce the detection zone length in the direction of flow to ~ 1 cm, thus making it a very small fraction of the reaction length. Before entering the multipass cell, a small fraction of the incident beam was diverted and measured at photodiode A. Upon exiting, the transmitted probe beam was measured at photodiode B and the outputs from the two photodiodes were ratioed by using an analog divider having a response time of 10^{-5} s. The purpose of this ratioing technique was to normalize fluctuations in the dye laser power. The resulting output from the divider was sampled every 500 ns by a transient digitizer. Integration times were typically around 50 s for the measurements of each NO₃ concentration. By this method, $\sim 5 \times 10^{11}$ NO₃ cm⁻³ could be detected with S/N = 1 for 50-s integration.

The concentration of NO_3 in the absorption cell was determined by

$$[NO_3] = \ln \left(I_0 / I \right) / \sigma l \tag{I}$$

where I is the measured output of the analog divider in the presence of NO₃ and I_0 is the output of the divider in the absence of NO₃. I_0 was routinely checked before and after each run by adding excess NO slightly upstream of the absorption cell, thus titrating away all NO₃. The I_0 values determined by utilizing this method were shown to be identical with those determined by shutting off the microwave discharge. The absorption cross section of NO₃, σ , used at 662 nm to determine the NO₃ concentration was 1.78×10^{-17} cm²/molecule.⁶ The path length of the absorption cell, I, was calibrated by using known amounts of O₃ and the absorption cross section of NO₃, typically between 0.5×10^{13} and 1.0×10^{13} molecule/cm³, was checked at each injector position by shutting off the NO₂ flow and measuring the absorbance of NO₃.

In order to minimize vibrational perturbations in the experimental system, the entire apparatus was mounted on an optical table equipped with a vibration isolation system. The mechanical pump was connected to the experimetnal system through a set of bellows to decouple any vibrations between the pump and isolation table.

 NO_2 mixed with He or N_2 was passed from a 12-L bulb through a 70-cm absorption cell before entering the injector of the flow tube. The flow tube was designed such that the reaction-zone portion of the injector was never exposed to ambient air, thus minimizing possible contamination and the subsequent changes in wall loss rate of NO₃. The concentration of NO₂ was continuously monitored by using the 366-nm line from a Hg pen-ray lamp that was isolated by a band-pass filter and detected by a RCA 1P28 photomultiplier tube. The output current from the photomultiplier tube was measured by an electrometer. The incident light intensity from the Hg lamp was checked before and after each run by shutting off the NO₂ flow and flushing the absorption cell with diluent gas. The NO₂ concentrations were calculated by using an absorption cross section of 5.75×10^{-19} $cm^2/molecule$ at 365 nm.⁸ In no case did the amount of NO₂ tied up as N_2O_4 exceed 1.2%. By using this procedure, we could determine the concentration of NO_2 with an absolute accuracy of 5%.

The inside surface of the entire apparatus (i.e., inside of the flow tube and the outer wall of the injector) was coated with halocarbon wax in order to reduce the loss of NO_3 to the walls.

⁽³⁾ Kircher, K. C.; Margitan, J. J.; Sander, S. P. J. Phys. Chem. 1984, 88, 4370.

⁽⁴⁾ Croce de Cobos, A. E.; Hippler, H.; Troe, J. J. Phys. Chem. 1984, 88, 5083.

⁽⁵⁾ Malko, M. W.; Troe, J. Int. J. Chem. Kinet. 1982, 14, 399.

⁽⁶⁾ Ravishankara, A. R.; Wine, P. H. Chem. Phys. Lett. 1983, 101, 73.

⁽⁷⁾ Nicolet, M. Etude des reactions chimiques de lozone dans la Stratosphere.

⁽⁸⁾ Wine, P. H.; Kreutter, N. M.; Ravishankara, A. R. J. Phys. Chem. 1979, 83, 3191.



Figure 2. Pseudo-first-order decays in the presence of excess NO₂ at 298 K and a total pressure of 6 torr of N₂: (a) $[NO_2] = 11.4 \times 10^{13}$ molecule/cm³; (b) $[NO_2] = 17.3 \times 10^{13}$ molecule/cm³; (c) $[NO_2] = 2.19 \times$ 10^{14} molecule/cm³; (d) [NO₂] = 3.16×10^{14} molecule/cm³; (e) [NO₂] = 4.2×10^{14} molecule/cm³.

The wall loss rate has been estimated to be $<1 \text{ s}^{-1}$. The pressure inside the flow tube was measured (after the absorption cell) by a MKS capacitance manometer. The pressure gradient between the NO₃ absorption cell and the pressure port was always less than 5% of the measured pressure. The flow rates of all gases into the experimental system were measured by utilizing calibrated mass-flow transducers. HNO3 (Baker, reagent grade) was purified by distilling a mixture of HNO₃ and concentrated H₂SO₄ (Fischer, reagent grade) at 298 K and collecting HNO₃ at 77 K. NO₂ (99%, Matheson Gas Products) was mixed with UHP O_2 and cryopumped at 77 K, then degassed. F2 (1% in He, Spectra Gases), He (UHP, Matheson Gas Products), N₂ (UHP, Spectra Gases), and NO (99%, Matheson Gas Products) were all used without further purification.

Results and Discussion

I. Chemical Kinetics. All experiments were carried out under pseudo-first-order conditions with [NO₂]/[NO₃] always greater than 10, but typically 50. The pseudo-first-order loss of NO_3 is described by the following integrated rate equation

n
$$[NO_3]_0 / [NO_3]_t = (k_1 [NO_2])(d/v + C)$$
 (II)

where d is the injector displacement along the flow tube, v is the average flow velocity in the flow tube, and C is a constant representing the time delay between the injector position at zero displacement and the NO₃ detection zone. This "end effect" or time delay results from the injector position zero being upstream of the detection zone and the different cross-sectional areas of the flow tube and the absorption cell. The above equation assumes that all NO₃ decay processes are pseudo first order in NO₃ and the surface removal of NO₃ is independent of NO₂ added. k', the pseudo-first-order rate constant, is determined from the slopes of $\ln [[NO_3]_t/[NO_3]_0]$ vs. d. plots (examples of which are shown in Figure 2). The intercept of these plots gives C. The bimolecular rate constants, k_1 , are determined from the slopes of k' vs. $[NO_2]$ plots by using linear least-squares analyses. A typical k' vs. [NO₂] plot is shown in Figure 3. For the rate constant determinations at 0.5 torr of N_2 and 1 torr of He, the effect of NO_2 as a third body was significant and had to be accounted for. Under these conditions, the measured k' is given by

$$k' = k_1[M][NO_2] + k_4[NO_2][NO_2]$$
 (III)

which can be rearranged to give

$$k' / [NO_2] = k_1[M] + k_4[NO_2]$$
 (IV)



[NO2] (1014MOLECULE/CM3)

Figure 3. k' vs. [NO₂] plot for NO₂ + NO₃ + M(N₂) at 298 K: (a) 6 torr of N_2 ; (b) 5 torr of N_2 ; (c) 4 torr of N_2 ; (d) 3 torr of N_2 ; (e) 2 torr of N₂.

where k_1 and k_4 are the termolecular rate constants for M and NO₂ as third bodies, respectively. This analysis assumes that the loss rate of NO₃ to the walls is independent of $[NO_2]$ or is very small as shown by zero intercepts in plots of k' vs. [NO₂] at higher pressures. Thus, a plot of $k'/[NO_2]$ vs. $[NO_2]$ yields the bimolecular rate constant at the respective pressure of M as the intercept; in addition, the termolecular rate constant can be determined from the slope of this plot. The termolecular rate constant for M = NO₂ (k_4) was found to be (1.68 ± 0.63) × 10⁻²⁹ cm⁶ molecule⁻² s⁻¹ and (3.8 ± 2.4) × 10⁻²⁹ cm⁶ molecule⁻² s⁻¹ at 1 torr of He and 0.5 of torr N_2 , respectively. The errors were derived only from the error in the intercept of the fit to the above equation. A value of $(2.7^{+2.4}_{-1.5}) \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹ better reflects the value of k_{NO_2} and the associated errors in our measurements.

The linearity of the logarithmic decays of NO₃ as a function of injector position over typically 2 1/e times validated the existence of first-order kinetics in NO3 and showed that any interferences from competing reactions were negligible. As a further check for complications from possible secondary and/or radical-radical reactions, the initial [NO₃] was varied by more than a factor of 3 in several experiments and no significant changes were observed in the pseudo-first-order rate constant (k').

The rate constant for reaction 1 was studied at 298 K over the pressure range of 0.5-6 torr of N2 and 1-8 torr of He with average flow velocities ranging between 500 and 1500 cm/s. The results for this investigation are shown in Table I where the listed uncertainties represent two standard deviations. Since the [NO₂] was measured directly, these error limits depict the accuracy of the measurements. The present rate constant data clearly show that even at the low pressures of our study reaction 1 is in the falloff region between third- and second-order kinetics (as anticipated from previous kinetic data for the thermal unimolecular decomposition of N₂O₅).^{1a-f,2a,b,5}

II. Falloff Parameters. Troe and co-workers^{5,9-12} have developed a semiempirical method based on statistical theories for

- (10) Luther, K.; Troe, J. Symp. (Int.) Combust., [Proc.], 17, 1978 1979, 535
- (11) Troe, J. Ber. Bunsenges. Phys. Chem. 1983, 87, 161.

(12) Gilbert, R. G.; Luther, K.; Troe, J. Ber. Bunsenges. Phys. Chem. 1983, 87, 169. (13) Wine, P. H.; Thompson, R. J.; Ravishankara, A. R.; Semmes, D. H.; (13) Wine, P. H.; Thompson, R. J.; Ravishankara, A. R.; Semmes, D. H.;

Gump, C. A.; Torabi, A.; Nicovich, J. M. J. Phys. Chem. 1984, 88, 2095.

⁽⁹⁾ Troe, J. J. Phys. Chem. 1979, 83, 114.

TABLE I: Rate Constants for the Reaction

 $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

P8 K as a Function of Pressure and Diluent Gas				
pressure.	$k_1(\pm 2\sigma)$, $\times 10^{-14}$ cm ³ /molecule s			
torr	M = He	$M = N_2$		
0.5ª		3.6 (±2.0)		
1.0ª	2.58 (±0.70)	4.5 (±1.0)		
2.0	5.29 (±0.20)	8.7 (±1.4)		
2.0	5.27 (±0.14)	8.8 (±0.8)		
2.0	5.73 (±0.28)			
	5.43 (±0.38)	8.75 (±1.3)		
3.0	7.20 (±1.40)	12.5 (±2.4)		
4.0	8.78 (±0.98)	15.6 (±3.4)		
4.0	8.46 (±0.94)			
	8.62 (±1.36)			
5.0	9.50 (±1.60)	16.8 (±3.6)		
5.0	9.55 (±2.28)			
	9.53 (±1.86)			
6.0		20.3 (±2.8)		
6.0		19.7 (±1.8)		
		20.0 (±3.2)		
7.1	11.9 (±0.4)			
8.0	12.7 (±1.8)			

^a The value of $k_1[M]$ was obtained from the intercept of a plot of $k_1'/[NO_2]$ vs. $[NO_2]$ (eq IV). See text for details.

TABLE II: Falloff Parameters for $T = 298 \text{ K}^a$

М	F _c	$k_0, \mathrm{cm}^6/$ (molecule ² s)	$k_{\infty}, \mathrm{cm}^3/$ (molecule s)
He	0.55	9.5×10^{-31}	1.45×10^{-12}
N ₂	0.47	2.12×10^{-30}	1.85×10^{-12}
N ₂ ^b	0.40	2.32×10^{-30}	1.84×10^{-12}
No	0.60	1.97×10^{-30}	1.40×10^{-12}
N_2^{d}	$0.565-6.97 \times 10^{-3}T$	2.7×10^{-30}	1.6×10^{-12}

^a Derived by fitting eq I to the rate constant data of this study along with Kircher et al. for M = He and with Croce de Cobos et al. and Kircher et al. for $M = N_2$. ^bParameters fitted with rate constant data of this study and that of Croce de Cobos et al.⁴ ^cParameters fitted with rate constant data of this study and that of Kircher et al.³ ^dParameters obtained by Kircher et al.³ by fitting their data using F_c calculated by Malko and Troe.⁵

approximating bimolecular rate constants for association reactions in the falloff regime. The utilization of such a theory helps provide, within the framework of current understanding of association reactions, an analytical expression useful in experimental studies as well as in atmospheric modeling to predict the behavior of such reactions as a function of pressure and temperature. In order to obtain a reasonable comparison for our rate constant data with those of other investigations at higher pressures, we have utilized the following expression^{5,9-12} (an approximate form) to fit our data

$$k[\mathbf{M},T] = \frac{k_0[\mathbf{M}]}{1 + \left(\frac{k_0}{k_{\infty}}\right)[\mathbf{M}]} F_c \left\{ 1 + \left(\log\left(\frac{k_0}{k_{\infty}}\right)[\mathbf{M}]\right)^2 \right\}^{-1}$$
(V)

where $k_0(M,T)$ is the third-order low-pressure limiting rate constant, for bath gas M at temperature T, $k_{\infty}(T)$ is the second-order high-pressure limiting rate constant at temperature T, and $F_c(M,T)$ is the falloff curve broadening factor at the center of the curve (i.e., when $k_0[M] = k_{\infty}$). Definitions of the adjustable parameters given in eq V have been described in detail previously.^{5,9-14}

TABLE III: Summary of Recent Cited Values of K_{eq} for N₂O₅ + M \Rightarrow NO₃ + NO₂ + M at 298 K

investigation	$K_{\rm eq}(298), \times 10^{10} {\rm molecule/cm^3}$		
Patrick and Golden ¹⁶	5.42		
Graham and Johnston ¹⁷	4.28		
NASA ¹⁸	5.24		
Kircher et al. ³	3.07		
Tuazon et al. ¹⁹	2.91		
this work	2.50, ^a 4.85, ^b 3.64 ^c		

^{*a*} Using Viggiano et al.'s data for k_{-1} . ^{*b*} Using Connell and Johnston's data for k_{-1} . ^{*c*} Using a combination of Viggiano's and Connell and Johnston's for k_{-1} .

TABLE IV: Estimated Vibrational Frequencies for N2O5

mode	frequency, cm ⁻¹	mode	frequency, cm ⁻¹
NO ₂ antisym	1728	NO ₂ twist	55
stretch		NO_2 antisym stretch	1728
NO ₂ sym stretch	1338	NO ₂ sym stretch	1247
NO ₂ deformation	743	NO antisym stretch	860
NO ₂ rock	614	(N-O-N)	
(in-plane)		NO ₂ deformation	743
NO sym stretch (N-O-N)	353	NO_2 rock (in-plane) Two internal rotations	353
N-O-N deformation	85		
NO ₂ wag (out-of-plane)	614		

TABLE V: Calculated Values at 298 K for Z_{LJ} and $k_{0rec}^{sc a}$

A. Low Vibrational Frequencies of Adduct Treated as Hindered Rotors

М	$\frac{Z_{\rm LJ}, \times 10^{14}}{\rm cm^3/(molecule s)}$	$k_{0rec}^{sc}, \times 10^{29}$ cm ⁶ /(molecule s)	
He	2.97	3.19	
N_2	2.15	2.31	

B. Low Vibrational Frequencies of Adduct Treated as Free Rotors

М	$Z_{\rm LJ}$, $\times 10^{14}$ cm ³ /(molecule s)	$k_{0rec}^{sc}, \times 10^{29}$ cm ⁶ /(molecule s)	
He	2.97	6.00	
N_2	2.15	4.36	

^a Using $E_0 = 22.8$ kcal/mol and $K_{eq} = 2.50 \times 10^{10}$ molecule/cm³. Details of k_{0rec}^{sc} calculations are given elsewhere.^{13,14}

Using a nonlinear least-squares program, we have fit our data along with the higher pressure results of Kircher et al.³ and Croce de Cobos et al.⁴ for $M = N_2$, and along with the results of Kircher et al.³ for He to eq V. The values of k_0 , k_∞ , and F_c at 298 K were determined by floating all three parameters and iterating until the best fit of eq V to the input data was achieved. The results are indicated in Table II, and falloff curves calculated from these values are shown in Figure 4. The range of k_∞ values is a measure of the error is estimating k_∞ from such a set of data. For the purposes of atmospheric modeling, the falloff parameters calculated by using all available data to date (i.e., line 2 of Table II) are recommended.

In addition to calculating the falloff parameters for reaction 1 in the above fashion, k_0 and k_{∞} at 298 K were determined by nonlinear curve fitting of the input data to eq V by using calculated values for F_c similar to the calculations undertaken by Patrick and Golden.¹⁴

The thermal decomposition data of Viggiano et al.^{2a} were used in conjunction with the results of this study and those of Croce de Cobos et al.⁴ and Kircher et al.³ in determining the equilibrium constant, K_{eq} , at 298 K. A value $k_{-1}/k_1 = 2.5 \times 10^{10}$ molecule/cm³ at 298 K was obtained over the pressure range of 10–700 torr of N₂. (A comparison of the K_{eq} derived in this study with those determined or calculated in other studies is shown in Table III.) From the equilibrium constant, the enthalpy of reaction was determined to be $\Delta H_f^{\circ}(298) = 22.4$ kcal/mol. When this enthalpy result was combined with the tabulated values¹⁴ for the heats of

⁽¹⁴⁾ Patrick, R.; Golden, D. M. Int. J. Chem. Kinet. 1983, 15, 1189.

TABLE VI:	Summary of	Calculated	Falloff	Parameters at	298 K
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A. Derived in This Study					
М	ߢ	k_0 , $\times 10^{-30}$ cm ⁶ /(molecule s)	$k_{\infty}, \times 10^{-12}$ cm ³ /(molecule s)	F_{c}^{d} $(S_{k} = S_{eff})$	$\frac{F_{c}^{d}}{(S_{k} = S_{eff} + 1)}$
He	0.036	1.15	2.50	0.30 ^a	
N_2	0.114	2.64	1.98	0.35ª	
He	0.036	1.03	2.65		0.21ª
N_2	0.145	3.34	2.07		0.26 ^a
He	0.019	1.13	2.15		0.34 ^b
N_2	0.055	2.40	1.92		0.39
He	0.017	1.04	1.70	0.45 ^b	
N_2	0.049	2.15	1.52	0.52	
-		B. De	etermined in Other Studies		
М	β ^c	F _c	k_0 , $\times 10^{-30}$ cm ⁶ /(molecule s)	$k_{\infty}, \times 10^{-12}$ cm ³ /(molecule s)	ref
He		0.60	1.2 (±0.4)	1.40 (±0.14)	3
N2		0.60	$2.0(\pm 0.5)$	$1.40(\pm 0.14)$	3
N ₂		0.36	$3.0(\pm 1.5)$	2.2 (± 0.5)	4
N ₂	0.13	0.33	2.2	()	14
N ₂		0.60	2.2 (±0.1)	1.0 (±0.8)	2

^a Low adduct frequencies as hindered rotors. ^b Low adduct frequencies as free rotors. $^c\beta = k_0^{\text{wc}}/k_0^{\text{sc}}$. $^dS_k = S_{\text{eff}} + (E_a - E_0)/RT$ where E_{aw} is the Arrhenius activation energy for adduct decomposition in high-pressure limit and E_0 is the critical energy for adduct decomposition.



Figure 4. Falloff curves for M = He and N_2 at 298 K. For M = He, rate constant data of this study are plotted along with the higher pressure results of Kircher et al. For $M = N_2$ our data are plotted along with the higher pressure results of Kircher et al. and Croce de Cobos et al. The low-pressure limiting rate coefficients, $k_0[M]$, and high-pressure limiting rate coefficients, k_{∞} , given in Table II are shown as dashed lines.

formation for NO_2 and N_2O_5 , the heat of formation for NO_3 was determined to be $\Delta H_f^{\circ}(298) = 17.2 \text{ kcal/mol.}$ Both these values are in good agreement with those recently obtained by Kircher et al.⁸ Similarly if the value given by Connell and Johnston^{2a} (which includes all previous measurements from Johnston's group) for k_{-1} is used, then the calculated value of K_{eq} at 298 K = 4.85 \times 10¹⁰ molecule/cm³ and the $\Delta H_{\rm f}(298) = 16.83$ kcal/mol for NO₃. In these calculations, the entropy and heat capacities of NO₃ were calculated by assuming that the symmetry of NO₃ is D_{3h} , and the vibration frequencies for NO₃ are those guessed on the basis of known frequencies of HNO₃. For NO₂ and N_2O_5 , the entropy and heat capacity information were taken from JA-NAF tables.¹⁵ Because of the uncertainties in the value of K_{eq} , error bounds for ΔH_f values cannot be ascertained.

Heat capacities calculated according to formalisms provided in the JANAF thermochemical tables¹⁵ were used in determining $E^{\circ}_{0} = \Delta H_{0}^{\circ}$, the critical energy for dissociation of N₂O₅. The vibrational frequencies¹⁶ given in Table IV along with E°_{0} and

the calculated values for Z_{LJ} , k_0^{sc} and K_{eq} given in Table V (parts A and B) were used in theoretically calculating F_{c} . Details of this calculation have been presented in previous publications^{13,14} and, therefore, will not be repeated here. The low vibrational frequencies of the adduct were treated as free rotors in one case and as hindered rotors (with torsional frequency of $\sim 60 \text{ cm}^{-1}$) in the other. The values for k_0 and k_{∞} were then determined by fixing F_c to the calculated value and iterating until the best fit of eq V to the input data was obtained. The results are summarized in Table VI (part A), and a comparison of the falloff parameters for reaction 1 determined in other recent studies is given in Table VI (part B). It is necessary to point out that we have used a fixed value of F_c with no allowance given for its variation with pressure. Such treatments have been carried out by Troe and co-workers.^{11,12} However, within the uncertainties of K_{eq} and experimental errors in k_1 , it seems superfluous to use an elaborate analysis.

Since this work represents the only measurements of k_1 at pressures below 10 torr, a direct comparison with other rate constant data in this pressure regime is not possible. However, from the examination of Table VI and Figure 4, several observations can be made. There is reasonable unanimity in the falloff parameters determined for reaction 1 by the various investigations shown in Table VI. The divergence in the specific values appears acceptable given the range of adjustable parameters utilized in the calculations. The differences between the calculated F_c values (listed in Table VIA) and the fitted F_c values (listed in Table II) can be attributed largely to the uncertainty in the low vibrational frequencies for N_2O_5 . The F_c values seem to be quite low for a molecule (N_2O_5) having seven atoms. When the falloff parameters in Figure 4 are used, there is good agreement in the extrapolation of our kinetic data to the higher pressure results of Kircher et al.³ (20-700 torr of He, N_2). Thus, the pressure dependency of the rate constant for reaction 1 has now been determined over an extremely large pressure range with relatively good agreement between the three studies. In order to reasonably complete the kinetic data base on reaction 1, an examination of the temperature dependence of k_1 at pressures below 20 torr is clearly needed. This information would be extremely pertinent in further elucidating the stratospheric chemistry of NO₃.

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^{(15) &}quot;JANAF Thermochemical Tables", 2nd ed.; 1970.
(16) Hisatune, I. C.; Devlin, J. P.; Wada, J. Spectrochim. Acta. 1962, 18, 1641.

⁽¹⁷⁾ Graham, R. A.; Johnston, H. S. J. Phys. Chem. 1978, 82, 254.
(18) Demore, W. B.; Molina, M. J.; Watson, R. T.; Golden, D. M.;
Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. "JPL Publication 83-62"; Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 1983. (19) Tuazon, E. C.; Sanhueza, E.; Atkinson, R.; Carter, W. P. L.; Winer,

A. M. Pitts, Jr., J. N. J. Phys. Chem. 1984, 88, 3095.