Kinetics of the Reaction NO + $O_3 \rightarrow NO_2 + O_2$ from 212 to 422 K

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The reaction of nitric oxide with ozone has been studied over a wide range of temperature (212–422 K) by utilizing the discharge flow/mass spectrometric technique. The pseudo-first-order decay of ozone was measured in the presence of a large excess concentration of nitric oxide. The value of the bimolecular rate coefficient at 299 K and the Arrhenius expression determined are $k = (1.80 \pm 0.08) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 299 \text{ K})$ and $k = (3.16 \pm 0.90) \times 10^{-12} \exp(-(1556 \pm 80)/T)$ cm³ molecule⁻¹ s⁻¹. These results are compared with previous measurements.

Introduction

The reaction between nitric oxide and ozone

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

is important in both the natural and polluted atmosphere.^{1,2} Reaction 1 is partially responsible for regulating stratospheric ozone and the stratospheric [NO₂]/[NO] ratio. As such, its Arrhenius parameters are essential components of photochemical models of the atmosphere. At present, only the temperature dependence kinetics study of Birks, Shoemaker, Leck, and Hinton³ (203-361 K) is recommended by the NASA⁴ and CODATA⁵ evaluations for use in photochemical models. Recent experience (see NO + HO₂ \rightarrow NO₂ + OH, for example⁶) has shown that all kinetic and photochemical data should be independently confirmed in order to ensure the reliability of the results of photochemical model calculations.^{4,5}

There have been several other studies of reaction 1 in addition to that of Birks et al. at either room temperature⁷⁻¹⁴ or over relatively restricted temperature ranges.¹⁵⁻¹⁷ Huie, Herron, and Brown¹⁸ studied reaction 1 over nearly

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the same temperature interval as Birks et al. (224–364 K). Although their results are in good agreement with Birks et al., several of their plots of the pseudo-first-order rate constant, k' vs. nitric oxide concentration, [NO], display statistically significant but physically meaningless negative intercepts. To date, this study remains unpublished.

At the time of the completion of this work a new study of reaction 1 was reported by Lippmann, Jesser, and Schurath (283-443 K).¹⁹ This study was also in substantial agreement with the results of Birks et al. over their common temperature interval (283-361 K). However, they were unable to work at temperatures relevant to the middle and lower stratosphere due to the limitations of their experimental apparatus. Consequently, an additional study that encompasses the temperature ranges treated by the previous workers is necessary to ensure that the kinetics of reaction 1 are well characterized at temperatures relevant to the stratosphere and troposphere.^{4,5}

Experimental Section

The discharge flow/mass spectrometric system has been described previously and will be the subject of only a brief outline here.^{20,21} Å 2.5-cm diameter pyrex flow tube is interfaced to a modular multistage (three or four) vacuum chamber. Three differentially pumped stages were used in these experiments. The flow tube is sampled by a series of three pinholes leading to an electron-impact quadrupole mass spectrometer. The combination of collision-free sampling and low background pressure results in high sensitivity for both stable and labile species. The detection limit for O_3^+ (m/e 48) with an unmodulated beam and analogue signal processing is 3×10^9 molecule cm⁻³. Pressure is measured at the center of the flow tube reaction zone by using a calibrated capacitance manometer. Under the conditions of this study corrections for viscous pressure drop were unnecessary. The temperature was controlled by flowing methanol (212-273 K) or ethylene glycol (299-422 K) from a thermostatically controlled circulating

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TABLE I: Summary of	Experimental	Results
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<i>Т</i> , К	no. of experiments	$10^{-11}[O_3]_0, \text{ cm}^{-3}$	10 ⁻¹⁴ [NO] ₀ , cm ⁻³	k', \mathbf{s}^{-1}	$10^{15}k_1$, cm ³ molecule ⁻¹ s ⁻¹	
422	10	1.0-10.0	7.58-29.5	40.0-231	82.0 ± 4.8^{a}	
361	12	2.0 - 7.5	6.52 - 31.6	29.0-129	42.4 ± 3.0	
299	24	0.5-18.2	5.57-36.6	9.70-63.8	18.0 ± 0.8	
273	8	1.53 - 2.24	15.3-58.9	19.4-57.0	9.55 ± 0.36	
241	9	7.60	21.2 - 174	11.3-73.7	4.88 ± 0.24	
212	12	5.11	59.8-194	14.4 - 45.0	2.23 ± 0.06	

^a Error limits correspond to twice the standard deviation.

bath through a pyrex outer jacket that surrounds the entire reaction zone. The flow tube temperature is measured by two chromel-constantan thermocouples placed in the temperature control jacket at opposite ends of the reaction zone. The temperature remained constant within ± 0.1 K during each experimental run. Dilute O₃/He mixtures (<0.5%) were admitted to the flow tube upstream of the reaction zone by means of a circular loop injector. Nitric oxide entered the flow by means of a coaxial moveable injector. Flow rates were measured by calibrated linear mass flow meters.

Ozone was prepared by discharging a Tesla coil through oxygen (Linde UHP, 99.999%). The product was condensed at 77 K and pumped on to remove the O2 impurity. The O_3 was then mixed with helium and stored in 5-L pyrex bulbs. This method is safe only when small amounts of ozone are required (<0.02 g in this case). For larger amounts, the ozone should be trapped on silica gel at dry ice temperature. Initial ozone concentrations were determined by titrating the O_3 with excess NO and measuring the NO₂⁺ (m/e 46) signal. This was then compared to a previously calibrated NO_2^+ signal. The nitric oxide (Matheson CP Grade, >99.0%) was passed through an Ascarite trap to remove impurity NO_2 before admission to the flow tube. The helium carrier gas (Linde UHP, 99.999%) was passed through a zeolite trap at 77 K before entering the flow tube by way of a side arm.

Results

Table I summarizes the experimental conditions and the results obtained in this study. Total pressure was varied between 1.0 and 2.2 torr and flow velocity from 700 to 1500 cm s⁻¹. The results showed that k_1 is independent of both of these parameters. The decay of the O_3^+ (m/e 48) signal was monitored in the presence of a large excess concentration of NO. Typical decays ranged from a factor of 3 to a factor of 600. Pseudo-first-order conditions were maintained throughout ($[NO]_0/[O_3]_0 \ge 10^3$). Consequently, the decay rates could be analyzed by means of eq I, where k' is the pseudo-first-order rate coefficient and

n
$$([O_3]_0/[O_3]_t) = k't = k_1[NO]t$$
 (I)

 k_1 is the bimolecular rate coefficient for reaction 1. Figure 1 shows three typical decay plots $(\ln ([O_3]_0/[O_3]_t) \text{ vs. } t)$. The linearity of the plots verifies that the reaction is first order in $[O_3]$. The value of $k'(-d \ln [O_3]/dt)$ from each experimental run was obtained from the slope of the associated decay plot. The slopes were computed by means of a $1/[\ln ([O_3]_0/O_3]_t)]^2$ weighted linear least-squares fitting routine.²² Each value of k' was corrected for axial diffusion.²³ In general, the magnitudes of the corrections were less than 3%. The diffusion coefficients for O_3 in He were calculated, after allowing for the small difference in molecular weights, from the data reported by Marrero and

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Figure 1. The reaction NO + $O_3 + O_2$. Typical first-order decay plots for $[O_3]$ in the presence of various excess concentrations of NO at 422 K.

Mason for ⁴⁰Ar in He.²⁴ No corrections for radial diffusion were necessary.

The variation of the pseudo-first-order rate constant, k', with nitric oxide concentration, [NO], at each temperature is shown in Figure 2. All plots are linear with zero or negligible intercepts, indicating that the reaction is first order in [NO] and that the system is reasonably well behaved. The bimolecular rate constants (listed in Table I) were obtained from weighted linear least-squares fits to these plots. The error limits listed in Table I are twice the standard deviation. Overall experimental uncertainty is estimated at $\pm 15-20\%$. As an alternate method of analysis, the bimolecular rate constant at each temperature can be computed from the mean of the values of k'/[NO] taken from each experimental run. When analyzed in this way, the data reported here yield values of k_1 that differ from those reported in Table I by an average of 2.5% with a maximum difference at 6.7%. This excellent agreement is the result of there being zero or

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$$pD = \frac{1.521 \times 10^{-2} T^{1.552}}{[\ln (T/4.10 \times 10^7)]^2 \exp(1.71/T)} \text{ atm cm}^2 \text{ s}^{-1}$$

 $D(299 \text{ K}, 1.0 \text{ torr}) = 521 \text{ cm}^2 \text{ s}^{-1}.$

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Figure 2. The reaction NO + $O_3 \rightarrow NO_2 + O_2$. Variation of the pseudo-first-order rate constant, k', with [NO] at (**●**) 212 K; (**■**) 241 K; (**▲**) 273 K; (**△**) 299 K; (**□**) 261 K; (O) 422 K. Two data points at both 212 and 422 K are omitted for convenience.

TABLE II: Values for k_1 at Approximately 298 K

$10^{14}k_1, \text{ cm}^3$ molecule ⁻¹ s ⁻¹	<i>Т</i> , К	ref
1.73 ± 0.09	297	3
1.81 ± 0.13	29 8	7
1.70	290	8
1.41	298	9
2.10	298	10
1.73 ± 0.1	29 8	11
4.65	303	12
1.4	293	13
2.1	296	14
2.22 ± 0.12	301	18
2.14 ± 0.11	304	19
1.80 ± 0.08	299	this work

negligible intercepts in the k' vs. [NO] plots.

An arrhenius expression for reaction 1 from 212 to 422 K was obtained from a weighted linear least-squares fit of $\ln k_1$ vs. 1/T as shown in Figure 3. The plot is linear over the entire temperature range. The resulting Arrhenius expression is

$$k_1 = (3.16 \pm 0.90) >$$

 $10^{-12} \exp(-(1556 \pm 80)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (II)



Figure 3. The reaction NO + $O_3 \rightarrow NO_2 + O_2$. Arrhenius plot over the range 212–422 K. $k_1 = (3.16 \pm 0.90) \exp(-(1556 \pm 80)/T) \text{ cm}^3$ molecule⁻¹ s⁻¹.

The error limits correspond to twice the standard deviation. When the alternate (mean) values of k_1 mentioned in the previous paragraph are used, a second Arrhenius expression may be obtained that is identical with II within experimental error:

 $k_1 = (2.99 \pm 0.90) \times 10^{-12} \exp(-(1533 \pm 80)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (III)

Equation II is the preferred expression.

Discussion

Experimental room temperature values for k_1 are listed in Table II. Most of the results reported are in the $(1.7-2.1) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ range. The results reported by Ghormley et al.,⁹ Ford et al.,¹² and Cough and Thrush¹³ may be discounted as they vary significantly from the rest. The remaining data center around two values, $\sim 1.8 \times 10^{-14}$ and $\sim 2.1 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, with no clear way to differentiate between them.

Table III lists the results of this work and the other temperature dependence studies of reaction 1. As mentioned earlier, the Arrhenius parameters reported in ref 15–17 should be discarded due to their low values relative to the results of the more recent studies and the relatively restricted temperature ranges over which they were de-

TABLE III: Summary of Temperature Dependence Studies of the Reaction NO + $O_3 \rightarrow NO_2 + O_2$

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temp r	ange, K	A factor ^a	E/R^{b}	$10^{14}k_1(298 \text{ K})^{a,c}$	ref	
198-	-230	1.3×10^{-12}	1260 ± 150	1.96	16	
216	-322	$9.5 imes 10^{-13}$	1230 ± 75	1.53	15	
245	-345	$2.0 imes 10^{-12}$	1275 ± 110	2.77	17	
203-	-361	$(2.34 \pm 0.23) \times 10^{-12}$	1450 ± 50	1.80	3	
283	-433	$(4.3 \pm 0.6) \times 10^{-12}$	1598 ± 50	2.02	19	
224	-364	$(3.47 \pm 0.48) \times 10^{-12}$	1533 ± 64	2.02	$18^{d,e}$	
$212 \cdot$	-422	$(3.16 \pm 0.90) \times 10^{-12}$	1556 ± 80	1.71	this work ^{d}	

^a cm³ molecule⁻¹ s⁻¹. ^b K. ^c Computed from the Arrhenius expression. ^d Error limits correspond to twice the standard deviation. ^e Using the values of k_1 derived from the slopes of the k' vs. [NO] plots, $k_1 = (8.85 \pm 6.48) \times 10^{-12} \cdot (\exp(-(1799 \pm 194)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

termined. Overall, our results are in good agreement with Birks et al., Lippmann et al., and Huie et al. It should be pointed out that Huie et al. determined k_1 at each temperature by taking the mean of the ratios of k'/[NO]. This approach was taken as a result of the negative intercepts mentioned in the Introduction. If the values of k_1 had been obtained from the slopes of the k' vs. [NO] plots, a significantly different Arrhenius expression would have resulted:

$$k_1 = (8.85 \pm 6.48) \times 10^{-12} \exp(-(1799 \pm 194)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (IV)}$$

The ln k_1 vs. 1/T plot of Birks et al., from data obtained by using the discharge flow/mass spectrometric technique, displayed a slight curvature. The authors attributed this observation to the possibility that the two-product channels of reaction 1

$$NO + O_3 \rightarrow NO_2(^2A_1) + O_2 \tag{1a}$$

$$NO + O_3 \rightarrow NO_2^*(^2B_1) + O_2$$
 (1b)

have different activation energies. It was shown that the best fit to their data was obtained from a sum of two Arrhenius expressions corresponding to the two product channels. Utilizing a stopped-flow/chemiluminescent technique, Lippmann et al. were able to observe both the overall reaction and channel 1b. In agreement with this

work and Huie et al., they observed no curvature in their $\ln k_1$ vs. 1/T plot over the temperature range studied. It was shown that their data were fit equally well by single or biexponential Arrhenius expressions. The differences between values of k_1 calculated from the biexponential Arrhenius expression of Lippmann et al. and our data are comparable to our experimental uncertainty (15-20%). This observation plus the fact that the data of Lippmann et al. were fit equally well by an Arrhenius expression with a single exponential term leads to the conclusion that one should not expect to observe the nonlinearity reported by Birks et al. over the temperature range of this study.

For the purposes of tropospheric and stratospheric modeling, the temperature dependence of reaction 1 now seems to be well understood. Although the value of k_1 at 220 K (lower stratosphere) computed from our results is 16% lower than that calculated from the study of Birks et al., the resulting change in predicted stratospheric ozone depletion by chlorofluorocarbons is negligible.

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Theoretical Study of Protonated Isocyanic Acid

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Self-consistent field calculations have been performed for protonated HNCO. The most stable form is protonated at nitrogen, H_2NCO^+ , with a planar Y-shaped structure. The energy of protonation is calculated to be 187 kcal/mol. A metastable isomer protonated at oxygen, HNCOH⁺, is found to be about 18 kcal/mol less stable. but with a large barrier against unimolecular rearrangement to H_2NCO^+ . These results are in good accord with recent ion cyclotron resonance experiments. Implications for interstellar chemistry are discussed briefly.

Introduction

The structure and energies of protonated species have traditionally been of interest due to the pivotal role they play in aqueous acid-base chemistry. More recently attention has focused on these species because of the key role they appear to play in interstellar chemistry.¹ The present study was motivated by interest in this latter field. However, it appears that H_2NCO^+ has not been the subject of previous ab initio investigations, and results of this study should be of general use.

Three of the currently unidentified radioastronomical lines are found to be precise harmonics (within a few parts in 10^6) of a common fundamental frequency.² Such an occurrence is quite unlikely to be coincidental; the most plausible explanation being that these represent $J + 1 \rightarrow$ J transitions in a linear or nearly linear molecule. (For a slightly nonlinear species, for example, with only hydrogen atoms off axis, these lines would correspond to K= 0 transitions; levels with K > 0 lie at higher energy and

are not expected to be populated at low interstellar temperatures.) The absence of intervening harmonics suggests that these are successive transitions which unambiguously fixes the quantum numbering and determines the rotation constant as $B_0 = 10.691$ GHz. As discussed by Thaddeus et al.,² constraints of interstellar chemistry and estimates for rotation constants can be used to reduce the plausible candidates to two: protonated carbon dioxide, HOCO+ and cyanic acid, HOCN. The former has been discussed in detail previously.^{3,4} The latter is a metastable isomer of isocyanic acid, HNCO, which is abundant in interstellar space; extensive theoretical studies of HNCO and HOCN are available,^{5,6} which indicate that the latter is about 20

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