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Temperature and Pressure Dependence of the Rate Constant for the ClO + NO_2 Reaction

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The rate constant for the reaction ClO + NO_2 + M has been measured between 150 and 600 Torr and at 298 and 213 K using a turbulent flow technique with high-pressure chemical ionization mass spectrometry for the detection of reactants. This work represents the first experimental evaluation of this rate coefficient at temperatures below 248 K. The results are in excellent agreement with the values recommended by the NASA Panel for Data Evaluation (DeMore et al., JPL Publication 97-4, 1997).

Introduction

The association reaction of ClO with NO_2 (reaction 1) is of importance for the chemistry of the stratosphere; it affects the Cl-catalyzed destruction of ozone through the formation of $ClONO_2$.

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (1)$$

As a consequence of its relatively slow rate of photolysis, $ClONO_2$ acts as a temporary reservoir for both ClO and NO_2. In addition, reaction 1 ties together the ClO_x (Cl, ClO) and NO_x (NO, NO_2, NO_3) families, both of which are involved in the catalytic destruction of stratospheric ozone. Knowledge of the rate of reaction 1 is therefore of considerable significance in evaluating the effects of Cl-catalyzed destruction of ozone in the stratosphere.

The rate coefficient of reaction 1 (k_1) has been measured in several different ways;[1−14] in general, the results reported from these measurements are in good agreement with one another. However, these studies have not included measurements at temperatures below 248 K. Also, the identities of the products of reaction 1 were investigated at 298 K by Margitan[15] and by Cox et al.[16] and at 253−298 K by Burrows et al.[11] All three groups concluded that chlorine nitrate, $ClONO_2$, is the only product, in disagreement with earlier suggestions that another isomer such as ClOONO was also formed (see, e.g., ref 14). On the other hand, the formation of such an isomer would not have been observed in those experiments if the ClO−ONO bond strength is less than ~15 kcal/mol, because at temperatures above 253 K the isomer would rapidly decompose, regenerating the reactants ClO and NO_2.

To further investigate the kinetics of reaction 1 at temperatures representative of the stratosphere, we have utilized a turbulent-flow system, developed in our laboratory,[17] coupled to a chemical ionization mass spectrometer (CIMS). Using this system to monitor the pseudo-first-order decay rate of ClO in excess NO_2, k_1 is determined in nitrogen at pressures from 150 to 600 Torr and at temperatures of 298 and 213 K.

Experimental Section

A schematic diagram of the experimental apparatus is shown in Figure 1 and is similar to that used in our previous studies.[18,19] The jacketed flow tube is constructed from 22 mm i.d. Pyrex tubing, the walls of which are coated with Halocarbon wax (Halocarbon Products Inc.). A large flow of nitrogen (ranging from 50 to 130 STP L min^{-1}) is injected at the rear of the flow tube. The flow tube is pumped by a rotary pump (Edwards 2M80). Nitrogen dioxide is injected through a moveable injector consisting of a 6 mm o.d. Pyrex tube. A propeller-like Teflon piece (a "turbulizer") designed to enhance turbulent mixing is fixed to the end of the moveable injector. A portion of the gases in the flow tube is sampled into the ion−molecule region via a variable aperture. The ion−molecule region is constructed from 13 mm o.d. Pyrex tubing and is connected to a mechanical pump. The moveable ion source is placed orthogonal to the flow tube. A quadrupole mass spectrometer (ABB Extrel Merlin) is located at the end of the ion−molecule region. All gas flows are monitored with calibrated mass flow meters (Tylan). The pressures in the flow tube and the ion−molecule region are monitored using a 0−1000 Torr capacitance manometer (MKS Baratron).

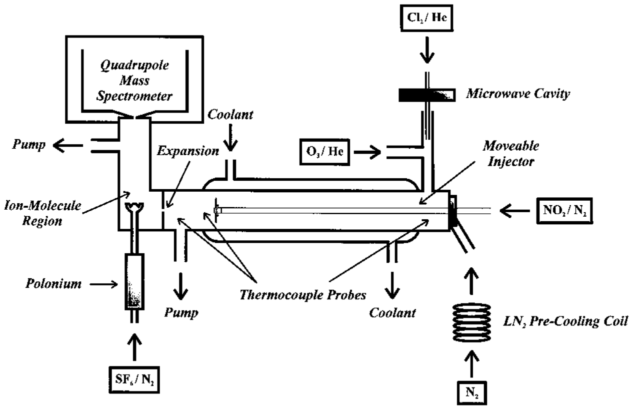

Figure 1. A schematic diagram of the apparatus used in this study.

The temperature of the flow tube is controlled to within 2 K by flowing a coolant (HCFC-123) at the desired temperature through the jacket on the exterior of the flow tube. The nitrogen carrier gas is precooled to the same temperature by passing it through a copper coil immersed in liquid nitrogen. The carrier gas temperature is maintained with heating tape regulated by an electronic controller (Omega CN76000) in conjunction with a type-T thermocouple. The temperature within the flow tube is monitored using type-T thermocouples located at the rear of the flow tube and immediately upstream of the variable aperture. The temperature profile along the flow tube is checked by placing a type-T thermocouple at the end of the moveable injector and moving it along the length of the flow tube.

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ClO is produced in the rear of the flow tube via the reaction

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \qquad (2)$$

Chlorine atoms are produced by combining a 2.0 STP L min^{-1} flow of He (99.9999%), which has passed through a molecular sieve trap held at 78 K, with a 0.3−3 STP mL min^{-1} flow of 1% Cl_2 (>99.9%) in He mixture, which then passed through a microwave discharge produced by a Beenakker cavity operating at 60 W. To produce ClO, the Cl atoms are injected into the flow tube via a sidearm inlet located at the rear of the flow tube and are mixed with an excess of ozone. O_3 is generated by passing O_2 (99.994%) through an OREC ozonizer, and the O_3 is stored in a silica gel trap immersed in a dry ice−ethanol bath. O_3 is introduced into the system by passing a 2−30 STP mL min^{-1} flow of helium through the trap. NO_2 is introduced into the flow tube via the moveable injector by mixing a flow of 1% NO_2 with a 1 STP L min^{-1} flow of nitrogen. In all experiments $[NO_2] \gg [ClO]$; the NO_2^- signal ($m/e = 46$) always remains constant, indicating that pseudo-first-order conditions are maintained. Blank runs (with no NO_2 flowing) are carried out to ensure that ClO^- signal (m/e 51) is not affected by movement of the injector.

NO_2, O_3, and ClO are chemically ionized using SF_6^- as the reagent ion. SF_6^- is generated by passing a 10 STP L min^{-1} flow of N_2 through a Po(210) Nuclecel ionizer (NRD Inc.). The generated reagent ion is then carried into the ion−molecule region through a moveable injector constructed from 6 mm o.d. stainless steel. A fan-shaped turbulizer is attached to the end of the moveable inlet to enhance mixing of the reagent ion with the sampled flow from the flow tube. All of the species observed in this study are ionized by SF_6^- via electron transfer, enabling all of the species to be detected by their parent ions.

Ions are detected with a quadrupole mass spectrometer in a three-stage differentially pumped vacuum chamber. Ion−molecule gases (neutrals and ions) are drawn into the front chamber through a 0.8 mm aperture which is held at a potential of −2 V. The ions are then focused by a stainless steel plate of 4 cm o.d. and 2 mm i.d. held at −20 V. The front vacuum chamber is evacuated by a mechanical pump (Varian SD-450) and held at approximately 2 Torr. The ions are further focused by a 4 cm o.d. and 0.6 mm i.d. stainless steel plate held at −30 V and passed into a second chamber, which contains the quadrupole mass filter (ABB Extrel, Merlin) and is pumped by a turbomolecular drag pump. The rear chamber, which holds the multiplier assembly, is pumped by a second turbomolecular pump. Both turbomolecular drag pumps (Balzers TMU 520) are backed by the same rotary pump. Under typical operating conditions, the ion−molecule region is at a pressure of ~30 Torr and the rear chamber is at a pressure of $\sim 2 \times 10^{-6}$ Torr.

Results and Discussion

Assessment of Detector Sensitivity. Dilute mixtures of known composition of NO_2 in nitrogen are injected into the flow tube via a calibrated flow meter with no other reactant gases present, and the NO_2^- signal is monitored. From a linear plot of $[NO_2]$ vs NO_2^- signal, we estimate that the sensitivity for NO_2 is 7×10^7 molecules cm^{-3} for a signal-to-noise ratio of one and a time constant of 20 ms. Also, the sensitivity was found to be independent of pressure and temperature. The NO_2 concentrations are corrected to take into account equilibrium concentrations of N_2O_4 in the gas mixtures used. Under the experimental conditions the lifetime of N_2O_4 formed by the equilibrium

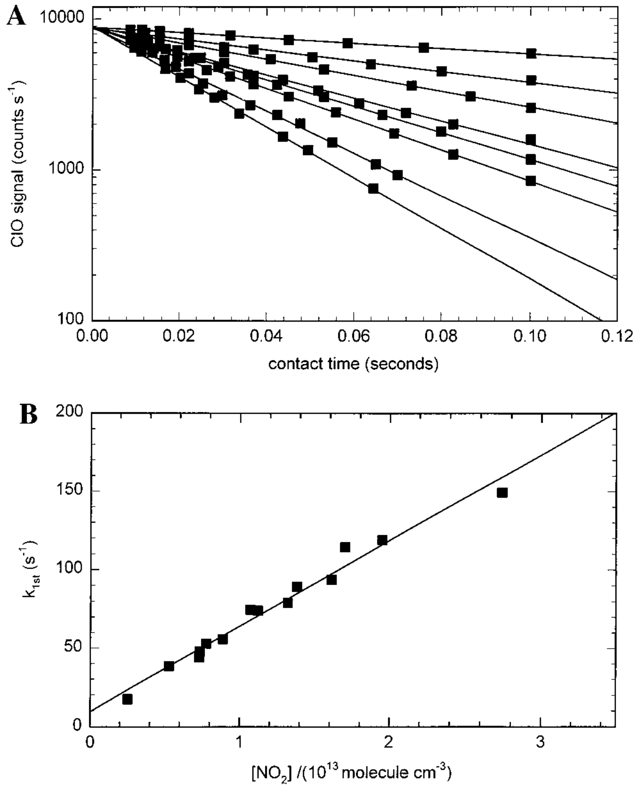

Figure 2. (A) Typical set of pseudo-first-order plots. (B) Typical plot of k_{1st} as a function of NO_2.

$$\mathrm{NO_2} + \mathrm{NO_2} \rightleftharpoons \mathrm{N_2O_4} \qquad (3)$$

is comparable to the time of mixing.[20] This assumption is corroborated by the fact that on the time scale of the experiment no change in NO_2^- signal is observed.

Calibration of the ClO^- signal is achieved by adding NO to the flow tube via the moveable injector at a constant contact time of 20 ms and by monitoring the resultant NO_2 formed by reaction with ClO

$$\mathrm{ClO} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{Cl} \qquad (4)$$

Sufficient NO is added to ensure complete removal of ClO, as shown by measuring a steady NO_2^- signal with increasing [NO]. The production of a Cl atom in reaction 4 requires that the titration of ClO be performed under complete conversion of O_3. The presence of excess O_3 would alter the stoichiometry of the ClO → NO_2 conversion by regeneration of ClO through the reaction of Cl with O_3. Cl atoms are therefore added incrementally to a constant flow of O_3 until O_3^- is no longer detected, indicating that the concentration of O_3 is close to zero. This procedure is repeated for several different O_3 concentrations, resulting in a linear plot of ClO^- signal vs [ClO]. We estimate that the sensitivity for ClO is 5×10^7 molecules cm^{-3} for a signal-to-noise ratio of one and a time constant of 20 ms and is independent of pressure and temperature.

Kinetics. The rate coefficient for reaction 1 is measured by monitoring ClO concentration profiles at $m/e = 51$ under pseudo-first-order conditions with $[ClO] = (7-20) \times 10^{10}$ molecules cm^{-3} and $[NO_2] = (2-60) \times 10^{12}$ molecules cm^{-3}. First-order decay rates (k_{1st}) are obtained both by a linear regression of the plots of ln(ClO^- signal) vs contact time (as shown in Figure 2A) and by a nonlinear fit of the plots of (ClO^- signal) vs contact time. Within experimental error, both methods yield the same values of k_{1st}. This process is repeated for at least 10 different values of $[NO_2]$ at each pressure studied.

TABLE 1: Summary of the Second-Order Rate Coefficients Obtained from This Study

temp (K)	press. (Torr)	k (cm^3 molecule^{-1} s^{-1})^a
298	150	$(7.66 \pm 0.66) \times 10^{-13}$
298	200	$(9.25 \pm 0.84) \times 10^{-13}$
298	248	$(1.02 \pm 0.07) \times 10^{-12}$
298	314	$(1.33 \pm 0.09) \times 10^{-12}$
298	364	$(1.49 \pm 0.10) \times 10^{-12}$
298	400	$(1.54 \pm 0.11) \times 10^{-12}$
298	415	$(1.55 \pm 0.13) \times 10^{-12}$
298	430	$(1.60 \pm 0.09) \times 10^{-12}$
298	503	$(1.67 \pm 0.18) \times 10^{-12}$
298	550	$(1.76 \pm 0.19) \times 10^{-12}$
298	600	$(2.05 \pm 0.10) \times 10^{-12}$
213	150	$(2.15 \pm 0.08) \times 10^{-12}$
213	200	$(3.00 \pm 0.35) \times 10^{-12}$
213	250	$(3.19 \pm 0.27) \times 10^{-12}$
213	300	$(3.80 \pm 0.29) \times 10^{-12}$
213	350	$(4.59 \pm 0.30) \times 10^{-12}$
213	400	$(4.96 \pm 0.38) \times 10^{-12}$
213	450	$(5.47 \pm 0.34) \times 10^{-12}$
213	500	$(5.90 \pm 0.59) \times 10^{-12}$
213	600	$(6.24 \pm 0.61) \times 10^{-12}$

^{a} The quoted errors are 2σ based on 95% confidence limits.

As shown in Figure 2B, the values k_{1st} are then plotted vs [NO$_2$], which is determined directly from the known concentration in the mixture flowing through the calibrated flow meter. These data points are fitted with a linear least-squares routine, the slope providing the bimolecular rate constant, k_1. Table 1 lists the effective bimolecular rate coefficients obtained in this study. This approach for determining bimolecular rate constants assumes that deviations from the plug flow approximation are negligible. Under the conditions in our turbulent flow tube, Seeley et al.[18] estimated that these deviations result in apparent rate constants that are ~3% below actual values assuming a reaction probability γ for ClO loss at the flow tube walls of 10^{-4} (and, at most, 8% below for γ values approaching unity). Hence, the flow corrections are neglected, as they are smaller than the sum of other likely errors in the measurements of gas flows, temperature, detector signal, pressure, and absolute NO$_2$ concentrations.

Figure 3A shows the pressure dependence of the effective bimolecular rate coefficient for reaction 1 at 298 K observed in this study. Also included in this figure are data from three previous[5,8,10] studies conducted at pressures that directly overlap those used in this work. The solid line is the pressure dependence as suggested by DeMore et al.,[14] which is of the form

$$k(\mathrm{M},T) = \left(\frac{k_0(T)[\mathrm{M}]}{1 + (k_0(T)[\mathrm{M}]/k_\infty(T))}\right)0.6^{\{1+[\log_{10}(k_0(T)[\mathrm{M}]/k_\infty(T))]^2\}^{-1}} \tag{5}$$

with

$$k_0(T) = k_0^{300}(T/300)^{-n}$$

and

$$k_\infty(T) = k_\infty^{300}(T/300)^{-m}$$

For the ClO + NO$_2$ reaction in air, the parameters recommended by DeMore et al. are $(1.8 \pm 0.3) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} for the low-pressure rate coefficient k_0^{300}, $(1.5 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for the high-pressure rate coefficient k_∞^{300}, and 3.4 ± 1.0 and 1.9 ± 1.9 for the temperature coefficients n and m, respectively. The dashed lines in Figure 3A represent the upper and lower limits in $k(\mathrm{M},T)$ as associated with the quoted errors in the values of k_0 and k_∞.

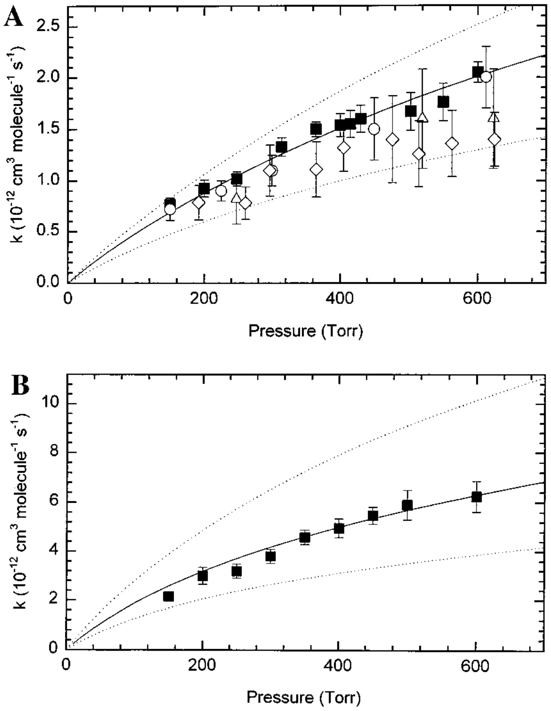

Figure 3. (A) Pressure dependence of the reaction of ClO + NO$_2$ at 298 K: (■) this work; (○) Cox and Lewis;[5] (△) Handwerk and Zellner;[10] (◇) Dasch et al.;[8] (—) recommended falloff curve from DeMore et al.;[14] (···) upper and lower values of the falloff curve based on errors in k_0 and k_∞ as suggested by DeMore et al.[14] (B) Pressure dependence of the reaction of ClO + NO$_2$ at 213 K: (■) this work; (—) recommended falloff curve from DeMore et al.;[14] (···) upper and lower values of the falloff curve based on errors in temperature dependence (n and m) as suggested by DeMore et al.[14]

Lee et al.[9] investigated the ClO + NO$_2$ reaction using both N$_2$ and O$_2$ as third bodies; we conclude from their study that within experimental error our results for N$_2$ should be applicable to air as well.

The pressure dependence observed in this study is in good agreement with the recommendation of DeMore et al.,[14] the work of Cox and Lewis,[5] and that of Handwerk and Zellner.[10] However, the work of Dasch et al.[8] is in fair agreement only up to 500 Torr; at higher pressures, their data show a deviation from the upward trend exhibited at lower pressures. Such a leveling off of k_1 at these pressures is inconsistent with the RRKM model of Smith and Golden.[21] We also carried out experiments at 213 K, and the pressure dependence of the bimolecular rate coefficient at this temperature is shown in Figure 3B. Once again the agreement with the values recommended by DeMore et al.[14] is good. In this figure the dashed lines represent the upper and lower values of $k(\mathrm{M},T)$ as associated with the quoted errors in the temperature-dependent coefficients m and n.

Considering the limited number of individual rate constant determinations conducted in this work (see Table 1), we do not list here rate parameters for eq 5 calculated from our measurements alone; within experimental error, these values are the same as those recommended by DeMore et al.[14]

The kinetics study of reaction 1 reported here suggests that no weakly bound isomer of chlorine nitrate is formed at significant rates at temperatures down to 213 K, since no unexpected increase in the rate of disappearance of ClO is observed at the lower temperatures.

Conclusions

Our data indicate that reaction 1 does have the pressure dependence and negative temperature dependence suggested by previous studies.[1−14] The results reported here represent an extension in the range of temperatures over which reaction 1 has been studied experimentally. In fact, our experiments appear to be the first ones conducted at a temperature below 248 K. Our results are in good agreement with previous higher temperature measurements extrapolated to 213 K. Hence, we believe that the rate coefficient of reaction 1 can be predicted reliably from the expression recommended by DeMore et al.[14] for temperatures and pressures representative of the stratosphere.

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