

KINETICS AND PRODUCT STUDIES OF THE BrO + ClO REACTION: IMPLICATIONS FOR ANTARCTIC CHEMISTRY

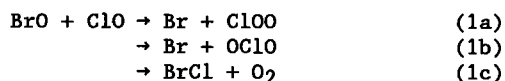
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Abstract. The reaction of ClO with BrO has been investigated by two independent techniques, discharge flow-mass spectrometry and flash photolysis-UV spectrometry, over the temperature range 220-400 K and the pressure range 1-760 torr. Rate constants have been determined for three product channels; a) Br + ClOO, b) Br + OClO, and c) BrCl + O₂. The rate constants for the overall reaction and each reaction branch were found to be inversely dependent on temperature and independent of pressure. The results for the temperature dependence of the overall rate constant from the discharge flow and flash photolysis studies are in excellent agreement, and collectively disagree substantially with the only previous temperature dependence study. Also, in contrast to previous studies, the channel forming BrCl is found to be significant ($\approx 8\%$). These kinetic measurements have an important impact on the modeling of Antarctic chemistry; for temperatures found in the Antarctic stratosphere the rate coefficients for the channels yielding ClOO and OClO are a factor of 2-3 larger than previously estimated. In addition, the BrCl channel, which has an impact on the nighttime partitioning of BrO_x and the diurnal variability of OClO, has been omitted from previous atmospheric models.

Introduction

The role of bromine-containing compounds in the depletion of stratospheric ozone has been recognized for several years [Watson, 1975; Wofsy et al., 1975; Yung et al., 1980]. Because bromine compounds are partitioned into their active forms (Br, BrO) to a much greater extent than the analogous chlorine-containing species, the efficiency of catalytic ozone destruction cycles involving bromine is much higher than those involving chlorine. At present, however, the overall impact of bromine chemistry on the stratosphere is difficult to assess because of uncertainties in the concentrations and identities of bromine-containing species. The recent observation of large decreases in springtime stratospheric ozone over Antarctica have renewed the interest in the role of bromine compounds. The reactions



have been invoked in several models [McElroy et al., 1986; Tung et al., 1986] to account for both

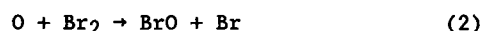
the recycling of ClO to Cl and the formation of OClO, which has been observed from the ground [Solomon et al., 1987].

Previous studies of reaction 1 have failed to elucidate fully the temperature and pressure dependences of the overall rate coefficient and the individual branching ratios. In this Letter, we present the results of two independent studies of reaction 1, using the techniques of discharge flow-mass spectrometry (DF/MS) and flash photolysis-ultraviolet absorption (FP/UV). The results of these studies are in substantial disagreement with the recent study of Hills et al. [1987, 1988] concerning both the temperature dependence of the overall reaction and the branching ratio for BrCl formation. More detailed accounts of this work will appear subsequently [Friedl and Sander, Sander and Friedl, submitted to J. Phys. Chem.].

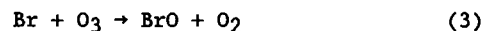
Experimental Section

Discharge Flow-Mass Spectrometry

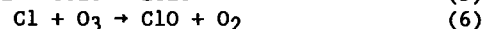
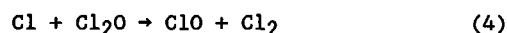
In the DF/MS study, a three-stage modulated molecular beam mass spectrometer using electron impact ionization was used in conjunction with a temperature-controlled (220-400 K) fast-flow reactor (flow velocity 1800 - 3000 cm s⁻¹). BrO and ClO radicals were produced in separate source regions using microwave discharges to produce the precursor Br, Cl and O atoms and were introduced interchangeably into the flow tube through a side-arm and a moveable injector. Pseudo first-order conditions were employed with ClO ((1-20) × 10¹² molecule cm⁻³) present in large excess over BrO ((1-3) × 10¹¹) molecule cm⁻³. BrO was produced using the reactions



and



ClO radicals were generated by reacting Cl₂O, OClO or O₃ with Cl, i.e.



Mass spectrometric calibrations for ClO, BrO, OClO and O₃ were obtained by titration with excess NO and measurement of the NO₂ produced. Other species (Br₂, Cl₂, BrCl, Cl₂O and O₂) were calibrated using absolute flow rate measurements. Detection limits for most species were in the range 10⁸ - 10⁹ molecule cm⁻³.

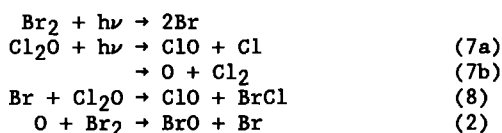
Flash Photolysis-Ultraviolet Absorption

In the flash photolysis study, a 1 m-long coaxial flash lamp/reaction cell which could be

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controlled in temperature over the range 215-400 K was used. The cell was coupled to an optical absorption system consisting of a xenon arc lamp or deuterium lamp probe beam, long-path (8 m) White-type optics and two spectrometers, one for the detection of ClO and Cl₂O at 277.5 nm, and the other for the detection of BrO at 338.5 nm and OC1O between 325 and 350 nm. The OC1O spectrometer used an optical multichannel analyzer (OMA) in conjunction with a fast shutter to obtain time-resolved spectra of the OC1O band system. Pseudo first-order conditions were employed with ClO ((3-60) × 10¹² molecule cm⁻³) present in large excess over BrO ((7-50) × 10¹¹ molecule cm⁻³). BrO and ClO radicals were produced by the photolysis (λ > 180 nm) of Br₂-Cl₂O mixtures:



Absolute concentrations were required for ClO and Cl₂O in the determination of the overall rate constant, k_1 , and for BrO and OC1O in the determination of the branching ratio for OC1O formation, k_{1b}/k_1 . The temperature dependence of the BrO cross section was determined in this study from titrations involving reactions 2 and 3. The temperature dependence of the ClO cross section over the entire A ← X band was measured by three independent methods using the O + OC1O reaction, OC1O photolysis and the Br + Cl₂O reaction. Cross sections for O₃, Cl₂O and OC1O were taken from the studies of Molina and Molina [1986], Lin [1976], and Wahner et al. [1987], respectively.

Results

Discharge Flow-Mass Spectrometry

The DF/MS system was used to measure the temperature dependences and branching ratios of reaction 1 over the temperature range 220-400 K at 1 torr total pressure of helium. Kinetic parameters were derived from about 100 experimental runs in which k_1' varied from 10 to 200 s⁻¹. The overall rate constant was determined using reaction 2 as the BrO source and reactions 4 and 5 as the ClO sources with atomic chlorine in excess. This approach eliminated potential complications due to the regeneration of BrO from the Br + O₃ and Br + OC1O reactions. BrO signals were followed over 3-4 decay lifetimes in most experiments. First-order kinetics were obeyed over the complete range of reaction conditions as indicated by the linearity of plots of ln[BrO] vs. time and k_1' vs. [ClO], where $k_1' = k_1[\text{ClO}]$. Plots of k_1' vs. [ClO] had negligible y-intercepts. The observed temperature dependence of k_1 is given by:

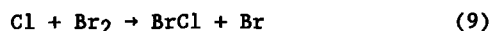
$$k_1 = (4.61 \pm 0.50) \times 10^{-12} \exp[(327 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors limits are ± 2σ. The quoted experimental errors include both the random component from the variation of k_1' with [ClO] and possible systematic errors from flow, pressure and temperature calibrations.

Extensive studies of the branching ratios of reactions 1a, 1b and 1c were carried out using several different chemical systems. These experiments are summarized as follows:

1) Determination of k_{1b} : The yield of OC1O was determined two ways. In the first method, absolute OC1O yields were measured relative to BrO removal under the same conditions as those described above for the measurement of k_1 . In the second method, BrO and ClO radicals were formed and rapidly recycled by the reactions of Br and Cl with a large excess of O₃. k_{1b} was determined directly from the rate of OC1O production from measurements of the BrO and ClO concentrations and a knowledge of the reaction time.

2) Determination of k_{1c} : The yield of BrCl was determined in the excess O₃ system in a manner analogous to the measurement of OC1O described above. By using [O₃]/[Br₂] ratios greater than 10⁴, it was established that the BrCl signals observed at m/e 116 were from reaction 1c and not from the rapid reaction



3) Determination of $(k_{1a} + k_{1c})/k_1$: The quantity $(k_{1a} + k_{1c})/k_1$ was determined by measuring the yield of BrCl under conditions of high [Br₂] ([Br₂] > 10¹³ molecule cm⁻³) such that all Cl atoms produced in reaction 1a are scavenged by Br₂ (reaction 9). The observed BrCl signal therefore corresponds to the sum of the contributions from reactions 1a and 1c. A second, independent method for the determination of this quantity involved the measurement of the isotope ³⁴O₂ which was formed in reactions 1a and 1c when isotopically labelled Br¹⁸⁰ reacted with Cl¹⁶⁰.

The results of these studies effectively characterize the temperature dependences of the rate coefficients for reactions 1a, 1b and 1c. The derived Arrhenius expressions for the three reaction channels are, in cm³ molecule⁻¹ s⁻¹,

$$\begin{aligned} k_{1a} &= (2.9 \pm 1.0) \times 10^{-12} \exp[(217 \pm 50)/T] \\ k_{1b} &= (1.6 \pm 0.4) \times 10^{-12} \exp[(426 \pm 50)/T] \\ k_{1c} &= (5.8 \pm 2.0) \times 10^{-13} \exp[(168 \pm 50)/T] \end{aligned}$$

Flash Photolysis-Ultraviolet Absorption

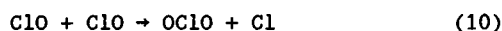
In order to determine the overall rate constant, k_1 , and the branching ratio for OC1O formation, k_{1b}/k_1 , it was necessary to measure the absorption cross sections for ClO and BrO under the same conditions of temperature, pressure and monochromator spectral resolution employed in the kinetics studies. As indicated above, the cross sections for both radicals were measured using several independent techniques to minimize the possibility of systematic error. The cross sections of both radicals at their respective band heads were observed to increase with decreasing temperature. This has been observed previously for BrO by Sander and Watson [1981].

The temperature dependence of k_1 was determined by measuring the first-order decay rate of BrO (k_1') in the presence of excess ClO. As in the DF/MS experiment, first-order plots of BrO decay and plots of k_1' vs. [ClO] were linear with negligible y-intercepts over the temperature and pressure range studied. A correction,

ranging from 10% to 30% and averaging about 20%, was applied to measured first-order rate constants to allow for the change in the background absorption at 277.5 nm due to the Cl₂O present in the cell. Rate constants were obtained from experiments in which k_1' varied from 500 to 10000 s⁻¹. No dependence on the total pressure of argon was found over the range 50-700 torr. The Arrhenius expression determined from about 100 kinetic runs in the flash photolysis study is given by:

$$k_1 = (6.11 \pm 1.00) \times 10^{-12} \exp [(236 \pm 50)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The branching ratio k_{1b}/k_1 was determined by measuring the OC1O yield as a function of the initial BrO concentration. Because of the spectral interference between the (7,0) band head of BrO and the continuum absorption of OC1O, a spectral method employing an optical multichannel analyzer was used to determine the OC1O concentration. OC1O spectra were acquired during a 1 ms integration period after reaction 1 had gone to completion. These spectra were corrected for baseline shifts associated with BrCl formation and fitted to OC1O calibrated reference spectra acquired at the appropriate temperature. Plots of the derived OC1O yield vs. [BrO]₀ were linear over a wide range of [BrO]₀. The branching ratios obtained by this method were 0.68 ± 0.12 and 0.59 ± 0.12 at 220 K and 298 K, respectively. Measurements at 400 K were not possible because of secondary OC1O formation by the reaction



As part of the study of the BrO + ClO reaction, the temperature dependence of the rate constant for the reaction



was measured. The Arrhenius expression was determined to be

$$k_8 = (2.14 \pm 0.89) \times 10^{-11} \exp[-(520 \pm 130)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 220 - 298 K.

Discussion

The rate coefficients for k_1 obtained in the DF/MS and FP/UV investigations are in excellent agreement indicating that there is no effect of pressure on the rate coefficient over the range 1 to 760 torr. Both studies obtain a significant negative temperature dependence for k_1 which is consistent with the observed behavior of other exothermic halogen monoxide disproportionation reactions [e.g. Sander and Watson, 1981; Sander, 1986]. Good agreement is also obtained concerning the branching ratio for OC1O formation with values of 0.55 and 0.68 being obtained at 220 K for the DF/MS and FP/UV studies, respectively. Also significant is the small but measurable BrCl product channel in the discharge flow study. This result is analogous to the observation of Br₂ as a product in the BrO + BrO reaction [Sander and Watson, 1981], as both channels require the formation of a four-center transition state.

While there have been several previous

measurements of the rate coefficient for reaction 1 at room temperature [Basco and Dogra, 1971; Clyne and Watson, 1977], there has been only one previous measurement of the temperature dependence. Hills et al. [1987, 1988] studied reaction 1 using discharge flow-mass spectrometry and measured a value for k_1 of about 8×10^{-12} cm³ molecule⁻¹ s⁻¹, independent of temperature over the range 241-408 K. This result is in significant disagreement with the present studies, as indicated in Figure 1. In addition, Hills et al. reported a value of < 0.02 for the BrCl branching ratio, in disagreement with our DF/MS study. Several possible reasons for these discrepancies are discussed by Friedl and Sander [submitted to J. Phys. Chem.].

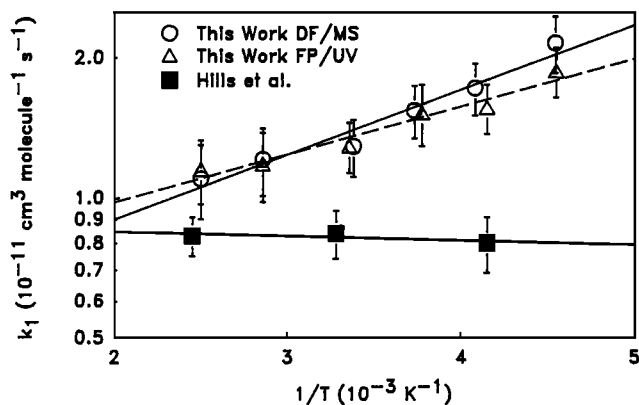


Fig. 1. Comparison of Arrhenius plots for the BrO + ClO reaction from this work and the study of Hills et al. [1987, 1988].

Atmospheric Implications

McElroy et al. [1986] showed that reaction 1a can lead to depletion rates for the ozone column in the Antarctic stratosphere that are comparable to those observed by TOMS [Stolarski, 1986] provided that the concentrations of ClO and BrO at high altitude are approximately 3.3 ppb and 25 ppt, respectively. Tung et al. [1986] also concluded that O₃ removal rates of 0.5% per day can be achieved with 24 hour averaged abundances of ClO and BrO at 18 km of 0.4 ppb and 20 ppt, respectively. Both calculations assumed a value for k_{1a} at stratospheric temperatures equal to the value measured at 298 K by Clyne and Watson (1977), i.e. $k_{1a} = 6.7 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

In the present study we have found that the value of k_{1a} increases with decreasing temperature such that, if the derived Arrhenius expressions are extrapolated to 180 K, k_{1a} is approximately 1×10^{-11} cm³ molecule⁻¹ s⁻¹. This result can be combined with measured concentrations of ClO ($\approx 1 - 2$ ppb) and BrO ($\approx 4 - 10$ ppt) taken during the 1986 and 1987 ground-based and airborne Antarctic campaigns [de Zafra, 1987; Anderson et al., 1988; Sanders et al., 1988] to provide a reassessment of the impact of the bromine-catalyzed destruction of ozone. Following the earlier calculations, we estimate that reaction 1a will be responsible for approximately 10-20% of the observed loss in column ozone in the Antarctic. This estimate is

in accord with a recent analysis by Salawitch et al. [1988] which includes the kinetic parameters for reaction 1 obtained in these studies.

Reaction channels 1b and 1c act to sequester ClO and BrO during the Antarctic night in the forms OClO and BrCl. Previous models have included reaction 1b but have omitted 1c. These models tend to overestimate the observed magnitude of the diurnal variation of OClO. (see Solomon, 1987). In this study we have established that reaction 1c is a small but significant channel of the BrO + ClO reaction. One atmospheric effect of this channel is to inhibit the nighttime conversion of ClO to OClO. The nighttime BrCl sink tends to reduce the diurnal OClO variation. Salawitch et al. [1988] have demonstrated that the inclusion of reaction 1c does indeed reduce the discrepancy between observed and calculated OClO diurnal variations.

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