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ABSTRACT

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STUDIES OF ClO AND BrO REACTIONS IMPORTANT IN THE POLAR STRATOSPHERE: KINETICS AND MECHANISM OF THE ClO + BrO AND ClO + ClO REACTIONS

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A. Introduction

The reactions,

$$\begin{aligned} BrO + ClO &\rightarrow Br + ClOO && (1a)\\ &\rightarrow Br + OClO && (1b)\\ &\rightarrow BrCl + O_2 && (1c) \end{aligned}$$

and

$$\begin{aligned} ClO + ClO &\rightarrow Cl + ClOO && (2a)\\ &\rightarrow Cl + OClO && (2b)\\ &\rightarrow Cl_2 + O_2 && (2c)\\ &\rightarrow (ClO)_2 && (2d) \end{aligned}$$

have assumed new importance in explaining the unusual springtime depletion of ozone observed in the Antarctic stratosphere. The mechanisms of these reactions involve the formation of metastable intermediates which subsequently decompose through several energetically allowed product channels. The resulting pressure and temperature phenomenology is complex, providing the motivation to study these reactions using both the discharge flow - mass spectrometric and flash photolysis - ultraviolet absorption techniques. These methods have also been used to explore aspects of the kinetics and spectroscopy of the ClO dimer.

B. Mass Spectrometric Studies of ClO + BrO and $(ClO)_2$

As part of a comprehensive study of the ClO + BrO reaction, kinetic and product determinations were performed at 1 torr total pressure in a temperature controlled discharge flow apparatus. Mass spectrometric detection was employed with continuous sampling of the flow tube through a three stage beam inlet system coupled to a quadrupole mass filter using electron impact ionization.

Kinetic studies were carried out under pseudo first-order conditions in excess ClO. In order to avoid possible regeneration of BrO within the reaction zone, radical sources were employed that did not use O_3, in particular $O + Br_2$ (excess) → BrO and Cl(excess) + Cl_2O → ClO. Possible depletion of BrO in the reaction zone by Cl atoms, generated in the ClO source and from both ClO +

ClO and BrO + ClO, was avoided by insuring fast conversion of Cl atoms to BrCl with excess Br_2. The results of these kinetics experiments reveal that the ClO + BrO reaction, like many of the halogen monoxide self reactions, displays a negative temperature dependence as shown in Figure 1.

Product yields were determined from four distinct sets of experiments. The first set employed conditions identical to those used for kinetic determinations. Simultaneous measurements of OClO and BrO were obtained, revealing that the channel yielding OClO constitutes a significant fraction of the overall reaction. The second set of experiments also employed conditions similar to those used for kinetic runs with the exception that the O atoms were generated using isotopically labelled molecular oxygen ($^{36}O_2$). In these experiments the production of $^{34}O_2$ was monitored simultaneously with the decay of $Br^{18}O$, providing a measure of the combined yield of the Cl atom and BrCl producing channels. A third set of measurements, which employed a ClO source of Cl + OClO(excess) and which focussed on detection of BrCl, measured the same two channels as did the second set. The results of these two sets were consistent with one another and with the conclusion of the first set of experiments. Results from the third set of experiments also strongly suggested that the reaction of Br with $(ClO)_2$ rapidly forms BrCl. In the fourth set of experiments, the channel forming BrCl was isolated by the addition of large amounts of O_3 to the flow tube. In these experiments the BrCl channel constituted the only loss mechanism for BrO. The results derived from this last series of experiments have important implications for the diurnal behavior of OClO in Antarctica as well as for reinterpretation of several previous studies of ClO_x + BrO_x reactions.

During the investigation of the ClO + BrO reaction it was discovered that under certain ClO source conditions a signal could be detected at m/e 102. This peak has tentatively been assigned to the ClO dimer. A temperature controlled, high pressure source region has subsequently been interfaced to the discharge flow - mass spectrometer system. We have successfully optimized ClO dimer production in this source and are in the process of characterizing the kinetic behavior of this species in the presence of O_3, OClO, and various atomic species.

C. Flash Photolysis Studies of BrO and ClO Reactions

Reactions 1 and 2 were studied using the flash photolysis - ultraviolet absorption technique. For the study of reaction 1, BrO and ClO were produced by rapid reactions following the broad-band photolysis of Br_2 - Cl_2O mixtures. BrO and ClO were simultaneously monitored by long-path absorption. In order to avoid some of the difficulties encountered in previous studies of this reaction, ClO was produced in excess over BrO, and conditions were chosen such that the secondary regeneration of BrO was negligible. From the analysis of first-order BrO decays, rate constants for reaction 1 were obtained over the temperature range 220-400 K and pressure range 50-700 torr. The temperature dependence of the yield of OClO from reaction 1 was determined using a novel time-resolved diode array spectrometer. Calibrated ultraviolet absorption spectra for both BrO and ClO were obtained between 220 and 400 K in order to interpret the kinetic and product studies of reaction 1. For the first time, determinations were made of the rate constant temperature dependence for the reaction

$$Br + Cl_2O \rightarrow BrCl + ClO$$

and of quantum yields for the photolysis of Cl_2O, i.e.

$$\begin{aligned} Cl_2O + h\nu &\rightarrow Cl + ClO & \Phi_1 \\ &\rightarrow O + Cl_2 & \Phi_2 \end{aligned}$$

Kinetic and spectroscopic studies of the ClO + ClO reaction were also carried out using this technique. The pressure and temperature dependences of the termolecular channel forming the ClO dimer were determined, and reaction products were studied using the gated diode-array spectrometer.

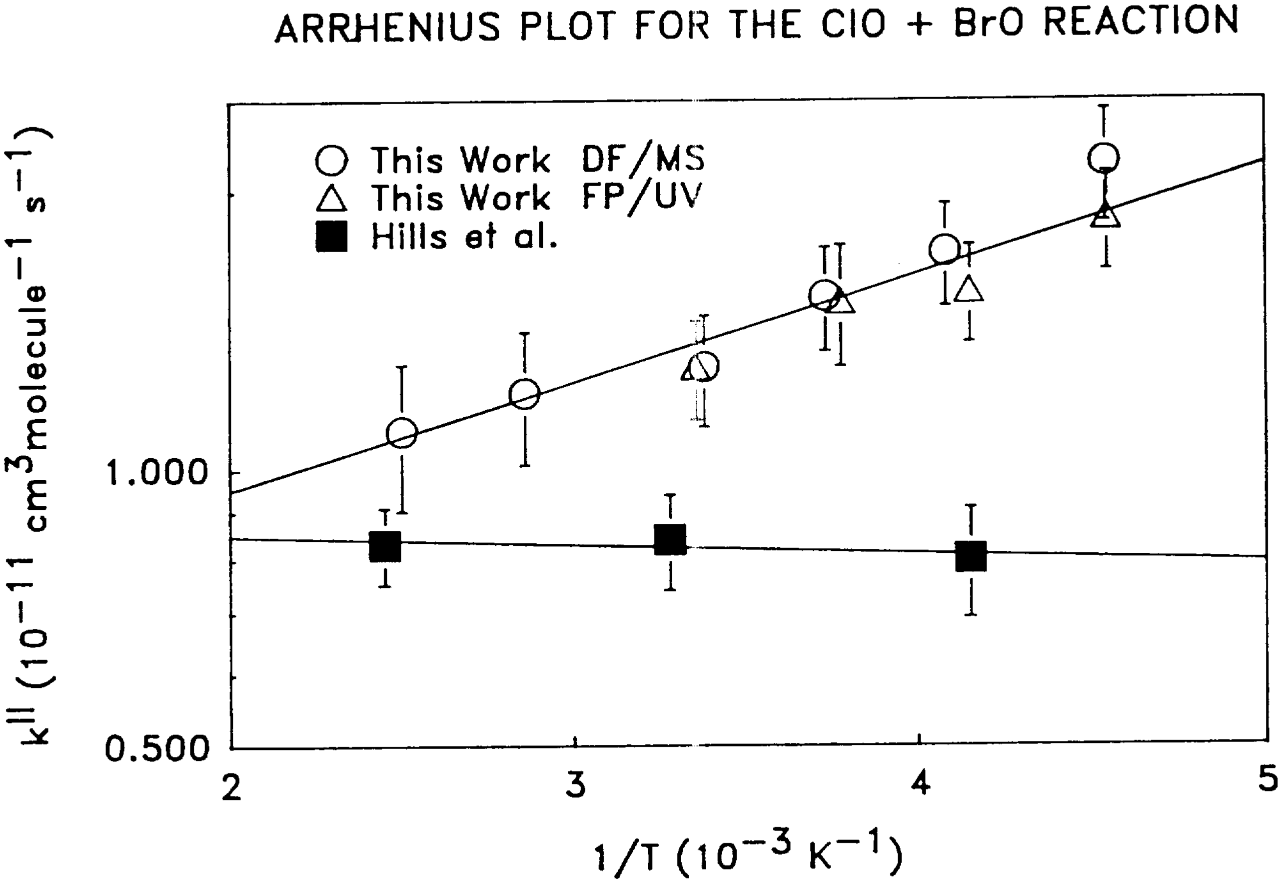

Figure 1. Temperature dependence of the BrO + ClO rate constant from this study and from Hills et al. (1987). DF/MS = Discharge Flow/Mass Spectroscopy, FP/UV= Flash Photolysis/Ultraviolet Absorption.