of their stated BrCl sensitivity ( $\approx 1.2 \times 10^{11}$  molecules cm<sup>-3</sup> for S/N = 2) and maximum allowed BrO concentration (5 × 10<sup>11</sup> molecules cm<sup>-3</sup>), it is difficult to justify such a low limit. Moreover, the electron capture cross section for isobutane is sufficiently large as to degrade the sensitivity of the mass spectrometer when excess isobutane is employed. Accordingly, an upper limit greater than 0.12 for the BrCl branching ratio appears to be more consistent with the reported data. This latter upper limit is consistent with the values obtained in the present work.

Qualitative evidence in support of a significant yield of BrCl in reaction 1 can be inferred from previously reported observations of BrCl( ${}^{3}\pi_{0^{+}}$ ) emission from reaction mixtures of Br and OCl-O.<sup>28-30</sup> Although initially this emission was attributed to the reaction of Br with ClOO,<sup>30</sup> this conclusion was based on an incorrectly low estimate of the ClOO decomposition rate. Alternatively, the occurrence of reaction 1c, where the nascent BrCl is electronically excited, provides a straightforward explanation for these observations. Recently, Toohey et al.<sup>17</sup> have shown that a model containing reaction 1c can predict the previously observed BrCl emission. They have also presented data on the yields of bromine atoms from reaction 1 that suggest a significant role for reaction 1c.

Implications for Atmospheric Chemistry. Following the revelation by Farman et al.<sup>10</sup> of an unprecedented drop in the

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springtime levels of ozone over the Antarctic region, a host of theories were proposed to explain this phenomenon. McElroy et al.<sup>11</sup> first emphasized the possible role of reaction 1a in the destruction of  $O_3$  under the special conditions existing in Antarctica. Ground-based observations of OClO made by Solomon et al.<sup>31</sup> at McMurdo Station have provided solid albeit circumstantial evidence for the occurrence of reaction 1. Recent attempts to model the role of reaction 1 in the Antarctic stratosphere have employed the room-temperature rate coefficient data of Clyne and Watson.<sup>11,32</sup> The present results reveal that the rate coefficient for reaction 1 depends inversely on temperature. Consequently, for temperatures typical of the Antarctic stratosphere (190 K), reaction 1 will take on added significance. In addition, the identification of reaction 1c, previously omitted in model calculations, provides a means for sequestering BrO during the night. The significance of these new findings is discussed in ref 33.

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# Kinetics and Product Studies of the Reaction CIO + BrO Using Flash Photolysis–Ultraviolet Absorption

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The flash photolysis-ultraviolet absorption method has been used to study the BrO + ClO reaction over the pressure range 50-700 Torr and temperature range 220-400 K. The rate constant for the overall reaction is given by  $k_1 = (6.1 \pm 1.2) \times 10^{-12} \exp[(240 \pm 60)/T] \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> ( $\pm 2\sigma$  error limits). Branching ratios for the reaction channel forming OClO were determined at 220 and 298 K and found to be  $0.68 \pm 0.10$  and  $0.59 \pm 0.10$ , respectively. Absolute UV absorption cross sections for ClO and BrO were determined as a function of temperature at the peaks of the 12-0 and 7-0 bands. In order to more fully understand the reaction mechanism used in the BrO + ClO study, the reactions Br + Cl<sub>2</sub>O  $\rightarrow$  ClO + BrCl and Cl<sub>2</sub>O +  $h\nu \rightarrow$  products were examined. The Arrhenius expression for the Br + Cl<sub>2</sub>O reaction was found to be  $k_3 = (2.1 \pm 1.8) \times 10^{-11} \exp[-(520 \pm 260)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $\pm 2\sigma$ ) over the temperature range 220-298 K. The quantum yield for the production of atomic oxygen from broad-band Cl<sub>2</sub>O photolysis ( $\lambda > 180$  nm) was found to be 0.25  $\pm 0.05$ .

## Introduction

The BrO + ClO reaction is an important process in the chemistry of the Earth's stratosphere because it links the catalytic ozone destruction cycles of the chlorine and bromine radical families. While the role that this reaction plays in the chemistry of the midlatitude stratosphere has been understood for some time,<sup>1</sup> the recent discovery of a massive springtime decline in the stratospheric ozone column over Antarctica has stimulated renewed interest in this reaction.<sup>2</sup> Data needs have focused on the temperature and pressure dependences of the rate coefficients for the three exothermic product channels

$$BrO + ClO \rightarrow Br + ClOO$$
 (1a)

$$\rightarrow$$
 Br + OClO (1b)

$$\rightarrow$$
 BrCl + O<sub>2</sub> (1c)

The previous paper<sup>3</sup> has discussed an experimental approach to this reaction that utilized the technique of discharge-flow mass spectrometry. In order to validate the results of that technique and to extend the pressure regime over the full 1–700-Torr range, we have studied reaction 1 using the flash photolysis-ultraviolet absorption method. Rate constants for reaction 1 were obtained over the temperature range 220–400 K and the branching ratio  $k_{1b}/k_1$  was determined at 220 and 298 K by monitoring the

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Figure 1. Ultraviolet absorption spectra of ClO (solid line) and Cl<sub>2</sub>O (dashed line) in the 265-305-nm spectral region.<sup>10,16</sup> The ClO spectrum was obtained with an optical multichannel analyzer that had a wider bandwidth than the monochromator used in the kinetics study. As a result, the cross sections at the band heads are lower than those measured here. ClO was monitored at the peak of the 12-0 band at 275.2 nm as indicated by the arrow. The procedure for correcting the measured ClO optical density for changes in the background absorption due to Cl<sub>2</sub>O is discussed in the text.

formation of OClO. As a necessary part of this study, aspects of the kinetics and photochemistry of  $Cl_2O$  were investigated, including the temperature dependence of the reaction

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

and the products of Cl<sub>2</sub>O photolysis.

### **Experimental Section**

The flash photolysis-absorption system has been described in detail previously.<sup>4</sup> The flash lamp/reactor consists of four concentric tubes, approximately 1 m long, comprising the reaction cell (1-in. i.d.), photolyzing light filter, xenon flash lamp, and cooling/heating jacket. Two identical cells were used: one constructed of quartz for use in the BrO + ClO kinetics and branching ratio studies and one constructed of Pyrex for use in Br + Cl<sub>2</sub>O kinetics and radical cross-section studies. The cell was operated in the continuously flowing mode, with all reagent and carrier gas flows being measured with calibrated mass flowmeters. The analytical light source was a 150-W xenon arc lamp or a 30-W deuterium lamp. The analytical beam was collimated and coupled into the reaction cell through 8-pass White-type optics with external mirrors. The optical path length was 800 cm. The exit beam passed through a dichroic beam splitter that directed part of the beam ( $\lambda > 300$  nm) to a 0.32-m focal length monochromator (150- $\mu$ m slit width, 0.18-nm resolution) equipped with a photomultiplier and a 1024 diode optical multichannel analyzer (OMA), used for the detection of BrO and OCIO. The other part of the exit beam was coupled into a 0.5-m monochromator (150- $\mu$ m slit width, 0.13-m fwhm resolution) and photomultiplier for the detection of ClO and Cl<sub>2</sub>O. Photomultiplier outputs were amplified, low-pass filtered, and digitized with an analog signal averager interfaced to a microcomputer.

ClO radicals were monitored by their absorption at the peak of the  $12-0 \Omega = 3/2$  subband (A  $\leftarrow$  X) at 275.2 nm<sup>5.6</sup> (Figure 1). BrO radicals were monitored at the peak of the 7-0  $\Omega = 3/2$ subband (A  $\leftarrow$  X) at 338.5 nm.<sup>7-9</sup> This band, which is the most intense in the progression, lies fortuitously between two OClO bands, as indicated in Figure 2. Both the BrO and ClO bands show rotational structure but are diffuse due to predissociation. The effective cross sections were therefore somewhat sensitive to



Figure 2. Ultraviolet absorption spectra of BrO (solid line) and OCIO (dashed line, ref 20). BrO was monitored at the peak of the 7–0 band at 338.5 nm as indicated by the arrow.

monochromator resolution (see Results). OCIO was monitored by examining the strong band progression that extends from 280 to 480 nm. The three bands with peaks at 329.22, 336.08, and 343.44 nm were used to quantify OCIO formation with use of the OMA to acquire the band spectra in real time.

Normally, the time required to obtain a 1024-channel spectrum from the OMA is about 16 ms. In order to quantify the OCIO production from the BrO + ClO reaction without interference from OCIO produced by the CIO + CIO reaction, it was necessary to reduce the OMA exposure time to 1 ms. This was accomplished with a fast electromechanical shutter sequenced to open both before and after the photolysis flash for a preset period to obtain the  $I_0$  and  $I_t$  spectra. OClO spectra from the OMA were processed by first coadding and converting to absorbance the spectra from 64 to 128 flashes. Since the exit slit function of the spectrometer overlapped several diodes, spectra were smoothed with a 7-point boxcar kernel. Because BrCl was formed in the reaction, the observed OCIO spectra usually displayed a variable base line offset due to the contribution of the BrCl continuum. Base-line correction was accomplished by subtracting from the smoothed spectrum a third-order polynomial obtained from a curve fit to the spectrum. The absolute OCIO yield was determined by fitting the experimental spectrum to a calibrated reference spectrum obtained at the same temperature.

One of the methods used in this study to measure the absorption cross section of ClO used a discharge-flow apparatus.<sup>10</sup> This system consisted of a 15-cm-i.d. flow tube pumped by a 650 cfm Roots blower/mechanical pump. The flow tube was fitted with single-pass ultraviolet absorption optics consisting of a deuterium lamp and a 0.3-m spectrometer interfaced to an optical multichannel analyzer. The path length was 152 cm.

Cl<sub>2</sub>O was prepared by the method of Schack and Lindahl.<sup>11</sup> Residual chlorine from the synthesis was removed by distillation at -112 °C. The purity of the Cl<sub>2</sub>O in the vapor above the liquid was at least 95% as determined by ultraviolet absorption.  $Cl_2O$ was introduced into the flash photolysis cell by flowing helium at 5 psia through a bubbler containing the pure liquid at -78 °C. Due to problems associated with sample storage, OClO was prepared in-line by flowing mixtures of 5% Cl<sub>2</sub> in helium through a trap containing NaOClO mixed with glass beads. Ultraviolet spectra of the exit gas stream indicated that all of the Cl<sub>2</sub> was converted to OClO within the experimental uncertainty.  $Br_2$  (J. T. Baker; 99.7% purity) was used after successive freeze-thaw cycles. O<sub>3</sub> was prepared by passing ultra-high-purity oxygen through a commercial ozonizer and using either a portion of the exit gas stream directly or by flowing helium over silica gel that had previously been saturated with ozone at -78 °C. Ultrahigh-purity argon and helium were used as received.

The mechanism employed in the study of the BrO + ClO reaction utilized the photolysis of  $Br_2$ -Cl<sub>2</sub>O mixtures at wavelengths longer than 200 nm (quartz cutoff). In this system, ClO

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radicals were formed by two processes: (1) from the  $Br + Cl_2O$  reaction

$$Br_2 + h\nu \rightarrow 2Br$$
 (2)

$$Br + Cl_2O \rightarrow BrCl + ClO$$
 (3)

and (2) from the direct photolysis of  $Cl_2O$ 

$$Cl_2O + h\nu \rightarrow Cl + ClO$$
 (4a)

$$\rightarrow O + Cl_2$$
 (4b)

The rate constant for reaction  $3^{12}$  and the product yields of Cl<sub>2</sub>O photolysis<sup>13-15</sup> have been studied previously, but there is considerable uncertainty concerning these parameters. Estimates for these parameters were obtained in this study and will be discussed below.

BrO radicals were formed by the  $O + Br_2$  reaction

$$O + Br_2 \rightarrow BrO + Br$$
 (5)

 $k_{\rm s}(298 \text{ K}) = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.32}$ 

The primary loss mechanism for BrO was reaction with ClO:

$$BrO + ClO \rightarrow Br + ClOO$$
 (1a)

$$\rightarrow$$
 Br + OClO (1b)

$$\rightarrow$$
 BrCl + O<sub>2</sub> (1c)

Bromine atoms formed in reaction 1a and 1b rapidly regenerated ClO by reaction with  $Cl_2O$  (reaction 3). The ClOO formed in reaction 1a rapidly dissociated to form  $Cl^{16}$ 

$$ClOO + M \rightarrow Cl + O_2 + M \tag{6}$$

Chlorine atoms formed by reaction 4a or reaction 6 then reacted with  $Br_2$  or  $Cl_2O$  to regenerate ClO:

$$Cl + Br_2 \rightarrow BrCl + Br$$
 (7)

$$k_7 = 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.17}$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO$$
 (8)

$$k_8 = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.16}$$

An important point concerning this mechanism is that there is no reaction path that can efficiently regenerate BrO; i.e., the products of the ClO + BrO reaction regenerate only ClO. The only reaction capable of regenerating BrO

$$Br + OCIO \rightarrow BrO + CIO$$
 (-1b)

$$k_{-10} = 4.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.18}$$

proceeded at a negligible rate under these conditions.

The ranges of initial reactant concentrations were as follows:  $[Cl_2O] = (0.6-2.0) \times 10^{15}$  molecules cm<sup>-3</sup>,  $[Br_2] = (0.2-6.6) \times 10^{15}$  molecules cm<sup>-3</sup>,  $[BrO]_0 = (1.0-7.0) \times 10^{12}$  molecules cm<sup>-3</sup>,

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Figure 3. First-order decay plots for BrO in the presence of excess ClO.



Figure 4. First-order decay constants for BrO, k', at 220 K ( $\blacktriangle$ ) and 298 K ( $\blacklozenge$ ).

 
 TABLE I: Summary of Overall Rate Coefficient Measurements for the BrO + CIO Reaction

temp, K	no. of measmts	$10^{11}k_{1}^{a}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
220	22	$1.87 \pm 0.23$
265	5	$1.52 \pm 0.23$
298	60	$1.29 \pm 0.16$
350	9	$1.18 \pm 0.20$
400	11	$1.15 \pm 0.18$

<sup>a</sup>Quoted uncertainties represent  $\pm 2\sigma$  error limits.

and  $[CIO]_0 = (0.3-6.0) \times 10^{14}$  molecules cm<sup>-3</sup>. Under these conditions, CIO was formed by reaction 3 on a time scale at least 10 times faster than its removal by reaction 1.

The CIO concentration remained essentially constant throughout the BrO decay period. The predominant CIO reaction path was disproportionation

$$ClO + ClO \rightarrow Cl + OClO$$
 (9a)

$$\rightarrow$$
 Cl + ClOO (9b)

$$\rightarrow Cl_2 + O_2$$
 (9c)

 $k_9 = 8.0 \times 10^{-13} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.16}$ 

$$ClO + ClO + M \rightleftharpoons (ClO)_2 + M$$
 (9d, -9d)

$$k_{\rm 9d} = 4.0 \times 10^{-32} (T/300)^{-2} \,\mathrm{cm^6 \ molecule^{-2} \ s^{-1.16}}$$

$$K_{eo} = 7.9 \times 10^{-27} \exp(8600/T) \text{ cm}^3 \text{ molecule}^{-1.16}$$

ClO removal occurred only through OClO formation (9a) and  $Cl_2$  formation (9c) since Cl or ClOO formation resulted in the regeneration of ClO. The ratio of the initial ClO half-life by reaction 9 to the BrO half-life by reaction 1 was greater than 40, indicating that no correction was required for ClO decay during the measurement period.

## Results

Kinetics of BrO Decays. The overall rate constant for reaction 1 was measured over the temperature range 220-400 K and



Figure 5. Spectrum of OClO formed as a product of the BrO + ClO reaction after averaging 128 flashes. The OMA exposure time was 1 ms, beginning 2 ms after the photolysis flash. The OClO yield is obtained by fitting a calibrated OClO reference spectrum to the experimental spectrum as shown.

pressure range 50-700 Torr of argon. Plots of ln (BrO absorbance) vs time were linear over 3-4 1/e times through the entire range of experimental conditions (Figure 3). The slopes of these plots are the pseudo-first-order rate constants,  $k_1'$ . A residual absorption was observed after the reaction was completed, consistent with the formation of BrCl by reactions 1c, 3, and 7. The ClO optical density was also recorded for each kinetic run. A mean ClO concentration was then calculated from the absorption cross section at the appropriate temperature. A concentration-dependent optical density correction factor was also applied, as discussed in text below. Bimolecular rate constants for reaction 1 were obtained from plots of  $k_1'$  vs [ClO]. These plots were linear with negligible y intercepts (Figure 4) over a range in ClO concentration that varied between 6 and 20, depending on temperature. The observed rate constants are listed in Table I and show a significant negative temperature dependence, ranging from  $(1.87 \pm 0.23) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 220 K to  $(1.15 \pm 0.18) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 400 K. The best-fit Arrhenius expression to the rate constant data is given by

 $k_1 =$ 

$$(6.1 \pm 1.2) \times 10^{-12} \exp[(240 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the quoted uncertainties represent the  $\pm 2\sigma$  error limits.

As indicated above, a correction was required in the determination of the ClO optical density. This was due to the fact that Cl<sub>2</sub>O absorbs a significant fraction of the probe beam at 275.2 nm, and small changes in Cl<sub>2</sub>O concentration from reactions 3 and 4 lead to relatively large changes in the base line. This effect causes the ClO optical density to be underestimated. A base-line correction was derived by estimating  $\Delta$ [Cl<sub>2</sub>O] from the reaction stoichiometry. It can be seen from the assumed reaction mechanism that the quantum yield for Cl<sub>2</sub>O destruction from both Br<sub>2</sub> and Cl<sub>2</sub>O photolysis is 2.  $\Delta$ [Cl<sub>2</sub>O] is therefore given by

$$\Delta[\text{Cl}_2\text{O}] = 2(f_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + f_{\text{Br}_2}[\text{Br}_2])$$

where  $f_{Cl_2O}$  and  $f_{Br_2}$  are the fractional photolytic dissociation rates of Cl<sub>2</sub>O and Br<sub>2</sub>, respectively. These parameters were measured at each photolysis flash energy used in the experiment by monitoring the disappearance of the pure compound before and after the flash. The calculated value of  $\Delta$ [Cl<sub>2</sub>O] for each kinetic run was used to correct the observed ClO optical density using a value of  $1.25 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> for the cross section of Cl<sub>2</sub>O at 275.2 nm.<sup>19</sup> This correction averaged about 20%, increasing with increasing flash energy.

Branching Ratio for OClO Formation. The branching ratio for OClO formation,  $k_{1b}/k_1$ , was determined by measuring the OClO yield relative to the initial BrO concentration after the BrO + ClO reaction had gone to completion. As indicated above, OClO was quantitatively determined with an optical multichannel analyzer (OMA) gated by a mechanical shutter with an exposure



Figure 6. OCIO yield vs  $[BrO]_0$  for the BrO + CIO reaction at 220 K ( $\blacktriangle$ ) and 298 K ( $\blacklozenge$ ).

time of about 1 ms. Figure 5 shows a typical OMA spectrum of OCIO produced from the BrO + CIO reaction along with the OCIO reference spectrum. OCIO reference spectra were acquired in separate experiments at the same temperature as the OCIO yield studies and subsequently calibrated with cross sections measured by Wahner et al.<sup>20</sup> Since these cross sections were measured at the same spectral resolution that was employed here (0.25 nm), no corrections for spectrometer resolution were necessary. The initial BrO concentration for each run was determined by extrapolating the first-order BrO decay curve to t = 0. By using somewhat lower initial CIO concentrations than those employed in the  $k_1$  determinations, BrO decayed slowly, allowing for improved estimates of the initial BrO optical density,  $\sigma I[BrO]_0$ . OCIO yields and initial BrO concentrations were measured in consecutive experiments that used identical reagent flows and photolysis flash energies. Measured values of the optical density were converted to initial BrO concentrations with BrO absorption cross sections at the appropriate temperature and spectral resolution. The procedures for measuring these cross sections will be described in text below.

The dependence of the OCIO product yield on  $[BrO]_0$  is shown in Figure 6. The branching ratios are given by the slopes of the plots. Values of  $0.59 \pm 0.10$  and  $0.68 \pm 0.10$  are obtained at 298 and 220 K, respectively. Measurements of the branching ratio at high temperature (400 K) were not possible because of the rapid formation of OCIO from the CIO self-reaction (reaction 9a). This reaction did not compete with reaction 1b at 298 K and below but was considerably faster at 400 K because of the 2.5 kcal mol<sup>-1</sup> activation energy for the reaction.

ClO Cross-Section Determination. In order to convert observed ClO absorbances into concentrations, it was necessary to measure the absolute absorption cross section for ClO under the experimental conditions employed. Three independent measurement techniques were used to minimize the possibility of systematic error. These were based on (1) the stoichiometric conversion of Br to ClO in excess  $Cl_2O$ , (2) the photolysis of OClO, and (3) the stoichiometric conversion of OClO to ClO in excess Cl. The first two measurements were carried out in the flash photolysis apparatus while the third method used a discharge-flow apparatus.

In the first method, bromine atoms were stoichiometrically converted to ClO by photolyzing  $Br_2$ -Cl<sub>2</sub>O mixtures in the Pyrex flash photolysis cell. The use of the Pyrex cell minimized the photolysis of Cl<sub>2</sub>O, while permitting the photolysis of  $Br_2$ :

$$Br_2 + h\nu \rightarrow 2Br \qquad (\lambda > 300 \text{ nm})$$
$$Br + Cl_2O \rightarrow ClO + BrCl$$

In each run in the  $Br_2$ -Cl<sub>2</sub>O system,  $[Br]_0$  could be estimated from the initial  $Br_2$  concentration and the fractional decomposition of  $Br_2$ . The latter quantity (which depended only on the photolysis flash energy) was determined in a series of experiments at different  $Br_2$  concentrations by photolyzing  $Br_2$  in the absence of Cl<sub>2</sub>O and measuring the change in  $Br_2$  optical density at 400 nm. In the

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TABLE II: Summary of CIO Ultraviolet Cross-Section Determinations at 275.2 nm

temp, K	method <sup>a</sup>	$10^{18}\sigma$ , <sup>b</sup> cm <sup>2</sup> molecule <sup>-1</sup>	
220	1	$9.76 \pm 0.98$	
220	2	$9.35 \pm 0.93$	
220	3	$9.99 \pm 1.0$	
		$av 9.70 \pm 0.97$	
298	1	$8.52 \pm 0.85$	
298	2	7.94 ± 0.79	
298	3	$8.63 \pm 0.86$	
		av $8.36 \pm 0.84$	
400	3	$7.84 \pm 0.78$	

<sup>a</sup> Methods: 1, Br + Cl<sub>2</sub>O titration; 2, OCIO photolysis; 3, Cl + OCIO titration. <sup>b</sup>Quoted uncertainties represent  $\pm 2\sigma$  error limits.

presence of excess Cl<sub>2</sub>O, Br was stoichiometrically converted into ClO. In these experiments, the ClO optical density at 275.2 nm was measured in a series of runs in which the initial  $Br_2$  concentration was varied. The ClO cross section was then given by

$$\sigma_{\rm ClO} = \frac{\sigma_{\rm Br_2}}{2} \frac{\Delta(\rm OD_{\rm ClO})/\Delta[\rm Br_2]}{\Delta(-\Delta \rm OD_{\rm Br_1})/\Delta[\rm Br_2]}$$

where the numerator in the second term is the slope of the plot obtained from the  $Br_2$ - $Cl_2O$  experiments and the denominator is the fractional dissociation of  $Br_2$  obtained from the system with  $Br_2$  only.

In the second method, OCIO was photolyzed in the Pyrex cell:

$$OC|O + h\nu \rightarrow O + C|O$$
 ( $\lambda > 300 \text{ nm}$ )

Atomic oxygen reacted either with ClO or OClO:

$$O + ClO \rightarrow Cl + O_2 \tag{10}$$

$$Cl + OClO \rightarrow 2ClO$$
 (11)

$$O + OCIO \rightarrow O_2 + CIO \tag{12}$$

In either case, the quantum yield for ClO formation is unity. In these experiments, OClO and ClO were monitored simultaneously. A series of runs were carried out in which  $OD_{ClO}$  was plotted against  $\Delta(OD_{OClO})$  at different initial OClO concentrations. From the slope of this plot, the ClO cross section could be derived from the expression

$$\sigma_{\rm ClO} = \sigma_{\rm OClO} \frac{\Delta(\rm OD_{\rm ClO})}{\Delta(\Delta(\rm OD_{\rm OClO}))}$$

Values of  $\sigma_{OCIO}$  at 397.9 nm were taken from the study of Wahner et al.^{20}

In the third method, a known initial concentration of OCIO was titrated with excess atomic chlorine in a flow system to produce a known ClO concentration (reaction 11). The OCIO spectrum was obtained by ultraviolet absorption from the OMA to obtain the spectrum in the 327–351-nm wavelength range. After the addition of Cl, the OCIO spectrum was again recorded to verify that OCIO had been completely converted to ClO. The ClO spectrum was scanned with the same spectrometer and spectral resolution employed in the flash photolysis study. ClO cross sections were determined from the relative absorbances of the ClO and OCIO spectra scaled by absolute OCIO cross sections.<sup>20</sup>

The results from the three ClO cross section determinations are given in Table II. Excellent agreement is observed between the three methods at 220 and 298 K. The consistency between the methods indicates that the reaction stoichiometries assumed for each system are correct and that there was no secondary formation or destruction of ClO. The apparent cross section at the peak of the 12–0 band decreases with increasing temperature, ranging from  $9.70 \times 10^{-18}$  to  $7.84 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> over the range 220–400 K. A significant increase in the peak-to-valley ratios in the banded region is also observed at decreasing temperatures. The ClO cross section was also observed to depend on the spectral resolution of the monochromator although this

TABLE III: Summary of BrO Ultraviolet Cross-Section Determinations at 338.5 nm

temp, K	method <sup>a</sup>	$10^{17}\sigma$ , <sup>b</sup> cm <sup>2</sup> molecule <sup>-1</sup>
220	1	$2.21 \pm 0.22$
298	1	1.71 ± 0.17
298	2	$1.64 \pm 0.16$

<sup>a</sup> Methods: 1, Br + O<sub>3</sub> titration; 2, O + Br<sub>2</sub> titration. <sup>b</sup> Quoted uncertainties represent  $\pm 2\sigma$  error limits.

dependence was not explicitly measured.

**BrO** Cross-Section Determination. The measurement of the BrO cross section at 338.5 nm was necessary for the determination of the OCIO branching ratio. As in the CIO cross-section measurement, more than one method was used to obtain the cross section. In the first, a measured amount of  $O_3$  was titrated with excess atomic bromine to produce a known concentration of BrO.

$$Br_2 + h\nu \rightarrow 2Br$$
 ( $\lambda > 300 \text{ nm}$ )

$$Br + O_3 \rightarrow BrO + O_2$$
 (13)

$$k_{13} = 1.7 \times 10^{-11} \exp(800/T)^{16}$$

For these experiments, high  $Br_2$  concentrations ( $[Br_2] > 1 \times 10^{16}$  molecules cm<sup>-3</sup>) and flash energies were required to produce a sufficient Br atom excess to drive reaction 13 to completion on a time scale that was short compared to BrO removal by the reaction

$$BrO + BrO \rightarrow 2Br + O_2$$
 (14a)

$$\rightarrow Br_2 + O_2$$
 (14b)

The BrO cross section was determined from a series of experiments at different O<sub>3</sub> concentrations in which the O<sub>3</sub> absorbance at 275.2 nm ( $\sigma_{O_3} = 5.79 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-121</sup>) and the BrO absorbance extrapolated to t = 0 were measured. The cross section was then given by

$$\sigma_{\rm BrO} = \sigma_{\rm O_3} \frac{\Delta(\rm OD_{\rm BrO})}{\Delta(\rm OD_{\rm O_3})}$$

where the ratio in the above expression is the slope of the  $OD_{BrO}$  vs  $OD_{O_3}$  plot.

In the second method, O atoms produced by  $O_2$  photolysis were titrated with excess  $Br_2$  to form BrO

$$O_2 + h\nu \rightarrow 2O \qquad (\lambda > 180 \text{ nm})$$
$$O + Br_2 \rightarrow BrO + O_2 \qquad (5)$$

The initial O atom concentration was estimated in each experiment from the  $O_2$  concentration and the fractional dissociation of  $O_2$ . The fractional dissociation was determined in separate experiments without  $Br_2$  in which atomic oxygen was stoichiometrically converted to  $O_3$ 

$$O + O_2 + M \rightarrow O_3 + M$$

and the  $O_3$  yield was measured. The BrO cross section was then given by

$$\sigma_{\rm BrO} = \sigma_{\rm O_3} \frac{\Delta(\rm OD_{\rm BrO})/\Delta[\rm O_2]}{\Delta(\rm OD_{\rm O_3})/\Delta[\rm O_2]}$$

where the numerator of the second term is the slope of the plot obtained from the  $Br_2$ -O<sub>2</sub> experiments and the denominator is the fractional dissociation of  $Br_2$ .

The results of these measurements are given in Table III. Good agreement between the two methods is observed at 298 K. As with ClO, the cross section increases as temperature decreases, a trend observed previously for BrO by Sander and Watson.<sup>9</sup> The dependence of the absorption cross section on the monochromator spectral resolution at the peak of the 7–0 band was also measured.

<sup>(21)</sup> Molina, L. T.; Molina, M. J. J. Geophys. Res. D 1986, 91, 14501.



**Figure 7.** Reaction  $Br + Cl_2O \rightarrow ClO + BrCl.$  Plot of first-order formation constants for ClO, k', vs [Cl<sub>2</sub>O] as a function of temperature.

The cross section varied from  $1.68 \times 10^{-17}$  to  $0.98 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> as the spectral bandwidth increased from 0.06 to 1.25-nm fwhm. Additional details concerning this measurement as well as a calibrated plot of the BrO spectrum are discussed by Wahner et al.<sup>22</sup>

Kinetics of the  $Br + Cl_2O$  Reaction. The reaction

$$Br + Cl_2O \rightarrow ClO + BrCl$$
 (3)

was used as the primary source of ClO radicals for the study of reaction 1. Since there had been only one quantitative determination of the rate coefficient for reaction 3, this reaction was examined in detail. In separate studies with the Pyrex photolysis cell, Br2-Cl2O mixtures were photolyzed. The reaction was studied by measuring the first-order formation of ClO radicals in the presence of excess Cl<sub>2</sub>O. The Cl<sub>2</sub>O concentration in the reaction cell  $[(1-20) \times 10^{14} \text{ molecules cm}^{-3}]$  was measured by ultraviolet absorption at the same wavelength as the ClO absorption, 275.2 nm. At 298 K, the absorption cross section measured by Lin<sup>19</sup> was used to derive the Cl<sub>2</sub>O concentration. Because cross sections were not available at other temperatures, the following method was used to derive  $\sigma_{Cl_2O}$  below 298 K. An effective vapor pressure above the Cl<sub>2</sub>O bubbler reservoir was determined by correlating the measured flow rate through the bubbler with the Cl<sub>2</sub>O absorbance in the reaction cell. This quantity was used to calibrate the actual Cl<sub>2</sub>O flow rate at other temperatures. At temperatures below 298 K, cross sections were obtained from plots of Cl<sub>2</sub>O optical density vs [Cl<sub>2</sub>O] as determined from flow rate measurements.

The rate constant  $k_3$  was determined from 40 kinetic runs carried out at 298, 265, 241, and 220 K at a total pressure of 100 Torr of argon. A first-order rate constant,  $k_3'$ , was obtained from each run from the observed ClO concentration profile by the relation

$$\ln \frac{[\text{ClO}]_{\infty}}{[\text{ClO}]_{\infty} - [\text{ClO}]} = k_3't$$

where  $k_3' \equiv k_3[\text{Cl}_2\text{O}]$ . For each run,  $[\text{ClO}]_{\infty}$  was determined from the measured absorbance at long reaction times. Characteristic times for reaction 3 were 10–100 times shorter than those for the fastest competing ClO loss process (ClO disproportionation), making it unnecessary to correct for secondary chemistry of ClO. Bimolecular rate constants,  $k_3$ , were obtained from plots of  $k_3'$ vs [Cl<sub>2</sub>O] at each temperature (Figure 7). These values are listed in Table IV. An Arrhenius plot (Figure 8) yields the following expression for the temperature dependence of  $k_3$ 

 $k_{3} =$ 

 $(2.1 \pm 1.8) \times 10^{-11} \exp[-(520 \pm 260)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

where the quoted uncertainties represent the  $\pm 2\sigma$  error limits. As

1	temp, K	no. of measmts	$10^{-12}k_{3}^{a}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
	220	10	$2.14 \pm 0.22$
	241	10	$2.11 \pm 0.22$
	265	10	$3.03 \pm 0.31$
	298	10	$3.79 \pm 0.38$

<sup>a</sup>Quoted uncertainties represent  $\pm 2\sigma$  error limits.



Figure 8. Arrhenius plot for the reaction  $Br + Cl_2O \rightarrow BrCl + ClO$ .

shown in Figure 8, there may be some curvature in the Arrhenius plot over the temperature range studied but this cannot be verified with the present data.

Products of  $Cl_2O$  Photolysis. Initial studies of reaction 1 used added  $O_2$  as a photolytic source of atomic oxgyen in order to produce BrO by the reaction of O with Br<sub>2</sub> (reaction 5). It was determined, however, that BrO could be formed in the absence of added  $O_2$ . Since reaction 5 is the only known source of BrO and  $Cl_2O$  is the only oxygen-containing species in the system, it was assumed that O atoms were formed directly from  $Cl_2O$ photolysis by one or both of the following routes

$$Cl_2O + h\nu \rightarrow O + Cl_2$$
 ( $\lambda < 719 \text{ nm}$ ) (4b)

$$Cl_2O + h\nu \rightarrow O + 2Cl$$
 ( $\lambda < 294 \text{ nm}$ ) (4c)

O atoms reacted either with  $Cl_2O$ 

$$O + Cl_2 O \rightarrow 2ClO \tag{15}$$

or with  $Br_2$  via reaction 5. It was possible to obtain independent estimates of the yield of atomic oxygen from  $Cl_2O$  photolysis by measuring the initial concentrations of ClO and BrO. These quantities are given by

$$2f_4\phi_{4a}[\text{Cl}_2\text{O}] + f_4\phi_{4b}\frac{k_{15}[\text{Cl}_2\text{O}]}{k_{15}[\text{Cl}_2\text{O}] + k_5[\text{Br}_2]} + 2f_2[\text{Br}_2]$$
(I)

$$[BrO]_0 = f_4 \phi_{4b} [Cl_2O] \frac{k_5 [Br_2]}{k_5 [Br_2] + k_{15} [Cl_2O]}$$
(II)

where  $f_4$  = fractional photolysis of Cl<sub>2</sub>O,  $f_2$  = fractional photolysis of Br<sub>2</sub>,  $\phi_{4a}$  = quantum yield for ClO formation from Cl<sub>2</sub>O photolysis, and  $\phi_{4b}$  = quantum yield for O formation from Cl<sub>2</sub>O photolysis. In eq I, the three terms represent the contribution to [ClO]<sub>0</sub> from (1) the Cl<sub>2</sub>O photolysis channel yielding ClO directly, (2) the O + Cl<sub>2</sub>O reaction where O atoms arise from Cl<sub>2</sub>O photolysis, and (3) the Br + Cl<sub>2</sub>O reaction. The derivation of eq I assumes that reaction 4b is the only source of O atoms in the system.

The parameters  $\phi_{4a}$  and  $\phi_{4b}$  were estimated from I and II.  $f_4$ and  $f_2$  were measured at specific flash energies by observing the photolytic disappearance of Cl<sub>2</sub>O and Br<sub>2</sub> in the absence of other reagents. With the use of these parameters and measurements of [ClO]<sub>0</sub>, [BrO]<sub>0</sub>, [Br<sub>2</sub>], and [Cl<sub>2</sub>O], a value of 0.25 ± 0.05 was obtained for  $\phi_{4b}$ . Because a broad-band photolysis source was used with a spectral distribution extending from visible wavelengths to a cutoff of about 180 nm, it was not possible to determine the wavelength dependence of the quantum yield.

<sup>(22)</sup> Wahner, A.; Ravishankara, A. R.; Sander, S. P.; Friedl, R. R. Chem. Phys. Lett. 1988, 152, 507.

#### Discussion

Mechanism of the BrO + ClO Reaction. Several aspects of the mechanism of reaction 1 have been discussed in the companion paper.<sup>3</sup> In order to explain the three product channels observed for reaction 1, the reaction must proceed through at least two different BrO-ClO adducts. It is reasonable to assume that the channel forming Br + OClO proceeds through a BrOClO structure while the Br + ClOO and BrCl +  $O_2$  channels proceed through a BrOOCl structure.

The XO + XO and XO + YO (X, Y = halogen) reactions show a wide range of pressure and temperature dependence phenomena that can be related to the details of the potential surfaces. The temperature dependence behavior of these reactions has been discussed by Friedl and Sander.<sup>3</sup> The pressure dependence manifests itself as an observed rate constant that has both a nonzero bimolecular (zero-pressure) component and a pressuredependent component as in the CIO + CIO and IO + IO reactions.<sup>23,24</sup> Other well-characterized reactions that exhibit this behavior include  $HO_2 + HO_2$  and  $OH + CO.^{25,26}$  A qualitative understanding of the relationship between the observed pressure dependence and the potential energy surface can be obtained by the Lindemann model extended to reactions with multiple decomposition pathways for the vibrationally excited intermediate, i.e.

$$XO + YO \xrightarrow{k_{11}} XO - YO^* \xrightarrow{k_{d2}} \text{ products}$$

$$\downarrow^{k_2[M]}$$

$$XOYO$$

The following expressions are obtained from this model<sup>24</sup>

$$k_{\text{obsd}} = \frac{k_{1\text{f}}(k_{d2} + k_2[M])}{k_{d1} + k_{d2} + k_2[M]}$$
(III)

$$k_{\rm II} = \frac{k_{\rm 1f} k_{\rm d2}}{k_{\rm d1} + k_{\rm d2}} \tag{IV}$$

$$k_{\rm III} = \frac{k_{1\rm f}k_2}{k_{\rm d1} + k_{\rm d2}} \tag{V}$$

$$k_{\infty} = k_{1f} \qquad (VI)$$

$$[\mathbf{M}]_{1/2} = \frac{k_{d1} + k_{d2}}{k_2}$$
(VII)

where  $k_{obsd}$  = observed rate constant for reactant disappearance,  $k_{\rm II}$  = bimolecular ([M] = 0) rate constant,  $k_{\rm III}$  = termolecular component,  $k_{\infty}$  = high-pressure limiting rate constant, and  $[M]_{1/2}$ = bath gas density at which  $k_{obsd} = (k_{\infty} + k_{II})/2$ . As in the analogous formulation for single-channel reactions, the dependence of  $k_{\rm III}$  on the well depth is weak, arising mainly from the energy dependence of the density of states.

The discharge-flow and flash-photolysis studies, taken together, indicate that the observed rate constant for the BrO + ClO reaction is independent of pressure between 1 and 700 Torr. As indicated above, these observations set an upper limit of  $4 \times 10^{-32}$  $cm^6$  molecule<sup>-2</sup> s<sup>-1</sup> for  $k_{III}$ . In terms of the two-channel model, three alternatives are suggested by this result, namely, (a) the reaction is in the high-pressure limiting region in this pressure range  $(k_2[M] \ll k_{d1} + k_{d2})$ , (b) the reaction is in the low-pressure limiting region and  $k_{\rm III}$  is too small to result in a measurable change in  $k_{obsd}$  ( $k_2[M] \gg k_{d1} + k_{d2}$ ), and (c)  $k_{II}$  and  $k_{\infty}$  are nearly the same, which renders most the question of whether  $k_{III}$  is large or small. These cases will be dealt with individually

Considering possibility a, unless  $k_{II}$  is only marginally smaller than  $k_{\infty}$ , the fact that  $k_{obsd}$  is as large as  $1.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1 Torr implies a value for  $\bar{k}_{\rm III}$  of 4 × 10<sup>-28</sup> cm<sup>6</sup> molecule<sup>-2</sup>  $s^{-1}$  or greater. This would be difficult to reconcile with the termolecular rate constant observed for the ClO + ClO reaction at 298 K (about  $4 \times 10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>) although  $k_{\text{III}}$  for BrO + ClO would be expected to be larger because of the higher density of states in the BrO-ClO adducts. Considering possibility b, if  $k_{\infty}$  were considerably larger than the 298 K rate constant of 1.3  $\times$  10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> measured here, then with the upper limit of 5 × 10<sup>-32</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> determined for  $k_{\rm III}$ , pressures >50-100 atm would be required to achieve the high-pressure limit. This is a regime that is difficult to access experimentally.

The third, and most likely, interpretation is that  $k_{\rm II}$  and  $k_{\infty}$  are nearly the same. As a counterexample, if  $k_{\infty}$  exceeded  $k_{\rm II}$  by a measurable quantity, a factor of 2, then from eq IV and VI above

$$\frac{k_{\infty}}{k_{11}} = \frac{k_{1f}}{k_{1f}k_{d2}/(k_{d1}+k_{d2})} > 2$$

which can be rearranged to give

 $k_{d1} > k_{d2}$ 

For a two-channel process in which the entropies of activation of the decomposition steps are not too dissimilar (as would be the case if both channels involve simple bond fissions), this condition can be met only if the overall bimolecular process is endothermic as, for example, in the reaction

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad \Delta H_0 = -49.5 \text{ kcal mol}^{-1}$$
$$\rightarrow H + NO_3 \qquad \Delta H_0 = 51.8 \text{ kcal mol}^{-1}$$

This is not the case for the BrO + ClO reaction. The above observations would fit into a consistent picture if  $k_{\rm II}$  and  $k_{\infty}$  were very similar and if both BrO-ClO isomers were bound with respect to Br + OClO and Br + ClOO by a few kilocalories per mole. It should be noted that, while the overall reaction does not exhibit a large pressure dependence, the branching ratio for BrCl formation could change considerably without producing a measurable change in the OCIO and CIOO branching ratios. This effect was observed in the IO + IO reaction in which the branching ratio for the reaction channel forming  $2I + O_2$  decreased from 0.4 to 0.2 over the pressure range 20-650 Torr.<sup>24</sup>

Comparison with Previous Studies. The results of previous studies have been discussed in the discharge-flow mass spectrometry (DF/MS) paper. This study is in excellent agreement with the room-temperature measurements of  $k_1$  by Clyne and Wath the 10th temperature measurements of  $k_1$  by Cryne and Watson<sup>18</sup> ( $k_1 = 1.34 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and Toohey and Anderson<sup>27</sup> ( $k_1 = 1.4 \times 10^{-11}$ ). Significantly lower values of  $k_1$  (298 K) were obtained by Basco and Dogra<sup>28</sup> ( $k_1 = 2.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and Hills et al.<sup>29,30</sup> ( $k_1 = 8.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ ). In the only previous study of the temperature dependence of  $k_1$ , Hills et al. determined that  $k_1$  was approximately independent of temperature over the range 241-408 K. This result is in substantial disagreement with this study and our DF/MS study in which  $E_a/R$  values of 240 ± 60 and 320 ± 40 K were obtained, respectively. Several possible reasons for the discrepancy have been suggested by Friedl and Sander.<sup>3</sup> The only previous study of this reaction at total pressures greater than a few Torr was that of Basco and Dogra.

Previous measurements of ultraviolet ClO cross sections have been reviewed by DeMore et al.<sup>16</sup> Because the spectrum is only partly rotationally resolved due to predissociation, the effective cross section is a function of spectral bandwidth and comparison between different studies is difficult. There have been no previous studies of the temperature dependences of the apparent band-head cross sections below 298 K. Clyne and Coxon<sup>33</sup> determined the

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<sup>(29)</sup> Hills, A. J.; Cicerone, R. J.; Calvert, J. G.; Birks, J. W. Nature 1987, 328. 405.

<sup>(30)</sup> Hills, A. J.; Cicerone, R. J.; Calvert, J. G.; Birks, J. W. J. Phys. Chem. 1988, 92, 1853.

<sup>(31)</sup> Ray, G. W.; Keyser, L. F.; Watson, R. T. J. Phys. Chem. 1980, 84, 1674.

<sup>(32)</sup> Clyne, M. A. A.; Monkhouse, P. B.; Townsend, L. W. Int. J. Chem. Kinet. 1976, 8, 425.

<sup>(33)</sup> Clyne, M. A. A.; Coxon, J. Proc. R. Soc. London, A 1968, 303, 207.

following relationship for the CIO cross section at the 11–0 band head relative to the 298 K value for the temperature range 294 K < T < 450 K:

$$\sigma_{294}/\sigma_T = 1 + 0.0036(T - 294)$$

The relative cross section at 400 K from this relation is 0.72 compared with 0.94 for the 12–0 band from this study.

There has been only one previous study of the Br + Cl<sub>2</sub>O reaction, by Basco and Dogra.<sup>12</sup> The method employed by Basco and Dogra was virtually identical with the one used here. Br<sub>2</sub>-Cl<sub>2</sub>O mixtures were irradiated in a flash-photolysis apparatus with the reaction being followed by the formation of ClO. The rate constant obtained by Basco and Dogra at room temperature,  $k_3 = (1.0 \pm 0.08) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is considerably smaller than the value obtained in our study,  $(3.8 \pm 0.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The large discrepancy in the results for  $k_3$  between the two studies is puzzling in view of the similarity between the methods. The primary differences between the two studies are the use by Basco and Dogra of very high initial Br concentrations (factor of 300 larger than ours) and their use of a filter to limit photolysis to wavelengths longer than 440 nm (vs  $\simeq 300$  nm in our system). The use of high ClO concentrations might be troublesome if ClO loss by the CIO + CIO reaction were competitive with CIO formation by reaction 3. At the total pressures used by Basco and Dogra (200 Torr of argon), this effect would be minimal. The difference in photolysis cutoff wavelengths between the two experiments also does not explain the discrepancy. While there is some Cl<sub>2</sub>O photolysis at 300 nm, the effect only produces a small amount of prompt ClO, which has no effect on reaction 3. Atomic chlorine produced in the photolysis reacts rapidly with Br<sub>2</sub> to produce Br, which is also produced in the photolysis flash. As noted by Ray et al.,<sup>31</sup> the determination by Basco and Dogra in the same study of the rate constant for the  $Cl + Cl_2O$  reaction was underestimated by more than a factor of 100. This suggests that there may have been a systematic error in their method for determining [ClO] that affected their analysis of the  $Br + Cl_2O$ reaction as well.

There have been several previous studies of the gas-phase photolysis of  $Cl_2O$ . Finkelnburg et al.<sup>13</sup> measured the quantum yield in the chlorine-photosensitized decomposition of  $Cl_2O$  at 436, 365, and 313 nm while Schumacher and Townend<sup>14</sup> carried out

the same experiments at 275 and 235 nm. Quantum yields were obtained that increased from 3.5 to 4.5 as the photolysis wavelength decreased. These observations were explained by assuming that the process

$$Cl_2O + h\nu \rightarrow 2Cl + O$$
 ( $\lambda < 294 \text{ nm}$ ) (4c)

became the dominant photolysis channel at the shorter wavelengths. Edgecombe et al.<sup>15</sup> and Basco and Dogra<sup>12</sup> used the flash photolysis technique to photolyze Cl<sub>2</sub>O with and without added Cl<sub>2</sub>. Both studies observed the kinetics of ClO, Cl<sub>2</sub>O, OClO, and Cl<sub>2</sub> in these systems. Edgecombe et al. reinterpreted the results of the Schumacher studies<sup>13,14</sup> as suggesting that the increased quantum yield at the shorter photolysis wavelengths was due to the combined effect of reaction 4c and the reaction

$$O + Cl_2O \rightarrow 2ClO$$

which was assumed to be slow in the earlier work. Basco and Dogra<sup>12</sup> measured quantum yields of  $4.9 \pm 1.0$  in both the direct and chlorine-sensitized photolysis experiments. The interpretation of all these experiments was hampered by an incomplete understanding of the rates and products of the ClO + ClO reaction, which was assumed to produce only Cl<sub>2</sub> and O<sub>2</sub>. Both Edgecombe et al. and Basco and Dogra assumed that the OClO observed in their experiments was due to the reaction

$$ClO + Cl_2O \rightarrow OClO + Cl_2$$

when, in fact, the ClO + ClO reaction can account for the OClO observed. Because of these complications, it is difficult to compare the branching ratios for  $Cl_2O$  photolysis from the earlier studies with the results from the present work.

It is not possible to determine from this study the relative importance of channels 4b and 4c. Further work on  $Cl_2O$  photolysis should focus on the wavelength-resolved yields for Cl and O atom production to determine whether channel 4c is operative beyond the threshold wavelength of 294 nm.

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**Registry No.** BrO, 15656-19-6; CIO, 14989-30-1; OCIO, 10049-04-0; Br, 10097-32-2; Cl<sub>2</sub>O, 7791-21-1; O, 17778-80-2.