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Kinetics of the BrO + ClO reaction and implications for stratospheric ozone

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The gas-phase reaction between BrO and ClO has been proposed as a potentially fast and synergistic mechanism of stratospheric ozone destruction. Further, it has been advanced¹ as a contributing factor to Antarctic springtime ozone column losses of ~40% from 1960 to 1985^{2,3}. Both dynamical⁴ and chemical theories^{1,5-8} have been advanced to explain the formation of the Antarctic 'ozone hole'. A major uncertainty in these theories has been the rate constant and product distribution of the BrO + ClO reaction as a function of temperature. Here we report the first direct measurements of these parameters. We show that this reaction could, indeed, account for a large fraction of the springtime ozone depletion over Antarctica and provide a source of chlorine dioxide of sufficient magnitude to explain the recent measurements of this species in the Antarctic stratosphere, provided that the stratosphere contains a sufficient quantity of bromine (~20 p.p.t.v.).

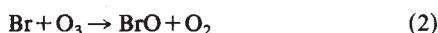
The reaction of BrO with ClO has the following accessible product channels:



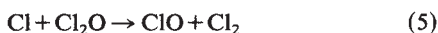
The sets of products Br + ClOO and BrOO + Cl are also possible, but we do not distinguish these from channel (1b) because of the rapid thermal dissociation of ClOO and BrOO to halogen atoms and molecular oxygen, both in our laboratory experiments and in the stratosphere.

We performed the kinetics investigations using the technique of discharge-flow mass spectrometry^{9,10} using the apparatus described in a recent publication¹¹. Figure 1 is a schematic diagram of the apparatus configuration. Selected ion monitoring measured the concentrations of all molecular species (for example, Cl₂, ClO, OClO, Cl₂O, Br₂, BrO, BrCl, NO and NO₂) during each experiment.

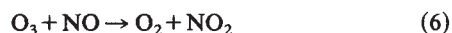
BrO and ClO were produced in separate flow streams via microwave discharge of trace Br₂ and Cl₂ in He to produce Br and Cl atoms, respectively, which were then reacted with ozone:



To determine whether the means of producing ClO influenced the experimental results, ClO was produced in two additional ways, by reaction of chlorine atoms with OClO and with Cl₂O:



Ozone concentrations were measured by reaction with excess NO



to substitute a stoichiometric amount of NO₂ for O₃. Absolute

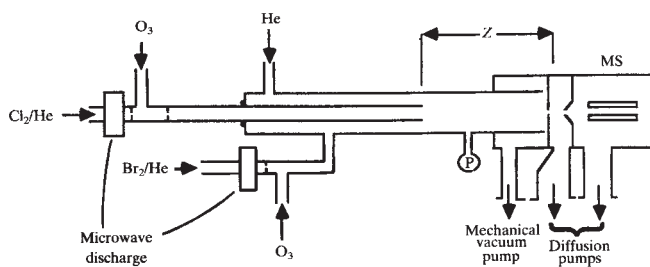
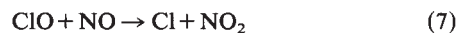


Fig. 1 Discharge-flow apparatus as configured for measurement of the rate constant and product distribution of the BrO + ClO reaction. ClO radicals are produced in the moveable inlet by microwave discharge of Cl₂ diluted in He and reaction of the Cl atoms with O₃. BrO radicals are produced analogously by reaction of Br with O₃ and are introduced to the flow tube via a fixed inlet. Reaction time is varied by moving the ClO source relative to the first sampling orifice of a differentially pumped quadrupole mass spectrometer. Reaction time is computed from this distance, Z, and the velocity of the carrier gas. The latter is established by a mechanical vacuum pump and is calculated from measurements of the total flow rate of gases into the flow tube, the cross-sectional area of the flow tube, and the pressure and temperature of the reaction zone.

calibration of NO₂ as an ion current at $m/e = 46$ was achieved by admitting known concentrations to the flow tube. The concentrations of ClO and BrO radicals were measured analogously to that of ozone via the reactions



and



Again, an excess of NO results in stoichiometric substitution of NO₂ for the species of interest, here either ClO or BrO.

The flow tube and both inner and outer surfaces of the movable injector were coated with phosphoric acid to reduce wall losses of reactive species. First-order losses of ClO and BrO on the flow-tube wall were measured at various times during this work and were always found to be negligible ($< 2 \text{ s}^{-1}$). All of the kinetics measurements were made under pseudo-first-order conditions, $[\text{ClO}]_0 \gg [\text{BrO}]_0$. This condition was checked via measurement of the ClO and BrO concentrations and by observing the linearity of pseudo-first-order decay plots. Helium served as the carrier gas, and the total pressure in the flow tube was in the range 1.1–1.5 torr.

A typical decay plot showing the loss of BrO in the presence of excess ClO is shown in Fig. 2. The upper plot shows BrO measurements taken with the ClO discharge turned off. This blank is performed to account for BrO destruction due to any heterogeneous loss of BrO on the injector surface. At all temperatures the slope of this plot was $< 1 \text{ s}^{-1}$, indicating negligible BrO surface loss. The lower plot shows the change in BrO signal as a function of increasing BrO + ClO reaction time. The negative value of the slope of a plot of $\ln(\text{BrO})$ against time is a first-order rate constant, k^1 . The bimolecular rate constant was calculated

Table 1 Data summary for the rate coefficient measurements

Number of measurements	Temperature (K)	k ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)*
32	241	8.0 ± 1.1
69	305	8.4 ± 1.0
13	408	8.3 ± 0.8

Average value: 8.2 ± 1.0 ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) where the uncertainty corresponds to the 95% confidence level and includes both random and possible systematic errors.

* Error shown is one standard deviation (precision only).

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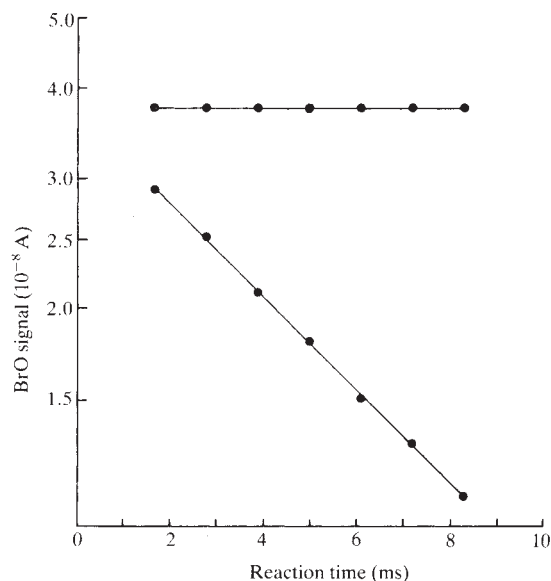


Fig. 2 Typical kinetics data for the BrO + ClO reaction. The upper plot is the variation in BrO ion current as a function of movable inlet position with the ClO source turned off. The lower plot shows the decrease in BrO signal as a function of injector position in the presence of excess ClO. Reaction conditions: $P = 1.30$ torr, $T = 305$ K, $[\text{ClO}] = 1.58 \times 10^{13}$ molecule cm^{-3} . The measured value of $k^1 = 142.7 \text{ s}^{-1}$ gives the result $k_1 = 9.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for this particular run.

for each kinetics run using the equation

$$k = \frac{k^1}{[\text{ClO}]}$$

Table 1 summarizes the results of 114 measurements of the rate constant for reaction 1 made in the temperature range 241–408 K. Within experimental error, the rate constant, k_1 , did not vary with temperature. Taking into account both random and possible systematic errors, we report $k_1 = (8.2 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the total rate constant for the reaction forming all possible products.

The branching ratio into channel 1a, Br + OCIO products, was measured by first calibrating ClO relative to OCIO. The reaction



was used in these calibrations. Ion currents at $m/e = 67$ and 51 were monitored as the Cl_2 discharge (Cl source) was turned on and off. The $\Delta m/e = 67$ signal was directly proportional to $[\text{OCIO}]$ change resulting from reaction 4. The $\Delta m/e = 51$ signal was the result of both changes in $[\text{ClO}]$ and $[\text{OCIO}]$ as the Cl source was modulated, because OCIO fragments by $\sim 50\%$ into ClO. The $m/e = 51$ signal was corrected for OCIO contribution using the method of Birks *et al.*⁹. The branching ratio into channel 1a was measured by monitoring $\Delta[\text{OCIO}]/\Delta[\text{ClO}]$ as BrO was turned on and off. The BrO source was modulated either by turning the Br_2 discharge on and off or by leaving it

on but interrupting the flow of Br_2 through the discharge.

The branching fraction into channel 1c, $\text{BrCl} + \text{O}_2$ products, was measured in a similar manner to that of channel 1a. The value $\Delta[\text{BrCl}]/\Delta[\text{ClO}]$ was measured as BrO was modulated. To measure the relative sensitivities of BrCl at $m/e = 116$ and ClO at $m/e = 51$, either excess Br_2 or excess O_3 was added to a stream of chlorine atoms to produce equal amounts of BrCl or ClO, respectively, according to the reactions:



The BrCl/ClO sensitivity ratio was determined over a wide range of concentration by varying the flow rate of Cl_2 through the microwave discharge. Modulation of the BrO source in the presence of ClO was found to result in a large modulation of the BrCl ion current at $m/e = 116$. However, this was found to be due to a secondary reaction of Cl atoms produced in channel 1b with Br_2 (reaction 9). The corresponding reaction of Br with Cl_2 is endothermic by $5.7 \text{ kcal mol}^{-1}$ and thus does not contribute to the BrCl signal. Addition of isobutane to the flow tube allowed Cl atoms to be removed from the reaction system. Under these conditions, no BrCl product could be detected.

The fast secondary reaction of Cl with Br_2 (reaction 9) allowed channel 1b to be quantified. By using a sufficiently large concentration of Br_2 (6×10^{13} molecules cm^{-3}), reaction 9 was forced to completion, and the branching ratio into channel 1b

Table 2 Summary of product distribution experiments

Temperature (K)	Number of experiments	Reaction products	Branching ratio ($\pm \sigma$)
305	18	(1a), Br + OCIO	0.53 ± 0.04
241	7	(1a), Br + OCIO	0.50 ± 0.01
305	9	(1b), Br + Cl + O ₂	0.44 ± 0.02
241	10	(1b), Br + Cl + O ₂	0.42 ± 0.05
305	4	(1c), BrCl + O ₂	0.00
Temperature averaged, sum of: (1a) + (1b) + (1c) = 0.95			
Temperature averaged branching ratios, normalized to 1.00:			
		Br + OCIO	$0.55 \pm 0.10^*$
		Br + Cl + O ₂	$0.45 \pm 0.10^*$
		BrCl + O ₂	$\leq 0.02^*$

* Uncertainty includes σ and an estimate of possible systematic errors.

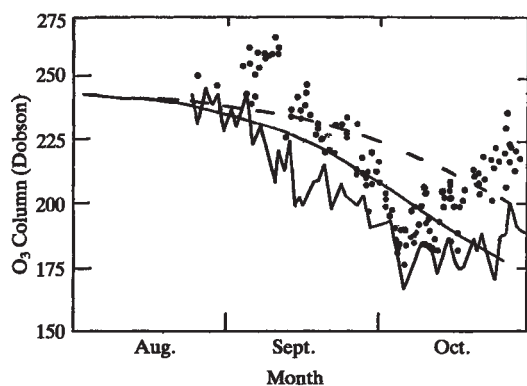


Fig. 3 Calculated time-dependent behaviour of the ozone column above 16 km at 80° S according to the model of Rodriguez *et al.*⁸ A mixing ratio of 20 p.p.t.v. inorganic bromine is assumed. Solid line: results using the rate constant of Clyne and Watson¹² for channel 1a of the BrO+ClO reaction; dashed line: results using the rate constant reported here. Model calculations do not allow ozone depletion due to photolysis of the ClO dimer. Satellite data³ for 74° S–78° S are observations over Halley Bay (points) and the minimum over all longitudes (jagged line).

is given by $\Delta[\text{BrCl}]/\Delta[\text{ClO}]$ upon modulation of the BrO source.

The measured branching ratios are summarized in Table 2. Independent measurements of channels 1a and 1b added to 95%, invariant of temperature in the range 241–408 K. The 5% discrepancy is certainly within the experimental error of the measurements. We attribute all of the products to channels 1a and 1b and recommend a branching ratio of 0.55 ± 0.10 for channel 1a and 0.45 ± 0.10 for channel 1b. Complete details of the measurements of the rate constant and product distribution for this reaction, including an analysis of all possible interfering reactions, will be reported elsewhere.

Combining the results of the measurements of the rate constant for product loss with the branching ratio for channel 1b gives a value of $3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for k_{1b} . This is 45% smaller than the value of $6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured by Clyne and Watson¹² and used in recent model calculations^{1,8}. In the pioneering work of Clyne and Watson, ClO and BrO were produced simultaneously by the reaction

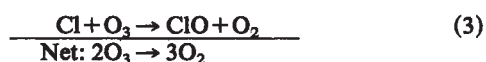
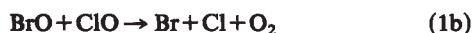


and the decays of BrO, ClO and OCIO monitored with time. Because reaction 10 is the reverse of reaction 1a, an equilibrium among the species of this reaction was approached. The lack of pseudo-first-order kinetics and interference from the reaction



also compromise the accuracy of this earlier study, which required computer modelling to extract the rate constant and branching ratios. Considering these complications in interpretation of the earlier work, the agreement of our work with that of Clyne and Watson is quite good.

Reaction 1 is of significance to the Antarctic stratosphere in that (1) it could provide a rapid means of ozone depletion, and (2) it could explain the recent observation of OCIO in this region of the atmosphere¹⁴. The catalytic cycle



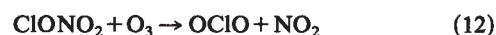
is particularly significant in that it does not require sunlight or atomic oxygen to destroy ozone. A major difficulty of all theories of the Antarctic ozone hole based on chlorine-catalysed ozone

depletion is the low concentrations of ClO expected for this region of the atmosphere. Until recently, the predominant forms of chlorine in the polar stratosphere were predicted by atmospheric models to be chlorine nitrate and HCl. Some theories invoke heterogeneous reactions on stratospheric cloud particles^{1,5,8} to convert oxides of nitrogen to nitric acid. Other theories rely on the condensation of nitric acid itself to form the polar stratospheric clouds^{6,7}. In this way the ClO concentration of the polar stratosphere is increased. In any case, measurements made by de Zafra during the 1986 National Ozone Expedition showed anomalously high ClO in the lower stratosphere of Antarctica¹³.

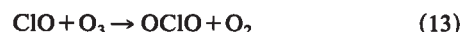
In Fig. 3, computer model results, incorporating our new value for k_{1b} are compared with earlier model results (see ref. 8 for details of the model) using the rate constant of Clyne and Watson and with observations of the ozone column³. Although our reduced rate constant results in less predicted ozone depletion, the possibility of a large fraction of the observed ozone depletion being due to the BrO+ClO reaction is still indicated if there is as much as 20 p.p.t.v. total inorganic bromine there.

The recent and unprecedented observation of OCIO in the Antarctic stratosphere¹⁴ and of its diurnal variation indicate that ClO is undergoing rapid cycling in this region of the atmosphere. The observed total column amounts of OCIO were found to be about 20–50 times larger than would be expected for standard homogeneous photochemistry. Furthermore, the BrO+ClO reaction is the only gas-phase reaction demonstrated to yield OCIO as a product. Thus, the observation of OCIO in the stratosphere is strong circumstantial evidence for channel 1a of the BrO+ClO reaction. If this channel is operative, the ozone destruction channel, channel 1b, is also operative.

We caution that other, as yet unknown reactions could possibly be the source of OCIO. In particular, the reactions



and



have been shown to be extremely slow in the gas phase⁹, but could possibly take place on the surfaces of polar stratospheric clouds. Assuming a particulate surface area⁷ of $10^{-7} \text{ cm}^2 \text{ per cm}^3$, the time constant for collision of any molecule with an aerosol particle is about 1 h. It was reported earlier that reaction 13 does take place on the surface of an uncoated silica flow tube at 298 K⁹. However, the surface-to-volume ratio in that reactor was $\sim 10^7$ times larger than that of polar stratospheric clouds. Molina and Molina¹⁵ have postulated the photolysis of the ClO dimer both as a possible source of OCIO and as a catalytic reaction for ozone destruction. However, the photolysis products of $(\text{ClO})_2$ have not yet been determined.

With respect to effects on ozone, the fate of OCIO produced in reactions 12 and 13 would most often be photolysis to regenerate ClO and produce atomic oxygen, which in turn reforms ozone. Therefore, these reactions, while producing OCIO, would be expected to have little effect on the ozone column. Laboratory studies of these and other heterogeneous reactions that might produce OCIO are called for. But such reactions remain speculative. Based on our present knowledge of reactions of chlorine species, the BrO+ClO reaction appears to be a potentially important reaction contributing to the formation of the ozone hole.

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High concentrations of chlorine monoxide at low altitudes in the Antarctic spring stratosphere: diurnal variation

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The Stony Brook ground-based remote sensing mm-wave spectrometer was used to measure chlorine monoxide in the stratosphere over McMurdo Station, Antarctica during the austral spring of 1986. From the data collected, we find strong evidence for abnormally high concentrations of ClO at low altitudes—as much as two orders of magnitude greater than standard theories predict at 20-km altitude at mid-latitudes. This low-altitude ClO changes cyclically on a diurnal basis, and also secularly during the September–October observing period. A study of the diurnal variation of the low-altitude ClO is presented here. We conclude that chlorine is crucially involved in the springtime destruction of Antarctic ozone.

The recently discovered and rapidly increasing depletion of ozone in the Antarctic spring seasons since the late 1970s^{1,2} has led to the suggestion of a variety of mechanisms to explain the phenomenon. Chemical theories involving chlorine have been likely candidates, due to the steady increase in chlorocarbons and chlorofluorocarbons reaching the stratosphere over the same time span. Other factors, so far unique to Antarctica, must also come into play however, or the observed large seasonal depletion of ozone would be seen on a worldwide basis.

The observation of large concentrations of ClO in the lower stratosphere (12–22 km) where the major depletions associated with the anomalous ozone hole are occurring³ would be strong evidence that chlorine chemistry is implicated in the phenomenon (perhaps augmented, but not replaceable, by other proposed mechanisms (for example refs 4–6)). Here we present evidence that just such large concentrations of ClO, exhibiting a strong diurnal variation, do exist at low altitudes during the Antarctic spring.

The presence of chlorine monoxide (ClO) in the middle to upper stratosphere is a direct indication of the catalytic conversion of O₃ to O₂ by chlorine. ClO has a mixing ratio profile determined by the balance between a number of photolytic and chemical reactions⁷. Under normal stratospheric conditions, the mixing ratio peaks at ~38 km⁸ and decreases rapidly with decreasing altitude below this level, at a rate of roughly 30% per km. The normal mixing ratio of ClO is predicted to be ~10⁻¹² at 20 km at tropical and temperate latitudes. One *in situ* balloon measurement exists down to ~22 km where ClO mixing ratios of ~10⁻¹¹ have been established⁸. In past ground-based mm-wave emission spectroscopy measurements^{9,10} we have been able to determine the chlorine monoxide mixing ratio profile down to ~28 km, below which the combination of emission-line pressure broadening and low mixing ratio yield a line-shape contribution too broad and weak to be reliably detected.

The chlorine-related ozone depletion theories for Antarctica have generally invoked various heterogeneous (surface) reactions on aerosols or 'ice' grains in an effort to speed up the rate of ozone destruction, as conventional gas-phase reactions have been shown^{11–13} to be too slow to account for the average rate of depletion observed in the Antarctic spring. New reaction routes involving ClO dimer formation¹⁴ and BrO+ClO reactions¹¹ have also been proposed to augment the rate of ozone depletion. The purely chemical theories also require low concentrations of NO_x, assumed to follow from sequestration of nitrogen in HNO₃ during the polar night. This prevents the suppression of active chlorine via reactions with NO_x.

During the National Ozone Expedition of 1986 at McMurdo Station, Antarctica, frequent balloon soundings of ozone were made up to 30-km altitude by Hofmann *et al.*³. These showed that ozone depletion, at least in the outward reaches of the polar ozone hole typically observed over McMurdo during the spring of 1986, occurs in highly structured layers, and may reach >90% reduction in selected layers within two months after the Antarctic spring sunrise exposes the stratosphere to photolytic chemistry. These observations pose an even more severe requirement on the depletion speed than previously realized.

Here we concentrate on the relatively early time period from 1–22 September, to emphasize the observed ClO concentration

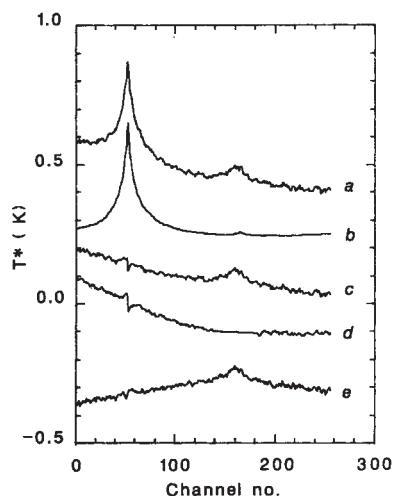


Fig. 1 Steps used in processing raw data, shown as curve (a). Curve (b) is a synthesized ozone background, including the $v_2 = 1$, $J = 18_{1,17} \rightarrow 18_{0,18}$ transition (left) and the much weaker $v_1 = 1$, $J = 14_{4,10} \rightarrow 15_{3,13}$ transition (near centre). Curve (c) = (a) - (b) and shows that residual instrumental curvature remains. Curve (d) is night-time data for >4 h after sunset at 45 km, with the remaining ClO signal suppressed. It contains the same instrumental curvature as (c). Curve (e) = (c) - (d).