IN SITU MEASUREMENTS OF BrO IN THE ARCTIC STRATOSPHERE

D. W. Toohey and J. G. Anderson

Department of Earth and Planetary Sciences and Department of Chemistry,
Harvard University, Cambridge, Massachusetts

W. H. Brune

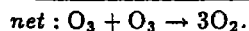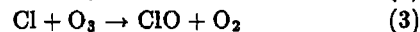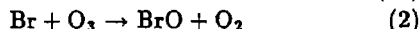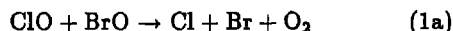Department of Meteorology, Pennsylvania State University, University Park

K. R. Chan

NASA Ames Research Center, Mountain View, California

Abstract. Mixing ratios of BrO have been measured in the arctic lower stratosphere with an instrument mounted on the NASA ER-2 aircraft. Observations from fourteen flights above the Arctic Circle in January and February of 1989 defined mixing ratios within the vortex of 4 ± 2 parts per trillion by volume (pptv) at a potential temperature of 400 K, rising to 8 ± 2 pptv at 470 K. These values are twice as large as values found at equivalent potential temperatures at lower latitudes, and are comparable to the mixing ratios found inside the antarctic polar vortex. Within the statistical uncertainty of the measurements, no BrO was observed in darkness at any time either inside or outside of the vortex, indicating that active bromine was sequestered in long-lived reservoirs, probably $BrONO_2$ and $BrCl$. These measurements, in conjunction with measurements of ClO, demonstrate that the interaction of bromine and chlorine could represent a major sink for ozone in the presence of sunlight.

Introduction

The suggestion that bromine compounds released at the earth's surface could destroy ozone in the stratosphere was first made in 1975 [Wofsy et al., 1975]. During the following decade, while research efforts focussed on quantifying the effects on ozone of chlorine atoms released by photolysis of chlorofluorocarbons in the stratosphere, bromine largely remained ignored. Only recently, after massive seasonal losses of ozone over Antarctica were reported, has this disparity been reduced. A renewed interest in bromine chemistry was initiated in part by the suggestion [McElroy et al., 1986] that bromine oxide (BrO) in the presence of enhanced concentrations of chlorine oxide (ClO) within the antarctic polar vortex could lead to substantial losses of ozone through the catalytic cycle

$$ClO + BrO \rightarrow Cl + Br + O_2 \qquad (1a)$$
$$Br + O_3 \rightarrow BrO + O_2 \qquad (2)$$
$$\underline{Cl + O_3 \rightarrow ClO + O_2} \qquad (3)$$
$$net: O_3 + O_3 \rightarrow 3O_2.$$

In contrast with the knowledge of chlorine chemistry obtained from fifteen years of in-situ and laboratory studies [WMO Report 16, 1986], analogous processes involving bromine remain poorly understood. Although the reactivities of related bromine and chlorine species are often similar, there are some important differences. Consequently, BrO represents a large fraction of the total

inorganic bromine budget [Yung et al., 1980], which is estimated to be less than 15 pptv [Brune and Anderson, 1986]. Yet these concentrations of BrO are small and pose a serious challenge to both ground-based and in-situ instruments.

The presence of BrO in the antarctic vortex was inferred from ground-based spectroscopic observations of OClO from McMurdo Station in 1986 [Solomon et al., 1987]. OClO, formed in the atmosphere primarily by the reaction

$$ClO + BrO \rightarrow OClO + Br, \qquad (1b)$$

was observed during twilight and in total darkness. The observed slant-column depths were consistent with enhanced abundances of ClO and the upper limit of 15 pptv of BrO established by midlatitude balloon measurements.

The first successful in-situ measurements of BrO in the stratosphere were made in the southern hemisphere during the AAOE campaign of 1987 [Brune et al., 1989a]. These observations showed that BrO mixing ratios within the southern polar vortex, ranging from 5 to 7 pptv, were somewhat enhanced compared to values found outside the vortex. Complementary ground-based studies of BrO and OClO during the same season [Solomon et al., 1989] provided additional strong evidence for occurrence of reaction (1) as well as information regarding the importance of a long-lived reservoir of BrO at night. From the slant-column measurements and a photochemical model, a mixing ratio of ≈ 7 pptv was derived for BrO, and it was concluded that photolysis of $BrONO_2$ in the morning twilight was more consistent with the observations than was photolysis of $BrCl$, a species formed by yet another channel of reaction (1),

$$ClO + BrO \rightarrow BrCl + O_2, \qquad (1c)$$
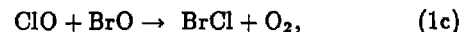
which represents about 10% of the overall reaction in laboratory studies [Toohey and Anderson, 1988; Friedl and Sander, 1989]. The ER-2-based observations, which were carried out in daylight, were unable to address this photochemical issue. However, they did demonstrate that a significant fraction ($\approx 20\%$) of the ozone depletion observed over Antarctica in 1987 was due to the catalytic cycle rate limited by the reaction of ClO with BrO [Anderson et al., 1989].

Several experiments were carried out in early 1988 to examine bromine and chlorine within the arctic vortex. Ground-based observations of OClO provided strong evidence again for the presence of BrO and enhanced concentrations of ClO inside the vortex [Solomon et al., 1988], while an in-situ study with the ER-2-based ClO-BrO instrument detected evidence of perturbed halogen chemistry outside the vortex [Brune et al., 1988]. We report here the results of recent measurements of BrO obtained during the AASE mission to the arctic stratosphere in January and February of 1989. As in the

companion paper that reports ClO observations [Brune et al., this issue, a], we will focus on three of the fourteen flights from Stavanger, Norway, across the Arctic Circle that occurred over the period from January 3 to February 10, 1989. In addition, we will draw upon measurements obtained on December 29, 1988, during a transit flight which passed over the continental United States. These results will be compared to previous measurements of BrO obtained over Antarctica and Canada in 1987 and 1988.

Experiment

The ClO–BrO instrument, which was mounted in a pod on the left wing of the NASA ER-2 aircraft, has been described in detail elsewhere [Brune et al., 1989b]. Detection of BrO is accomplished through addition of nitric oxide to a flow of air which is decelerated to ≈ 20 m s^{-1} with a double-ducted flow system. The reaction of BrO with NO is greater than 95% complete within 10 to 15 ms at the NO concentrations added ($\approx 10^{13}$ molecules cm^{-3}); the bromine detection system is positioned approximately 25 ms downstream of the NO injector. Bromine atoms formed by this reaction are then detected by resonance fluorescence with a density-dependent sensitivity ranging from $\approx 10^{-6}$ cts s^{-1}/(Br atom cm^{-3}) at the highest flight altitudes achieved, to $\approx 3 \times 10^{-7}$ cts s^{-1}/(Br atom cm^{-3}) at the minimum altitude the aircraft could sustain to allow for sufficient signal averaging. For background signals (which were also density dependent) of 5000 cts s^{-1}, a detection limit of $\approx$ (2–3) cts s^{-1} was obtained for signal averaging of one hour at most altitudes. Thus, BrO mixing ratios of 6 pptv could be detected with typical signal-to-noise ratios of 3 to 5.

The bromine lamp employed for the first half of the campaign was the same lamp as that used during the AAOE flights, the February flight series based at Moffett Field [Brune et al., 1988], and all test flights. This system has been calibrated at four separate instances. Both the absolute calibration (when scaled to the total background signal at an air density of 2.6×10^{18} molecules cm^{-3}) and the pressure dependence have varied less than 10% over more than 200 hours of operation in the stratosphere and in the laboratory. Calibrations used the rapid reaction of a measured amount of chlorine atoms with molecular bromine, and is described elsewhere [Brune et al., 1989a]. After the flight of January 30, 1989, this lamp was removed. The replacement lamp was calibrated after the flight series, and concentrations of bromine measured with this lamp over the last seven flights of the campaign were in good agreement with values observed during the first half of the flight series. Therefore, although the laboratory calibrations for the two lamps were different, there appears to be no significant systematic difference between bromine concentrations determined with the two systems.

Upon addition of nitric oxide to convert BrO to Br there is a small absorption of the background nonresonant scatter. By reproducing flight conditions in the laboratory, this correction to the bromine signal has been measured to be smaller than 10^{-17} cm^2 (molecule NO)$^{-1}$ for the lamps employed in these flights. In practice, accounting for this absorption leads to a positive offset of less than 1.5 pptv. Overall, it is estimated that the uncertainty in the BrO calibration is $\pm 35\%$ at the 2σ confidence level.

Observations

A typical ER-2 flight track consisted of a rapid ascent to maximum altitude, a hold at some potential temperature between 440 and 470 K while flying up the Norwe-

gian coast and then toward Spitzbergen, a turn-around at approximately local noon with a dive for a vertical scan, and finally a return leg at a different potential temperature back to Stavanger. These flight tracks were similar to those employed out of Punta Arenas, Chile, during the AAOE mission [Tuck et al., 1989]. We have selected three flights that illustrate key features of the bromine observations that were evident on most of the fourteen flights. Taken together, the flights of January 6, January 16, and February 10, sampled both inner- and outer-vortex air, and sampled inner-vortex air that was both illuminated and in total darkness. In addition, these flights, which span the entire series, serve to define the temporal evolution of BrO during the mission.

The BrO measurements for three flights appear in Figures 1 through 3, overlaid by the measurements of ClO. While these latter measurements are described in detail elsewhere [Brune et al., this issue, a], there are some important points that deserve review here. First, throughout the mission, every flight into the polar vortex revealed highly perturbed concentrations of ClO. Clearly, a significant fraction of the vortex air had been processed by polar stratospheric clouds (PSCs), at least at altitudes accessible to the ER-2. Both ClO and BrO are sensitive to concentrations of NO_2, which were significantly depleted within the vortex [Fahey et al., this issue]. The observations of high concentrations of ClO in air that has been in total darkness for at least 20 hours leads to the conclusion that a considerable fraction of ClO was bound up in a form other than $ClONO_2$. It is likely that the less stable species ClOOCl represents the major nighttime reservoir of ClO. Finally, as the mission progressed, the mixing ratios of ClO rose from several hundred pptv to over 1100 pptv by February 10. This increase was most likely due to increasing solar illumination with continued processing of air by PSCs.

The results for the first flight to encounter highly perturbed ClO, on January 6, appear in Figure 1. The potential temperature and solar zenith angles (SZA) for the entire flight track are shown by Brune et al. [this issue, a]. Interestingly, BrO was highest where ClO was low, and there was no BrO where ClO was highly perturbed. However, upon consideration of the SZA, we note that regions in which no BrO was observed were at very high angles, in this flight greater than 92°. Inversely, portions of the January 6 flight where BrO mixing ratios were high occurred where the ClO was low. The mixing
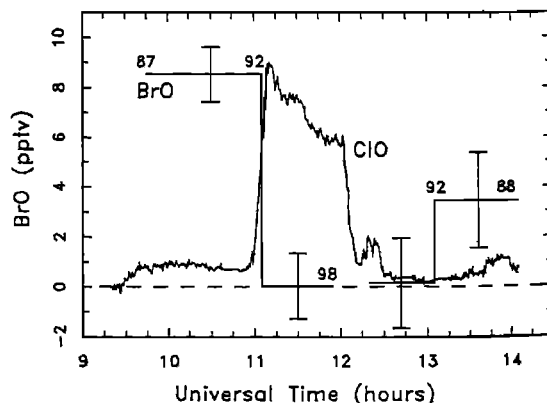

Fig. 1. Overlay of BrO and ClO mixing ratios for the flight of January 6, 1989. Horizontal bars represent time over which signal was averaged to obtain the 1σ statistical uncertainties represented as vertical bars. Numbers indicate solar zenith angles corresponding to various positions along the flight track. ClO axis units are unspecified.

ratio of BrO was 8.5±1.2 pptv along the outbound leg, which was flown at a potential temperature of 475 K, and 3.5±2 pptv along the inbound leg flown at 413 K. Even at this early stage in the flight series these BrO values were greater than values observed at comparable altitudes at midlatitudes and were similar to values observed within the antarctic vortex [Brune et al., 1989a]. Although ClO mixing ratios were relatively low at the start and the end of the flight, these outer-vortex values (25 pptv) were still considerably larger than values measured at midlatitudes at comparable altitudes and SZA [Brune et al., this issue, b], and thus represent a perturbation from typical midlatitude values.

The results obtained on January 16 were similar to those of January 6, and are shown in Figure 2. The mixing ratios of ClO were highly perturbed throughout the entire flight, while the behavior of BrO was identical to that for the flight of January 6. Once again, no BrO was observed at SZA greater than 92° and BrO values in sunlight were moderately high, even at a potential temperature of 400 K on the inbound leg. Within the statistical uncertainties of the measurements (typically ±1.5 pptv), at no time during any flight was BrO observed at solar zenith angles greater than 94°. At SZA greater than 90°, photolysis rates of $BrONO_2$ and BrCl decrease rapidly as the sun approaches the horizon (which is near 94° SZA at maximum ER-2 flight altitudes) [Solomon et al., 1989]. Thus, in darkness, BrO was likely sequestered in $BrONO_2$ or BrCl, or both. These observations also indicate that destruction of ozone by the catalytic cycle rate limited by the BrO + ClO reaction was terminated in darkness, even though ClO remained at moderate concentrations. In addition, the observations of zero BrO are important because they add confidence that the small offset due to absorption by NO is valid.

Results of the last arctic flight of the AASE campaign, on February 10, are summarized in Figure 3. The ER-2 flew over Iceland and Greenland staying in sunlight for the entire flight. Here, both the BrO and the ClO profiles strongly resemble those obtained over Antarctica [Brune et al., 1989a]. Within the arctic vortex the BrO mixing ratio was 8±2 pptv at 470 K. However, values outside the vortex were low (1–4 pptv), similar to those observed at midlatitudes. The mixing ratios of ClO early in the outbound leg and late in the return leg were the lowest values measured in sunlight during the latter half of the campaign. Indeed, meteorological analysis indicated that this outer-vortex air was drawn from significantly lower latitudes than earlier in the mission (D. S. McKenna, personal communication, 1989).
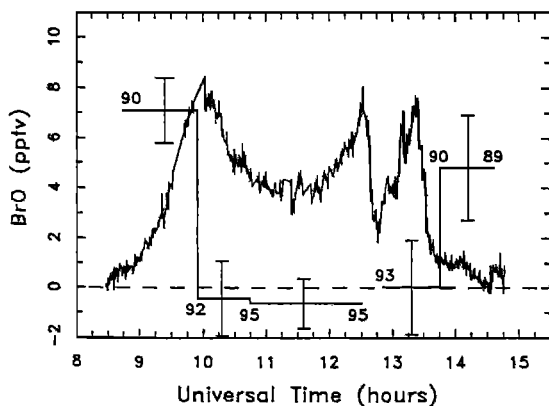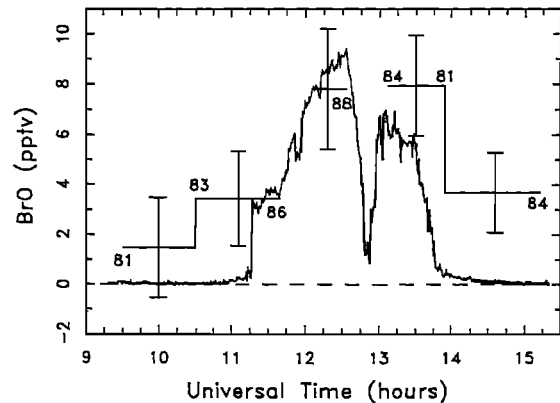

Fig. 3. Overlay of BrO and ClO mixing ratios for the flight of February 10, 1989. Data are represented as described in Figure 1 caption.

Near the end of the campaign, a number of measurements within sunlit portions of the vortex yielded values of 6 to 8 pptv (independent of SZA when SZA was less than 90°), while measurements obtained when ClO mixing ratios were observed to be low yielded values of 2 to 4 pptv. To highlight these differences, and also to compare to the measurements of BrO from over Antarctica, we plot the measurements as a function of potential temperature in Figure 4. Data obtained in air that had ClO mixing ratios typical of those found at midlatitudes are plotted as open symbols. Also included are data from the transit flight of December 29, 1988, which passed over the continental United States. There was indeed BrO enhancement within the two vortices, but much less than corresponding enhancements of ClO. BrO mixing ratios within the vortex were about twice as large as values at midlatitudes. This is consistent with the notion that BrO represents a major inorganic bromine species and reaches a maximum value with only a small reduction in NO_2 concentration.

Although there was a slight increase in mixing ratios of BrO over the course of the flight series, more likely

Fig. 2. Overlay of BrO and ClO mixing ratios for the flight of January 16, 1989. Data are represented as described in Figure 1 caption.
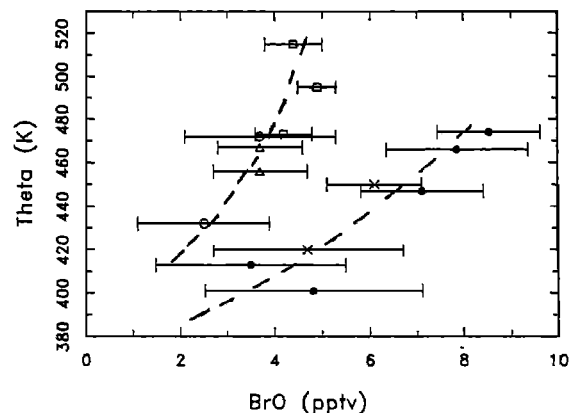

Fig. 4. Observed BrO mixing ratios for a number of flights as a function of potential temperature. Circles are from AASE flights, inner-vortex values represented by closed circles. × represent values from antarctic observations of Brune et al. [1989a], squares are from February 13, 1988, a flight over Canada [Brune et al., 1988], and triangles are from the transit flight of December 29, 1988, which passed over the continental US at midday. Dashed lines are for emphasis only.

this was due to the ability of the aircraft to reach higher potential temperatures as the vortex warmed than to any real temporal trend in the total burden of inorganic bromine or in its partitioning. While ClO concentrations rose markedly (as solar zenith angles decreased), BrO mixing ratios at a fixed potential temperature in sunlight remained fairly constant over the six-week period. This is consistent with observations from over Antarctica [Brune et al., 1989a]. If the partitioning of bromine was perturbed, as suggested by the significant perturbation in ClO, the burden of inorganic bromine in the stratosphere likely does not exceed 10 to 15 pptv, in contrast to a recent far-infrared emission mearurements at midlatitudes which found 25 pptv of HBr [Park et al., 1989]. However, a strong conclusion cannot be drawn until we know the details of heterogeneous reactions of HBr and $BrONO_2$ on PSC particles.

We can use the simultaneous measurements of BrO and ClO to estimate the rate of ozone loss due to reaction (1). Using a value of 1 part per billion of ClO in sunlight, consistent with the observations late in the mission, a rate of roughly 6×10^5 s^{-1} is derived for ozone loss, or equivalently, 0.5% each 12 hours of solar illumination. This loss rate is comparable to that observed within the Antarctic Ozone Hole. Therefore, should the arctic vortex remain stable into springtime, the interaction of bromine and chlorine could represent a significant sink for ozone in the arctic stratosphere.

Summary

Mixing ratios of BrO observed within the arctic lower stratosphere during daylight in January and February of 1989 were found to be enhanced by a factor of 2 over values normally found at midlatitudes. These observations are similar to those made over Antarctica in September, 1987. Values as large as 8 ± 2 pptv were observed late into the mission when more than a part per billion of ClO was measured. Within the statistical significance of the measurement, no BrO was observed at any time in complete darkness, indicating that BrO was tied up at night in long-lived reservoirs, most likely $BrONO_2$ and BrCl. These observations demonstrate the potential for significant loss of ozone, especially if vortex air masses were to experience significant solar illumination.

References

Anderson, J. G. et al., Kinetics of O_3 destruction by ClO and BrO within the antarctic vortex: An analysis based on in situ ER-2 data, *J. Geophys. Res.*, 94, 11,480–11,520, 1989.

Brune, W. H., and J. G. Anderson, In situ observations of midlatitude stratospheric ClO and BrO, *Geophys. Res. Lett.*, 13, 1391–1394, 1986.

Brune, W. H. et al., In situ northern mid-latitude observations of ClO, O_3, and BrO in the wintertime lower stratosphere, *Science*, 242, 558–562, 1988.

Brune, W. H., J. G. Anderson, and K. R. Chan, In situ observations of BrO over Antarctica: ER-2 aircraft results from 54°S to 72°S latitude, *J. Geophys. Res.*, 94, 16,639–16,647, 1989a.

Brune, W. H., J. G. Anderson, and K. R. Chan, In situ observations of ClO in the antarctic: ER-2 aircraft results from 54°S to 72°S latitude, *J. Geophys. Res.*, 94, 16,649–16,663, 1989b.

Brune, W. H. et al., In situ observations of ClO in the arctic stratosphere: ER-2 aircraft results from 59°N to 80°N latitude, *Geophys. Res. Lett.*, this issue, a.

Brune, W. H. et al., The sunrise and sunset variation of ClO in the lower stratosphere, *Geophys. Res. Lett.*, this issue, b.

Fahey, D. W., S. R. Kawa, and K. R. Chan, Nitric oxide measurements in the arctic winter stratosphere, *Geophys. Res. Lett.*, this issue.

Friedl, R. R., and S. P. Sander, Kinetics and product studies of the reaction ClO + BrO using discharge-flow mass spectrometry, *J. Phys. Chem.*, 93, 4756–4764, 1989.

McElroy, M. B. et al., Reductions of antarctic ozone due to synergistic interactions of chlorine and bromine, *Nature*, 321, 759–762, 1986.

Park, J. H., B. Carli, and A. Barbis, Stratospheric HBr mixing ratio obtained from far infrared emission spectra, *Geophys. Res. Lett.*, 16, 787–790, 1989.

Solomon, S. et al., Visible spectroscopy at McMurdo Station, Antarctica 2. Observations of OClO, *J. Geophys. Res.*, 92, 8329–8338, 1987.

Solomon, S. et al., Observations of the nighttime adundance of OClO in the winter stratosphere above Thule, Greenland, *Science*, 242, 550–555, 1988.

Solomon, S. et al., Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica 5. Observations of the diurnal variations of BrO and OClO, *J. Geophys. Res.*, 94, 11,393–11,403, 1989.

Toohey, D. W., and J. G. Anderson, Formation of BrCl ($^3\Pi_{0+}$) in the reaction of BrO with ClO, *J. Phys. Chem.*, 92, 1705–1708, 1988.

Tuck, A. F. et al., The planning and execution of ER-2 and DC-8 aircraft flights over Antarctica, August and September 1987, *J. Geophys. Res.*, 94, 11,181–11,222, 1989.

Wofsy, S. C., M. B. McElroy, and Y. L. Yung, The Chemistry of Atmospheric Bromine, *Geophys. Res. Lett.*, 2, 215–218, 1975.

World Meteorological Organization, *Atmospheric Ozone, 1985, Global Ozone Research and Monitoring Project*, Report No. 16, 1986.

Yung, Y. L. et al., Atmospheric bromine and ozone perturbations in the lower stratosphere, *J. Atmos. Sci.*, 37, 339–353, 1980.

D. W. Toohey and J. G. Anderson, Department of Earth and Planetary Sciences, Harvard Univerity, Cambridge, MA 02138.

W. H. Brune, Department of Meteorology, Pennsylvania State University, University Park, PA 16802.

K. R. Chan, NASA Ames Research Center, Moffett Field, CA 94035.