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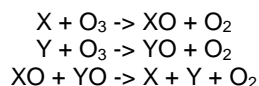
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## 1. INTRODUCTION

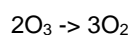
This paper reviews our current understanding of the source and behaviour of bromine in the troposphere and in particular of bromine explosion events. These events occur in the Arctic and Antarctic springtime and can lead to substantial or even complete boundary layer ozone depletion. This has been observed at several Arctic and Antarctic sites (e.g. Barrie et al., 1988; Bottenheim et al., 1990; Sturges et al., 1993; Solberg et al., 1996; Kreher et al., 1997). Theories involving bromine species in the depletion mechanism were confirmed by observations of high concentrations of filterable bromine (Barrie et al., 1988) and BrO (bromine oxide) accompanying ozone depletion events in the boundary layer (Hausmann and Platt, 1994; Tuckermann et al., 1997; Kreher et al., 1997; Wagner and Platt, 1998; Richter et al., 1998; Wagner et al., 2001).

## 2. MECHANISM & DISCUSSION

These observations suggest that the ozone depletion events are caused by halogen catalysis, mostly due to the following gas-phase chain reactions (e.g. Le Bras and Platt, 1995):

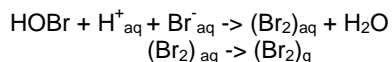


with  $X=Y=Br$ ,  $X=Br$  and  $Y=Cl$ , or possibly  $X=Br$  and  $Y=I$ , leading to the net result:



These catalytic reactions alone, however, are not sufficient to explain the release of the observed high BrO mixing ratios (up to 50 ppt) within a few days.

The additional mechanism necessary to liberate active bromine takes place via autocatalytic heterogeneous reactions involving sea-salt aerosol or the surface of sea ice (e.g. Fan and Jacob, 1992; Tang and McConnell, 1996; Vogt et al., 1996). They suggest that autocatalytic cycles involving sea salt particles liberate active gases such as BrCl and Br<sub>2</sub>, e.g. via HOBr reacting with Br<sup>-</sup> in aerosol particles to form Br<sub>2</sub>.




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Species in the gas phase are indicated by *g*, in the fluid phase by *aq* (e.g. Wagner et al., 2001). This means that one Br atom entering the fluid phase can release two Br atoms to the gas phase, leading to a possibly exponential growth, the so-called "bromine explosion" (Platt and Lehrer, 1997). Br<sub>2</sub> is then photolysed, yielding free bromine atoms that react with ozone to form BrO and, in turn, BrO reacts with itself, releasing bromine atoms again and thereby completing the ozone destroying cycle while preserving the bromine radicals (Wennberg, 1999). Also, with the return of sunlight in spring, the rate of Br<sub>2</sub> photolysis sharply increases and this in turn results in very high concentrations of BrO.

Since the turbulence mixing timescale is very fast in the planetary boundary layer and exchange of gases with the surface occurs quickly (within hours), this explains the sudden onset of the enhanced BrO events. This sudden onset can be observed clearly as strong enhancements in the BrO concentration (Kreher et al., 1997). Moreover, some evidence of BrO in the free troposphere has also been presented in the literature. Speculations about the sources of tropospheric BrO include the possibility that during polar spring BrO is transported from the boundary layer into the free troposphere through convection occurring over large ice leads i.e. openings in the pack ice (McElroy et al., 1999). Satellite observations of BrO made by GOME (Global Ozone Monitoring Experiment) show that the area of enhanced BrO in polar regions typically extends over 300 – 2000 km and that these events persist for 1 – 3 days (Wagner and Platt, 1988).

Wagner et al. (2001) find that the enhanced BrO concentrations observed by GOME are always over or near areas of frozen salt water (above sea ice or the frozen surface of the Caspian Sea) indicating that such conditions are necessary for the autocatalytic release of BrO and the build-up of enhanced BrO concentrations in the troposphere. Their observations suggest that the high BrO concentrations are due to autocatalytic bromine release from sea salt deposits on sea ice rather than to the degradation of unstable organic compounds containing halogens. This agrees with Platt (2000) reporting that attempts to identify BrO in the extra-polar marine environment have not been successful.

There have been, however, observations of episodes of elevated levels of BrO at mid-latitudes at the Dead Sea, Israel (Hebestreit et al., 1999; Matveev et al., 2001) and the Great Salt Lake, Utah, USA

(Stutz et al., 2002). It is somewhat surprising that although no activation of halogens has been observed in the marine environment, salt lakes such as the Great Salt Lake and the Dead Sea release a large amount of reactive halogens into the atmosphere. Hebestreit et al. (1999) and Stutz et al. (2002) attribute the presence of the reactive halogens to the presence of highly concentrated salt solutions or crystalline salt around the Great Salt lake and extended salt pans in the Dead Sea valley that can host heterogeneous reactions that cannot otherwise occur in the more diluted ocean salt water.

### 3. REMAINING QUESTIONS

Several studies provide evidence to support the autocatalytic release mechanism, discussed above, as reasonably well understood and well suited to explain existing observations (Vogt et al., 1996; Tuckermann et al., 1997). It is still unknown though what the source of the original bromine is that initiates the chemistry (Finnlayson-Pitts and Pitts, 1999), i.e. it is unclear what exactly triggers the bromine explosion events. Furthermore, it is still somewhat unclear whether the heterogeneous release mechanisms on aerosol surfaces are sufficient to explain the polar observations or if the presence of sea ice surfaces is necessary (Wagner et al., 2001, discussion above). Finally, our understanding of what maintains the bromine at the observed high concentration is not yet complete. Precise, vertically resolved measurements of the global distribution of BrO will ultimately be required to answer all of these questions.

### 4. OUR CONTRIBUTION

We have been measuring BrO using zenith sky UV/vis absorption spectroscopy at Arrival Heights, Antarctica since 1995. Several examples of BrO explosion events observed during springtime can be seen clearly in this 8 year data set. To further our understanding of the mechanisms leading to the bromine explosion events discussed here, a new retrieval technique developed to better distinguish between tropospheric and stratospheric partial columns of BrO is presented in the associated paper by R. Schofield et al. (2002).

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