The Participation of the Intermediates Chlorine, Bromine and Peroxy Radicals in Arctic Ozone Depletion during ARCTOC

Guest contribution

M. Martinez, T. Arnold, T. Klüpfel and D. Perner

Max-Planck-Institut für Chemie, Postfach 3060, Joh.-J. Becher Weg 27, D-55020 Mainz, Germany

Abstract

Within the EC-sponsored Arctic Tropospheric Ozone Chemistry (ARCTOC) project low ozone events, LOE, were studied at Ny Ålesund, Spitsbergen, in spring. BrO and O₃ were determined spectroscopically by DOAS. Peroxy radicals, HO₂/RO₂, and Cl/ClO mixing ratios were measured continuously and simultaneously by chemical amplification (ROₓ box). Under conditions with around 45 ppb ozone the ROₓ box signalled about 4 ppt of peroxy radicals at the daily noon maximum and zero at night. During low ozone events, LOEs, BrO reached up to 20 ppt. Then the daily maxima of the ROₓ box signals increased and at night ClO was found not exceeding 2 ppt. The detection limit for Cl/ClO was better than 1 ppt and new insights in the mechanism of halogen release and its participation in photochemical reactions in the boundary were obtained. Apparently both halogens were involved in ozone depletion with bromine playing the major role.

Introduction

While most trace gases are oxidised by OH radicals an occasional participation of chlorine atoms in atmospheric oxidation has been derived from hydrocarbon distribution patterns (Rudolph et al., 1997 and references therein). During low ozone events, LOEs, at polar sunrise halogens, mostly bromine, have been observed to play a major role in the ozone decomposition (Barrie et al., 1988). A minor participation of chlorine in LOEs was claimed by Jobson et al., (1994) and Ramacher et al., (1997).
The experiment for peroxyl radical HO₂/RO₂ detection by chemical amplification, called the ROₓ box (Hastie et al., 1991) and based on the OH/HO₂ radical catalysed chain oxidation of CO to CO₂ and NO to NO₂ was applied in order to learn more about the chemical reaction manifold. So far a possible sensitivity of the ROₓ box for other species had been generally ignored. At Ny Alesund sizeable ROₓ box signals during LOEs indicated an additional chain reaction other than that through OH/HO₂.

**Instrumental and results**

Two light paths of the differential optical absorption experiment, DOAS, reaching from zero up to about 400 m a.s.l. and the position of the ROₓ box, as described by Arnold (1997), are shown (Fig. 1).

BrO and O₃ observed by DOAS are given in Fig. 2 together with SO₂, NO₂ and total bromine and iodine (Martinez, 1998), also upper limits for ClO and IO were measured spectroscopically. The efficiency of the chain reaction or chain length, CHL, given by the number of NO₂ molecules produced from one primary radical was 155 ± 10 for CHLₓ and all ROₓ box signals in Fig. 3 are given in equivalents of those peroxy radicals. Chlorine supports the amplification through the chain process (1)–(4) (Hewitt et al., 1996).
Fig. 2: ARCTOC 1996 mixing ratios of trace gases and O₃ and BrO measured by long path absorption spectroscopy (DOAS). Total bromine and iodine by neutron activation.

\[
\begin{align*}
\text{ClO} + \text{NO} & \rightarrow \text{Cl} + \text{NO}_2 \\
\text{Cl} + \text{CO} + \text{M} & \rightarrow \text{CICO} + \text{M} \\
\text{CICO} + \text{O}_2 + \text{M} & \rightarrow \text{CICO}_3 + \text{M} \\
\text{CICO}_3 + \text{NO} & \rightarrow \text{Cl} + \text{CO}_2 + \text{NO}_2
\end{align*}
\]

(1) (2) (3) (4)

Calibration by dynamic dilution of $2.13 \times 10^9$ molec OCIO cm$^{-3}$ to 86 ppt yielded for CHL$_{cl}$ 300 ± 60. No corresponding oxidation of NO to NO$_2$ with up to 1 ppb of Br/BrO$_x$ was observed.

The detection limits for HO$_2$/RO$_2$ and for Cl/ClO were 1 and 0.5 ppt, respectively. At the end of April when 45 ppb O$_3$ were observed (Fig. 2) BrO
was zero. The RO<sub>x</sub> box signals followed the radiative flux and HO<sub>2</sub>/RO<sub>2</sub> reached 4 ppt HO<sub>2</sub>/RO<sub>2</sub> at noon and zero at night.

During LOEs elevated BrO (Fig. 2) was found and RO<sub>x</sub> box signals appeared at night (Fig. 3). During the day the RO<sub>x</sub> box signals were quite large and did not follow J(O<sub>3</sub>(O<sup>1</sup>D)) when low O<sub>3</sub> mixing ratios on May 5, 6, 8 and 9 precluded large radical yields from ozone photolysis. The high night-time signals of up to 2 ppt ClO persisted through May 9.

\[
\begin{align*}
J(O^1D) &\approx \begin{cases} 
2.0 \times 10^9 \\
1.5 \times 10^9 \\
1.0 \times 10^8 \\
5.0 \times 10^7 \\
0.0 \times 10^6
\end{cases}
\nonumber
\end{align*}
\]

\[
29 \text{ Apr} \quad 1 \text{ May} \quad 3 \text{ May} \quad 5 \text{ May} \quad 7 \text{ May} \quad 9 \text{ May} \quad 11 \text{ May} \quad 13 \text{ May} \quad 15 \text{ May} 
\]

\[
1996
\]

\[
O_3 = 0 \text{ ppb}
\]

Fig. 3: Ozone by DOAS and signals from RO<sub>x</sub> box (solid line) calibrated corresponding to HO<sub>2</sub>/RO<sub>2</sub>, J(O<sub>3</sub>(O<sup>1</sup>D)) during main ozone depletion episode.

**Discussion**

BrO was measured by DOAS and ClO by the RO<sub>x</sub> box. The RO<sub>x</sub> box apparently is sensitive to HO<sub>2</sub>/RO<sub>2</sub> and to Cl/ClO. At night, when the signal comes solely or overwhelmingly from Cl/ClO there is clear evidence for chlorine.

The primary source of halogen during that period of the year is sea salt bromide and chloride. During the bromine activation at polar sunrise from sea-salt on pack-ice the oxidation by HOBr activates chlorine also.

The lifetime of active chlorine is limited as Cl atoms react with hydrocarbons to yielding HCl. During the LOE from May 12 to 14 (Fig. 3) the RO<sub>x</sub> box signal persistently increased around midnight from zero to 1.5 ppt ClO. The highest signals in the early morning corresponding to 1.5–2.0 ppt Cl/ClO
Cl, Br and Peroxy Radicals in Arctic Ozone

decreased during the day (May 12, 13) demonstrating that H abstraction by Cl from hydrocarbons.

Conclusions

Halogen emission and ozone depletion at polar sunrise represents an important natural phenomenon (Perner et al., 1998).

The observation of Cl/ClO by the new RO\textsubscript{x} box amplification scheme allows in situ measurements of atmospheric active chlorine with a sensitivity of better than 1 ppt at ambient conditions close to the ground. In the processes leading to LOEs in arctic regions bromine and chlorine are involved. While bromine monoxide, BrO, reaches up to 20 ppt, not more than about 2 ppt Cl/ClO were found. The Cl atoms are regularly scavenged by hydrocarbons. Therefore the impact of chlorine in comparison with bromine is small.

Acknowledgements

The authors thank the CEC for financial support (EV5V-CT93-0318, ENV4-CT95-0005).

References


