



Efficiency of Br^- and I^- for activating chloride in sea-spray aerosol, derived from aerosol smog chamber experiments and model calculations

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Observations in the Arctic spring but even at mid-latitudes show that atomic Br and atomic Cl are produced in the boundary layer during NO_x -poor periods. The activation of Br is followed by destruction of ozone and production of BrO. The latter one has a dramatic influence on the mercury cycle. Model calculations show that halogen-containing radicals are produced in the presence of sea-spray aerosol and ozone using Br^- as a catalysing species. Besides the influence of Br^- a possible influence of I^- has been discussed (Vogt et al., 1999). Though iodide is a very minor trace compound in seawater ($\text{I}^-/\text{Br}^-/\text{Cl}^- = 1/1500/10^6$), a strong enrichment (up to a factor of 40) was observed in sea-spray, especially in the aged aerosol. The activating character of I^- is expected to exceed that of Br^- because it is a stronger nucleophile.

Effects of Br^- and I^- on halogen activation in sea-spray aerosol were investigated by aerosol smog chamber experiments accompanied by model calculations. Surprisingly, the observed ozone destruction is by a factor of about ten lower in the presence of iodide than in the presence of bromide (both in similar concentration). This indicates that much less I atoms are formed than Br atoms. More complicated are the effects promoting the activation of Cl^- . At low initial ion concentrations of I^- or Br^- below $1 \mu\text{g}/\text{m}^3$ ($400 \mu\text{g}/\text{m}^3$ NaCl concentration) the observed production rate of atomic Cl is significantly higher in the presence of I^- than of Br^- . At high initial ion concentrations above $2 \mu\text{g}/\text{m}^3$ the production rate of atomic Cl is up to three times higher in the presence of Br^- . The model calculations show that the activation of chloride

in the presence of Br^- occurs mainly by the production of HOBr followed by uptake into the aerosol and reaction with Cl^- . In contrast to this finding HOI is immediately formed by the rapid reaction of dissolved ozone with I^- : $\text{O}_3(\text{aq}) + \text{I}^- \Rightarrow \text{OI}^- + \text{O}_2(\text{aq})$ ($k = 4.2 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$, seven orders of magnitude faster than the analogous reaction with Br^-). On the other hand, I^- is rapidly transformed to the very inactive IO_3^- by the self reaction of IO ($\text{IO}(\text{aq}) + \text{IO}(\text{aq}) \Rightarrow \text{IO}_2^- + \text{HOI} + \text{H}^+$) followed by further oxidations e.g. by IO_2^- , H_2O_2 or HOCl .

References:

Vogt, R., R. Sander, R. von Glasow, and P.J. Crutzen, Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, *J. Atmos. Chem.* **32** (1999) 375-395.