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Kinetic smog-chamber studies on halogen activation from a simulated salt pan, using dry and wet NaCl/NaBr surfaces

Sergej Bleicher (1), Natalja Balzer (1), Cornelius Zetzsch (1,2), Joelle Buxmann (3), and Ulrich Platt (3)

(1) Atmospheric Chemistry Research Laboratory, Bayreuth Center of Ecology and Environmental Research, University of Bayreuth, Germany, (2) Fraunhofer-Institute of Toxicology and Experimental Medicine, Hannover, Germany, (3) Institute of Environmental Physics, University of Heidelberg, Germany

Field experiments and laboratory studies have shown that atomic Br and Cl are released from sea-salt aerosol and saline soils. This halogen release is based on the uptake of gaseous HOX by aqueous, acidified salt surfaces. Br and Cl play an important role in atmospheric ozone depletion and the destruction of hydrocarbons. Furthermore, Secondary Organic Aerosol (SOA) and HUmic LIke Substances (HULIS) may take part in these reaction cycles by halogenation and production of volatile organic halogen compounds.

Aerosol smog-chamber facilities (coolable to -25°C) enable us to simulate the halogen release mechanism under arctic tropospheric conditions. Mechanistic and kinetic studies are carried out to investigate the influence of SOA and HULIS on halogen cycles and to determine halogenated gaseous and solid organic products.

The present laboratory measurements study halogen activation from salt surfaces, which are similar to typical salt pan environments. In these experiments we placed different artificial salt mixtures with NaCl/NaBr ratios up to 300:1 on a Teflon pan located in a Teflon chamber with a volume of 3.5 m^3. Under clean air conditions we inject ozone and a mixture of non-methane hydrocarbons with well-known reactivities against OH and Cl and irradiated the chamber with a solar simulator. Beside the usual observing instruments like an ozone monitor and a gas chromatograph we used Differential Optical Absorption Spectroscopy (DOAS) in a White cell with a light path up to 320 m to observe various gas-phase species including BrO radicals. A dry air / dry salt pan environment showed no ozone depletion and no halogen activation. At relative humidity above 50%, a rapid ozone depletion (4.7 h half-life) was observed, which is much faster than for pure NaCl under the same conditions (77 h). Furthermore, the mixed salt was acidified with H_2SO_4 to a pH value of 4.3, no difference in ozone depletion and halogen activation was observed at this point.

The DOAS measurements are the first simultaneous observations of ozone depletion and BrO radicals in the laboratory. Using the radical clock technique we measured concentration time profiles of OH and Cl with integrated values up to $8 \cdot 10^{10}$ molec/cm^3 for OH and up to $5 \cdot 10^8$ molec/cm^3 for Cl.

With such halogen release out of a salt pan we can study the halogenation of SOA particles in environmentally relevant conditions.

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