



Autocatalytic halogen release from salt droplets and saltpans

S. Bleicher (1), J. Buxmann (2), N. Balzer (1), T. Riedel (3), J. Thornton (3), U. Platt (2), C. Zetzsch (1,4)

(1) Atmospheric Chemistry Research Laboratory, University of Bayreuth, Bayreuth, Germany, cornelius.zetzsch@uni-bayreuth.de, (2) Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany, (3) Department of Atmospheric Science, University of Washington, Seattle, WA, USA, (4) Fraunhofer-Institute for Toxicology and Experimental Medicine, Hannover, Germany

Reactive bromine and chlorine species are known to have an impact on the ozone concentration, to change the chemical balance of nitrogen oxides and to have an influence on human health: through their reactions with hydrocarbons (HCs) among other trace gases and increased deposition of toxic compounds (like mercury). Especially the formation of higher halogen oxides (OIO, OBrO) and the role of chlorine in tropospheric chemistry are not clear yet.

We present experiments on halogen activation from salt mixtures of NaCl/NaBr and salt droplet aerosols, simulating saltpans and sea spray in an illuminated Teflon chamber. The starting conditions influence the total amount of released halogens, so we varied the amounts of aerosol surface, NO_x and HCs, monitoring the time profiles of the HCs by gas chromatography in order to determine the time profiles of OH and Cl. The chemical ionization mass spectrometer (CIMS) of the University of Washington was used to observe stable halogen species in a short campaign, and a multi-reflection cell (White-type) of the University of Heidelberg, coupled with Differential Optical Absorption Spectroscopy (DOAS), was employed to measure BrO, ClO and OCIO.

We observe a qualitative difference in Br₂ release between the saltpan and the sea salt aerosol experiments: While BrO increases immediately to very high levels up to 6 ppb in the saltpan experiments (Buxmann et al., 2011), formation of BrO is delayed in the aerosol studies. This delay varies from about five to ten minutes after switching the solar simulator on, depending on HCs and NO_x concentrations. Furthermore, we observe a “chlorine explosion” with Cl₂ mixing ratios of up to 12 ppb (by CIMS) as a function of the initial HC and NO_x conditions. More than 3 ppb ClO, 3.5 ppb OCIO and 650 ppt BrO were observed at initial levels of 150 ppb NO₂ and of 770 ppb O₃, leading to an ozone depletion rate of 0.6 ppb/s. The influence of NO_x was tested on simulated sea spray alone. Due to the intermediate formation of BrNO₃ and its rapid uptake, releasing Br₂, the ozone depletion was a factor of 3-5 faster in that case. However, one mechanistic explanation for the rapid BrO increase in saltpan experiments could be a photolabile precursor, such as OBrO, having a large photolysis frequency of 0.2 s⁻¹ in our chamber. A release of OBrO could be possible in the dark, as known from the oscillating Belousov-Zhabotinsky reaction. Remarkably high values of OCIO were observed, while the formation of OBrO is very likely. Such higher halogen oxides appear to be important intermediates in the release process of reactive bromine and chlorine species.

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