



Spectroscopic investigations of organic aerosol and its reaction with halogens, released by sea-salt activation

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The release of reactive halogen species from sea-salt aerosol offers a class of reactants for heterogeneous reactions of utmost importance. These heterogeneous reactions have been overlooked so far, although they may occur with internal and external mixtures of sea-salt aerosol and organic aerosol or organic matter. Such reactions might constitute sources of gaseous organohalogen compounds or halogenated organic aerosol in the atmospheric boundary layer. Infrared and UV/VIS spectroscopy provide an insight into chemical processes at reactive sites of the organic phase on a molecular level.

Model studies of heterogeneous reactions of halogens with different kinds of (secondary) organic aerosols and organic matter were performed using a 700L smog chamber with a solar simulator. The model compounds alpha-pinene, catechol and humic acid have been chosen as precursors/material for the condensed, organic phase of the aerosol. After formation of the secondary organic aerosol or preparation of the organic material and the sea-salt solution the reaction was carried out using molecular chlorine and bromine in the presence of simulated sunlight. Chemical transformation of the organic material was studied using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) on a ZnSe crystal and diffuse reflectance UV/VIS spectroscopy. An electrostatic precipitator was developed to deposit the aerosol particles on the ATR crystal as a thin film. On the other hand, longpath-FTIR spectroscopy with a 40m White-cell allows us to monitor both the condensed and gas phase of the aerosol in situ in the smog chamber directly.

These spectroscopic techniques enable us to characterize different organic aerosol particles and their functional groups at reactive sites on these particles as well as to study aerosol formation and transformation directly. The heterogeneous reaction of reactive halogen species with organic material at atmospheric conditions leads to small reactive molecules like phosgene. Methyl groups (and possibly other C-H containing groups) on the aerosol particles are destroyed completely to form HCl and HBr. Also carbon oxygen bonds are affected by the reaction with these halogens. The heterogeneous reaction of organic aerosol with halogens leads to structural and functional changes of the aerosol particles and therefore to modified atmospheric behavior.