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Influence of secondary organic aerosols (SOA) on bromine explosion in smog-chamber experiments

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Br and Cl play an important role in atmospheric ozone depletion and destruction of hydrocarbons. Secondary organic aerosol (SOA) may take part in these reaction cycles by halogenation and production of volatile organohalogens. It is then expected that the presence of SOA slows down the catalytic bromine release via "Bromine Explosion" (auto catalytic release of reactive bromine from salt surfaces) since the halogens in the organohalogens are missing as reactive compounds.

Based on this theory, a new experimental setup was developed in which a substrate (solid crystalline NaCl/NaBr mixture, substituting environmental samples and serving as the source for halogen) was placed on a Teflon pan located in an aerosol smog-chamber (FEP 200A Dupont, total volume 3500 L). SOA was formed during the ozone-initiated oxidation of α-pinene, catechol and guaiacol, respectively. Mechanistic and kinetic studies were carried out to investigate the influence of SOA on the bromine explosion and to determine the possible halogenated compounds in the gaseous and particulate phase originating from the salt pan.

Three different types of experiments were investigated: (1) SOA and (2) the salt pan were placed in the Teflon chamber separately, and (3) SOA was placed together with the salt pan into the chamber. All experiments were carried out under similar conditions (T 20°C, relative humidity 60%, NaCl/NaBr =300/1). (1) With SOA only we observed a notable ozone depletion during the first 5-30 minutes, which corresponds to the typical timeframe of SOA formation for the different precursor substances. The total lifetime of ozone was more than 10 h. (2) With salt pan only a complete ozone depletion was observed within the first 10 minutes. This rapid depletion can be explained by the "Bromine Explosion". During this experiment a maximum BrO mixing ratio of 6500 ppt was measured by DOAS (Differential-Optical-Absorption-Spectroscopy). (3) With salt pan and SOA the BrO formation showed a delay, and its maximum mixing ratio of 150 ppt was one order of magnitude lower than without SOA. The total lifetime of ozone was about 3 h.

The Br-radical concentration was calculated on the basis of the ozone depletion; from our experiments we estimate values of bromine concentration around 20 ppt and 2 ppt for salt pan experiments with and without secondary organic aerosols, respectively.

The experiments showed that the presence of SOA modifies the kinetics of halogen cycles in the gas phase and leads to changes of the physico-chemical characteristics and size of SOA itself.

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