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Formation of halogen-induced secondary organic aerosol (XOA)

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Reactive halogen species (RHS) are very important due to their potential of stratospheric ozone depletion and surface ozone destruction. RHS seem to interact with precursors of secondary organic aerosol (SOA) similarly to common atmospheric oxidants like OH radicals and ozone. The potential interaction of RHS with preformed SOA has recently been studied (Ofner et al., 2012). Although aerosol formation from reaction of RHS with typical SOA precursors was previously studied (e.g. Cai et al., 2006), no data are available on bromine-induced aerosol formation from organic precursors yet.

An aerosol smog-chamber was used to examine the halogen-induced secondary organic aerosol (XOA) formation under atmospheric conditions using simulated sunlight. With a concentration of 10 ppb for the organic precursor, 2 ppb for molecular chlorine, and 10 ppb for molecular bromine, the experimental setup is close to ambient conditions. By combined measurements of the aerosol size distribution, ozone and NO_x mixing ratios, as well as the decay of the organic precursor, aerosol yields and aerosol growth rates were determined. The decay of the organic precursor was analyzed by capillary gas chromatography coupled with flame-ionization detection (GC-FID) and the aerosol size distribution was measured using a Scanning Mobility Particle Sizer (SMPS). Additionally, with the decay rate of the precursor and the calculated photolysis rates of molecular halogen species, based on the well-known spectrum of the solar simulator, mechanistic details on the XOA formation pathways can be determined.

We observed XOA formation even at very low precursor and RHS concentrations with a diameter mode at 10-20 nm and a number concentration up to 1000000 particles cm-3. While the XOA formation from chlorine is very rapid, the interaction of bromine with the organic precursors is about five times slower. The aerosol yield reached maximum values of 0.01 for the reaction of chlorine with α-pinene and 0.0004 for bromine with α-pinene.

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References:

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