



BrO loss due to secondary organic aerosols

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One major source of heterogeneous released reactive halogen species (RHS) is primary aerosol from sea-salt particles, ejected by sea spray. Photoactivated RHS emissions, such as atomic Br and BrO radicals, can play a key role in the destruction of atmospheric ozone, influencing HO_x and NO_x chemistry. Through aerosol interaction they show potential indirect effects on global climate.

The formation of RHS can be significantly reduced in the presence of organic aerosols. Additionally, halogen species were found to change the aerosol size distribution, the presence of functional groups and the optical properties. Furthermore, they may form halogenated species in the condensed phase of the organic aerosol - although the inhibition of the formation of RHS has not been quantified before. The interaction of secondary organic aerosols (SOA) from predominantly aliphatic (α -pinene) or aromatic (catechol and guaiacol) precursors and heterogeneously released halogens was studied in smog-chamber experiments. BrO and OCIO released from salt aerosols were detected by a White system in combination with Differential Optical Absorption Spectroscopy (DOAS). The size and number distribution of aerosols from salt droplets ($\sim 150\text{nm}$ - 1000nm) and from SOA ($\sim 5\text{nm}$ - 150nm) was quantified by a SMPS (Scanning Mobility Particle Sizer) to obtain typical surface areas of $10^3 \mu\text{m}^2/\text{cm}^3$ and $2 \times 10^2 \mu\text{m}^2/\text{cm}^3$, respectively. In the absence of SOA a BrO production rate per salt aerosol surface area of $5.2 \times 10^{11} \text{ molec}/\text{cm}^2\text{s} = 8500 \text{ pmol}/\text{m}^2\text{s}$ has been measured. This confirms model assumptions for BrO formation over the Dead Sea, where the Br₂ flux of $80\text{-}154 \text{ pmol}/\text{m}^2\text{s}$ and HOBr flux = $800 \text{ pmol}/\text{m}^2\text{s}$ was increased by a factor of 20-30 to explain high BrO mixing ratios. In the presence of SOA from α -pinene, catechol and guaiacol the formation rate was significantly reduced. In a first approximation, neglecting gas phase reactions, the BrO loss rate regarding the surface area of SOA was calculated to be $42 \times 10^{11} \text{ molec}/\text{cm}^2\text{s}$, $12 \times 10^{11} \text{ molec}/\text{cm}^2\text{s}$ and $10 \times 10^{11} \text{ molec}/\text{cm}^2\text{s}$ for α -pinene, catechol and guaiacol, respectively. In the presence of SOA about 150 ppt of OCIO were formed, which is not completely understood yet, but acidification by organic acids might trigger a chlorine release.

Model studies of the experiments including gas and particulate phase reactions will be presented in order to help explain reaction pathways and to estimate accommodation coefficients. In conclusion, we found a reduced formation of BrO in the presence of SOA, and therefore less Br-catalysed O₃ destruction. We also show the first quantitative BrO loss rate due to SOA, where α -pinene shows 4 times higher loss rate compared to catechol and guaiacol.