



Halogen-induced organic aerosol (XOA) formation and decarboxylation of carboxylic acids by reactive halogen species – a time-resolved aerosol flow-reactor study

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Reactive halogen species (RHS) are released to the atmosphere from various sources like photo-activated sea-salt aerosol and salt lakes. Recent studies (Cai et al., 2006 and 2008, Ofner et al., 2012) indicate that RHS are able to interact with SOA precursors similarly to common atmospheric oxidizing gases like OH radicals and ozone. The reaction of RHS with SOA precursors like terpenes forms so-called halogen-induced organic aerosol (XOA). On the other hand, RHS are also able to change the composition of functional groups, e.g. to initiate the decarboxylation of carboxylic acids (Ofner et al., 2012).

The present study uses a 50 cm aerosol flow-reactor, equipped with a solar simulator to investigate the time-resolved evolution and transformation of vibrational features in the mid-infrared region. The aerosol flow-reactor is coupled to a home-made multi-reflection cell (Ofner et al., 2010), integrated into a Bruker IFS 113v FTIR spectrometer. The reactor is operated with an inlet feed (organic compound) and a surrounding feed (reactive halogen species). The moveable inlet of the flow reactor allows us to vary reaction times between a few seconds and up to about 3 minutes. Saturated vapours of different SOA precursors and carboxylic acids were fed into the flow reactor using the moveable inlet. The surrounding feed inside the flow reactor was a mixture of zero air with molecular chlorine as the precursor for the formation of reactive halogen species.

Using this setup, the formation of halogen-induced organic aerosol could be monitored with a high time resolution using FTIR spectroscopy. XOA formation is characterized by hydrogen-atom abstraction, carbon-chlorine bond formation and later, even formation of carboxylic acids. Several changes of the entire structure of the organic precursor, caused by the reaction of RHS, are visible. While XOA formation is a very fast process, the decarboxylation of carboxylic acids, induced by RHS is rather slow. However, XOA formation from aliphatic or aromatic precursors is coupled to the formation of carboxylic acids by saturation of reactive radical sites with oxygen, but carboxylic acids themselves can be destroyed by RHS, leading to further fragmentation of the carbon structure.

References

- Cai, X., and Griffin, R. J.: Secondary aerosol formation from the oxidation of biogenic hydrocarbons by chlorine atoms, *J. Geophys. Res.*, 111, D14206/14201-D14206/14214, 2006.
- Cai, X., Ziemba, L. D., and Griffin, R. J.: Secondary aerosol formation from the oxidation of toluene by chlorine atoms, *Atmos. Environ.*, 42, 7348-7359, 2008.
- Ofner, J., Krüger, H.-U., and Zetzsch, C.: Circular multireflection cell for optical spectroscopy, *Appl. Opt.*, 49, 5001-5004, 2010.
- Ofner, J., Balzer, N., Buxmann, J., Grothe, H., Schmitt-Kopplin, Ph., Platt, U., and Zetzsch, C.: Halogenation processes of secondary organic aerosol and implications on halogen release mechanisms, *Atmos. Chem. Phys.*, 12, 5787-5806, 2012.