

Modeling Study on Halogen Activation from Cloud Droplets

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Sea salt particles are the main direct emitted particles on a global scale by mass. Field measurements show a release of halogens from sea salt particles into the gas phase (Ayers et al., 1999). These activated halogens influence the oxidation capacity of the maritime boundary layer (Spicer et al., 1998) due to higher concentrations of radicals. Halides are also found in cloud droplets. The aim of this study is to determine whether they lead to significant amounts of activated halogens. It is expected that in cloud droplets the importance of radical chemistry will increase comparing to the known reaction patterns in sea salt particles because of different conditions like higher pH values and lower ionic strength.

To analyze such processes a very complex multiphase mechanism is used. The gas phase reactions are characterized by RACM (Stockwell et al., 1997; Regional Atmospheric Chemistry Mechanism), and the aqueous phase reactions are taken from CAPRAM 2.4 (MODAC mechanism) (Ervens et al., 2001; Chemical Aqueous Phase Radical Mechanism). To describe the reactions of halogen containing compounds an additional module was developed (HALOGEN 2.1). This module contains reactions of halogen species in both the gas and the aqueous phase and also includes phase transfer processes of the species.

A box model was used to clarify the most important pathways leading to halogen atoms in the gas phase. The mechanism of halogen activation depends on the scenario which was used to describe the aerosol. Different pathways of halogen activation were identified for clean and polluted conditions.

The influence of the direct uptake of $\text{Cl}\cdot$ and $\text{Br}\cdot$ was another part of the study. The phase transfer of these radicals is possibly an important source of these radicals in the gas phase. In the maritime case the concentration of $\text{Br}\cdot$ is in the order of 10^4 molecules per cm^3 and 10^3 molecules per cm^3 of $\text{Cl}\cdot$. Although the concentration of halides in cloud droplets is estimated to be 4 orders of magnitude lower than in sea salt particles (Vogt et al., 1996) the amount of activated halogens is in the same order of magnitude.

References

- Ayers G. P., R. W. Gillett, J. M. Caine, J. M. Dick; Chlorine and Bromine Loss from Sea-Salt Particles in Southern Ocean Air, *J. Atmos. Chem.* 33 (1999) 299-319.
- Herrmann, H., B. Ervens, H.-W. Jacobi, R. Wolke, P. Nowacki, R. Zellner; CAPRAM 2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry., *J. Atmos. Chem.* 36 (2000) 231-284.
- Ervens, B., H. Herrmann, G. V. Buxton, G. A. Salmon, J. Williams, F. Dentener, C. George, P. Mirabel; CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, (2001) in preparation.
- Spicer, C. W., E. G. Chapman, B. J. Finnlaysen-Pitts, R. A. Plastrige, J. M. Hubbe, J. D. Fast, C. M. Berkowitz; Unexpectedly High Concentrations of Molecular Chlorine in Coastal Air, *Nature* 394 (1998) 353-356.
- Stockwell, W. R., F. Kirchner, M. Kuhn; A New Mechanism for Regional Atmospheric Chemistry Modeling, *J. Geophys. Res.* 102 (D22) (1997) 25847-25879.
- Vogt, R., P. J. Crutzen, R. Sander; A Mechanism for Halogen Release from Sea-Salt Aerosol in the Remote Marine Boundary Layer, *Nature* 383 (1996) 327-330.