Laser-based Laboratory Studies of Cl-Reactions in Aqueous Solution

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During the last years halogen activation became an often used terminus in atmospheric chemistry (Vogt et al., 1996; Sanders and Crutzen, 1996). Model calculations indicate that halogene-atom chemistry does not only play a role in gas-phase chemistry but also in the chemistry of aerosol particles and cloudwater (Herrmann et al., 1999, 2000). Therefore in this study the absorption spectrum of aqueous chlorine and reactions of $Cl_{(aq)}$ with different organics were investigated.
Chlorine atoms were generated by excimer-laser-photolysis of aqueous solutions containing HOCl as well as aqueous solutions containing chloroacetone as chlorine atom precursor substance at 248 nm according to:

$$HOCl + h\nu\ (\lambda = 248\ nm) \rightarrow OH + Cl$$
$$CH_3COCH_2Cl + h\nu\ (\lambda = 248\ nm) \rightarrow CH_3COCH_2 + Cl$$

For the spectroscopic investigations a time resolved laser-photolysis-broadband-diode-array-absorption experiment was used. For the kinetic investigations a laser-photolysis-longpath-laser-absorbance (LP-LPA) apparatus was used.
With a number of organic substances the Cl atom reacts via the abstraction of an H-atom, according to:

$$Cl + RH \rightarrow R + HCl$$

A correlation between the strength of the C-H bond and the rate of the H-atom-abstraction reaction was found. This correlation can be used to estimate reaction rates of H-atom-abstraction reactions of Cl atom from extrakinetical data (i.e. BDE).
The results that were obtained in this study can be used in modelling studies and though may be helpful for a better understanding of the tropospheric aqueous phase.

Literature

Herrmann, H., B. Ervens, P. Nowacki, R. Wolke and R. Zellner, Chemosphere **38**, 1223 (1999).
Herrmann H., B. Ervens, H.-W. Jacobi, R. Wolke, P. Nowacki and R. Zellner, J. Atmos. Chem. 36, 231 (2000).
Vogt R., P.J. Crutzen and R. Sander, Nature **383**, 327 (1996).
Sander R. and P.J. Crutzen, J. Geophys. Res. **101**, 9121 (1996).