

Laser-based studies of reactions of important atmospheric radicals with organic compounds in the aqueous phase

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Motivation and Background

Free radicals play an important role for the chemistry of organic compounds in the troposphere. In order to evaluate the impact of free radical chemistry in the tropospheric aqueous phase, many kinetic and spectroscopic data are needed. Since atmospheric oxidation reactions represent not only a sink process for organic compounds, but also a source for new species, information about the reaction products are required as well. These new species may have different toxic properties from their precursor compounds or affect other important atmospheric processes (e.g. particle mass production, atmospheric oxidation potential, acid rain). Based on the experimental data a detailed aqueous phase mechanism was developed. With these mechanism the importance of the aqueous phase chemistry for atmospheric processes can be evaluated.

Experimental

For the laboratory studies different Laser Photolysis Long Path Absorption (LP-LPA) setups were used.

For photolysis of the corresponding radical precursor compounds an EXCIMER lasers was used. The laser can be operated at different wavelengths (e.g. $\lambda = 248$ nm, 351 nm). The attitude of the wavelengths depends which radical precursor is used.

As analytical light source a Hg-Xe lamp, a deuterium lamp and different cw-lasers were used. In dependence of the analytical light source used a monochromator-photomultiplier, a photodiode, a Diodearray detector and CCD camera was used as detector.

Up to now many different radical reactions with alcohols, aldehydes, ketones, mono- and dicarboxylic acids, esters as well as phenols in aqueous phase were examined [1,3,4,5,6,7,8,9,10].

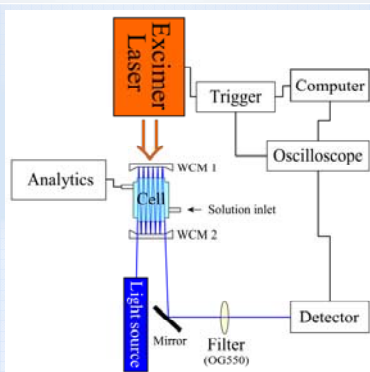


Figure 1: Laser photolysis long path absorption setup (LP-LPA).

The kinetic measurement of the radical reactions can as function of the temperature ($278\text{K} \leq T \leq 318\text{K}$), which ion strength ($0 \text{ mol l}^{-1} \leq I \leq 3 \text{ mol l}^{-1}$) and the pH value ($0.5 \leq T \leq 9$) are accomplished. All measurements were done under condition of pseudo first order. Therefore, reactants were added in at least ten times excess.

To produce the radicals different precursor will be used. In case of the halogen radicals the appropriate halogenated acetone compound will be used. The NO_3 radical can be produced by peroxodisulfat or nitrate with different wavelengths. These three mentioned radicals can be observed directly using their optical absorption properties. For kinetic investigation of OH radicals which was formed by photolysis of H_2O_2 , mostly the well characterized competition kinetics thiocyanate system [2] was used due to formation of peroxy radicals as reaction products which have an overlapping absorption with the OH radical.

Spectroscopic studies

Spectroscopic investigations are done in order to study the formation of transient reaction products (e.g. organic peroxy radicals) or to parameterize the spectroscopic properties of the reactants and products. Figure 2 shows for example the measured absorption spectra of Cl and Br.

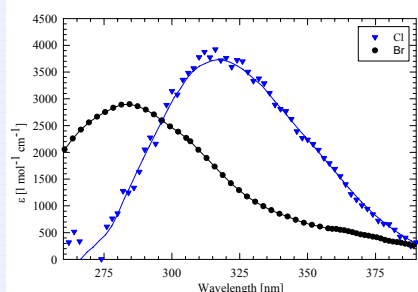


Figure 2: Normalized absorption spectra of the chlorine and bromine atom [3,4].

Such spectroscopic information is necessary for the kinetic investigation, for example to study the recombination reactions of organic peroxy radicals in aqueous solution.

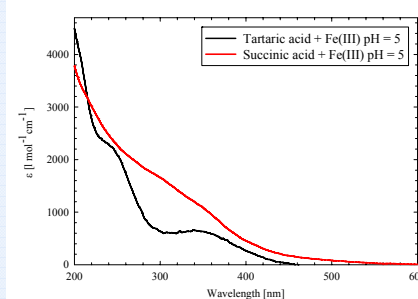


Figure 5: Normalized absorption spectra of iron complexes with dicarboxylic acids at pH = 5.

Furthermore, spectroscopic studies are done to investigate the photochemistry of environmentally important iron species. Photolysis of iron-complexes with UV-radiation initiates radical production in the atmospheric liquid phase and in the surface ocean. Model complexes of iron with ligands in the categories polycarboxylates, keto-carboxylates, hydroxymates and catecholates will be used to investigate radical quantum yields and organic products to clarify the fate of important organics and iron at the sea-atmosphere interface and in marine particles and clouds.

Product studies

Apart from transient species also the formation of stable oxidation products is studied, applying an offline coupling of laser photolysis experiments with liquid chromatography/mass spectrometry (LP-LC/MS, Figure 1). In first experiments the oxidation of phenols in aqueous solution was investigated. The results obtained showed the formation of highly toxic mono- and dinitrophenols as well as condensation products (dimers and trimers; see Figure 3). Especially the formation of these condensation products might be relevant to the atmospheric particle mass production.

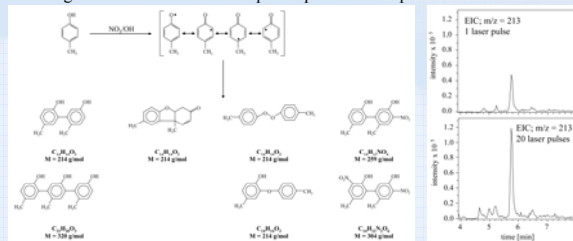


Figure 3: Shows the possible polymerization products (left) and the conversion in dependence of laser pulses (right) [5].

Kinetic studies

In order to describe the multiphase chemistry, kinetic information on the implemented reactions are essential. Using the setup in Figure 1, atmospheric relevant radical reactions are studied as a function of the pH, the temperature and the ionic strength (Figure 7). Based on the kinetic data the importance of atmospheric reactions can be assessed.

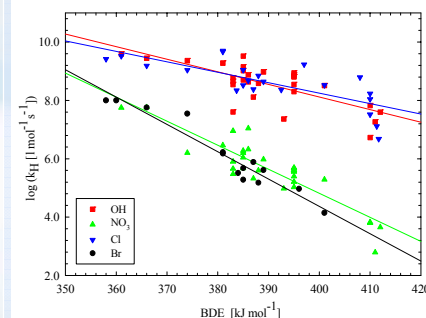


Figure 4: Evans-Polanyi plot of $\log k_H [\text{M}^{-1}\text{s}^{-1}]$ vs. bond dissociation energy (BDE) [kJ mol^{-1}] for OH, NO_3 , Cl and Br reactions [1,3,4,6,7,8,9,10].

Figure 4 shows a comparison of the reactivity and selectivity of four investigated radicals. From this picture the following reactivity row can be set up: $\text{OH} \approx \text{Cl} > \text{NO}_3 > \text{Br}$. However, correlations between the rate constants obtained and extra kinetic parameters are also used to estimate unknown rate constants for the mechanism development and to get information on the underlying reaction mechanism.

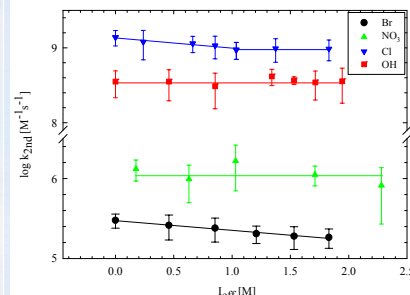


Figure 7: Ionic strength dependencies of formaldehyde with the investigated radicals (Cl, Br, OH and NO_3) [1,3,4,6,7,8].

Aqueous Phase Chemistry Mechanism

CAPRAM (Chemical Aqueous Phase Radical Mechanism, [11]) is a detailed aqueous phase mechanism which was developed for the application in tropospheric multiphase models. CAPRAM 3.0i contains with 777 reactions a complex implementation of aqueous phase inorganic as well as organic chemistry including organic species containing different functional groups with up to four carbon atoms. Therefore, CAPRAM is the most detailed aqueous phase mechanism and an adequate tool for model studies of the tropospheric aerosol processing.

For model studies, CAPRAM 3.0i is coupled to an extended version of the gas phase mechanism RACM-MIM2 [12] with 281 reactions. Phase transfer processes are treated by means of the resistance model of Schwartz [13] considering Henry's equilibrium, gas phase diffusion and mass accommodation coefficients.

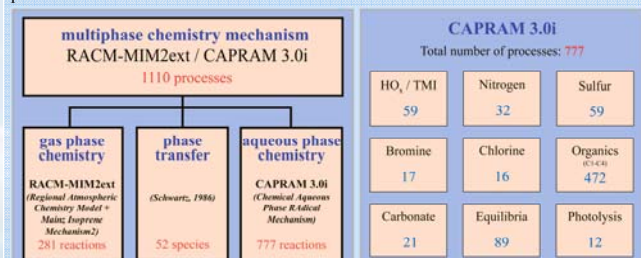


Figure 6: Scheme of the multiphase mechanism RACM-MIM2ext / CAPRAM 3.0i (left) and the number of processes in the chemical subsystems of CAPRAM (right).

References

- [1] H. Herrmann, *Chem. Rev.*, 103, 4691, 2003. [2] M. Chin and P.H. Wine, *J. Photochem. Photobiol.*, A 69, 17, 1992. [3] Donati, A., Dissertation, University of Leipzig, 2002. [4] Parajuli, K., Dissertation, University of Leipzig, 2007. [5] Hoffmann, D., Poster, 106. Hauptversammlung der Deutschen Bunsen-Gesellschaft für Physikalische Chemie, 2007. [6] Wicktor, F., Dissertation, University of Leipzig, 2009. [7] de Semanville, P. G., Hoffmann, D., George, C., Herrmann, H., *Phys. Chem. Chem. Phys.*, 9, 958, 2007. [8] Gligorovski, S., Dissertation, University of Leipzig, 2005. [9] P. Barzaghi and H. Herrmann, *Phys. Chem. Chem. Phys.*, 4, 3669, 2004. [10] S. Gligorovski and H. Herrmann, *Phys. Chem. Chem. Phys.*, 2004. [11] Herrmann, H., Tilgner, A., Majdik, Z., Barzaghi, P., Gligorovski, S., Poulain, L., Monod, A., *Atmospheric Environment*, 39 (23-24), 4351 – 4363, 2005. [12] Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A., Wahner, A., *Journal of Atmospheric Chemistry*, 55 (2), 167 – 187, 2006. [13] Schwartz, S., In: Jaeschke, W. (Ed.), *Chemistry of Multiphase Atmospheric Systems*, NATO ASI Series. Springer, Berlin, pp. 415-471, 1986.