

LASER-BASED STUDIES OF OH/RO₂ REACTIONS FOR CLOUD AND AEROSOL CHEMISTRY

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Introduction

Hydrocarbon oxidation in the aqueous tropospheric particle phase is mainly initiated by H-atom abstraction by hydroxyl radicals (OH). A second step leads to the formation of peroxy radicals by oxygen addition (Zellner and Herrmann, 1995). In order to assess their importance kinetic data for reactions with relevant organic compounds are needed. The rate constants and the activation energies of reactions of the OH-radical with organic compounds have been investigated for different temperatures and high ionic strengths.

Experimental Methods

Most kinetic investigations of the OH-radical in aqueous solution have been performed by competition kinetics. The problem of the often used SCN⁻-method is the possible side reaction of HO₂SCN⁻ and/or SCN⁻ which possibly could also react with the substrate. As a consequence, the obtained rate constant would be overestimated. A direct method was developed to determine the time dependence of OH-radical concentrations in the aqueous phase. An OH source was developed and spectroscopically investigated with the help of a CCD-Camera. The OH-radical is formed by excimer laser flash photolysis of water at 193 nm.

Results

The obtained absorption spectrum of the OH-radical is in reasonable agreement with the known literature spectra (Nielson et al., 1976 or Jayson and Parson, 1973). Using these data (extinction coefficient $\epsilon_{(\text{OH})10,244} = 500 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-1}$) the experimental setup was modified to observe the formation of RO₂-radicals. In the kinetic investigations of the RO₂-formation the interference by HO₂-radicals and OH-decay were taken into account. The HO₂-radical is absorbing at 244 nm ($\epsilon_{10,244} = 1080 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-1}$). The analyzing light source for the kinetic investigations is an internal frequency doubled Argon-ion-laser with an output wavelength of 244 nm (near the absorption maximum of the OH-radical and RO₂-radical). The detector unit used is a sensitive photo-diode connected to a digital oscilloscope. With this setup it is possible to measure rate constants of OH-radicals with relevant organic substances for tropospheric chemistry at different temperatures and ionic strengths via RO₂ product build-up kinetics.

The reactions of OH with atmospherically relevant substances like dicarboxylic acids, hydroxydicarboxylic acid and diketones and their temperature and ionic strengths dependencies were investigated to increase our knowledge of tropospheric chemistry.

References

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