

# LASER-BASED STUDIES OF OH/RO<sub>2</sub> REACTIONS FOR CLOUD AND AEROSOL CHEMISTRY

J. HESPER and H. HERRMANN

Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig.

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## INTRODUCTION

Free radicals play an important role in the chemistry of the aqueous tropospheric particle phase (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, i.e. by competition of two reactions with a known and a unknown rate constant. One of the standard competition kinetics methods for OH reactions in solution makes use of thiocyanate (Chin and Wine, 1994).

The problem of this method is the possible side reaction of HOSCN<sup>-</sup> and/or SCN<sup>-</sup> which possibly could also react with the substrate. As a consequence, the obtained rate constant would be overestimated. For this method a good knowledge of the competitor kinetics (rate constants at different temperatures, ionic strengths, pH-values and the exact reaction pathway) is needed. A direct method was developed to determine the time dependence of OH-radical concentrations in the aqueous phase. An OH source was developed and with the help of a CCD-Camera spectroscopically investigated. In Figure 1 the instrumental setup for spectroscopic investigations is shown.

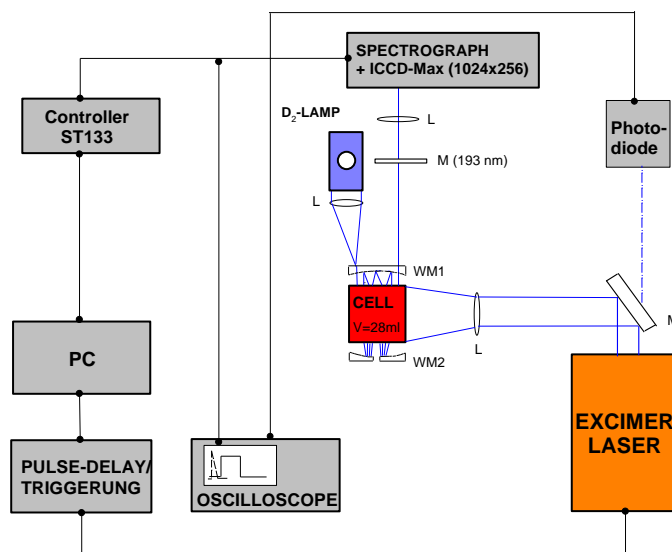


Figure 1. Laser-photolysis-longpath-absorption (LP-LPA) apparatus for the study of radical reactions.

The OH-radical is formed by excimer laser flash photolysis of water at 193 nm (active medium ArF):



The analyzing light source is a water-cooled Deuterium lamp (UV-light) folded 8 times through the cell (28ml) by the help of mirrors (WM1 and WM2) in White configuration to increase the sensitivity of the system. A CCD-Camera/grating combination was used to measure the absorption spectra of the radicals in the range of 200 nm to 400 nm.

The obtained absorption spectrum of the OH-radical is in reasonable agreement with the known literature spectra e.g. Nielson, S.O., B.D. Michael and E.J. Hart (1976) or Jayson, G.G. and B.J. Parson (1973). Using these data (extinction coefficient  $\epsilon_{(\text{OH})244,10} = 500 \text{ l}\cdot\text{mol}^{-1}\text{cm}^{-1}$ ) the experimental setup was modified to observe the formation of RO<sub>2</sub>-radicals. In the kinetic investigations of the RO<sub>2</sub>-formation the interference by HO<sub>2</sub>-radicals and OH-decay were taken into account. The HO<sub>2</sub>-radical is absorbing at 244 nm ( $\epsilon_{10,244} = 1080 \text{ l}\cdot\text{mol}^{-1}\text{cm}^{-1}$ ).



The analyzing light source is now a internal frequency doubled Argon-ion-laser with an output wavelength of 244 nm (near the absorption maximum of the OH-radical and RO<sub>2</sub>-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 organic substances of relevance for tropospheric chemistry at different temperatures and ionic strengths via RO<sub>2</sub> product build-up kinetics.

## CONCLUSIONS

The first investigations were performed to evaluate the kinetic setup. At first the reaction of OH with ethanol was investigated.



The hydroxy-alkyl-radical (CH<sub>3</sub>CHOH) quickly reacts with oxygen to build a hydroxyethylperoxyl radical CH<sub>3</sub>C(O<sub>2</sub>)HOH. After the correction the following rate constant was obtained.

$$k_{2\text{nd}} = (2.0 \pm 0.3) \cdot 10^9 \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$$

It is in good agreement with the known literature (e.g. Park and Getoff (1992);  $k_{2\text{nd}} = 1.9 \cdot 10^9 \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$ ). This reaction was also investigated in the present study in the temperature interval from 288 K to 328 K to obtain the activation energy  $E_A$

$$E_A (\text{OH} + \text{Ethanol}) = 14 \pm 4 \text{ kJ/mol.}$$

No data on the T-dependence are available from literature. The system was also investigated the first time at different ionic strengths (NaClO<sub>4</sub> as an inert salt). The reactions of OH with atmospherically relevant substances like dicarboxylic acids, hydroxydicarboxylic acid and diketones and their temperature and ionic strengths dependencies will be investigated next to increase our knowledge of tropospheric chemistry.

## ACKNOWLEDGEMENTS

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