Laser-Based Studies of OH/RO_2 Reactions for Cloud and Aerosol Chemistry

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Motivation

Hydrocarbon oxidation in the tropospheric aqueous particle phase is mainly initiated by H atom abstraction by the hydroxyl radicals (OH). A second step leads to the formation of peroxyl radicals by oxygen addition (Zellner and Herrmann, 1995). In order to assess the importance of such processes kinetic data for reactions with relevant organic compounds are needed. In the present study, the rate constants of OH radical reactions with organic compounds have been investigated for different temperatures. The intention of this work is to increase the knowledge in this area by using a new technique. Usually competition kinetic methods were used to determine rate constants of the OH radical with organic compounds, because the direct detection is difficult (low extinction coefficient of OH, overlapping absorption with organic peroxyl radicals). The new method follows the absorption/time profile at 244 nm (near the absorption maximum of OH radical) taking the interference of RO_2 and HO_2 into account.
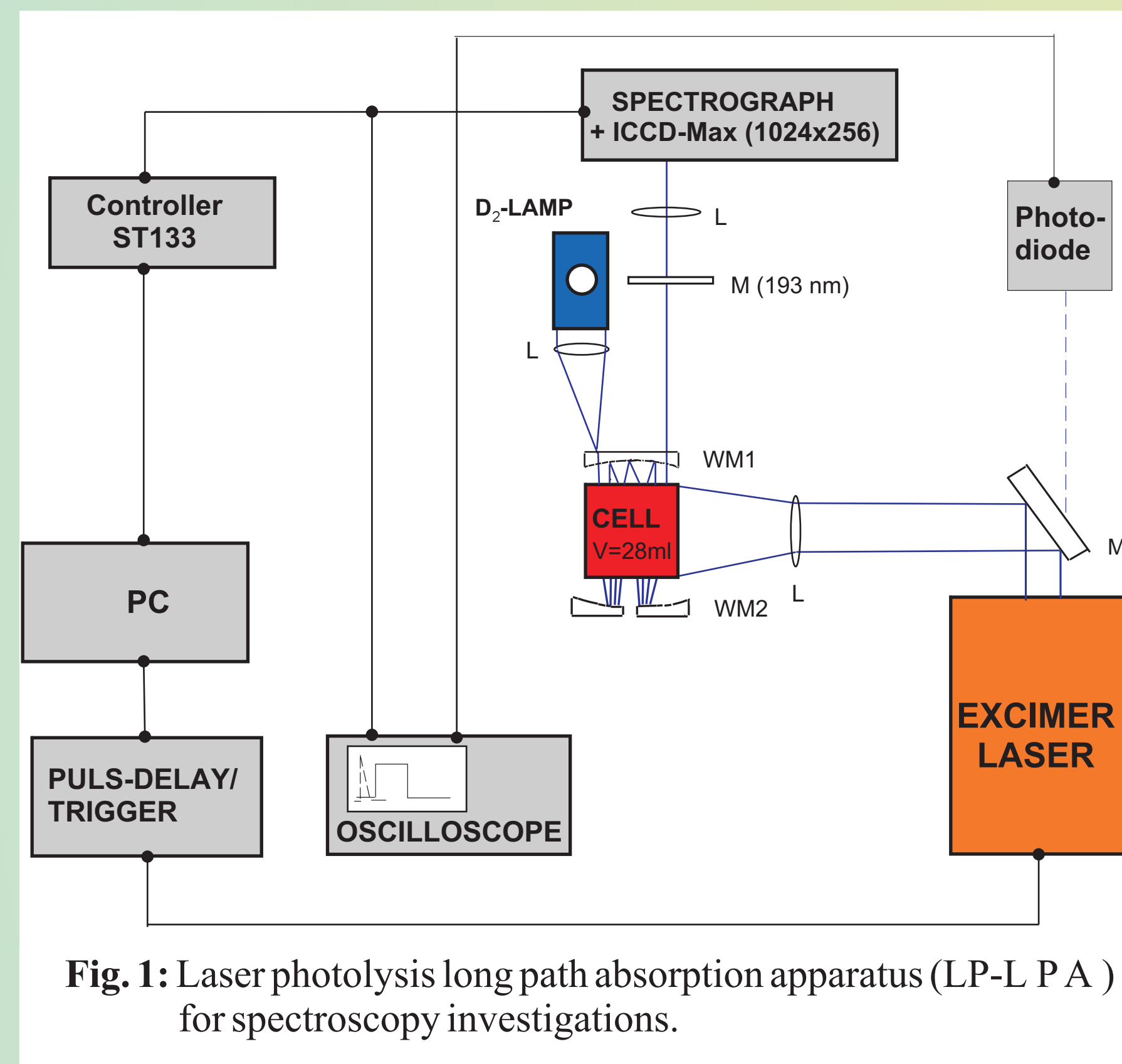
Spectroscopic Investigations

A new method was developed to determine the time dependence of OH radical reactivity in the aqueous phase. Figure 1 shows the schematic representation of the experimental setup used for spectroscopic investigations. An OH source was developed and spectroscopically investigated with a CCD-Camera /Grating combination. The OH radical is formed by excimer laser photolysis of water at 193 nm:

$$H_2O + h\nu \,(193\text{ nm}) \longrightarrow H + OH$$
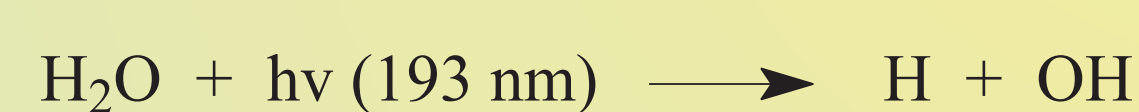
The analysing light source is a water cooled Deuterium lamp (UV-light). The output is focussed and folded 8 times through the cell (28 ml) by means of two mirrors (WM1 and WM2) in White configuration to increase the sensitivity of the system.
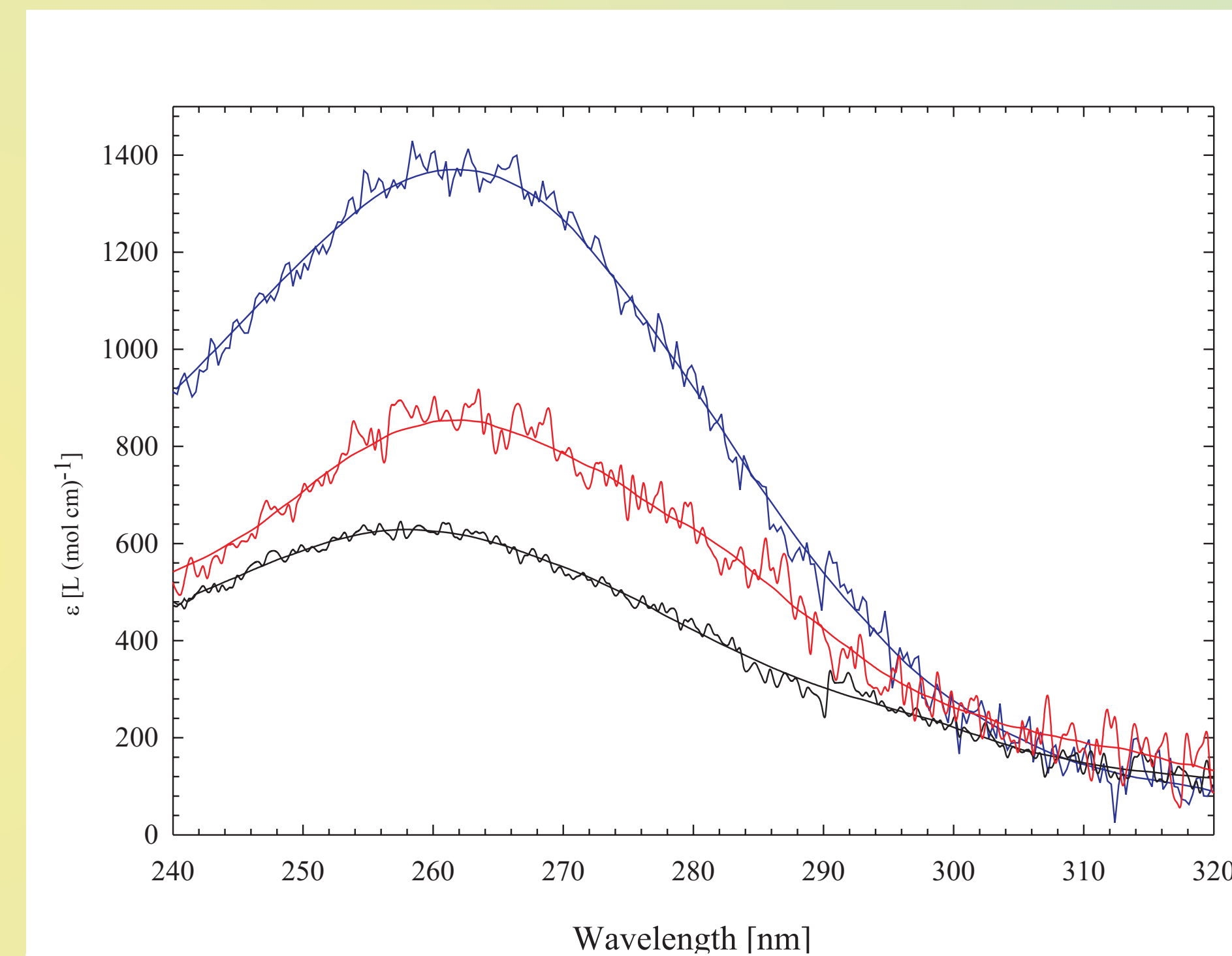

Fig. 1: Laser photolysis long path absorption apparatus (LP-L P A) for spectroscopy investigations.

Fig.2: Absorption spectra of the D,L-malic acid- (blue line), glutaric acid - (black line) and the adipic acid- peroxyl radical (red line).

Calculating the rate constant of OH radicals, the absorption characteristics of the respective peroxyl radicals (RO_2) are needed. Substances of atmospheric relevance like dicarboxylic acids, hydroxy-dicarboxylic acid etc were investigated. The absorption spectra of the peroxyl radicals of D,L-malic acid, glutaric acid and adipic acid were measured because no literature spectra were available. The absorption spectra of the D,L-malic acid peroxyl radical (blue line), the glutaric acid peroxyl radical (black line) and of adipic acid peroxyl radical (red line) are shown in Figure 2. For each spectrum 2000 single spectra were averaged to obtain a good signal to noise ratio.

Kinetic Investigations

The experimental setup was modified to measure OH kinetics by following the build-up of RO_2 radicals and taking the interference by HO_2 radicals and the OH decay into account. The analysing light source for the kinetic investigations is an internal frequency doubled Argon ion laser with an output wavelength of 244 nm. The detection unit used is a sensitive photo-diode connected to a digital oscilloscope. The RO_2, HO_2 and the OH radicals are absorbing at 244 nm ($\varepsilon\,(HO_2) = 1080\text{ l mol}^{-1}\text{cm}^{-1}$; $\varepsilon\,(OH) = 500\text{ l mol}^{-1}\text{cm}^{-1}$; e.g. ε (Malic acid peroxyl radical) = $1030\text{ l mol}^{-1}\text{cm}^{-1}$.

With this setup it is possible to study the reactivity of OH radicals with organic substances like dicarboxycylic acids, hydroxycarboxylic acid, alcohols etc. at different temperatures and ionic strengths. The obtained absorption/time profiles were corrected by using the equations shown on the right side. For pseudo first order conditions the reactant (RH) was added in excess. The solution was saturated with oxygen (O_2) in order to make the reaction OH + reactant the rate determining step.

Reaction scheme:

$$H_2O + h\nu \,(193\text{ nm}) \longrightarrow H + OH$$

Absorbance

$$lg(I_0/I) = \varepsilon \cdot c \cdot d$$

$$1/d \; lg\,(I_0/I) = \varepsilon_{OH}[\cdot OH]_t + \varepsilon_{RO2}\,[RO_2]_t + \varepsilon_{HO2}[HO_2]_{end}$$

with

$$[HO_2]_{end} = [RO_2]_{end}$$

$$[\cdot OH]_t = [RO_2]_{end} - [RO_2]_t$$

$$[RO_2]_t = \frac{\frac{1}{d}\cdot lg\left(\frac{I_0}{I}\right) - \varepsilon_{OH}\cdot[RO_2]_{end} - \varepsilon_{HO2}\cdot[RO_2]_{end}}{\varepsilon_{RO2} - \varepsilon_{OH}}$$

$$[RO_2]_{end} = \frac{1}{d\,(\varepsilon_{RO2} + \varepsilon_{OH})}\cdot lg\left(\frac{I_0}{I}\right)$$
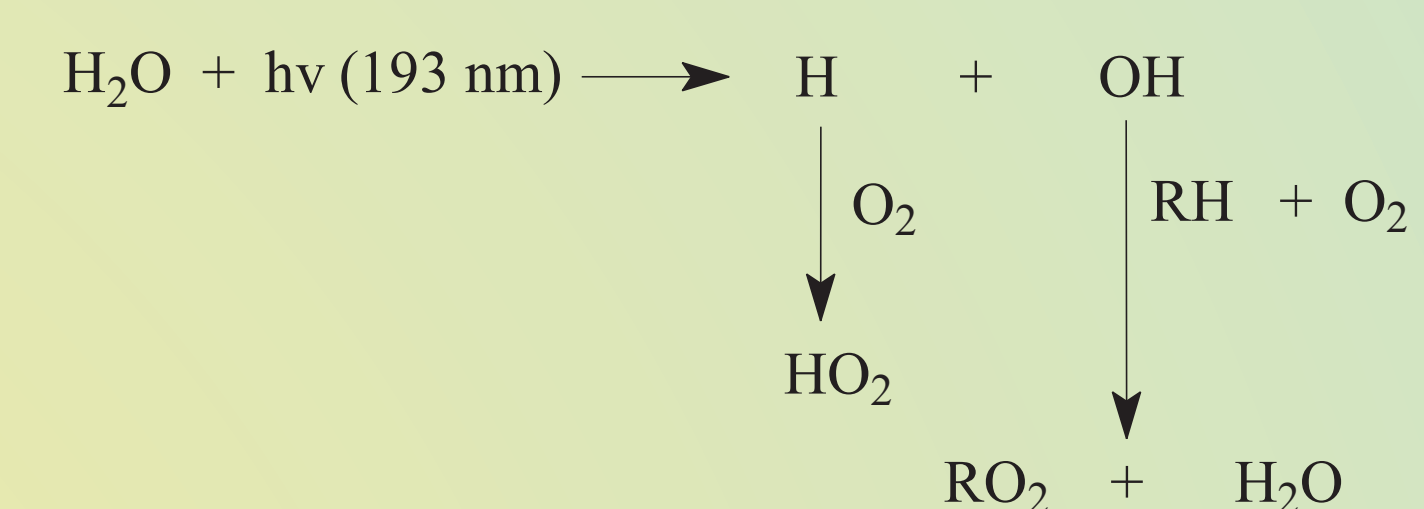
In order to obtain kinetical data for reactions of OH radicals with atmospheric relevant substance were investigated in the temperature interval between 278 - 328 K. The Arrhenius plot of OH + D,L-malic acid is shown as an example (Figure 3). The obtained rate constant at 298 K is in reasonable agreement with the literature value given by Cabelli and Bielski, 1985: $k(298) = 8.2 \cdot 10^8\,1(\text{mol s})^{-1}$
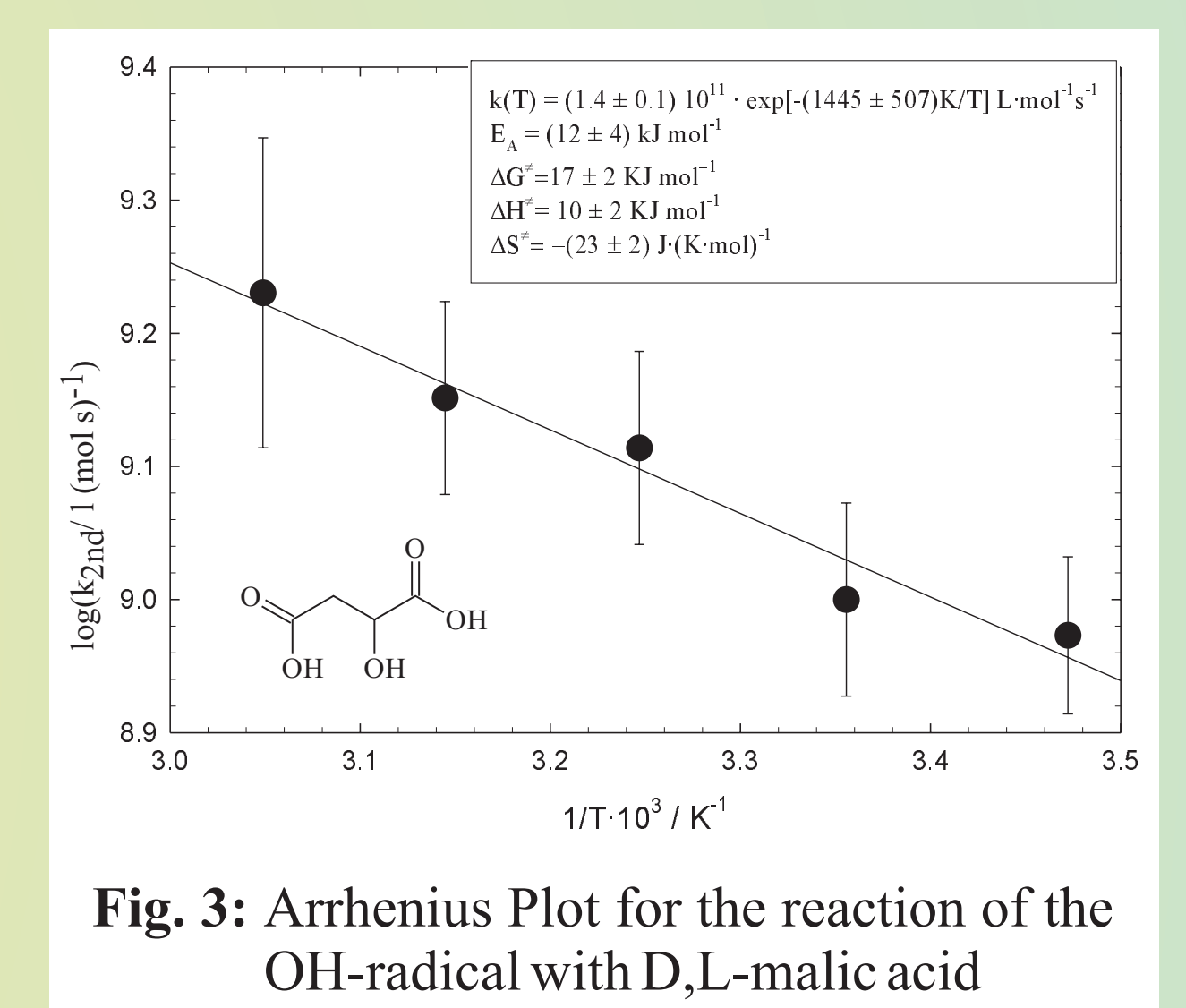

Fig. 3: Arrhenius Plot for the reaction of the OH-radical with D,L-malic acid

Reactant	pH	k(298 K) [l (mol s)$^{-1}$]	E_A [kJ mol^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J (K mol)$^{-1}$]
Alcohol						
Ethanol	2.0	$(2.0 \pm 0.3)\cdot 10^9$	14 ± 4	13 ± 2	16 ± 2	$- (23 \pm 2)$
2-Propanol	2.0	$(1.9 \pm 0.4)\cdot 10^9$	16 ± 4	7 ± 2	14 ± 2	$- (23 \pm 2)$
Hydroxydicarboxylic acid						
D,L-Malic acid	1.5	$(1.0 \pm 0.2)\cdot 10^9$	12 ± 4	17 ± 2	10 ± 2	$- (12 \pm 1)$
Dicarboxylic acid						
Glutaric acid	2.0	$(5.1 \pm 0.9)\cdot 10^9$	19 ± 6	16 ± 3	17 ± 3	$- (3 \pm 1)$

Table 1: Measured rate constants and thermochemical parameters for the reaction of OH with atmospheric relevant compounds.

Summary and Outlook

An OH radical source in aqueous solution was further developed. The OH radical and the peroxyl radicals were investigated in the wavelength region from 200 to 300 nm and 230 to 400 nm, respectively.
A new method was developed to determine OH reactivity with substances of atmospheric relevance by following the build up kinetic of the RO_2 radicals at 244 nm and taking the interference by HO_2 radicals and OH decay into account.
The obtained kinetic data will be implemented in a tropospheric multiphase model (CAPRAM2.4) to better understand the formation and degradation processes of higher hydrocarbons in cloud droplets or liquid aerosol particles.

References

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