Kinetic and spectroscopic investigations of OH radical reactions with tropospheric relevant compounds in aqueous solution

J. Hesper, P. Barzaghi and H. Herrmann

Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany

Introduction

The high reactivity and the ubiquity of OH radical make it one of the most important sink for volatile organic compounds both in the gas and aqueous tropospheric phases and as a consequence one of the most studied radical (Fynlayson-Pitts and Pitts, 2000). Furthermore, current tropospheric chemistry model predict that the conversion of organic compounds in the aqueous phase is dominated by the OH chemistry in daylight conditions (Ervens et al., 2004). The radical oxidation processes of organic compounds are driven by OH radicals, which are reacting with the compounds considered in this study through an H-abstraction mechanism. In literature rate constants for the reactions of OH with organics in aqueous solution were usually determined using kinetic competition methods with the help of reference rate constant, such as thiocyanate (see Herrmann, 2003 for a review). Only in the case of the reactions of OH with methanol, ethanol, 2-propanol and tert-butyl alcohol the rate constants have been obtained by direct optical absorption measurement at room temperature (Alam et al., 2003). A direct method was developed and applied for the study of the reactivity of OH radical towards organic compounds in aqueous phase. Spectroscopic and kinetic investigations were carried out using a laser flash photolysis long path laser absorption (LFP-LPLA) setup by means of which the reactions of OH with: (**1**) 2-propanol, (**2**) 1-butanol, (**3**) 2-butanol, (**4**) propionaldehyde, (**5**) butyraldehyde, (**6**) acetone, (**7**) 2-hydroxy-3-butanone, (**8**) D,L- malic acid, (**9**) D,L-maleate dianion, (**10**) glutaric acid, (**11**) D,L-glutarate dianion, (**12**) adipic acid, (**13**) adipate dianion, (**14**) pimelic acid, (**15**) pimelate dianion, (**16**) suberic acid and (**17**) suberate dianion were studied.

Experimental

A laser photolysis long path absorption apparatus (LP-LPA) was used (Figure 1) to investigate the reactivity of OH radicals in condensed phase.

For the spectroscopic characterisation of the OH radical the laser flash photolysis of water at 193 nm was used.

$$H_2O + h\nu \ (\lambda = 193 \ nm, 400 \ mJ) \rightarrow H + OH$$

In the kinetic studies OH radicals were generated trough the laser flash photolysis of hydrogen peroxide at $\lambda = 248$ nm:

$$H_2O_2 + h\nu \ (\lambda = 248 \ nm, 650 \ mJ) \rightarrow 2 \ OH$$

In experimental setup for the spectroscopic investigations the laser photolysis long path absorption apparatus is coupled with a CCD-camera / grating used as detector.
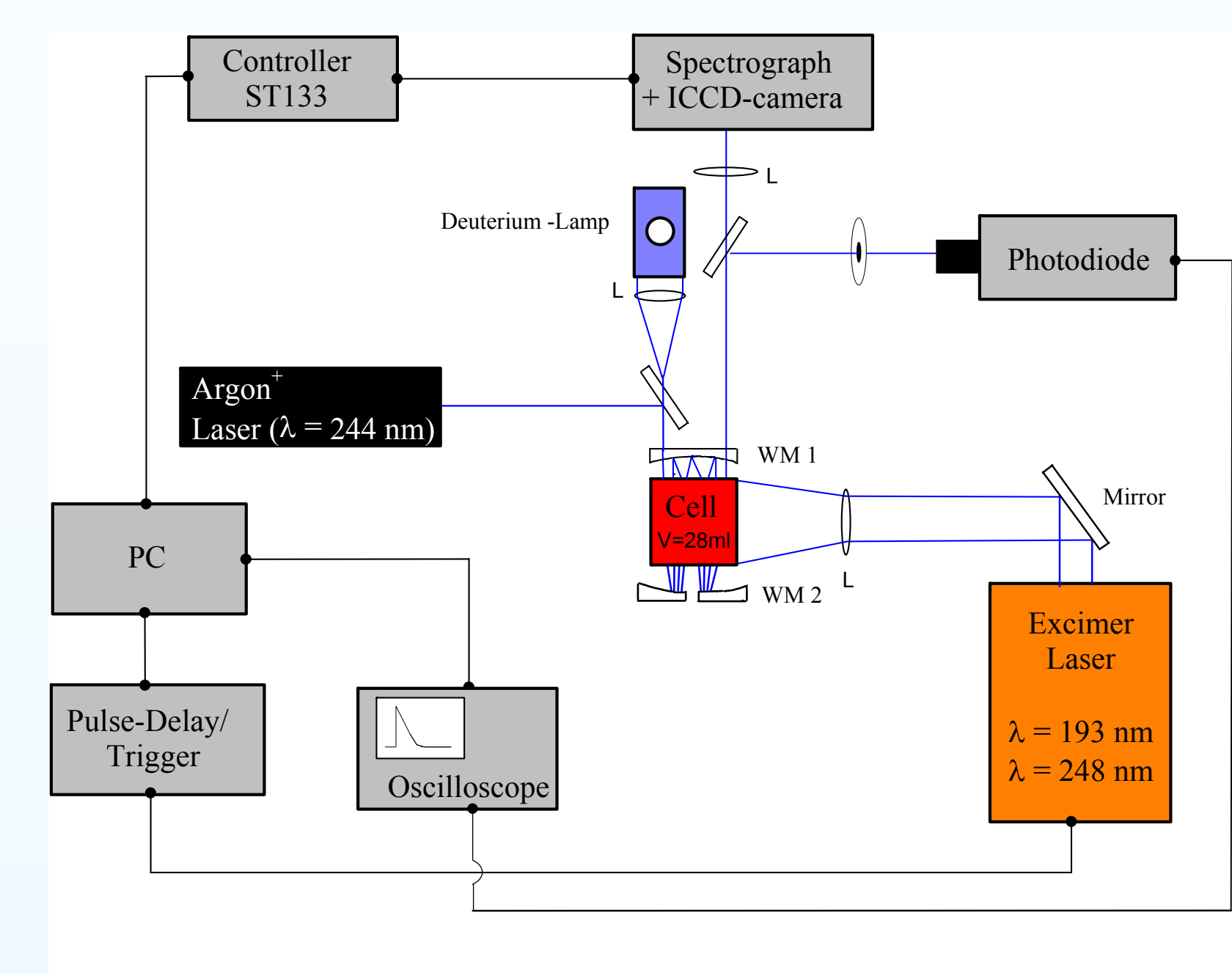
Figure 1: Experimental set-up of laser photolysis long path absorption (LP-LPA) experiment

For kinetic investigations a modified setup is used. The broadband UV-light source (water cooled deuterium lamp is changed to a frequency doubled argon$^+$-laser ($\lambda = 244$ nm). Thus, time resolved absorption profiles at one single wavelength can be followed using a photodiode as a detector.
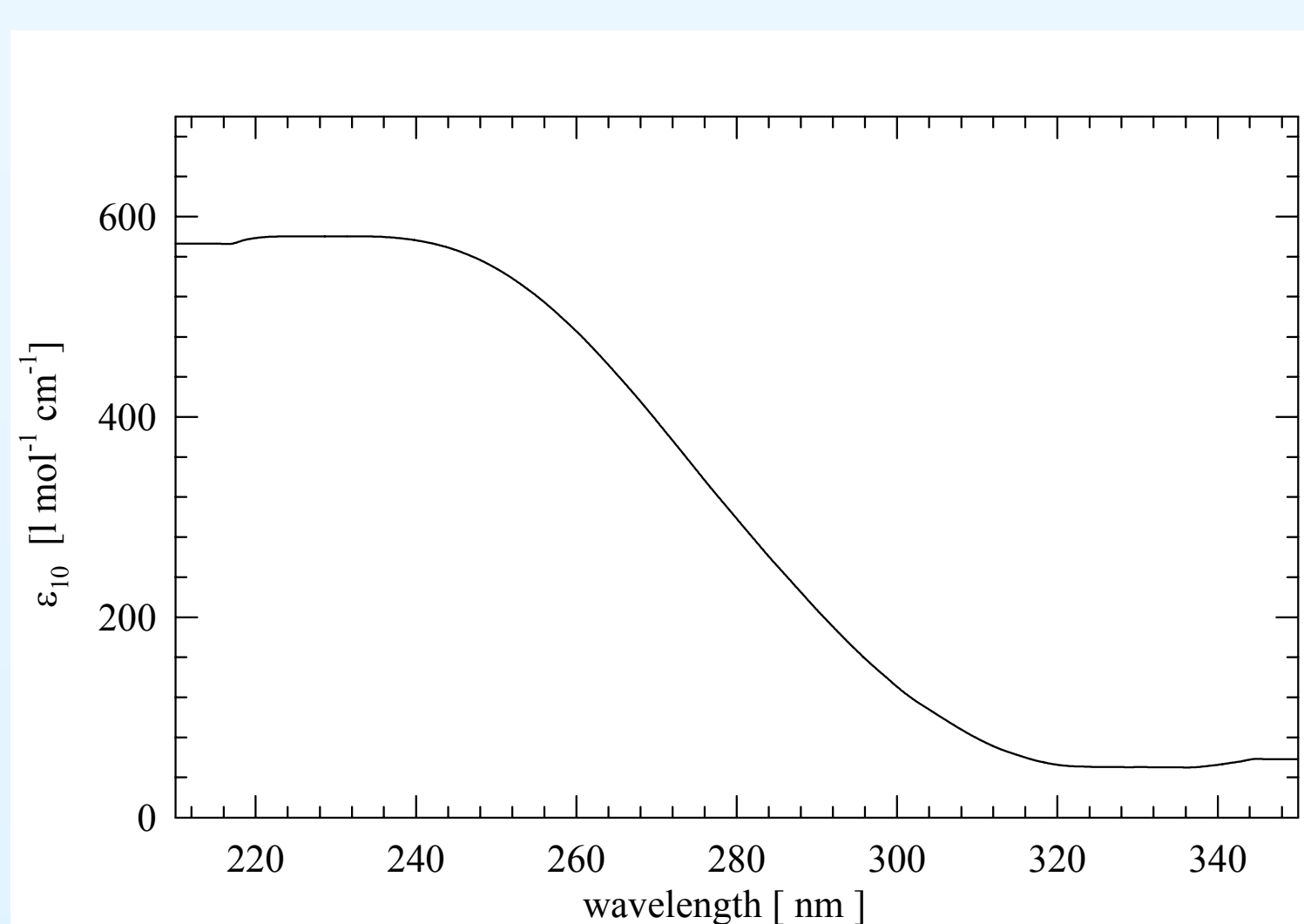

Figure 2: Absorption spectra of OH radical in aqueous phase

The OH absorption spectrum in aqueous solution is much different from its absorption spectrum in the gas phase. In fact, in aqueous solution the maximum absorption is found around $\lambda = 235$ nm as shown in Figure2.

This leads to the idea to use an internally frequency-doubled Ar$^+$-laser to directly monitor the absorption of OH at $\lambda = 244$ nm. However, when organic substances are investigated, the decay of absorption of OH is overlapped by the rising absorption of the organic radicals, or, in the presence of oxygen, the organic peroxyl radicals. Hence, to derive the rate constant for the reaction of OH with an organic substrate RH in the presence of oxygen, the observed intensity vs. time profile has to be numerically treated accordingly. The method requires the knowledge of the absolute absorption coefficient of the peroxyl radical formed at $\lambda = 244$ nm.

Furthermore, signals recorded by a digital oscilloscope were transferred to a computer. The reaction cell as well as the reservoir tank are fully thermosted and allow to perform kinetic investigations in a temperature range between 278K to 328 K.

Results and Discussions

The reactions of OH with most of the saturated aliphatic organics in aqueous solution are suggested to proceed via the abstraction of the most loosely bound hydrogen atoms present in the organic molecule. The resulting carbon-centred radicals, are known to react with oxygen at rates which are close to diffusion controlled (von Sonntag, 1987). Thus, the oxidation reaction chain proceeds with an almost diffusion controlled addition of a molecule of oxygen to the alkyl radical with the formation of the corresponding peroxyl radical and the rate constant is estimated to be k = 2·10⁹ l mol⁻¹ s⁻¹. The main spectral properties of organic peroxyl radicals obtained in the present study are summarised in Figure 3 and Table 1.
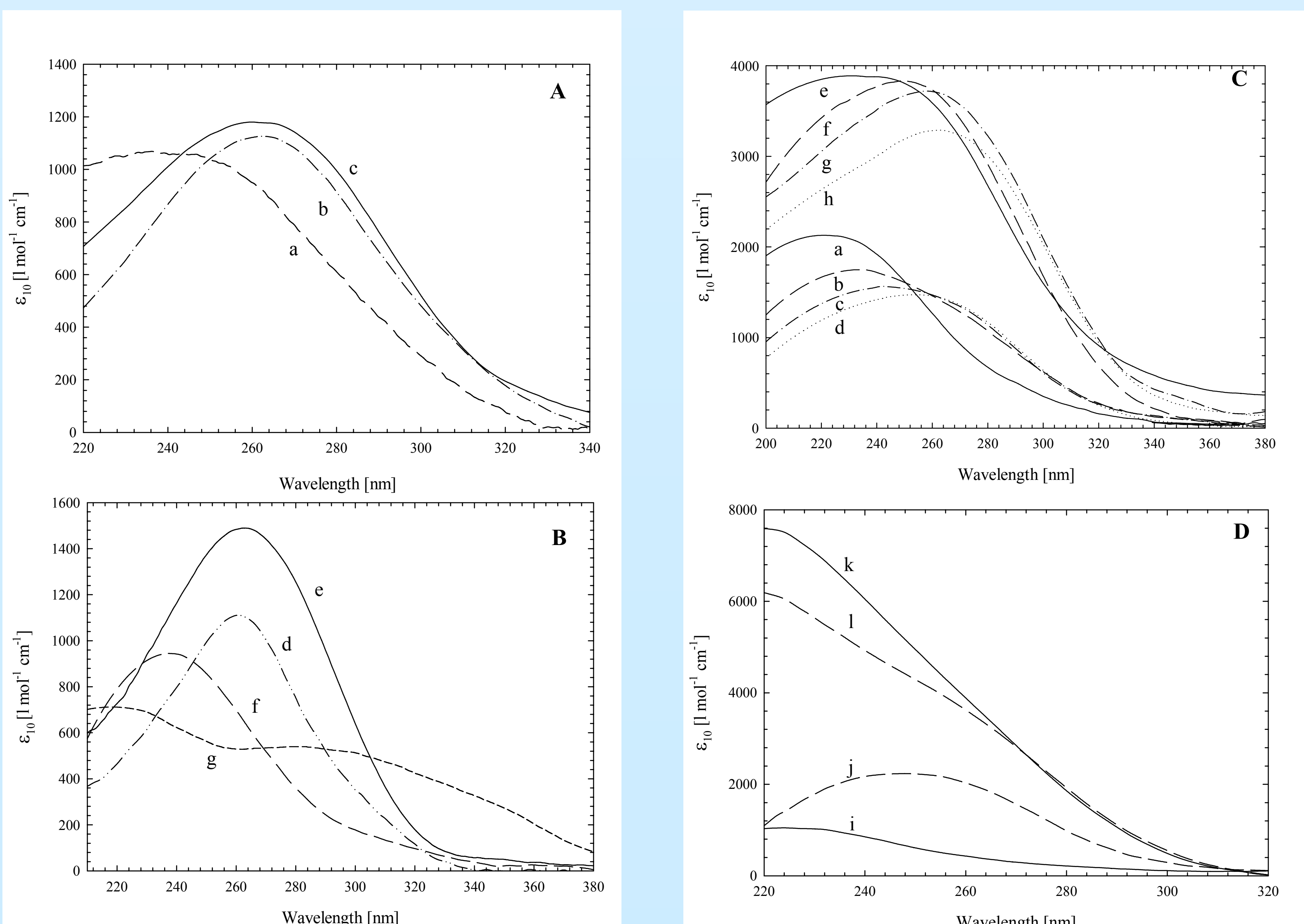
Table 1: Spectroscopic data of peroxyl-radicals in aqueous solution

Spectra Nr.		Parent Compound	pH	λ_{max} (nm)	ε_{10} (l mol⁻¹ cm⁻¹)
3A	a	2-Propanol	6.0	248	1060
	b	1-Butanol	6.0	260	936
	c	2-Butanol	6.0	260	1180
3B	d	Propionaldehyde	5.8	260	1110
	e	Butyraldehyde	5.8	263	1490
	f	Acetone	6.0	217	712
	g	2-Hydroxy-3-butanone	5.8	236	945
3C	a	Glutaric acid	2.0	224	1818
	b	Adipic acid	2.0	234	1680
	c	Pimelic acid	2.0	244	1560
	d	Suberic acid	2.0	255	1470
	e	Glutarate (dianion)	9.0	234	3885
	f	Adipate (dianion)	9.0	250	3845
	g	Pimelate (dianion)	9.0	260	3770
	h	Suberate (dianion)	9.0	262	3330
3D	i	Tartronic acid	0.5	224	1160
	j	D,L-Malic acid	0.5	248	2235
	k	Tartronate (dianion)	9.0	219	8470
	l	Malate (dianion)	9.0	214	6830

In oxygen saturated solution, the H-atom abstraction by the OH-radical (R-a) becomes the rate determining step due to the diffusion controlled reaction of the corresponding alkyl-radical (R-b):

$$OH + RH \rightarrow H_2O + R \quad (R\text{-}a)$$
$$R + O_2 \rightarrow RO_2 \quad (R\text{-}b)$$
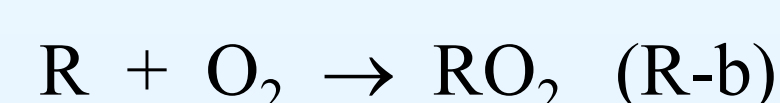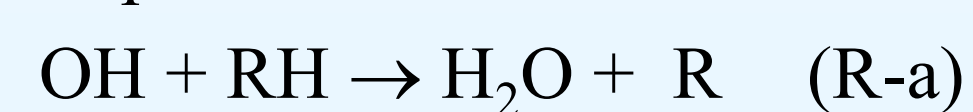
and with $[RH] \gg [OH]$, $[O_2] \gg [R]$

Thus, the absorption/time profile measured at l = 244 nm can be taken to calculate the rate constant of the OH-radical reaction by following the build up of the peroxyl-radical and by taking the absorption of the OH-radical into account.

The kinetic data obtained in this study show a good agreement with recent literature studies (Ervens et al., 2003; Gligorovski and Herrmann, 2004). The obtained results are summarised in Table 2.

Table 2: Kinetic data for the reaction of OH with organic compounds in aqueous solution.

	Compound	k (298 K) (l⁻¹ mol⁻¹s⁻¹)	A (l⁻¹ mol⁻¹s⁻¹)	E_A (kJ mol⁻¹)
	Alcohols			
R-1	2-propanol	$(2.1 \pm 0.2) \cdot 10^9$	$(6.1 \pm 0.3) \cdot 10^{10}$	8 ± 2
R-2	1-butanol	$(4.1 \pm 0.8) \cdot 10^9$	$(1.0 \pm 0.1) \cdot 10^{11}$	8 ± 1
R-3	2-butanol	$(3.5 \pm 0.4) \cdot 10^9$	$(7.4 \pm 0.3) \cdot 10^{10}$	8 ± 3
	Carbonyl Compounds			
R-4	Propionaldehyde	$(2.8 \pm 0.3) \cdot 10^9$	$(2.6 \pm 0.1) \cdot 10^{11}$	11 ± 3
R-5	Butyraldehyde	$(3.9 \pm 1.0) \cdot 10^9$	$(8.1 \pm 0.3) \cdot 10^{10}$	8 ± 3
R-6	Acetone	$(1.3 \pm 0.1) \cdot 10^8$	$(8.4 \pm 0.4) \cdot 10^{10}$	16 ± 3
R-7	2-Hydroxy-3-butanone	$(2.9 \pm 1.0) \cdot 10^9$	$(2.9 \pm 0.1) \cdot 10^{11}$	11 ± 3
	Dicarboxylic acids and corresponding dianions			
R-8	D,L-Malic acid	$(7.1 \pm 1.3) \cdot 10^8$		
R-9	D,L-Maleate dianion	$(8.4 \pm 1.0) \cdot 10^8$		
R-10	Glutaric acid	$(6 \pm 2) \cdot 10^8$		
R-11	Glutarate dianion	$(1.0 \pm 0.2) \cdot 10^9$		
R-12	Adipic acid	$(1.7 \pm 0.3) \cdot 10^9$		
R-13	Adipate dianion	$(2.4 \pm 0.2) \cdot 10^9$		
R-14	Pimelic acid	$(2.4 \pm 0.7) \cdot 10^9$		
R-15	Pimelate dianion	$(2.9 \pm 0.8) \cdot 10^9$		
R-16	Suberic acid	$(5.0 \pm 0.4) \cdot 10^9$		
R-17	Suberate dianion	$(5.8 \pm 0.3) \cdot 10^9$		

Summary and Conclusions

✓ The current method allows to measure rate constants of OH-radicals with tropospheric relevant organic substances at different temperatures and ionic strengths via peroxyl radicals product build-up kinetics.

✓ The method is independent of reference reactions needed for competitions kinetic methods

✓ The presented results are in good agreement with literature data

✓ The kinetic data obtained from this study will be implemented in the tropospheric multiphase model CAPRAM

Figure 3: Absorption spectra of the peroxy radicals investigated in this study (see Table 1)

Literature

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