

Laser-based Studies of Aqueous Phase Radical Reactions of Relevance for Tropospheric Chemistry

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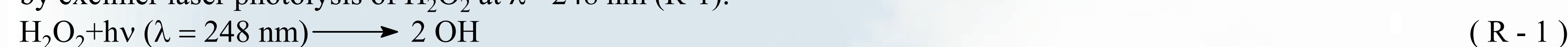
Introduction

Oxygenated organic compounds are either directly emitted to the atmosphere as fuel additives or solvents or they are formed in the troposphere as intermediate products of chemical degradation of other volatile organic compounds. Their presence in the atmosphere also results in formation of other secondary pollutants and tropospheric ozone. Furthermore, more polar intermediates and products will be formed upon their gas phase oxidation which could be transferred to the aqueous phase. The major degradation pathways of these organic compounds might be the reaction with OH, NO₃ and halogens radicals in the tropospheric aqueous phase. Part of the presented kinetic data have been implemented in the new version of our tropospheric multiphase chemistry model, i.e. CAPRAM 3.0 (Herrmann et al., 2005).

Experimental

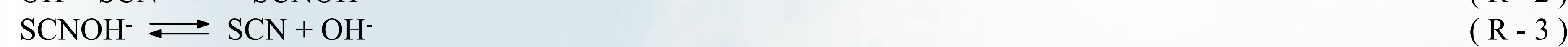
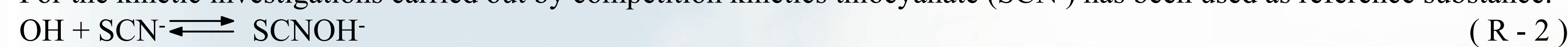
Using a laser-photolysis-long-path-laser-absorption (LP-LPLA) technique rate constants for the reactions of important atmospheric radical with oxygenated organic compounds have been measured.

The temperature dependency of the rate constant has been investigated for the reaction of OH with oxygenated organic compounds using a direct method based on RO₂ build-up kinetic (Figure 1a). The formation of the OH radicals was initiated by excimer laser photolysis of H₂O₂ at λ = 248 nm (R-1).



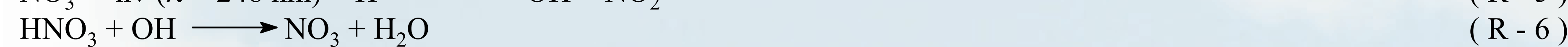
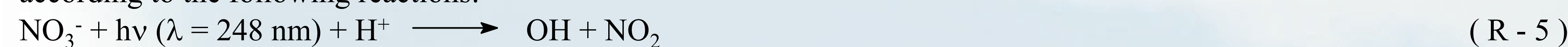
Using as analytical light source an Ar⁺ laser at λ = 244 nm, time resolved absorption profiles at one single wavelength can be followed using a photodiode as a detector.

For the kinetic investigations carried out by competition kinetics thiocyanate (SCN⁻) has been used as reference substance.



The (SCN)₂⁻ radical is strongly absorbing light 475 nm. Therefore the analysis light was emitted by an cw-laser at λ = 473 nm (Figure 1b). The temperature dependent rate constant on reaction OH + SCN⁻, reported by Chin and Wine (k = 1.24 · 10¹⁰ M⁻¹s⁻¹ at 298 K) has been applied as reference data set.

NO₃ radicals were generated by flash photolysis of nitrate anions at λ = 248 nm under acidic conditions (pH = 0.5) according to the following reactions:



The temporal change of the NO₃ concentration was followed using a He-Ne laser operated at λ = 632.8 nm (Figure 1c).

Br-atoms in aqueous solution have been generated by photolysis of bromoacetone operating at λ = 248 nm by an excimer laser.



A high pressure mercury xenon lamp has been used as an analytical light. The decay of Br-atoms is followed by using its absorption at λ = 297 nm which is close to the absorption maxima of Br-atoms (Figure 1d).

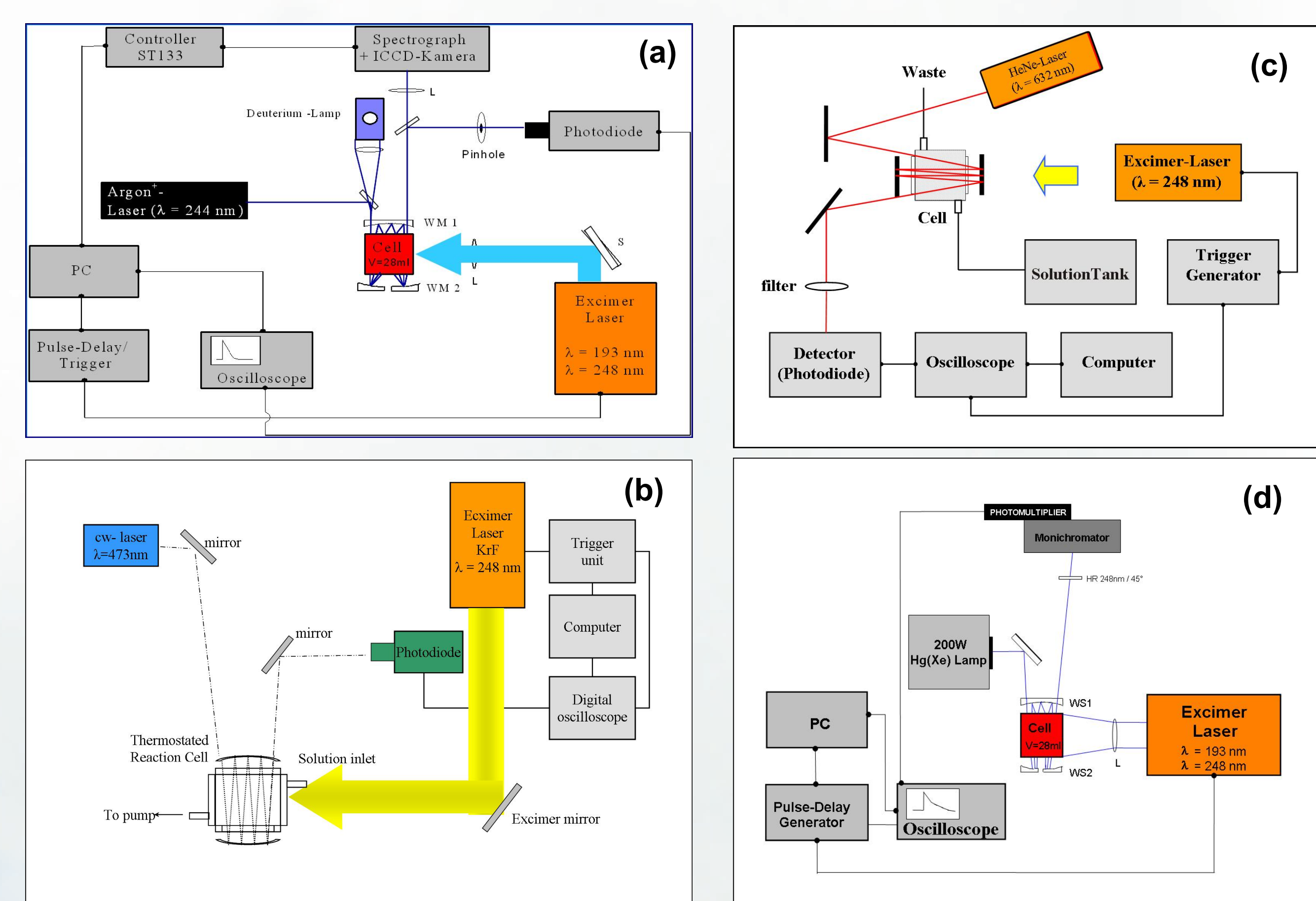


Figure 1. Schematic of the experimental set-ups used for the study of reaction of: (a) OH semi-direct method; (b) OH kinetics competition method; (c) NO₃ radical; (d) Br-atom with oxygenated organic compounds in aqueous solution.

Results and Discussions

Table 1. Summary of kinetic results obtained for the reactions of important atmospheric radical species with oxygenated organic compounds in aqueous solution.

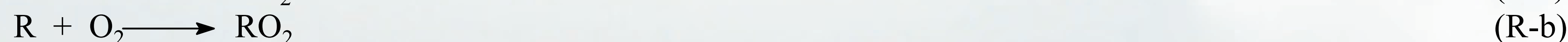
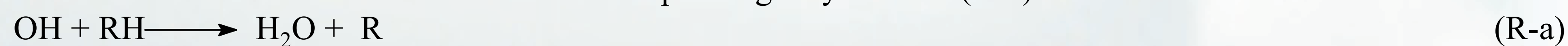
Compound	Radical	k (298 K) (l ⁻¹ mol ^l s ⁻¹)	A (l ⁻¹ mol ^l s ⁻¹)	E _A (kJ mol ⁻¹)	Remarks
Alcohols					
2-propanol	OH	(2.1 ± 0.2) · 10 ⁹ (2.1 ± 0.9) · 10 ⁹	(6.1 ± 0.3) · 10 ¹⁰ -	8 ± 2 -	a b
	Br	(1.8 ± 0.4) · 10 ⁶	(7.8 ± 1.2) · 10 ¹⁰	26 ± 10	
1-butanol	OH	(4.1 ± 0.8) · 10 ⁹	(1.0 ± 0.1) · 10 ¹¹	8 ± 1	a
2-butanol	OH	(3.5 ± 0.4) · 10 ⁹	(7.4 ± 0.3) · 10 ¹⁰	8 ± 3	a
	Br	(1.5 ± 0.2) · 10 ⁶	(2.0 ± 0.1) · 10 ⁹	18 ± 4	
Carbonyl Compounds					
Propionaldehyde	OH	(2.8 ± 0.3) · 10 ⁹	(2.6 ± 0.1) · 10 ¹¹	11 ± 3	a
	Br	(5.7 ± 2.0) · 10 ⁷	(1.1 ± 0.1) · 10 ⁹	5 ± 2	
	NO ₃	(5.8 ± 1.6) · 10 ⁷	(3.0 ± 0.5) · 10 ¹¹	22 ± 11	
Butyraldehyde	OH	(3.9 ± 1.0) · 10 ⁹	(8.1 ± 0.3) · 10 ¹⁰	8 ± 3	a
	Br	(1.0 ± 0.2) · 10 ⁸	(4.7 ± 0.6) · 10 ⁹	7 ± 6	
	NO ₃	(5.6 ± 2.3) · 10 ⁷	(5.0 ± 0.4) · 10 ¹⁰	17 ± 4	
Isobutyraldehyde	OH	(2.9 ± 1.0) · 10 ⁹	(3.0 ± 0.1) · 10 ¹⁰	6 ± 3	b
	Br	(1.0 ± 0.2) · 10 ⁸	(6.7 ± 2.2) · 10 ⁸	5 ± 17	
Acetone	OH	(1.3 ± 0.1) · 10 ⁸	(8.4 ± 0.4) · 10 ¹⁰	16 ± 3	a
	Br	(2.1 ± 0.6) · 10 ⁸	(3.4 ± 0.4) · 10 ¹¹	18 ± 11	b
2-butanone	OH	(1.5 ± 0.7) · 10 ⁹	(5.1 ± 0.6) · 10 ¹¹	15 ± 8	b
	NO ₃	(2.2 ± 0.4) · 10 ⁷	(4.0 ± 0.9) · 10 ¹¹	24 ± 15	
Diacetyl	OH	(2.8 ± 0.6) · 10 ⁸	(4.3 ± 0.3) · 10 ¹²	24 ± 5	b
Acetylacetone	OH	(7.6 ± 1.1) · 10 ⁸	(1.1 ± 0.1) · 10 ¹¹	12 ± 5	b
Acetoin	OH	(2.9 ± 1.0) · 10 ⁹	(2.9 ± 0.1) · 10 ¹¹	11 ± 3	a
Dicarboxylic acids and corresponding dianions					
Mesoxalic acid		(1.8 ± 0.3) · 10 ⁸	(3.8 ± 0.8) · 10 ¹⁰	13 ± 13	b
D,L-Malic acid		(7.1 ± 1.3) · 10 ⁸			a
D,L-Maleate dianion		(8.4 ± 1.0) · 10 ⁸			a
Glutaric acid		(6.0 ± 2.0) · 10 ⁸			a
Glutarate dianion		(1.0 ± 0.2) · 10 ⁹			a
Adipic acid	OH	(1.7 ± 0.3) · 10 ⁹			a
Adipate dianion		(2.4 ± 0.2) · 10 ⁹			a
Pimelic acid		(2.4 ± 0.7) · 10 ⁹			a
Pimelate dianion		(2.9 ± 0.8) · 10 ⁹			a
Suberic acid		(5.0 ± 0.4) · 10 ⁹			a
Suberate dianion		(5.8 ± 0.3) · 10 ⁹			a

a) kinetic data obtained with the semi-direct method; b) kinetic data obtained with the competition kinetics method.

Semi-direct method vs kinetics competition method

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-centered 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 peroxy radical and the rate constant is estimated to be k = 2 · 10⁹ M⁻¹s⁻¹.

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):



and with [RH] >> [OH], [O₂] >> [R]

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

The kinetic data obtained in this study with the semi-direct method show a good agreement with the data obtained from kinetic competition method and recent literature studies (Ervens et al., 2003; Gligorovski and Herrmann, 2004; Herrmann, 2003). The obtained results are reported in Table 1.

Reaction with alcohols

Considering available literature and the data presented here, alcohols appear to react with OH radicals with rate constants increasing with the increasing of the length of the carbon atom linear chain carrying the hydroxyl group.

The reactions of OH with alcohols show to proceed three order of magnitude faster than the reactions with Br-atom, whereas Cl-atom has a comparable reactivity to OH (Wicktor et al., 2003).

Reactions with carbonyl compounds

In the aqueous phase, carbonyl compounds are also reacting through an H-abstraction mechanism with OH, NO₃ and Br. It can be seen that OH radicals represent also in the case of aldehydes and ketones the most reactive species, however smaller differences in rate coefficients respect to Br have been observed.

Whereas OH and Br show activation energies (E_A) activation similar, NO₃ radical presents a stronger influence of the temperature on the rate constants (Table 1).

Reactions with dicarboxylic acids

In this work only the reactions of OH with different dicarboxylic acids have been reported. The rate constant obtained for the not dissociate form of the diacids are in good agreement with existing literature (Hesper et al., 2005). To the best knowledge of the authors, the reaction of OH with the anionic form of the acids have been measured for the first time.

It can be seen that the dianionic form react always faster than the corresponding acid, furthermore this difference in the reactivity seems to become smaller with the increase of the number of the carbon atoms (Table 1).

Reference

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Acknowledgements

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