

Motivation

The degradation of hydrocarbons in the atmosphere produces mainly oxygen-containing organic compounds. The presence of these compounds, for example acetone, in the troposphere strongly influences atmospheric key processes. Such oxygenated species are, for example, carriers of reactive nitrogen and are easily photolysed, producing free radicals and so influence the oxidizing capacity and the ozone-forming potential of the atmosphere and may also contribute significantly to the organic component of aerosols. But knowledge of the distribution and sources of oxygenated organic compounds is limited. Oxidation reactions of water soluble organic compounds in the atmospheric aqueous phase (cloud droplets, fog, rain, deliquescent particles) can be as fast as in the gas phase, but lead to different reaction products or different product distributions. Figure 1 shows the state of the art reaction scheme of the degradation of acetone in aqueous solution, but there are significant differences within the data from the literature. The objective of this work is to identify and characterize the various transient species formed in the oxidation of carbonyl compounds such as acetone. This characterization is necessary to measure rate constants of elementary reaction steps in the course of the degradation process. The spectroscopic and kinetic information will allow to clarify issues in the acetone chemistry and gives better understanding of the atmospheric fate of carbonyl compounds.

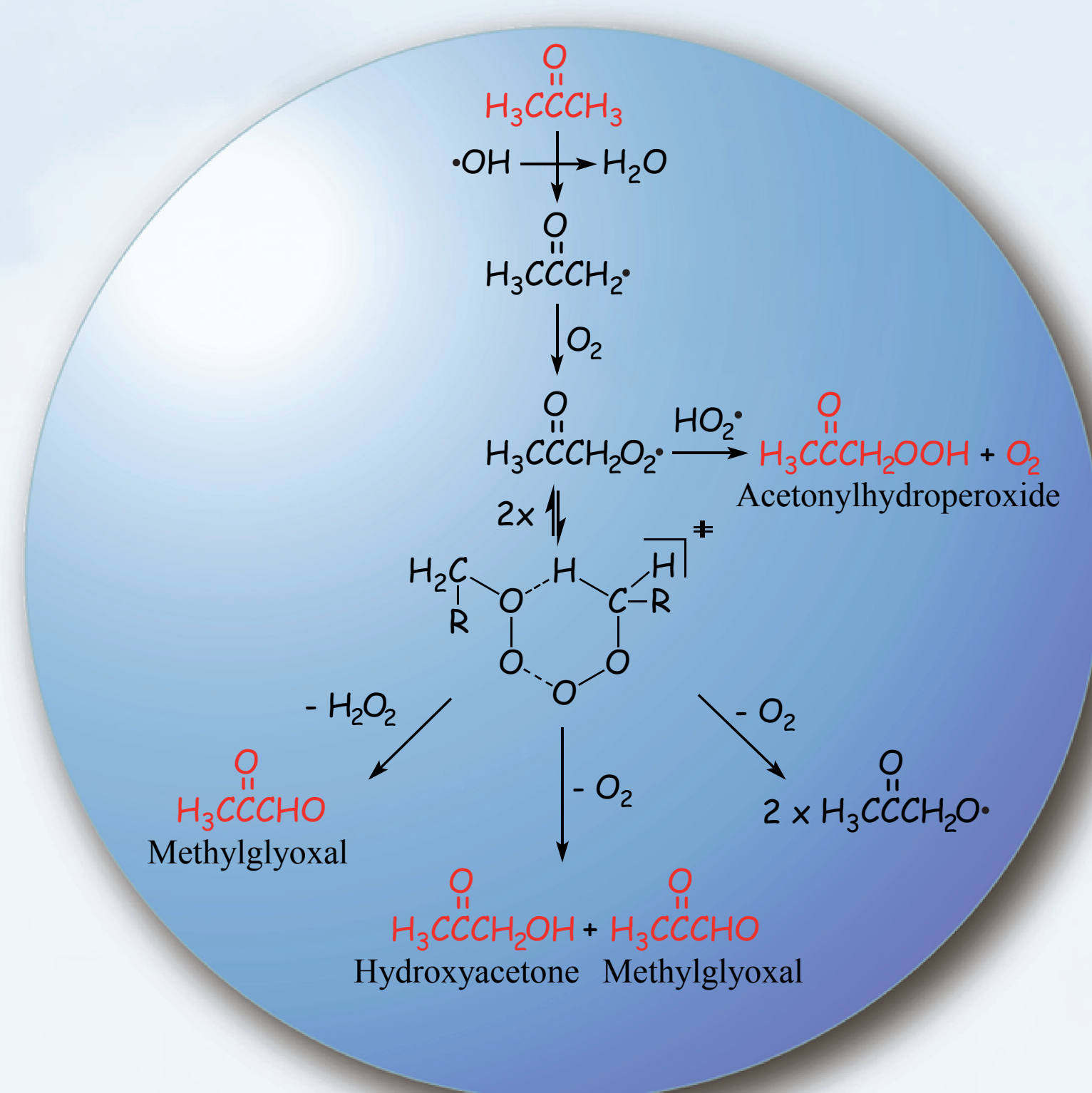


Figure 1: Reaction scheme of acetone in the aqueous phase.

Experimental

For the kinetic and spectroscopic investigations a Laser Photolysis Long Path Absorption (LP-LPA) setup was used (Figure 2).

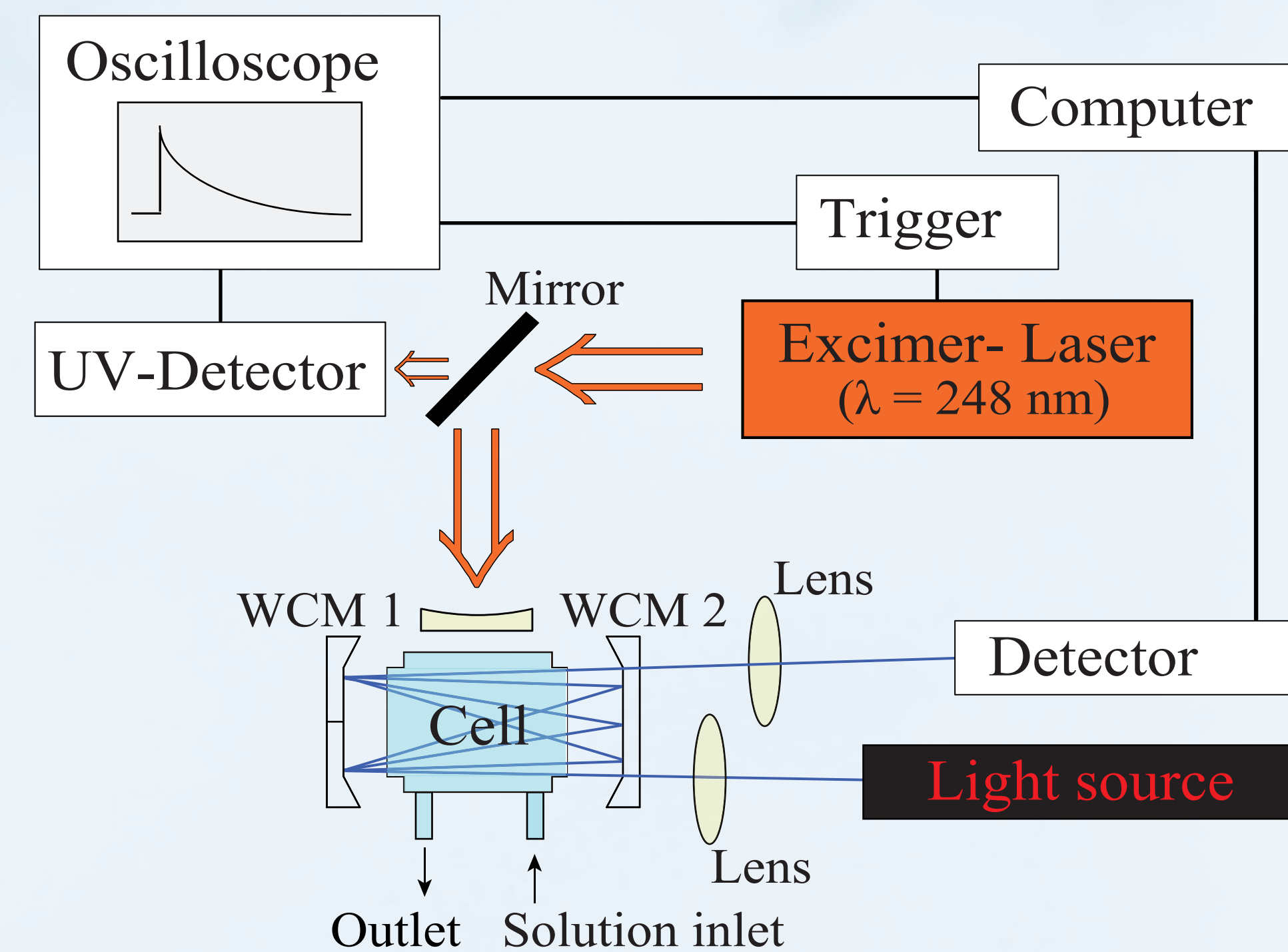
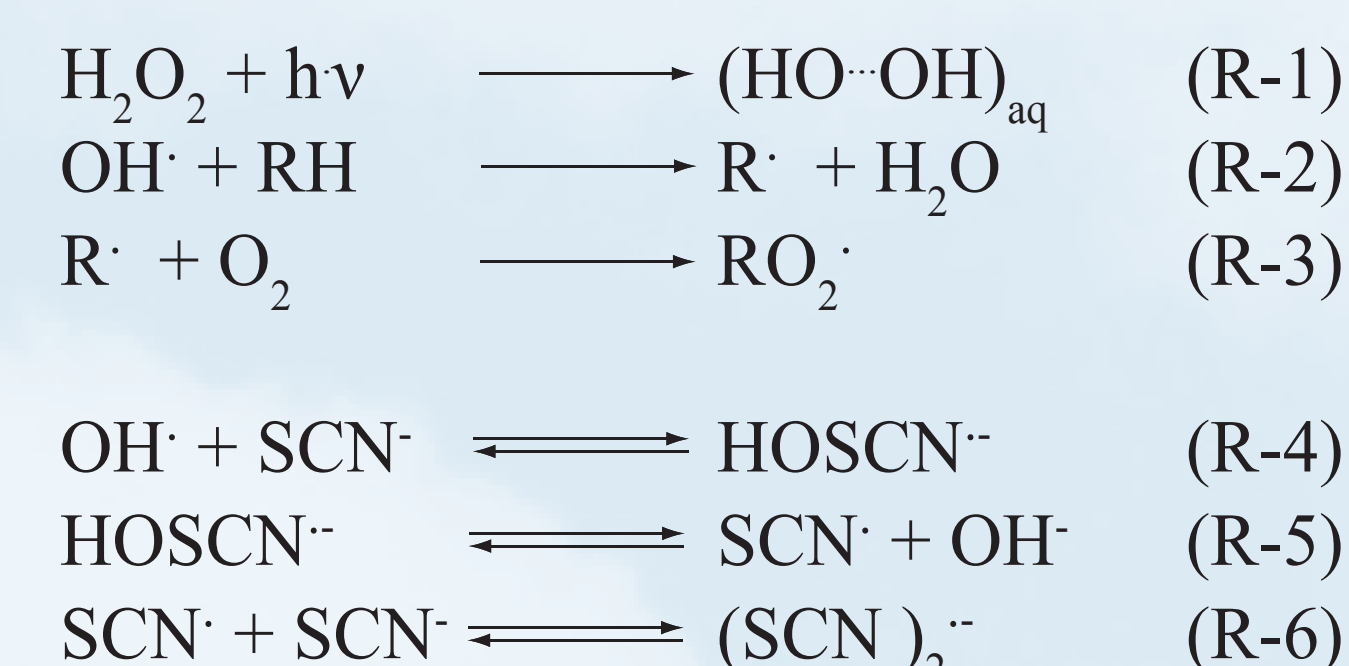


Figure 2: Laser photolysis long path absorption setup (LP-LPA).

For the kinetic investigation of OH radicals, which was formed by photolysis of H₂O₂ (R-1), mostly the well characterized competition kinetics thiocyanate system (R-4) - (R-6) (Chin and Wine, 1992) was used. Direct OH kinetic measurements can not be done due to formation of peroxy radicals as reaction products which have overlapping absorption. The (SCN)₂⁻ radical anion absorbs strongly at λ = 475 nm with an extinction coefficient of ε = 7600 M⁻¹ cm⁻¹ (Figure 2). As analytical light source a cw-lasers at λ = 473 nm and as detector a photodiode were used.



For spectroscopic investigation of the peroxy radicals (R-1) - (R-3) in the oxygen saturated aqueous solution a gated CCD camera coupled with a grating spectrograph as detector in combination with a deuterium lamp as analytical light source was used. With this technique time resolved spectra (at different delay times after the excimer laser pulse) of the reactants and products can be recorded. The accuracy of flash photolysis dosimetry is important for determining values of the extinction coefficient ε for the peroxy radicals which are required to measure the rate constants of the recombination. Since OH radical absorbs rather weakly, and only in the deep UV region of the spectrum, the direct measurement of the OH radical concentration is difficult. In order to characterize the dose of excimer laser energy inside the cell, the competition kinetics (R-4) - (R-6) was used. The Lambert-Beer's Law was applied with ε((SCN)₂⁻) to calculate the initial OH concentration. The OH concentration was used to calculate the energy inside the measuring cell (ε(H₂O₂) = 25.65 ± 1 M⁻¹cm⁻¹, Φ = 1 (Hunt and Taube, 1952)). This energy was used to calculate the formed the peroxy radical concentration.

Spectroscopic studies

Spectroscopic investigations are done in order to study the formation of transients (organic peroxy radicals) and to characterize the spectroscopic properties of the reactants and organic peroxy radicals. In Figure 3 – 5 the spectra of the organic peroxy radical of the following parent carbonyl compounds (a) acetone, (b) hydroxyacetone and (c) methylglyoxal are shown. In the case of the acetonylperoxy radical (Figure 3) the resulting spectrum is in a good agreement with the absorption spectrum obtained by Zegota, 1986. On the other hand the gas phase spectrum published by Cox et al., 1990 indicates that the extinction coefficient of the acetonylperoxy radical should be lower. The data for the transients from hydroxyacetone (Figure 4) and methylglyoxal (Figure 5) are currently not available in the literature.

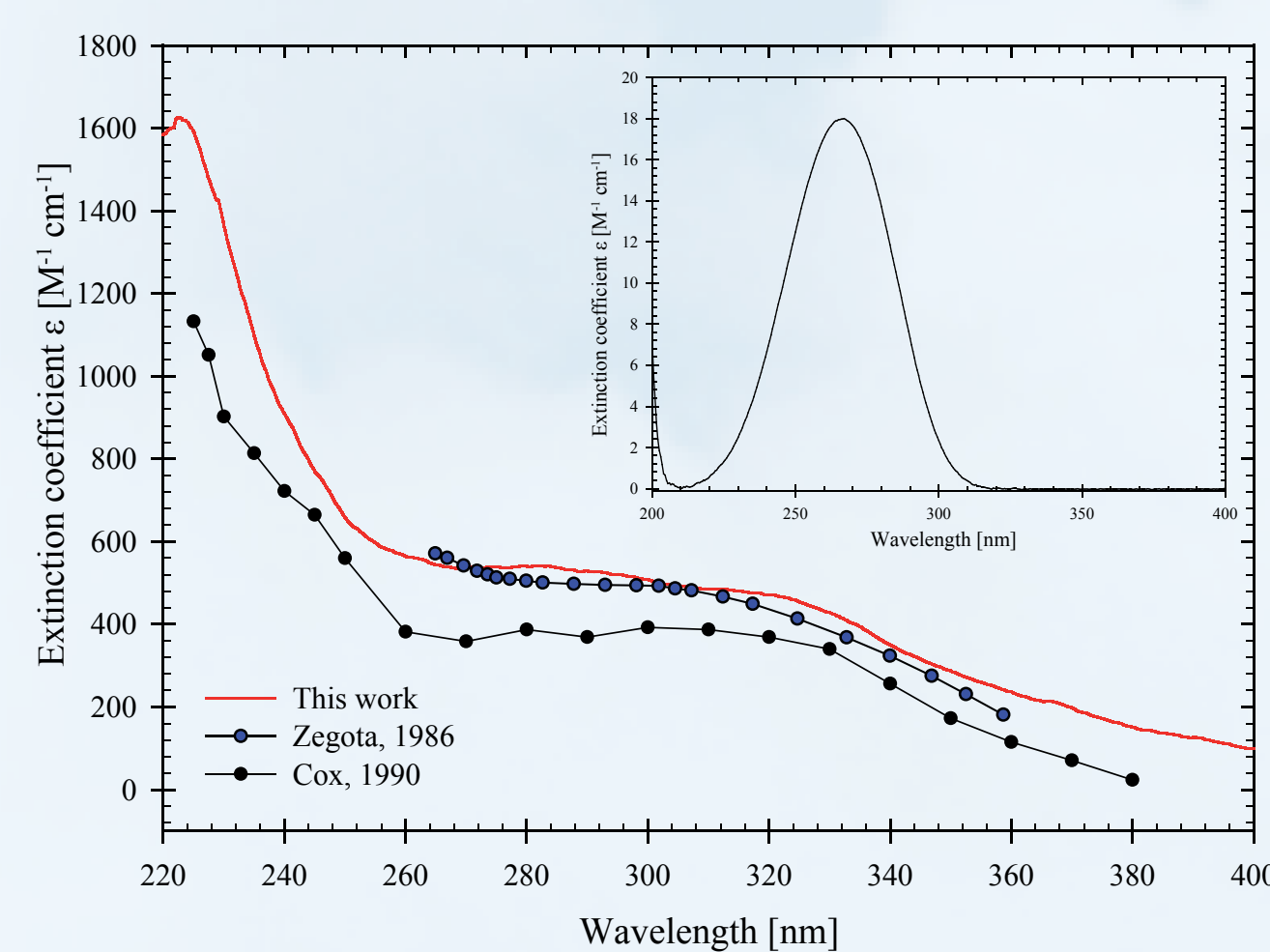


Figure 3: Spectrum of the observed peroxy radical measured in an oxygen saturated solution containing 6·10⁻⁴ M acetone and 2·10⁻⁴ M hydrogen peroxide. The spectrum was taken 45 μs after the pulse. The spectrum of acetone is shown in the inset.

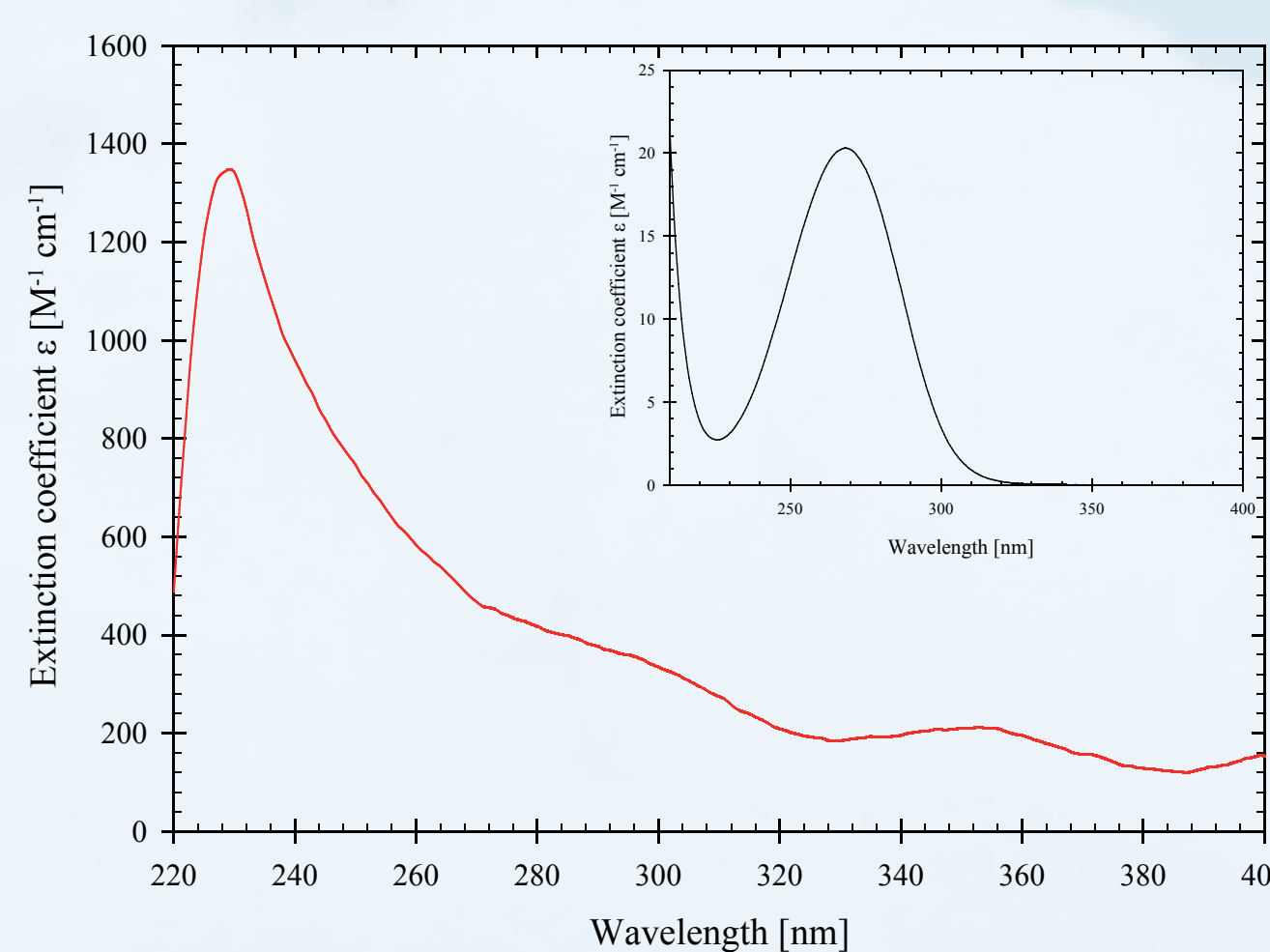


Figure 4: Spectrum of the observed peroxy radical measured in an oxygen saturated solution containing 6·10⁻⁴ M hydroxyacetone and 2·10⁻⁴ M hydrogen peroxide. The spectrum was taken 15 μs after the pulse. The spectrum of hydroxyacetone is shown in the inset.

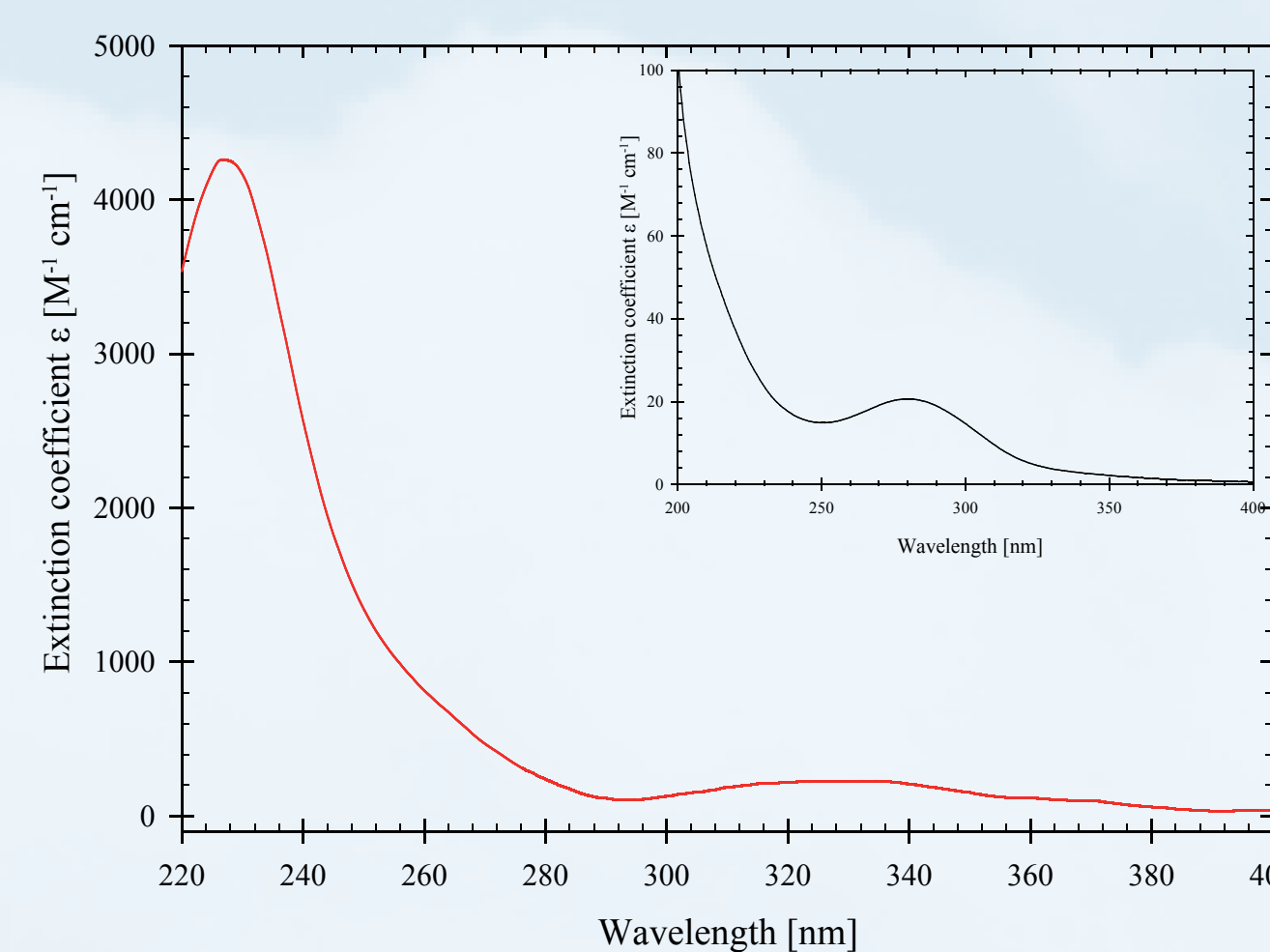


Figure 5: Spectrum of the observed peroxy radical measured in an oxygen saturated solution containing 6·10⁻⁴ M methylglyoxal and 2·10⁻⁴ M hydrogen peroxide. The spectrum was taken 15 μs after the pulse. The spectrum of methylglyoxal is shown in the inset.

Kinetic studies

The kinetic reinvestigation of the OH radical reactions with small carbonyl compounds were done to confirm the rate constants of these reactions. These rate constants are needed to describe the formation of the transients (organic peroxy radicals). In Table 1 the measured rate constants and activation parameters are summarized. Figure 6 shows the Arrhenius plots for the OH reactions with methylglyoxal and pyruvic acid.

Table 1: Measured rate constants and activation parameters for the investigated OH reactions in aqueous solution.

Reactant	k _{298K} [M ⁻¹ s ⁻¹]	E _A [kJ mol ⁻¹]	A [M ⁻¹ s ⁻¹]	ΔG [‡] [kJ mol ⁻¹]	ΔH [‡] [kJ mol ⁻¹]	ΔS [‡] [J mol ⁻¹ K ⁻¹]
Methylglyoxal	(6.6 ± 0.2) · 10 ⁸	12 ± 2	(8.6 ± 0.3) · 10 ¹⁰	23 ± 4	10 ± 1	(-44 ± 1)
Pyruvic acid pH = 0	(8.5 ± 1.2) · 10 ⁸	13 ± 8	(1.6 ± 0.2) · 10 ¹¹	22 ± 16	11 ± 6	(-39 ± 5)
Pyruvic acid pH = 6	(1.3 ± 0.2) · 10 ⁹	22 ± 12	(7.4 ± 1.2) · 10 ¹²	21 ± 15	19 ± 10	(-7 ± 1)

Table 2: Comparison of the measured rate constants and activation energies with literature data.

	k _{298K} [M ⁻¹ s ⁻¹]	E _A [kJ mol ⁻¹]	A [M ⁻¹ s ⁻¹]	
Acetone				
	(1.0 ± 0.2) · 10 ⁸	/	/	This work
	(1.7 ± 0.6) · 10 ⁸	/	/	MOST Report
Hydroxyacetone				
	(1.2 ± 0.3) · 10 ⁹	/	/	This work
	(1.2 ± 0.1) · 10 ⁹	9 ± 7	(4.0 ± 0.5) · 10 ¹⁰	Gligorovski, 2005
Methylglyoxal				
	(5.3 ± 0.4) · 10 ⁸	/	/	Monod, 2005
	(6.6 ± 0.2) · 10 ⁸	12 ± 2	(8.6 ± 0.3) · 10 ¹⁰	This work
	(1.1 ± 0.1) · 10 ⁹	13 ± 6	(2.9 ± 0.3) · 10 ¹¹	Ervens et al., 2003
Pyruvic acid				
pH = 0	(8.5 ± 1.2) · 10 ⁸	13 ± 8	(1.6 ± 0.2) · 10 ¹¹	This work
pH = 0	(1.2 ± 0.4) · 10 ⁸	23 ± 4	(1.0 ± 0.1) · 10 ¹²	Ervens et al., 2003
pH = 6	(1.3 ± 0.2) · 10 ⁹	22 ± 12	(7.4 ± 1.2) · 10 ¹²	This work
pH = 5.5	(7.0 ± 2.0) · 10 ⁸	19 ± 4	(1.3 ± 0.1) · 10 ¹²	Ervens et al., 2003
pH = 9	2.7 · 10 ⁷	/	/	Kraljic, 1967

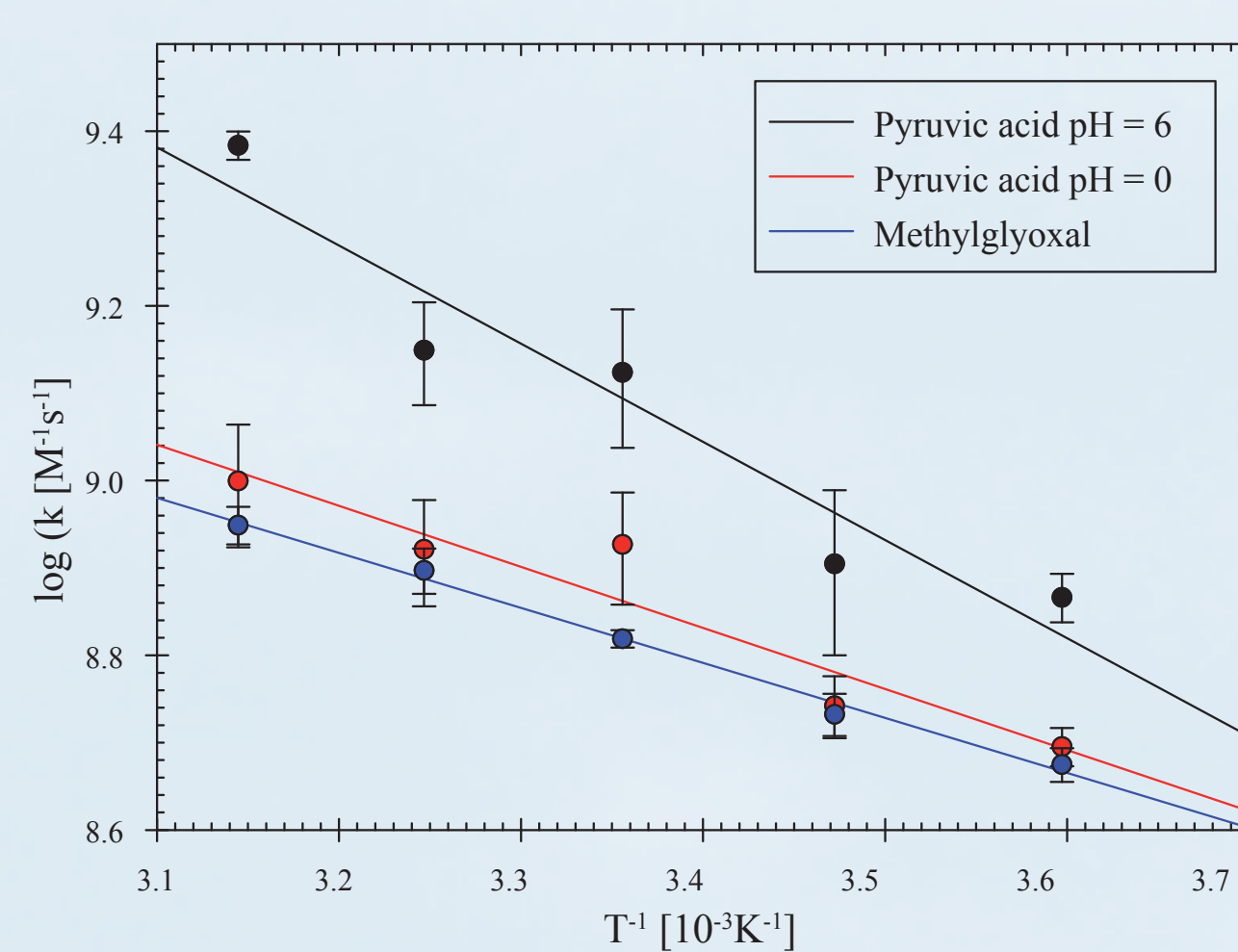
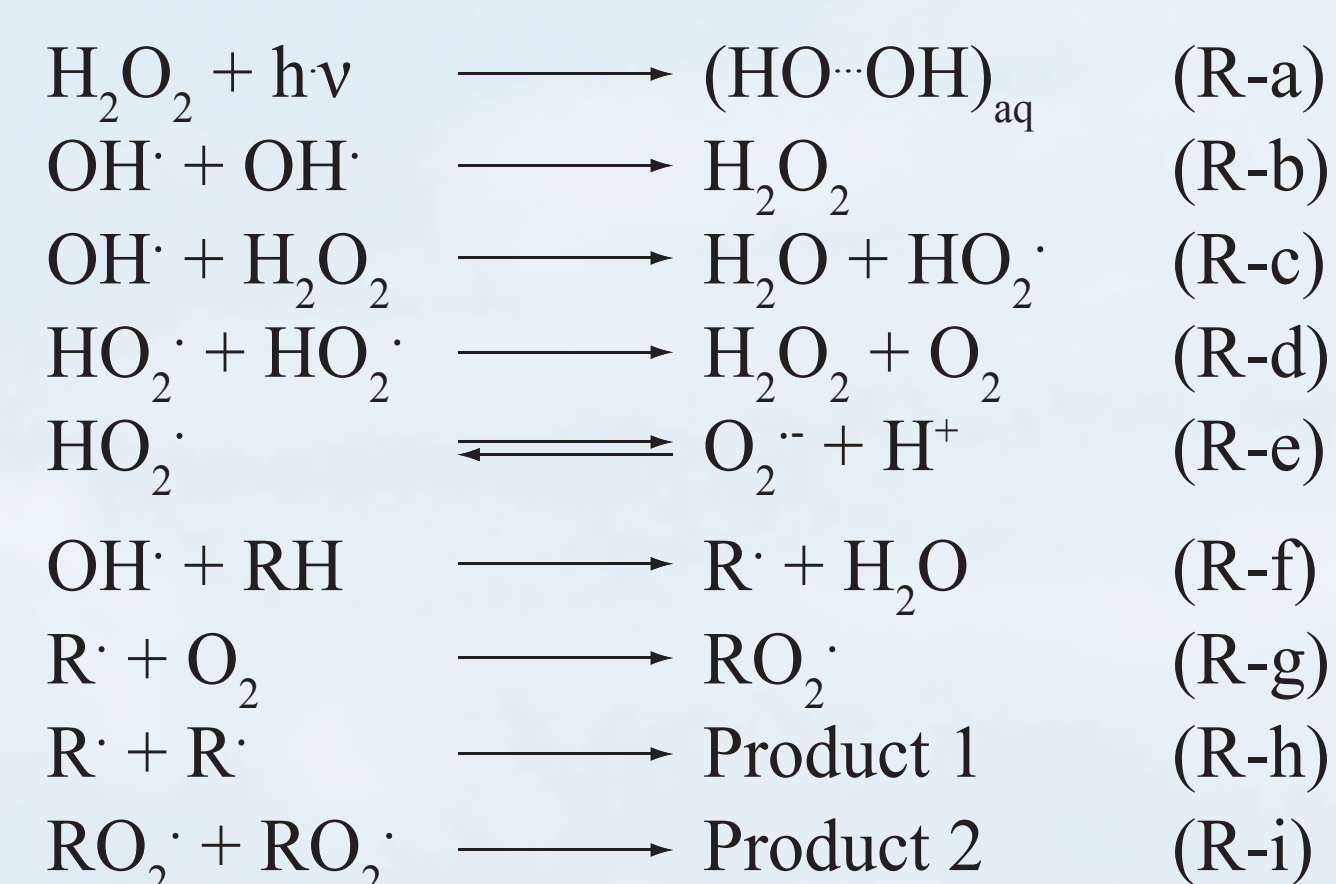


Figure 6: Arrhenius plot for the OH reaction with Methylglyoxal and Pyruvic acid

Modeling

The peroxy radical concentration has been calculated by using a GEPASI model. This model (37 Reactions) takes into account side reaction of HO_x radicals in the reaction cell. The most important reactions are shown in following.



Summary and Outlook

Spectroscopic investigations were performed in order to study the formation of transients (organic peroxy radicals) and to characterize the spectroscopic properties of the reactants and organic peroxy radicals. The kinetic reinvestigation were performed to confirm the rate constant of the OH radical reactions with small carbonyl compounds. To accomplish the aim of this study the following tasks must be successfully completed: A) Stepwise identification and quantification of the OH driven oxidation products. B) Kinetic studies on the recombination reactions of organic peroxy radical in aqueous phase. C) Validation of the oxidation pathway with continued irradiation experiments under tropospheric aqueous phase conditions.

References

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