Oxidation of Glyoxal in the Aqueous Phase

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Motivation

- Volatile and semivolatile organic compounds (VOCs) are emitted into the atmosphere in large amounts from biogenic and anthropogenic sources

- In the gas phase and the aqueous phase (cloud droplets, fog, rain and deliquescent particles) these VOCs will be oxidized to semivolatile carbonyl compounds

- Semivolatile carbonyl compounds such as glyoxal could be important for formation of secondary organic aerosol (SOA) by partitioning between gas- and liquid phase of pre-existing particles

- Initiation of oxidation process by radicals (OH and NO_3) under formation of peroxy radicals and substituted organics

- Oxidation pathways of glyoxal after H-atom abstraction still uncertain

- Buxton et al., 1997 (dilute solutions < 1 mM, typical concentration for cloud water) peroxy radical formation with a rate constant of $k = 1 \times 10^9$ M^{-1} s^{-1}

- Lim et al., 2010 (concentrations > 1 mM) formation of peroxy radicals minor important because of lower rate constant of $k = 1 \times 10^6$ M^{-1} s^{-1} estimated after Guzman et al., 2006

- The difference in the oxygen addition rate constants might lead to different oxidation products and yields in the aqueous solution
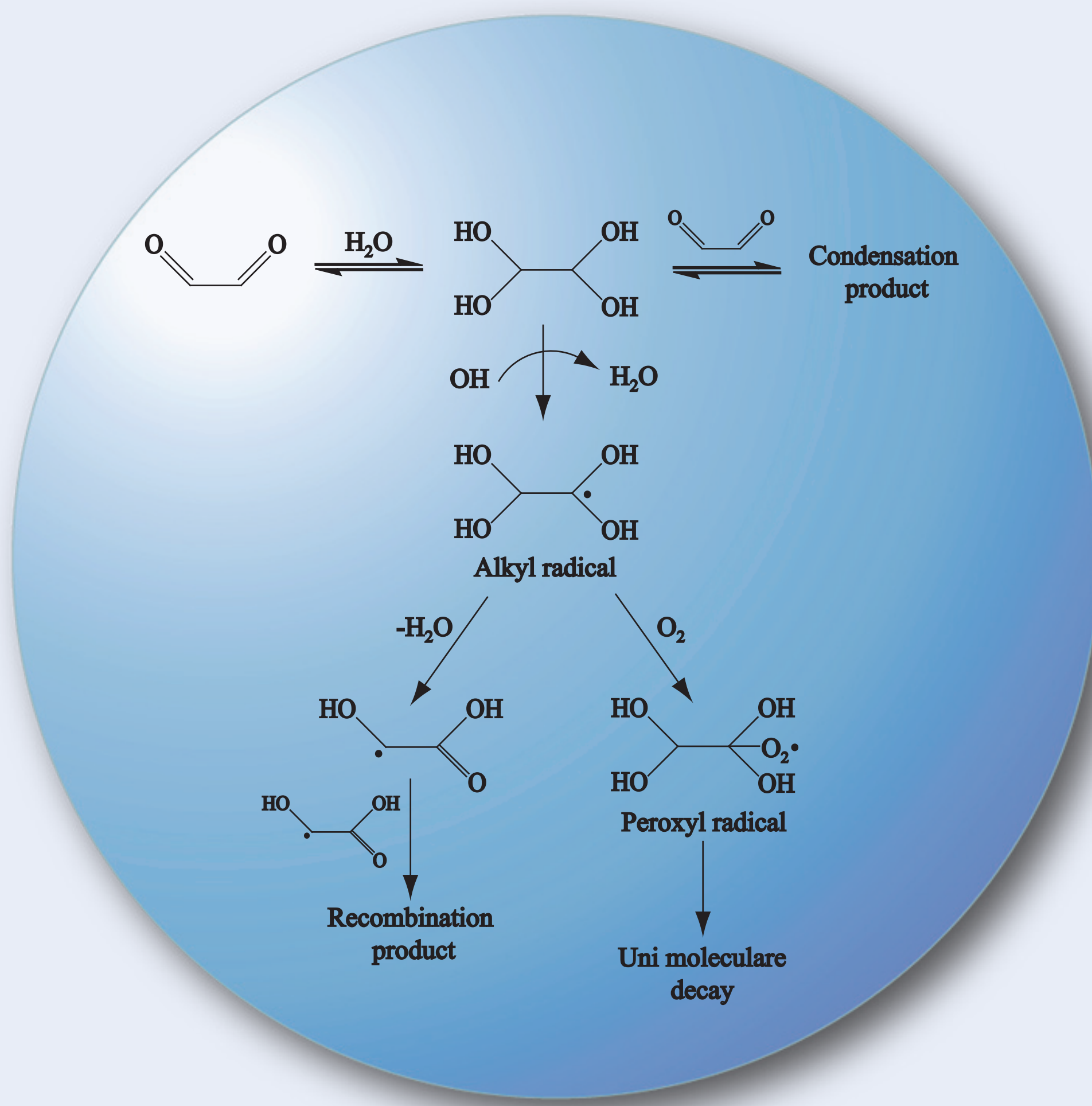

Figure 1: Glyoxal oxidation by OH radicals in aqueous solution.

Methods

- Investigation of formation and decay with Laser Photolysis Long Path Absorption (LP-LPA) setup (Figure 2)
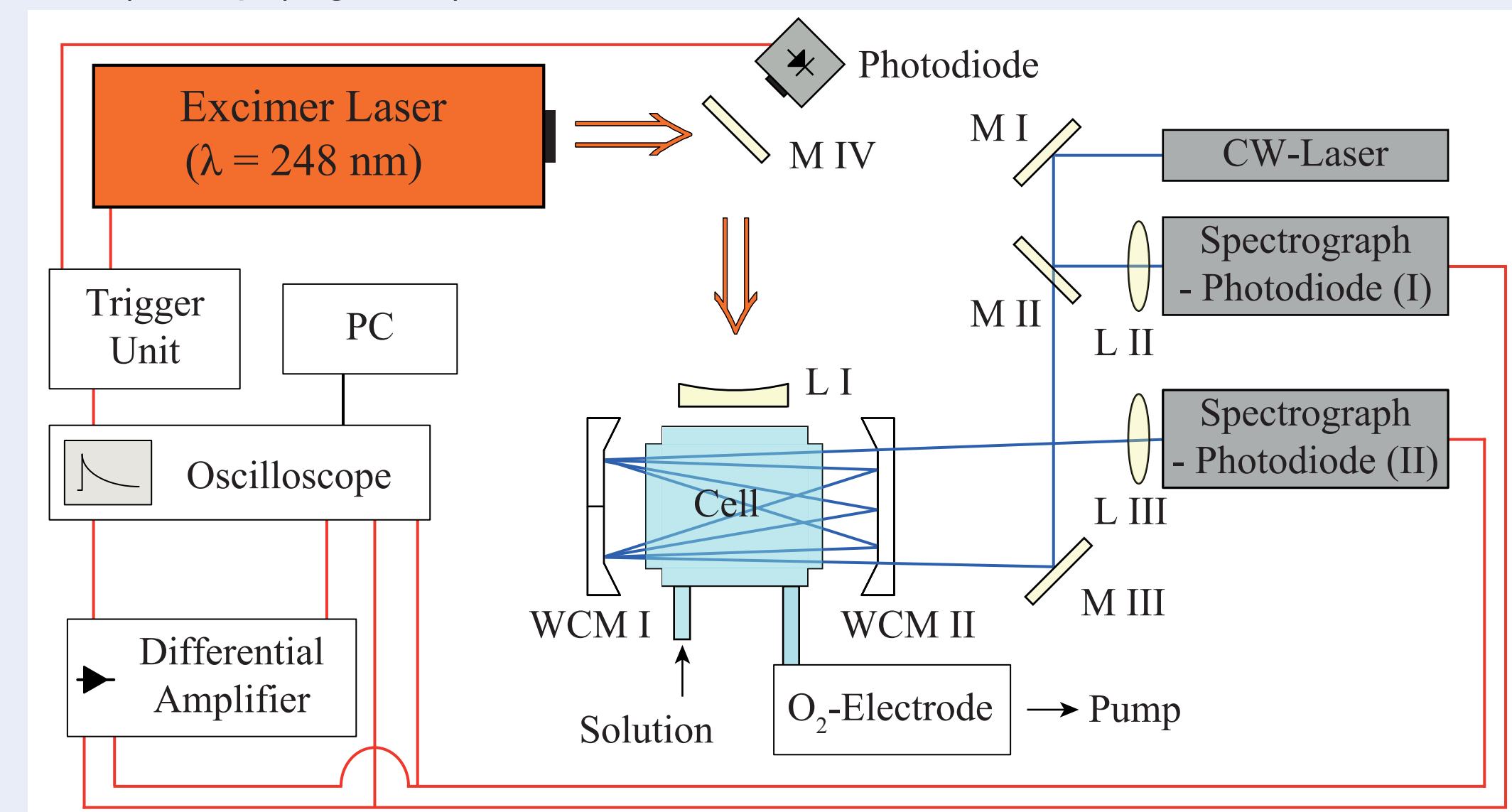

Figure 2: Laser Photolysis Long Path Absorption setup (LP-LPA).

- Analyical light sources: λ = 244 nm: direct detection of alkyl or peroxy radicals
  λ = 442 nm: investigations of alkyl radicals + O_2, OH and SO_4^- radical reactivity
  λ = 635 nm: NO_3 radical reactions

- Radical sources:
  OH: $H_2O_2 + h\nu$ (λ = 248 nm) ⟶ 2 OH
  SO_4^-: $S_2O_8^{2-} + h\nu$ (λ = 248 nm) ⟶ 2 SO_4^-
  NO_3: $S_2O_8^{2-} + h\nu$ (λ = 351 nm) ⟶ 2 SO_4^-
  $SO_4^- + NO_3^-$ ⟶ $SO_4^{2-} + NO_3$
  R/ RO_2: $H_2O_2 + h\nu$ (λ = 248 nm) ⟶ 2 OH
  OH + RH ⟶ R
  R + O_2 ⟶ RO_2

Results

R + O_2 measurement (competition kinetics)

- The rate constant of the addition reaction of oxygen to the glyoxyl alkyl radical was investigated with a competition kinetics method from Adams et al., 1969

- This pulse radiolysis method was modified and successfully tested for laser flash photolysis conditions

- As alkyl radical scavenger the ferricyanide complex was used and observed at λ = 442 nm

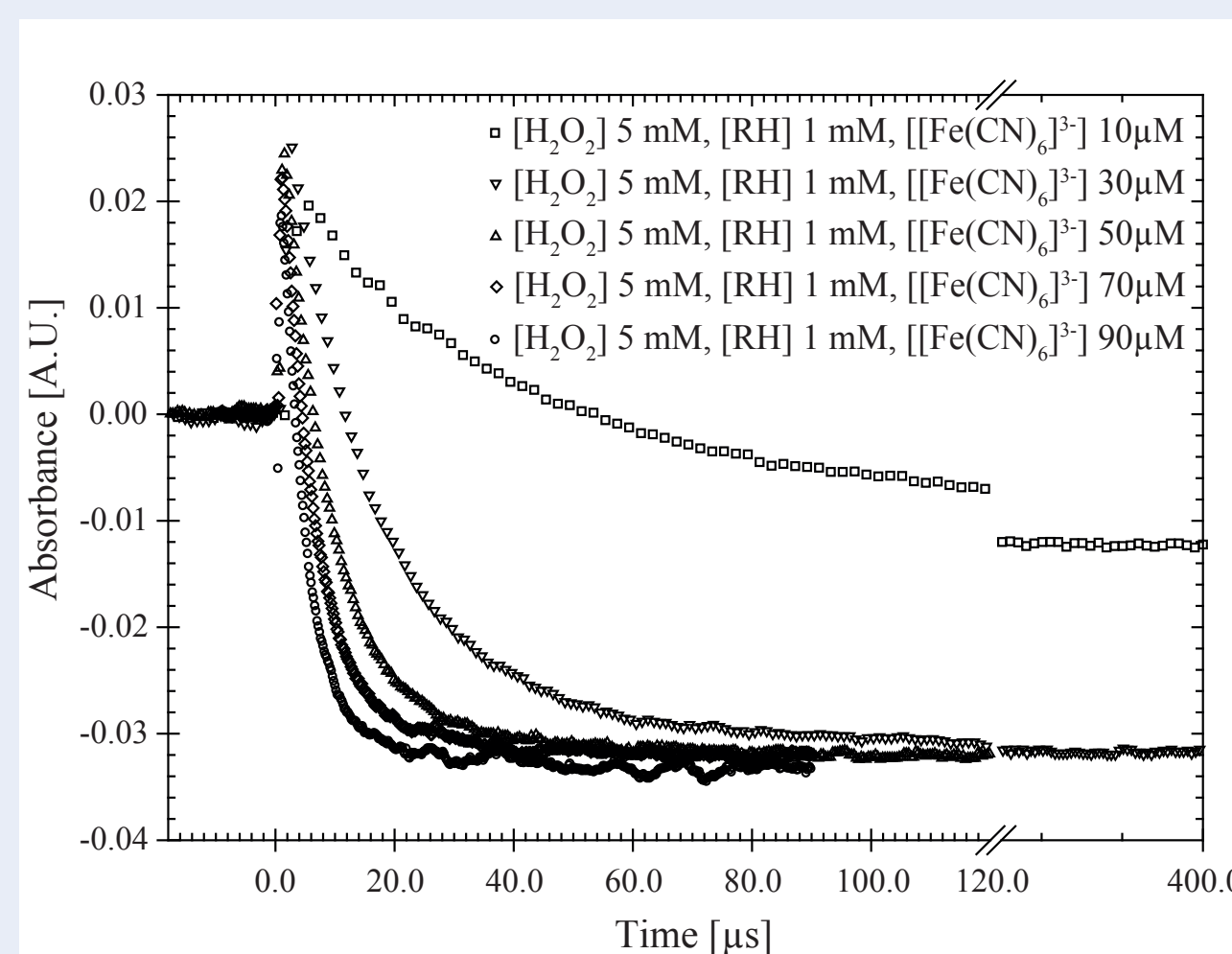

Figure 3: Absorption change at λ = 442 nm during the bleaching reaction of the glyoxyl radical with ferricyanide in the aqueous solution.
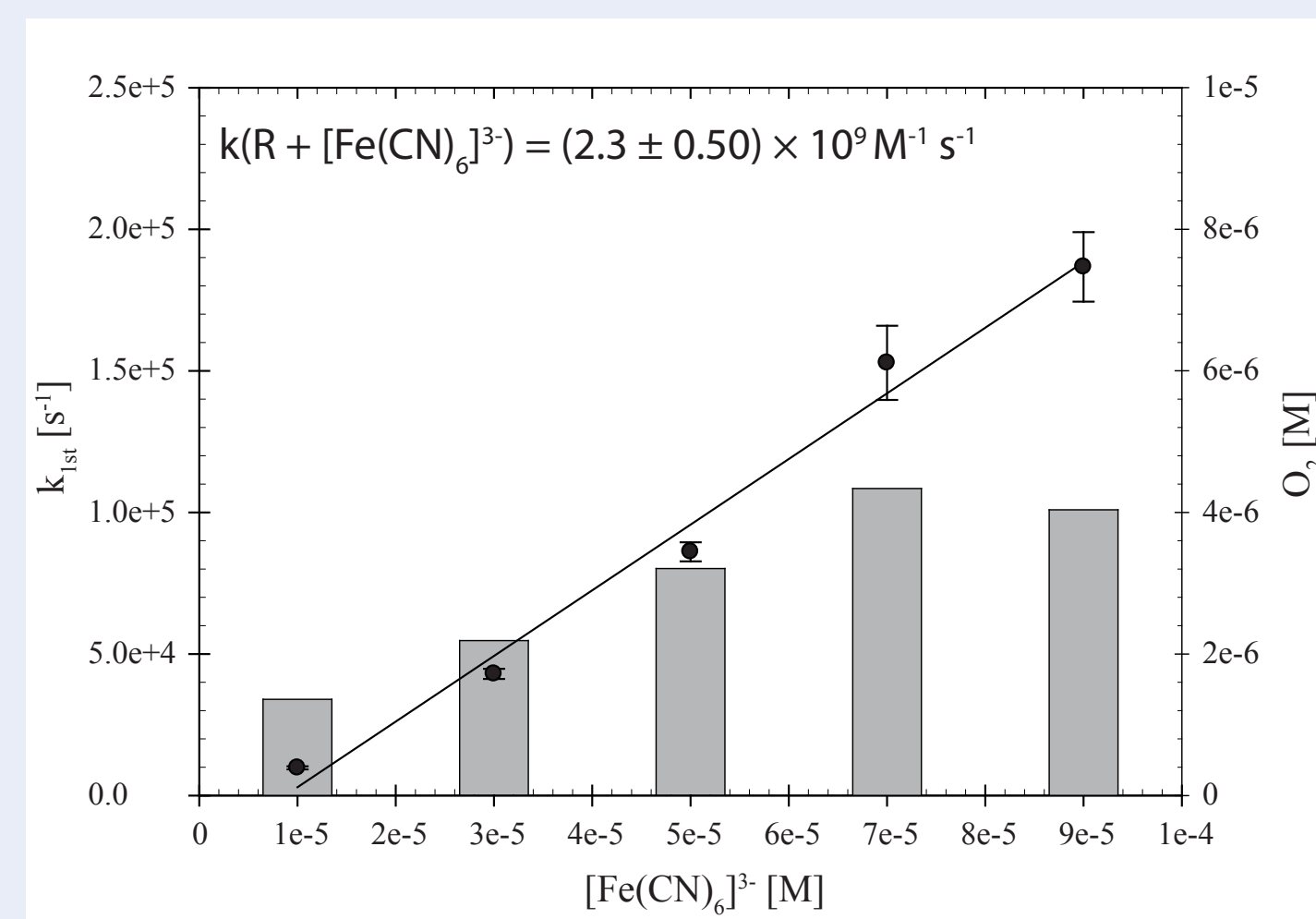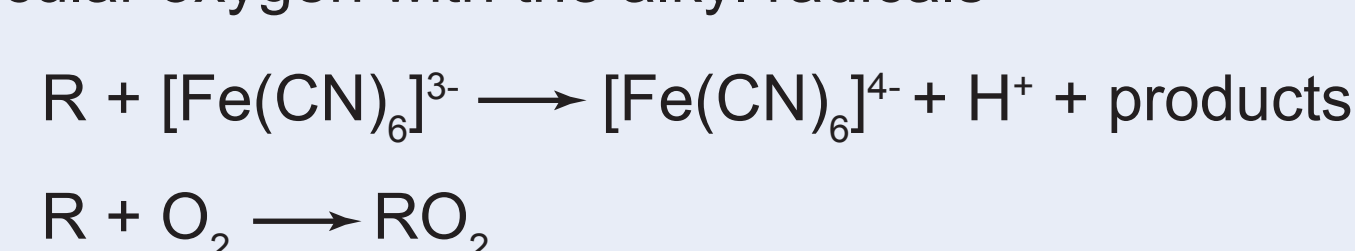

Figure 4: Determination of the reference rate constant for the bleaching reaction of the glyoxyl radical with ferricyanide in the aqueous solution.

- Competition between the electron transfer reaction of the ferricyanide and the addition reaction of molecular oxygen with the alkyl radicals

R + $[Fe(CN)_6]^{3-}$ ⟶ $[Fe(CN)_6]^{4-}$ + H^+ + products

R + O_2 ⟶ RO_2

$$\frac{E_0}{E} = 1 + \frac{k_{R+O_2}[O_2]}{k_{ref.}[[Fe(CN)_6]^{3-}]}$$

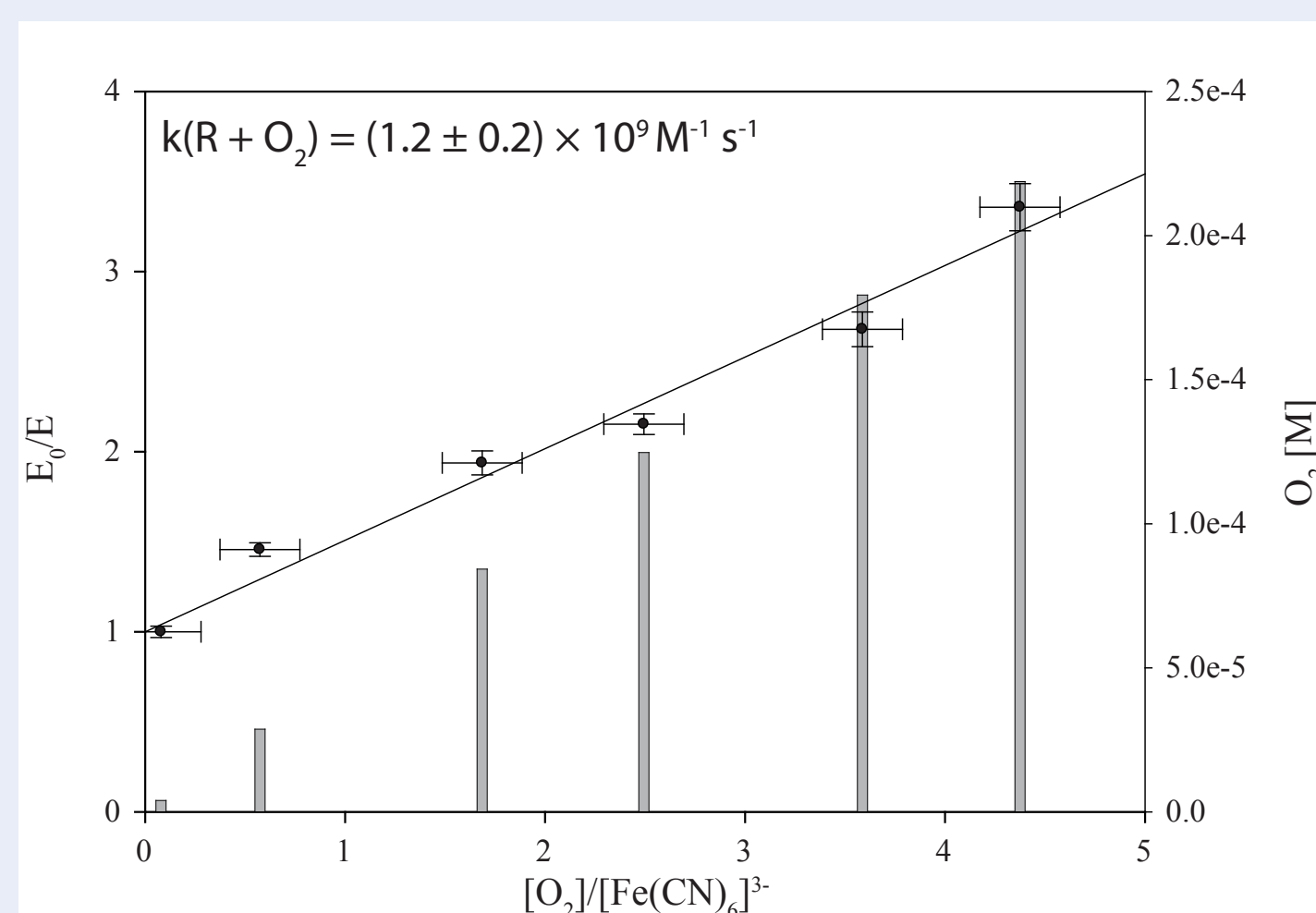- The bleaching reaction forms ferrocyanide which not absorbed at λ = 442 nm

Figure 5: Plot of absorbance ratio against the concentration ratio.

The addition reaction of alkyl radicals to molecular oxygen by the formation of peroxy radicals is not slow!

$k_{R+O_2} = 10^9$ $M^{-1}s^{-1}$, not $k_{R+O_2} = 10^6$ $M^{-1}s^{-1}$

R + O_2 measurement (optical detection method)

- Direct observation of the formed alkyl and peroxy radical species at λ = 244 nm

- Determination of $k(R + O_2)$ with a model mechanism which includes reactions of HO_X-radicals, of acid base equilibriums, alkyl and peroxy radicals
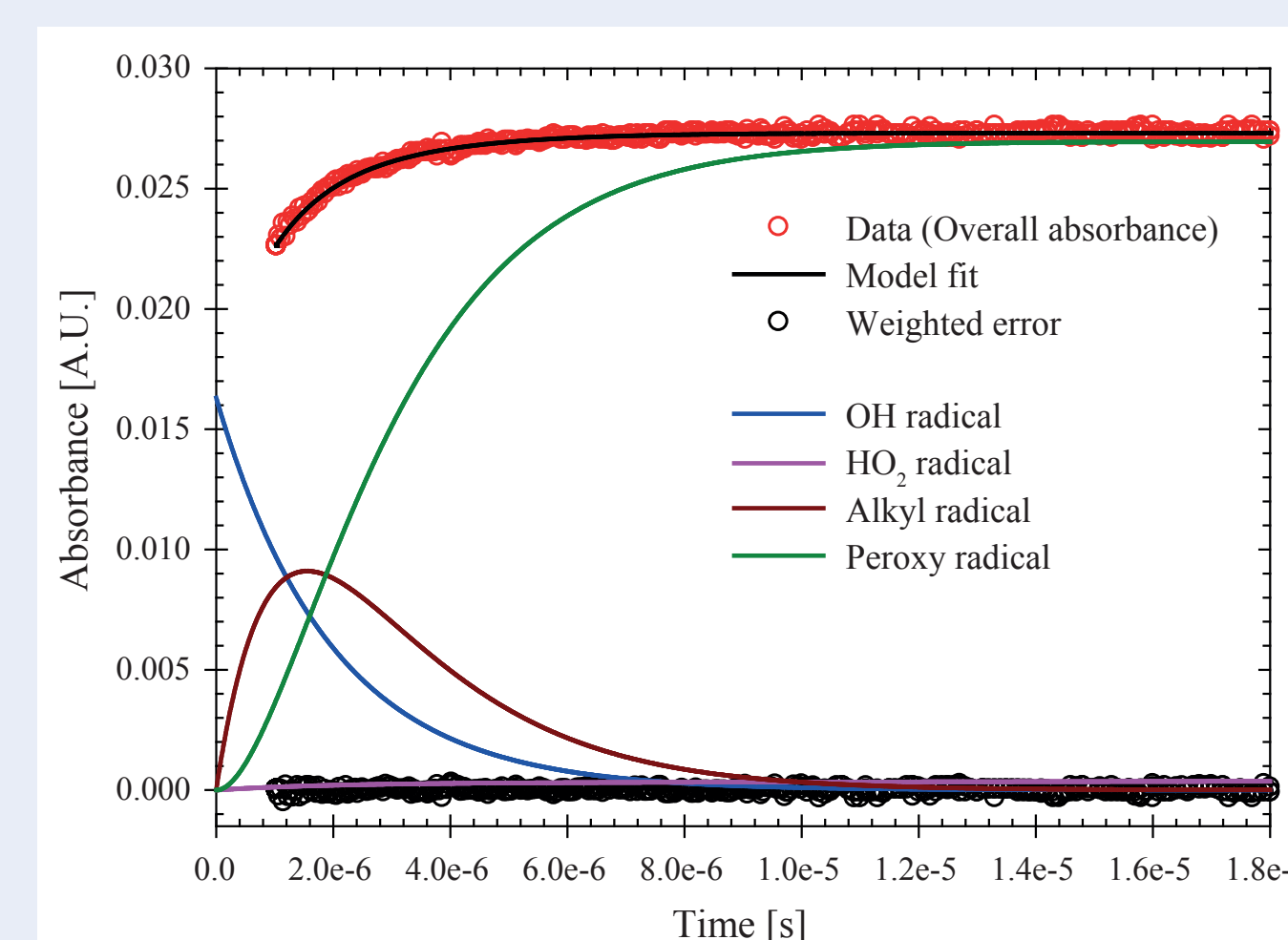

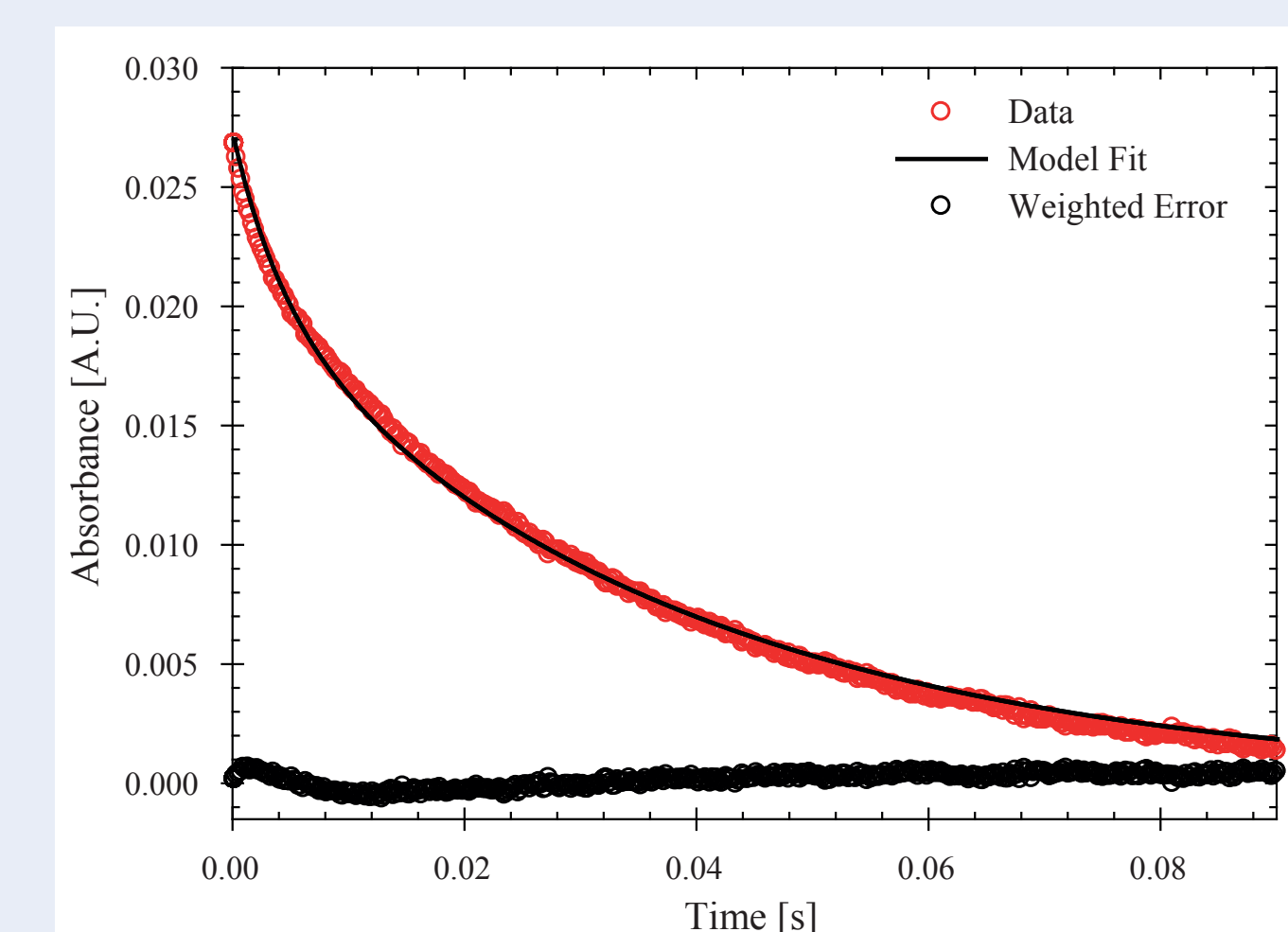Figure 6: Modelled absorption traces in O_2 saturated aqueous solution for short time steps.

Figure 7: Modelled absorption traces in O_2 saturated aqueous solution for long time steps.

- The modelling of the experimental data of an O_2 saturated aqueous solution gives the rate constant $k(R + O_2) = (1.2 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, the molar absorption coefficient of the glyoxyl alkyl radical $\varepsilon(R) = 1168$ M^{-1} cm^{-1} and of the glyoxylperoxyl radical $\varepsilon(RO_2) = 892$ M^{-1} cm^{-1}

- The obtained results are in good agreement with Buxton et al., 1997 with a rate constant $k(R + O_2) = (1.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, a molar absorption coefficient for the alkyl radical $\varepsilon(R) = 1105$ M^{-1} cm^{-1} and for the peroxyl radical $\varepsilon(RO_2) = 941$ M^{-1} cm^{-1}

- Reaction order n = 1.2 from the absorption-time-profile (Figure 6) was obtained

- With considering the absorption of HO_2 radicals leads to a modelled $k_{1st} = 122$ s^{-1}

Reactions of OH, NO_3 or SO_4^- radicals with glyoxal

- In Table 1 and Figure 7 the temperature dependencies of the H atom abstraction reaction of glyoxal with eigther OH, NO_3 or SO_4^- radicals are shown

- The oxidation of glyoxal by OH or SO_4^- radicals is pH independent, with $k_{pH = 2} = (9.7 \pm 0.4) \times 10^8$ M^{-1} s^{-1} and $k_{pH = 9} = (1.2 \pm 0.1) \times 10^9$ M^{-1} s^{-1} for the OH radical and with $k_{pH = 2} = (2.2 \pm 0.4) \times 10^7$ M^{-1} s^{-1} and $k_{pH = 9} = (2.6 \pm 0.1) \times 10^7$ M^{-1} s^{-1} for the SO_4^- radicals

Table 1: Arrhenius parameters at pH = 6.

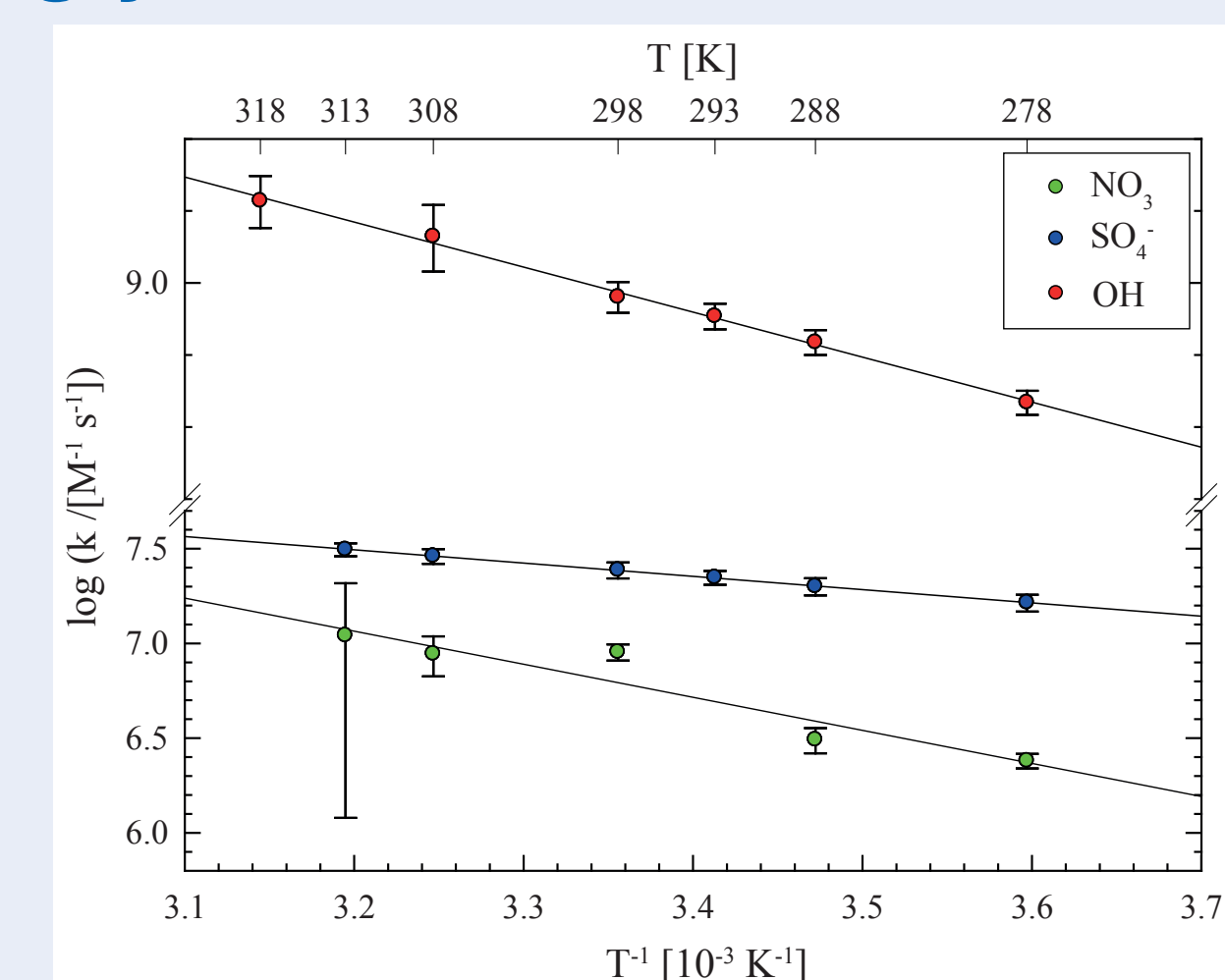| compound	$k_{298 K}$ [M^{-1} s^{-1}]	E_A [kJ mol^{-1}]	A [M^{-1} s^{-1}]
Glyoxal + OH	$(9.6 \pm 0.5) \cdot 10^8$	12 ± 1	$(1.2 \pm 0.1) \cdot 10^{11}$
Glyoxal + SO_4^-	$(2.4 \pm 0.2) \cdot 10^7$	13 ± 1	$(5.4 \pm 0.1) \cdot 10^9$
Glyoxal + NO_3	$(9.0 \pm 0.9) \cdot 10^6$	33 ± 21	$(4.5 \pm 1.3) \cdot 10^{12}$

Figure 7: Arrhenius plot of the oxidation reaction of glyoxal with OH, NO_3 and SO_4^- radicals.

Conclusions

- Temperature and pH dependent measurements of the H atom abstraction reaction of glyoxal by OH, NO_3 and SO_4^- radicals

- Determination of the rate constant of O_2 addition to glyoxyl alkyl radical with the ferricyanide competition kinetic method and a direct measurement at λ = 244 nm

- Fast O_2 addition to alkyl radicals ($k = 1 \times 10^9$ M^{-1} s^{-1}) from glyoxal oxidation! (confirmed by this work and Buxton et al., 1997)

- Uni moleculare decay of glyoxylperoxyl radical $k_{1st} = 122$ s^{-1}

Literature

Adams, G. E., and R. L. Willson (1969), Pulse Radiolysis Studies on the Oxidation of Organic Radical in Aqueous Solution, Trans. Faraday Soc., 65, 2981-2987. Buxton, G. V., T. N. Malone, and G. A. Salmon (1997), Oxidation of glyoxal initiated by OH in oxygenated aqueous solution, J. Chem. Soc. Faraday Trans., 93 (16), 2889-2891. Chin, M., and P.H. Wine (1992), A temperature-dependent kinetics study of the aqueous phase reactions OH + SCN⁻ ⟶ SCNOH⁻ and SCN + SCN⁻ ⇌ (SCN)₂⁻, J. Photochem. Photobiol. A: Chem., 69 (1), 17-25. Guzman, M. I., A. J. Colussi, and M. R. Hoffmann (2006), Photoinduced Oligomerization of Aqueous Pyruvic Acid, J. Phys. Chem. A, 110 (10), 3619-3626. Lim, Y. B., Y. Tan, M. J. Perri, S. P. Seitzinger, and B. J. Turpin (2010), Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521-10539.