OH radical driven oxidation process of Pyruvic acid and Lactic acid in aqueous solution

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Motivation

- Volatile and semivolatile organic compounds are emitted into the atmosphere in large amounts from biogenic and anthropogenic sources
- The tropospheric multi-phase system consists of the gas phase and a suspended aqueous phase (cloud droplets, fog, rain and deliquescent particles)
- Semivolatile carbonyl compounds such as acids could be important for secondary organic aerosol (SOA) formation by partitioning between gas- and liquid phase of pre-existing particles
- Initiation of oxidation process by OH radicals under formation of peroxy radicals and substituted organics
- Photochemical oxidation pathways of pyruvic acid are still under discussion by Guzman et al., 2006, Griffith et al., 2013 and Reed Harris et al., 2014.
- Adams et al., 1969 measured a rate constant of $k \approx 10^9$ M^{-1} s^{-1} of the peroxy radical formation in the aqueous phase
- Guzman et al., 2006 estimated a 3 orders of magnitude lower rate constant, which implies a minor importance of the peroxy radical formation in the aqueous phase
- The difference in the oxygen addition rate constants leads to a change of the reaction pathways and results in different product distributions in the aqueous solution
- The aim of this work was to clarify the difference in the rate constant of the oxygen addition reaction
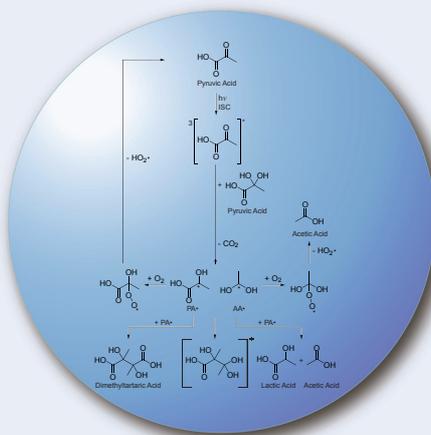
Figure 1: Photochemical oxidation of pyruvic acid in aqueous solution.

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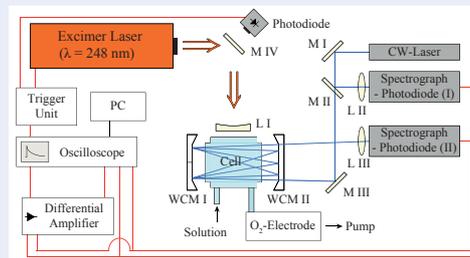
Figure 2: Laser Photolysis Long Path Absorption setup (LP-LPA).

- Analytical light sources: $\lambda = 405$ nm: OH radical competition kinetics
  $\lambda = 442$ nm: investigations of alkyl radicals + O_2
- Radical reactions:
  OH: $H_2O_2 + h\nu \longrightarrow 2\ OH$
  R/ RO_2: $OH + RH \longrightarrow R$
  $R + O_2 \longrightarrow RO_2$
  $R + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + H^+ + R'$
- The pulse radiolysis method from Adams et al., 1969 was modified and successfully tested for laser flash photolysis conditions (Schaefer et al., 2015)

$$\frac{A_0}{A} = 1 + \frac{k_{R+O_2}[O_2]}{k_{ref}[[Fe(CN)_6]^{3-}]}$$

Results

OH radical reactivity

- The H atom abstraction in the OH radical reaction occurs at the CH_3 group in the case of pyruvic acid/ pyruvate and at the CH group in the case of lactic acid/ lactate
- Activation parameters (Table 1) were derived from the Arrhenius expressions, which were obtained from the temperature dependent measurement of the rate constants of the aforementioned radical reactions
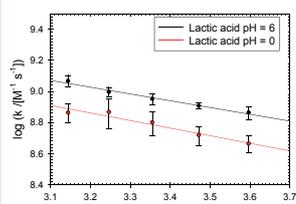
Figure 3: Temperature dependency of the OH radical reaction with lactic acid.
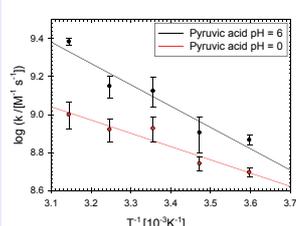
Figure 4: Temperature dependency of the OH radical reaction with pyruvic acid (Schaefer et al., 2012).

Measurement R + O_2 kinetics
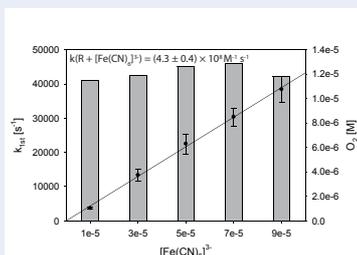
Figure 5: Determination of the reference rate constant for the bleaching reaction of the lactic acid alkyl radical with ferricyanide in the aqueous solution.
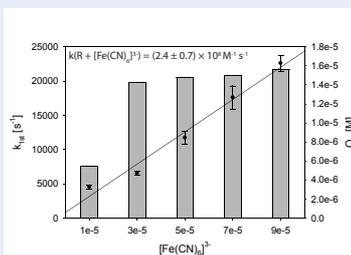
Figure 7: Determination of the reference rate constant for the bleaching reaction of the lactate alkyl radical with ferricyanide in the aqueous solution.
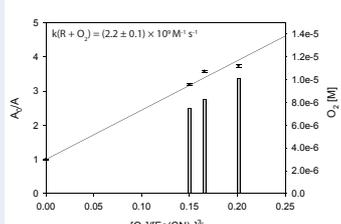
Figure 6: Plot of absorbance ratios against the concentration ratios in the case of lactic acid.
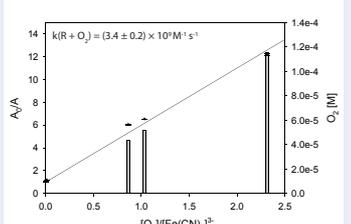
Figure 8: Plot of absorbance ratios against the concentration ratios for the lactate oxidation.

- The reference rate constant of the electron transfer reaction between the alkyl radical and the ferricyanide was derived from the slope in Figure 5 and Figure 7
- Adams et al., 1969 provided a value of $k = 1.5 \times 10^9$ M^{-1} s^{-1} of the electron transfer reaction of the lactate alkyl radical with ferricyanide
- The obtained value of the lactate alkyl radical is factor 6 smaller than the literatue value given by Adams et al., 1969
- In comparison the rate constant from Adams et al., 1969 of the electron transfer reaction of the glycolate alkyl radical can be given with $k = 5.0 \times 10^8$ M^{-1} s^{-1}
- From the product of the slope and the reference rate constant of either Figure 6 or Figure 8 the rate constant of the molecular oxygen addition reaction was derived
- The obtained rate constant of the addition reaction of the lactate alkyl radical with molecular oxygen is in good aggrement with the rate constant $k = 2.6 \times 10^9$ M^{-1} s^{-1} from Adams et al., 1969

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
$k_{R+O_2} = 10^6$ $M^{-1}s^{-1}$

Table 1: Arrhenius parameters of the OH radical reaction of lactic acid and pyruvic acid.

Compound	k_{298K} [$M^{-1}s^{-1}$]	E_A [kJ mol^{-1}]	A [$M^{-1}s^{-1}$]	$\Delta G^{\ddagger}$ [kJ mol^{-1}]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J K^{-1} mol^{-1}]
Lactic acid	$(6.3 \pm 1.1) \times 10^8$	9 ± 4	$(2.7 \pm 0.2) \times 10^{10}$	23 ± 12	7 ± 3	-54 ± -4
Lactate	$(8.9 \pm 0.8) \times 10^8$	8 ± 3	$(2.7 \pm 0.1) \times 10^{10}$	22 ± 7	6 ± 2	-54 ± -2
Pyruvic acid	$(3.2 \pm 0.6) \times 10^8$	15 ± 5	$(1.1 \pm 0.1) \times 10^{11}$	25 ± 10	12 ± 4	-42 ± -3
Pyruvate	$(7.1 \pm 1.8) \times 10^8$	25 ± 19	$(1.5 \pm 0.4) \times 10^{13}$	23 ± 23	23 ± 17	-0.8 ± -0.2

Summary and Conclusions

- Temperature and pH dependent measurements of the H atom abstraction reaction of lactic acid or pyruvic acid by OH radicals were done
- Determination of the rate constant of O_2 addition to the lactic acid alkyl radical and the lactate alkyl radical by the ferricyanide competition kinetic method
- Fast O_2 addition to alkyl radicals ($k \approx 10^9$ M^{-1} s^{-1}) from lactic acid or lactate oxidation! (confirmed the work of Adams et al., 1969)
- The estimated value of Guzman et al., 2006 ($k \approx 10^6$ M^{-1} s^{-1}) appears to low, therefore the general suggested value of $k \approx 10^9$ M^{-1} s^{-1} should be used

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. 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. Griffith, E. C., B. K. Carpenter, R. K. Shoemaker, V. Vaida (2013), Photochemistry of aqueous pyruvic acid, P. Natl. Acad. Sci. USA 2013, 110, 11714-11719. Reed Harris, A. E., B. Ervens, R. K. Shoemaker, J. A. Kroll, R. J. Rapf, E. C. Griffith, A. Monod, V. Vaida (2014), Photochemical Kinetics of Pyruvic Acid in Aqueous Solution, J. Phys. Chem. A 118, 8505-8516. Schaefer T.; J. Schindelka, D. Hoffmann and H. Herrmann (2012), Laboratory Kinetic and Mechanistic Studies on the OH-initiated Oxidation of Acetone in Aqueous Solution, J. Phys. Chem. A., 116 (24), 6317-6326. Schaefer T., D. van Pinxteren and H. Herrmann (2015), Multiphase Chemistry of Glyoxal: Revised Kinetics of the Alkyl Radical Reaction with Molecular Oxygen and the Reaction of Glyoxal with OH, NO₃, and SO₄⁻ in Aqueous Solution, Environ. Sci. Technol., 49 (1), 343-350.