

OXIDATION OF PYRUVIC ACID AND LACTIC ACID INDUCED BY OH RADICALS IN AQUEOUS SOLUTION

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Abstract

The tropospheric oxidation of volatile and semivolatile organic compounds (VOCs) can be induced by radical reactions, which can occur in the gas phase and in the liquid phase (cloud droplets, fog, rain or hygroscopic particles). These VOCs will be emitted either by anthropogenic or biogenic sources. In general, the degradation and conversion processes lead to more water-soluble organic compounds, e.g., carboxylic acids. In the literature, the photo-induced oxidation pathway of pyruvic acid is described by two concepts (Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014). The first one states the formation of lactic acid alkyl radicals, which react afterwards with molecular oxygen to peroxy radicals with a rate constant of $k \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. (Griffith et al., 2013; Reed Harris et al., 2014) The other one assumes that, the peroxy radical formation is a minor reaction pathway beside the alkyl radical addition reaction to pyruvic acid. A smaller rate constant of $k = 1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ for the peroxy radical formation was obtained. (Guzman et al., 2006) The difference in the rate constants of the oxygen addition is of about three orders of magnitude that clearly leads to different oxidation products and yields in aqueous solution. To clarify the difference in the rate constant of the oxygen addition, spectroscopic and kinetic investigations of the alkyl and peroxy radicals have been performed by use of a laser photolysis - long path absorption (LP-LPA) setup. The temperature and pH dependent measurements of the H atom abstraction reaction by OH radicals of lactic acid $k = (6.3 \pm 1.1) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, lactate $k = (8.9 \pm 0.8) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, pyruvic acid $k = (3.2 \pm 0.6) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and pyruvate $k = (7.1 \pm 1.8) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ were performed, in order to characterize the first oxidation step. In the second step the electron transfer reaction of the ferricyanide with the lactic acid alkyl radical $k = (4.3 \pm 0.4) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and the lactate alkyl radical $k = (2.4 \pm 0.7) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ were determined. By using these reference constants the molecular oxygen addition reaction with lactic acid alkyl radical $k = (2.2 \pm 0.1) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and the lactate alkyl radical $k = (3.4 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ have been obtained. According these findings and the confirmation of the work of Adams and Willson, 1969, the estimated value of Guzman et al., 2006 ($k \approx 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$) appears to low.

Keywords

OH radical reaction, Peroxy radical formation, Aqueous phase.

Introduction

Pyruvic acid can be formed in the troposphere either primarily the photooxidation of biogenic or anthropogenic precursors and can be found in both the gas and aqueous phase (Sempere et al., 1994; Veres et al., 2011). Previous and current studies on atmospherically relevant aqueous phase processes have focused on organic reactions with OH radicals, (Ervens et al., 2003, Schaefer et al., 2012) whereas the photolysis of organics, e.g. ketones and aldehydes might also play a role in SOA formation processes. (George et al., 2014)

However, the aqueous-phase photolysis of pyruvic acid including the resulting products is different from that in the gas-phase and is more controversial (Vesley and Leermakers, 1964; Guzman et al., 2006; Griffith et al., 2013; Reed Harris et al., 2014). In both concepts the triplet-state pyruvic acid reacts with another pyruvic acid molecule and form the lactic acid alkyl radical. The differences between the both concepts are in the subsequent reactions. The first one states that, the peroxy radical formation is a minor reaction pathway beside the alkyl radical recombination reaction as well as the alkyl radical addition reaction to pyruvic acid. A smaller rate constant of $k = 1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ for the peroxy radical formation was obtained (Guzman et al., 2006). The other one assumes that, the formation of lactic acid alkyl radicals, leads to peroxy radicals by the addition with molecular oxygen with a rate constant of $k \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Griffith et al., 2013; Reed Harris et al., 2014). The difference in the rate constants of the oxygen addition is of about three orders of magnitude that clearly leads to different major 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 of the formed alkyl radical.

Experimentals

The investigations of the kinetic of the OH radicals and of the alky radicals towards either ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) or molecular oxygen in an aqueous solution were conducted by using a Laser Flash Photolysis - Differential Amplified Laser - Long Path Absorption (LFP-DAL-LPA) setup.

Laser Flash Photolysis - Differential Amplified Laser - Long Path Absorption (LFP-DAL-LPA)

The LFP-DAL-LPA setup (Figure 1) is based on a continuous flow cell. The OH radicals were generated in a high-purity silica cell of 28 cm³ volume by the photolysis at $\lambda = 248 \text{ nm}$ of the precursor hydrogen peroxide (H_2O_2) initiated by an excimer laser (COMPEX 201, Lambda Physics). The White cell mirror configuration

was adjusted for 8 passes giving an absorption path length of 32 cm (White, 1942). A differential amplifier system with two photodiodes (S1336-44BQ, Hamamatsu) was used as the detector. The differential amplifier system was used to improve the signal-to-noise ratio (SNR) of the detected signal. The combination of a monochromator and a photodiode was used to avoid interferences due to scattered light from the excimer laser.

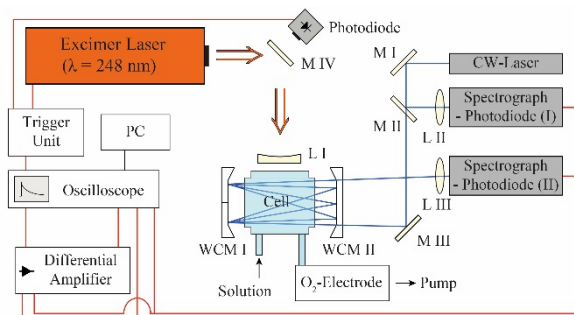
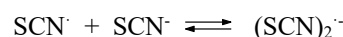
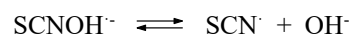
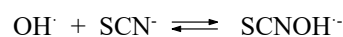
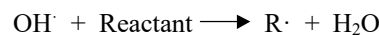
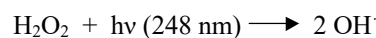


Figure 1. Scheme of the LFP-DAL-LPA system

The time dependencies of the formed radicals were observed at $\lambda = 405 \text{ nm}$ in case of the OH radical competition kinetic or $\lambda = 442 \text{ nm}$ in case of the alkyl radical competition kinetic. The concentration of the dissolved oxygen (O_2) in the aqueous solution has been adjusted by flushing with argon gas and measured with a Clark electrode (REK 1-1, Biolytik) which was connected to the measurement cell.

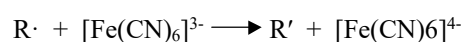
OH competition kinetics

The direct observation of the OH radicals is difficult, due to the low absorption in the deep UV (Herrmann et al., 2010) and the overlap absorption from other formed species e.g. alkyl or peroxy radicals. To investigate the rate constant of an oxidation reaction of the OH radicals with organic reactants the common method of the competition kinetics with the rhodanide anion as reference reactant was used (Chin and Wine, 1992).



Ferricyanide Competition Kinetics

The reactivity of the alkyl radical towards dissolved oxygen was investigated by using a modified competition kinetic method (Schaefer et al., 2015).



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As reference reactant the ferricyanide ($K_3[Fe(CN)_6]$) was used, which reacts with alkyl radicals ($R\cdot$) by electron transfer yielding the nonabsorbing ferrocyanide at $\lambda = 442$ nm.

Results and Discussion

The H atom abstraction reactions of OH radicals with lactic acid, lactate, pyruvic acid and pyruvate were measured as a function of the pH and T in aqueous solution.

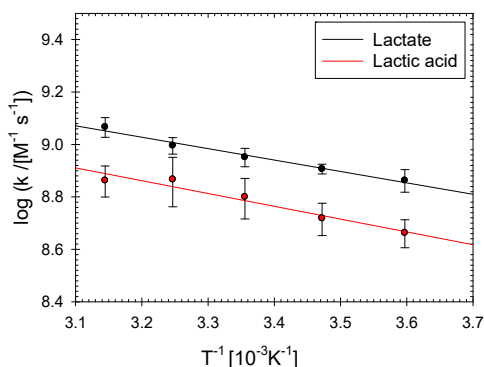


Figure 2. Temperature dependency of the OH radical reaction with lactic acid and lactate

The rate constants at $T = 298$ K and their corresponding Arrhenius parameters from the present work are summarized in Table 1.

Table 1. Summary of the obtained second order rate constants and Arrhenius parameters

OH radical	$k_{298K} /$ $L mol^{-1} s^{-1}$	$E_A /$ $kJ mol^{-1}$	$A /$ $L mol^{-1} s^{-1}$
Lactic acid	$(6.3 \pm 1.1) \times 10^8$	9 ± 4	$(2.7 \pm 0.2) \times 10^{10}$
Lactate	$(8.9 \pm 0.8) \times 10^8$	8 ± 3	$(2.7 \pm 0.1) \times 10^{10}$
Pyruvic acid	$(3.2 \pm 0.6) \times 10^8$	15 ± 5	$(1.1 \pm 0.1) \times 10^{11}$
Pyruvate	$(7.1 \pm 1.8) \times 10^8$	25 ± 19	$(1.5 \pm 0.4) \times 10^{13}$

The OH radical reactions of the carboxylic acids appear to be pH-dependent with a faster rate constant in the case of the deprotonated form of the acid. 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. The obtained rate constants and the activation parameters of the lactic acid/ lactate and pyruvic acid/ pyruvate are in a good agreement with literature values (Martin et al., 2009; Ervens et al., 2003).

In order to investigate the alkyl radical reaction with dissolved oxygen in the aqueous solution the protonated and deprotonated form of the lactic acid was oxidized by OH radicals. The formed α -hydroxy alkyl radical reacts with the ferricyanide in an electron transfer reaction to pyruvic acid and ferrocyanide. The averaged first-order rate constants derived from the change of the absorption at $\lambda = 442$ nm during the bleaching reaction are linear to

the ferricyanide concentration (Figure 3). From the slope of the plot, the bimolecular rate constant of the lactic acid alkyl radical reaction with ferricyanide was determined $(4.3 \pm 0.4) \times 10^8 L mol^{-1} s^{-1}$.

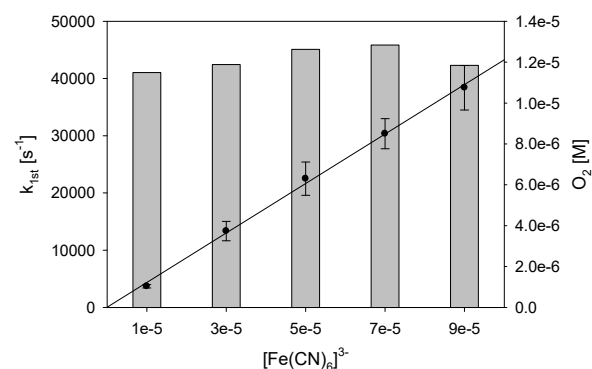


Figure 3. Determination of the reference rate constant for the bleaching reaction of the lactic acid alkyl radical with ferricyanide in the aqueous solution.

The rate constant of the lactate alkyl radical reaction with ferricyanide can be given with $k = (2.4 \pm 0.7) \times 10^8 L mol^{-1} s^{-1}$. The obtained value of the lactate alkyl radical is factor 6 smaller than the value ($k = 1.5 \times 10^9 L mol^{-1} s^{-1}$) given by Adams and Willson, 1969. In comparison the rate constant of the electron transfer reaction of the glycolate alkyl radical can be given with $k = 5.0 \times 10^8 L mol^{-1} s^{-1}$ (Adams and Willson, 1969).

The electron transfer reaction of the aforementioned alkyl radicals was used as reference constant in the competition reaction with dissolved oxygen. The linear regression with forcing to vertical intercept of 1 in Figure 5 leads to a rate constant for the reaction of the lactic acid alkyl radical with O_2 of $k = (2.2 \pm 0.1) \times 10^9 L mol^{-1} s^{-1}$.

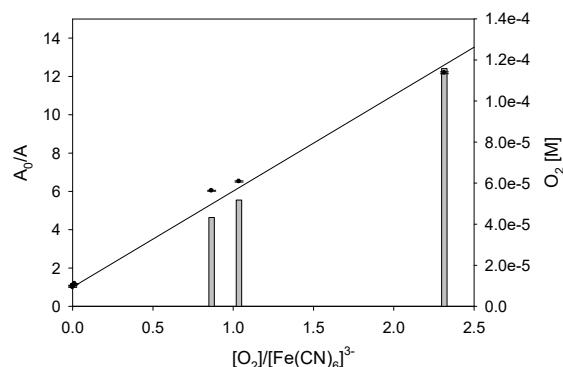


Figure 4. Determination of k_{2nd} by plotting the ratio of the absorptions against the ratio of the concentrations in the case of lactic acid

In case of lactate alkyl radical the rate constant of the addition reaction with molecular oxygen can be calculated with $k = (3.4 \pm 0.2) \times 10^9 L mol^{-1} s^{-1}$ and is in good agreement with the rate constant $k = 2.6 \times 10^9 L mol^{-1} s^{-1}$ from Adams and Willson, 1969.

Summary and Conclusion

In this study the temperature and pH dependent measurements of the H atom abstraction reaction of either the protonated or deprotonated form of lactic acid or pyruvic acid by OH radicals were performed. Furthermore, the rate constant of O₂ addition to the lactic acid alkyl radical and the lactate alkyl radical by using the ferricyanide competition kinetic method was determined. The obtained rate constants can be given with $k \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ of the molecular oxygen addition reaction, which confirms the work of Adams and Willson, 1969. Due to this, the estimated value of Guzman et al., 2006 ($k \approx 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$) appears to be low, therefore the general suggested value of the molecular oxygen addition reaction $k \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ should be used.

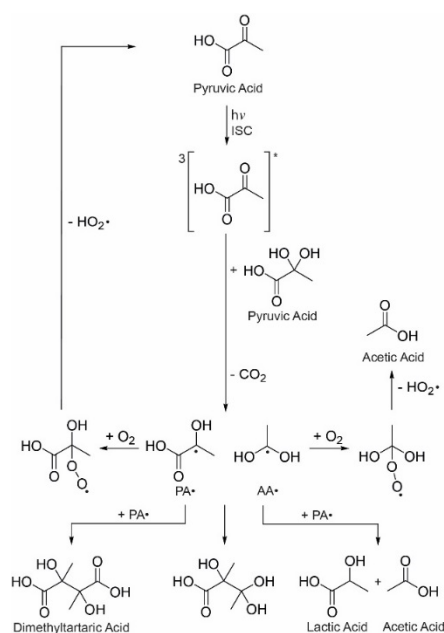


Figure 5. Revised photo-induced pyruvic acid oxidation mechanism from Reed Harris et al., 2014

According to the findings of this study the photo-induced pyruvic acid oxidation mechanism from Reed Harris et al., 2014 should be used.

Acknowledgments

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