



Kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solutions

L. Schöne and H. Herrmann

Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany

Correspondence to: H. Herrmann (herrmann@tropos.de)

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Abstract. Free radical reactions are an important degradation process for organic compounds within the aqueous atmospheric environment. Nevertheless, non-radical oxidants such as hydrogen peroxide and ozone also contribute to the degradation and conversion of these substances (Tilgner and Herrmann, 2010). In this work, kinetic investigations of non-radical reactions were conducted using UV/Vis spectroscopy (dual-beam spectrophotometer and stopped flow technique) and a capillary electrophoresis system applying pseudo-first order kinetics to reactions of glyoxal, methylglyoxal, glycolaldehyde, glyoxylic, pyruvic and glycolic acid as well as methacrolein (MACR) and methyl vinyl ketone (MVK) with H_2O_2 and ozone at 298 K. The measurements indicate rather small rate constants at room temperature of $k_{2\text{nd}} < 3 \text{ M}^{-1} \text{ s}^{-1}$ (except for the unsaturated compounds exposed to ozone). Compared to radical reaction rate constants the values are about 10 orders of magnitude smaller ($k_{\text{OH}\cdot} \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$). However, when considering the much larger non-radical oxidant concentrations compared to radical concentrations in urban cloud droplets, calculated first-order conversion rate constants change the picture towards H_2O_2 reactions becoming more important, especially when compared to the nitrate radical. For some reactions mechanistic suggestions are also given.

mosphere; others are formed secondarily by chemical or physical processes. Volatile organic compounds (VOCs) are oxidised in the gas phase according to their reactivity, leading to less volatile products. Due to increasing solubility, the uptake to the aqueous phase of cloud or fog droplets or deliquescent particles is enhanced. Especially in atmospheric aerosols, organic compounds account for a large fraction of up to 75 % of the total PM_{10} mass (Zhang et al., 2007). Regardless of which phase is considered, the main sink for organics in the troposphere is the oxidation by radicals such as $\text{OH}\cdot$ (at daytime), or $\text{NO}_3\cdot$ (especially at night) and other radicals for the aqueous systems. Therefore, mainly $\text{OH}\cdot$ radical photooxidation studies have been conducted in the past concerning the atmospheric transformation of organics. Glyoxal has been subject of several photochemistry studies (e.g. Carlton et al., 2007; Galloway et al., 2011; Zhao et al., 2012); however, carboxylic acids (Charbouillot et al., 2012) such as pyruvic acid (Guzman et al., 2006; Carlton et al., 2006) have also been investigated as well as glycolaldehyde (Beeby et al., 1987; Perri et al., 2009) and the unsaturated compounds methacrolein and methyl vinyl ketone (Liu et al., 2009; Liu et al., 2012). Nevertheless, Tilgner and Herrmann (2010) showed in a scoping study that some non-radical reactions with hydrogen peroxide or ozone and organic accretion reactions like aldol condensation or dimerisation have comparable first-order conversion rate constants to those of $\text{OH}\cdot$ or $\text{NO}_3\cdot$. At present, the proper implementation of such processes in models is hindered by the scarcity of kinetic and mechanistic data. Most available kinetic parameters originate from thermodynamical calculations or estimations.

1 Introduction

The troposphere is a complex mixture of gases, liquid substances and particulate constituents (e.g. Herrmann et al., 2010). Some components are emitted primarily into the at-

Table 1. Experimental details.*

Reactant	Oxidant	pH	Method & λ /nm	ϵ (oxidant) at λ /M ⁻¹ cm ⁻¹	ϵ (reactant) at λ /M ⁻¹ cm ⁻¹	c(oxidant)/M	c(reactant)/M
Pyruvic acid	H ₂ O ₂	1	CE	–	–	0.05–0.25	0.005
Pyruvate	H ₂ O ₂	7	CE	–	–	0.008–0.024	0.012
Glyoxylic acid	H ₂ O ₂	1	CE	–	–	0.5–1.5	0.025
Glyoxylate	H ₂ O ₂	7	CE	–	–	0.03–0.12	0.001
Glycolaldehyde	H ₂ O ₂	5	PE 229	63.6	10.5	0.001	0.02–0.2
Glyoxal	H ₂ O ₂	5	PE 233	54.0	0.4	0.028	0.56–1.68
Methacrolein	H ₂ O ₂	5	SF 310	29.8	0.5	0.02	1–3
Pyruvic acid	O ₃	1	PE 260	3300	4.8	5×10^{-5}	$(1–12.5) \times 10^{-3}$
Pyruvate	O ₃	7	PE 260	3300	51.0	3×10^{-5}	$(0.9–7) \times 10^{-3}$
Glyoxylic acid	O ₃	1	PE 260	3300	0.7	5×10^{-5}	$(0.1–10) \times 10^{-3}$
Glyoxylic acid/glyoxylate	O ₃	3	PE 260	3300	1.3	5×10^{-5}	$(1–7.5) \times 10^{-3}$
Glyoxylate	O ₃	7	PE 260	3300	2.1	5×10^{-5}	$(1–5) \times 10^{-3}$
Glycolic acid	O ₃	1	PE 260	3300	0.4	5×10^{-5}	$(1–37.5) \times 10^{-3}$
Glycolate	O ₃	7	PE 260	3300	2.2	5×10^{-5}	$(1–15) \times 10^{-3}$
Glycolaldehyde	O ₃	5	PE 260	3300	34.7	5×10^{-5}	$(1–15) \times 10^{-3}$
Glyoxal	O ₃	5	PE 260	3300	0.3	3×10^{-5}	$(0.9–3.6) \times 10^{-3}$
Methylglyoxal	O ₃	5	PE 260	3300	12.7	3×10^{-5}	$(0.7–2.1) \times 10^{-3}$
Methacrolein	O ₃	2	SF 260	3300	10.0	6×10^{-5}	$(0.6–1) \times 10^{-4}$
Methyl vinyl ketone	O ₃	2	SF 260	3300	7.7	6×10^{-5}	$(0.6–1) \times 10^{-4}$

* CE = capillary electrophoresis, PE = Perkin Elmer (dual-beam spectrometer), SF = stopped flow technique. Path length = 1 cm for PE and SF, $T = 298$ K.

The present work aims to improve the lack of kinetic and mechanistic data for reactions of hydrogen peroxide and ozone with organic compounds relevant for the tropospheric multiphase system. Reactants are pyruvic acid/pyruvate, glyoxylic acid/glyoxylate, glycolic acid/glycolate, glycolaldehyde, glyoxal, methylglyoxal, methacrolein and methyl vinyl ketone. Most of the mentioned species are products from the oxidation of isoprene, one of the largest single sources of organic carbon in the troposphere (Guenther et al., 2006; Sharkey et al., 2008). Especially glyoxal and methylglyoxal gained enormous attention in recent studies since they contribute largely to the formation of organic particulate matter (Lim et al., 2013, and references therein). Van Pinxteren et al. (2005) provide cloud water concentrations of glyoxal, methylglyoxal, glycolaldehyde, methacrolein and methyl vinyl ketone measured at a rural site (Mt. Schmücke, Germany) of maximum 88.5, 55.8, 95.8, 0.5 and 3.1 μM , respectively. Munger et al. (1990, 1995), Collett et al. (1990) and Matsumoto et al. (2005) state similar values at significant levels. The results from the kinetic investigations are compared to the few available reported values and the atmospheric relevance of the reactions studied is discussed in comparison to model studies.

2 Experimental

Table 1 summarises the experimental details of the kinetic investigations. Most measurements were conducted making

use of the optical properties of the reacting substances. All measurements were conducted at 298 K. For the acids, the pH was adjusted to pH 1 and pH 8 to measure both the neutral and anionic form, respectively. For the aldehydes, no pH-altering substances were added, resulting in values of pH 4.5 to 5.5.

2.1 Studies of ozone reactions

Pseudo-first order kinetics were applied for the ozone investigations using a dual-beam UV/Vis spectrophotometer (LAMBDA 900, Perkin Elmer). Consequently, the reactants' concentrations were held in excess over the ozone concentration (see Eq. 2). The depletion of ozone was recorded with time by tracking its absorbance at $\lambda = 260$ nm ($\epsilon = 3300 \text{ M}^{-1} \text{ cm}^{-1}$, Hart et al., 1983). The initial reactant concentrations were chosen to be $(7–22) \times 10^{-4}$ M, depending on the spectral conditions between reactant and oxidant, and $c_0(\text{O}_3) = 5 \times 10^{-5}$ M, respectively. As a reaction vessel, a 3.2 ml sealed fused silica cuvette ($d = 1$ cm) was used. Measurements with the dual-beam spectrometer lasted a minimum of 5 min to several hours, with reactant mixing times of about 5 s because of manual pipetting. This very short mixing time is considered affordable given the very slow reaction rates.

The stopped flow technique was used (SF-61DX2, HI-TECH Scientific, UV/Vis detection) for faster reactions with unsaturated compounds like methacrolein and methyl vinyl ketone. The advantage of this method is the immediate start

of the absorbance recording in the moment of reactant mixing. The mixing time of the stopped flow technique is about 1 ms. As the measurement of an ozone reaction with an unsaturated compound lasted a minimum of 1 s, only the first data point ($t = 1.48$ ms) was discarded a priori. There was no deviation in linearity observed at the beginning of recording. Here, the concentration of ozone was also monitored at $\lambda = 260$ nm during the reaction, with initial concentrations of MACR and MVK being $(0.6-1) \times 10^{-4}$ mM and $c_0(\text{O}_3) = 6 \times 10^{-6}$ M, respectively. The pH was adjusted to pH 2. From the concentration-time profiles measured, pseudo-first order rate constants $k_{1\text{st}}$ (s⁻¹) can be obtained according to Eq. (3). Variation of the initial concentration of the reactant in excess enables calculation of the second-order rate constant $k_{2\text{nd}}$ (M⁻¹ s⁻¹, Eq. 2).



$$\frac{dc(\text{O}_3)}{dt} = -k_{2\text{nd}} \cdot c(\text{O}_3) \cdot c(\text{X}) \quad (1)$$

$$k_{1\text{st}} = k_{2\text{nd}} \cdot c(\text{O}_3) \quad \text{if } c(\text{X}) \gg c(\text{O}_3) \quad (2)$$

$$\frac{dc(\text{O}_3)}{dt} = -k_{1\text{st}} \cdot c(\text{O}_3) \quad (3)$$

Ozone was produced using the ozone generator 500 M (Fischer, Germany) with pure O₂ from a gas cylinder. Ozone “stock solutions” were prepared by introducing this ozone-enriched gas flow to an aqueous solution with an adjusted pH value. Ozone “stock solutions” were prepared freshly prior to each experiment as it decomposes in an aqueous solution (see Reactions R2 to R5). The ozone concentration in the “stock solution” was determined spectroscopically at 260 nm using the extinction coefficient by Hart et al. (1983). Subsequently, the stock solution was diluted to the requested concentration. The time between the end of bubbling and the start of the measurement was about one minute. Throughout the experiments with the dual-beam spectrometer, the decay of the ozone concentration was recorded simultaneously in the reference beam path in order to obtain the ozone decay solely resulting from the reaction with the organic compound.

2.2 Studies of H₂O₂ reactions

The reactions of H₂O₂ with the target reactants proceeded slowly enough to allow manual pipetting to mix reactant aliquots and start the reaction while recording the time with a stopwatch. Total volumes were 25 ml; 0.3 ml volume samples were withdrawn at time intervals from 10 s up to some minutes. In cases where the UV/Vis spectra of H₂O₂ and the respective reactant showed appreciable differences without interfering absorptions in certain wavelength ranges, these reactions were kinetically investigated using UV/Vis spectroscopy. Pyruvic acid/pyruvate and glyoxylic acid/glyoxylate were quantified by capillary electrophoresis

(CE) because of an overlap of their UV spectrum with that of H₂O₂ making a kinetic analysis using UV spectroscopy impossible. The reaction was simply stopped by adding 3 ml of catalase stock solution to each sample (0.3 ml). The stock solution was prepared by solving 400 μ l of catalase in 50 ml MilliQ water. According to the product information, catalase acts as catalyst in the following two-step reaction: $2 \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O}$. In the first step, H₂O₂ is reduced and the enzyme is oxidised yielding water as product. In the second step, H₂O₂ as well as the previously oxidised enzyme get reduced, leading to water and O₂ as products. How fast the reaction occurs, depends on the concentration of catalase and H₂O₂, being highest at high concentrations (Michaelis–Menten theory). During the conducted experiments both concentrations were comparably high (e.g. $c(\text{H}_2\text{O}_2) = 1$ M), thus the reaction of H₂O₂ with catalase is much faster than with the reactant. The rate constant of H₂O₂ + catalase was reported with $k_{2\text{nd}} = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Ogura, 1955). Tests revealed that the amount of catalase was sufficient to destroy H₂O₂ and stop the reaction with the organic acid (= reactant). This was concluded as no change in the concentration of the formed organic acids was observed over a period of a week after the reaction was stopped.

During CE measurements two buffer reservoirs are constantly filled with an electrolyte containing 2 mM 5-sulfosalicylic acid, 8 mM tris(hydroxymethyl)aminomethane and 0.001 % hexadimethrin bromide at pH 8.2. The reservoirs are connected by a fused silica capillary (82 cm) with an inner diameter of 75 μ m. A high voltage source is adjusted at 30 kV. Due to the electrolyte pH of 8.2 organic acids in the sample deprotonate and the so formed anionic compounds move towards the cathode, the migration speed depending on their size and charge. The detection was performed indirectly at $\lambda = 208$ nm (for details see ESM). Concentration-time profiles of the corresponding acid have been obtained and the kinetic data analysis occurs analogously to the ozone measurements. The CE also provides information of the products formed during the reaction.

As pseudo-first order conditions were applied, the reactant, whose concentration would not be recorded, was added in excess in order to keep its concentration constant during the measurements. For CE measurements the oxidant was in excess just as for methacrolein + H₂O₂ (because the acids and methacrolein were analysed), whereas the reactions of H₂O₂ with glycolaldehyde and glyoxal were conducted under aldehyde excess (where H₂O₂ was analysed). All experimental parameters are summarised in Table 1.

2.3 Chemicals

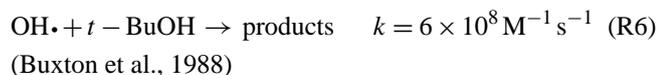
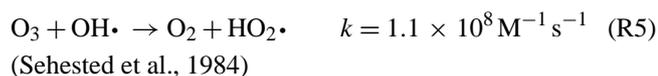
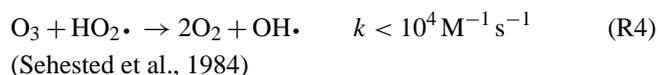
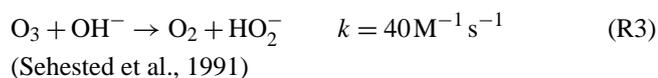
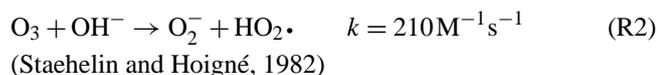
The following chemicals were used without further purification: ammonium sulfate (> 99 %, Riedel deHaën), sodium pyruvate (99 %, Merck), sodium phosphate dibasic dihydrate (> 98 %, Fluka), glycolaldehyde dimer (mixture from

stereoisomers, Aldrich), glycolic acid ($\geq 99\%$, Fluka), glyoxal (40% in water, Sigma Aldrich), glyoxylic acid monohydrate ($\geq 97\%$, Fluka), hexadimethrin bromide (HDB, $\geq 95\%$, Sigma Aldrich), catalase (from bovine liver, aqueous suspension, Sigma), methacrolein (95%, Aldrich), methylglyoxal (47% in water, Sigma), methyl vinyl ketone (99%, Aldrich), sodium phosphate monobasic (99%, Riedel de Haën), perchloric acid (70–72%, J. T. Baker), phosphoric acid (85%, Aldrich), oxygen (Premium), 5 sulfosalicylic acid (for electrophoresis, Sigma Aldrich), *tert*-butanol (99.7%, Fluka), tris(hydroxymethyl)aminomethane ($\geq 99.9\%$, Sigma Aldrich), hydrogen peroxide ($\geq 30\%$ in water, Fluka). All solutions were freshly prepared with MilliQ water ($18\text{ M}\Omega\text{ cm}^{-1}$). The pH was adjusted using a phosphate buffer system or perchloric acid.

3 Results and discussion

3.1 Ozone measurements

The ozone measurements were tested applying the system suggested by Hoigné and Bader (1983b) with *tert*-butanol as OH• scavenger. In an aqueous solution, ozone will degrade to form hydroperoxyl radicals HO₂• or hydroperoxide anions HO₂⁻ (Reactions R2 and R3) as well as oxygen or superoxide, respectively, as a consequence of its reaction with hydroxide ions. The initial involvement of hydroxide causes a dependence of this reaction on the pH. Since HO₂• is a quite reactive species, it reduces ozone forming even more reactive OH• radicals (Reaction R4). These will destroy ozone, leading again to HO₂• (Reaction R5). Taking OH• off the system by addition of a scavenger (R6) means preventing O₃ from being destroyed by the following cycle.



Additionally, the pH of the aqueous solution can be adjusted to an acidic milieu (e.g. pH 2) to slow down the rate of Reaction (R2) and suppress ozone decomposition.

Hoigné and Bader tested several OH• radical scavenging substances such as HCO₃⁻, PrOH, BuOH, NaHCO₃ or methyl mercury hydroxide, respectively, but *t*-BuOH was

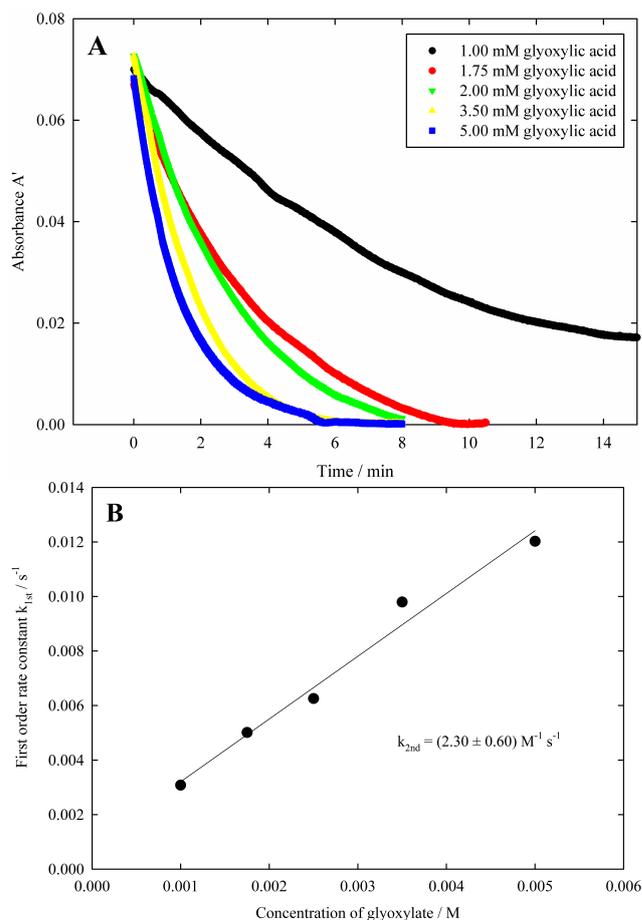


Fig. 1. (A) Absorbance-time profiles of ozone during the reaction with glyoxylate at pH 7. The initial concentration of ozone was about $c(\text{O}_3) = 5 \times 10^{-5}\text{ M}$. (B) Pseudo-first order rate constants k_{1st} plotted over the concentration of glyoxylate.

found to be the most appropriate scavenger (Hoigné and Bader, 1983a, b, 1985). Variation of *t*-BuOH beyond the suggested concentration led to a significantly smaller S/N ratio but showed no change in the results. Therefore, the proposed concentration of 15 mM *t*-BuOH was adopted within all ozone measurements, also in the present study.

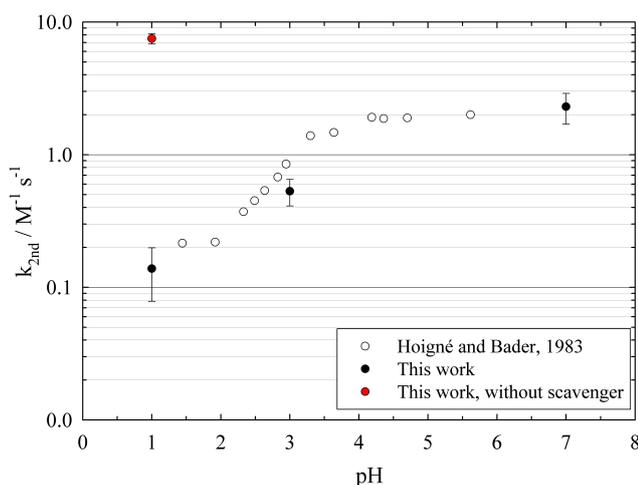
3.1.1 Monocarboxylic acids + ozone

Figure 1 shows the absorbance vs. time (left) and k_{1st} vs. $c(\text{glyoxylate})$ (right) plots for the reaction of glyoxylate with O₃ at pH 7 measured with the UV spectrometer. The pseudo-first order rate constant k_{1st} increases with increasing glyoxylate concentration, the slope corresponds to the second-order rate constant $k_{\text{glyoxylate}} = 2.30 \pm 0.60\text{ M}^{-1}\text{ s}^{-1}$.

The reaction of glyoxylic acid/ glyoxylate with ozone was studied at three different pH values to obtain a direct comparison to the work of Hoigné and Bader (1983b). Figure 2 shows the pH-dependent second-order rate constants from this work (black dots) and from Hoigné and Bader (1983b,

Table 2. Second-order rate constants [M⁻¹ s⁻¹] for the investigated systems. The uncertainties stated are statistical errors with the student *t* factor for the 95 % confidence level derived from linear regression analysis.

Substance	k _{2nd} /M ⁻¹ s ⁻¹	
	H ₂ O ₂	O ₃
Glyoxylic acid pH 1	(3.96 ± 0.91) × 10 ⁻³	0.14 ± 0.06
Glyoxylic acid/glyoxylate pH 3	–	0.53 ± 0.12
Glyoxylate pH 7	0.11 ± 0.01	2.30 ± 0.60
Pyruvic acid pH 1	0.12 ± 0.04	0.13 ± 0.03
Pyruvate pH 7	0.75 ± 0.16	0.98 ± 0.35
Glycolic acid pH 1	–	(5.50 ± 1.52) × 10 ⁻²
Glycolate pH 7	–	0.71 ± 0.05
Glycolaldehyde pH 5	0.04 ± 0.02	0.52 ± 0.10
Glyoxal pH 5	(1.67 ± 0.80) × 10 ⁻⁴	0.90 ± 0.17
Methylglyoxal pH 5	–	2.89 ± 0.72
Methacrolein pH 2	(7.56 ± 2.84) × 10 ⁻²	(2.25 ± 0.53) × 10 ⁴
Methyl vinyl ketone pH 2	–	(7.11 ± 1.06) × 10 ⁴

**Fig. 2.** Rate constants [M⁻¹ s⁻¹] plotted as a function of pH value for the reaction of glyoxylic acid/glyoxylate with ozone. Hoigné and Bader (1983b; white dots); this work (black dots); no scavenger used in this work (red dot).

white dots). The figure indicates good agreement between both studies.

Figure 2 furthermore includes one data point measured during this study at pH 1 where no scavenger was added to the solution (red dot). The resulting rate constant is highly overestimated due to the additional reduction of ozone by reactions with OH• (see Reaction R5). Adding a scavenger is therefore essential if reactions with ozone are investigated.

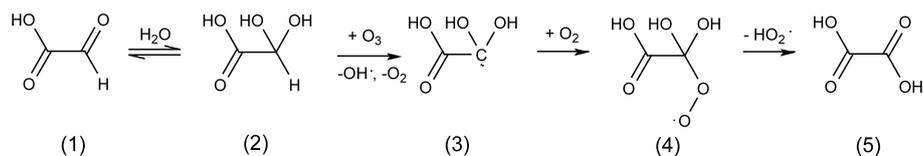
Hoigné and Bader do not suggest a reaction pathway of glyoxylic acid and ozone. Scheme 1 illustrates one tentative mechanism which is proposed here. In solution, most of the aldehyde group in glyoxylic acid is hydrated ($K_{\text{hydr}} = 1.09 \times 10^4 \text{ M atm}^{-1}$, Ip et al., 2009). With ozone in the system, the most weakly bound H atom at the carbon

atom (BDE = 337.2 kJ mol⁻¹, Dean and Lange, 1992) is abstracted, leading to an OH• radical from the decomposition of HO₃, molecular oxygen and an alkyl radical (3). This step is identical with the one proposed by Caprio et al. (1987). Holen et al. (1998) also suggest an H atom abstraction as well as the addition of ozone to the C=O double bond that can be neglected as glyoxylic acid is hydrated in solution. Subsequent reaction with the released O₂ forms a peroxy radical (4) which quickly decomposes to form oxalic acid (5) and an HO₂• radical. Caprio et al. (1987) and Holen et al. (1998) also identified oxalic acid as a product during the reaction of glyoxylic acid with ozone. This reaction can therefore be regarded as an additional reaction pathway to form oxalic acid which is the most abundant diacid in aqueous atmospheric environments (Myriokefalitakis et al., 2011). Nevertheless, it has to be noted that there were no product studies conducted within this work. Thus, the proposed mechanism is tentative.

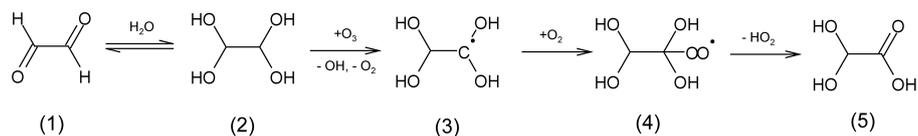
The additional formation of OH• and HO₂• radicals during this reaction makes it necessary to add a scavenger to the reacting system. Additionally, Caprio et al. (1987) state a much larger second-order rate constant of $k_{\text{glyoxylic acid}+\text{O}_3} = (20 \pm 0.5) \text{ M}^{-1} \text{ s}^{-1}$. The reasons for this discrepancy are the missing scavenger during their measurements and probably a different ratio of protonated and deprotonated acid forms since no pH value was declared.

The reaction of glycolic acid with ozone also leads, analogously to the mechanism just proposed, to the formation of glyoxylic acid and HO₂•. The rate constants measured here is $k_{\text{glycolic acid}+\text{O}_3} = (5.50 \pm 1.52) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

For the interaction of pyruvic acid with ozone no mechanism is proposed so far in the literature. The only suggestions include manganese as a catalyst, leading to acetic acid as well as O₂ and CO₂ (pH 2–4, Andreozzi et al., 1998). The rate constant measured in this work is $k_{\text{pyruvic acid}+\text{O}_3} = (0.13 \pm 0.03) \text{ M}^{-1} \text{ s}^{-1}$. Table 2 indicates a



Scheme 1. Proposed oxidation mechanism of (hydrated) glyoxylic acid exposed to ozone in an aqueous environment.



Scheme 2. Reaction mechanism for fully hydrated glyoxal reacting with ozone.

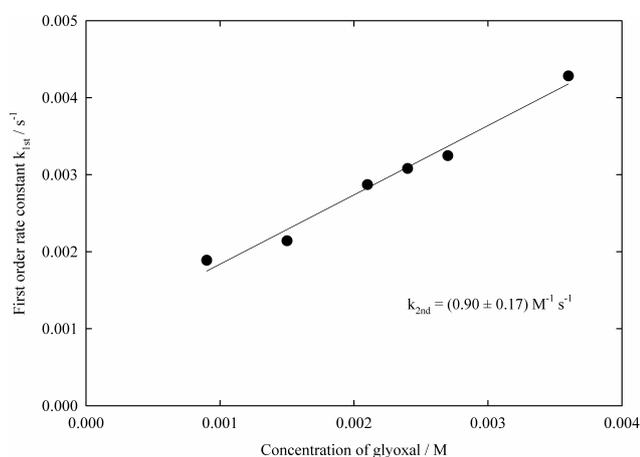


Fig. 3. Pseudo-first order rate constants k_{1st} plotted over the concentration of glyoxal during the reaction with ozone at pH 5. The initial concentration of ozone was about $c(O_3) = 3 \times 10^{-5}$ M. The slope corresponds to $k_{glyoxal+O_3} = (0.90 \pm 0.17) M^{-1} s^{-1}$.

higher reactivity of the deprotonated form of the acid compared to the protonated form by about one order of magnitude. The reason for this could be the stronger electron-withdrawing properties of the deprotonated carboxylate group, leading to different BDEs and therefore a more easily abstractable hydrogen at the neighbouring C atom.

3.1.2 Aldehydes + ozone

Figure 3 shows the dependence of the pseudo-first order rate constant on the glyoxal concentration during the reaction with ozone, which corresponds to a second-order rate constant of $k_{glyoxal+O_3} = (0.90 \pm 0.17) M^{-1} s^{-1}$. The other two aldehydes, methylglyoxal and glycolaldehyde, react with similar rate constants of $k_{methylglyoxal+O_3} = (2.89 \pm 0.72) M^{-1} s^{-1}$ and $k_{glycolaldehyde+O_3} = (0.52 \pm 0.10) M^{-1} s^{-1}$, respectively. The reactivities of the deprotonated forms of the acids are also in the same range (see Table 2).

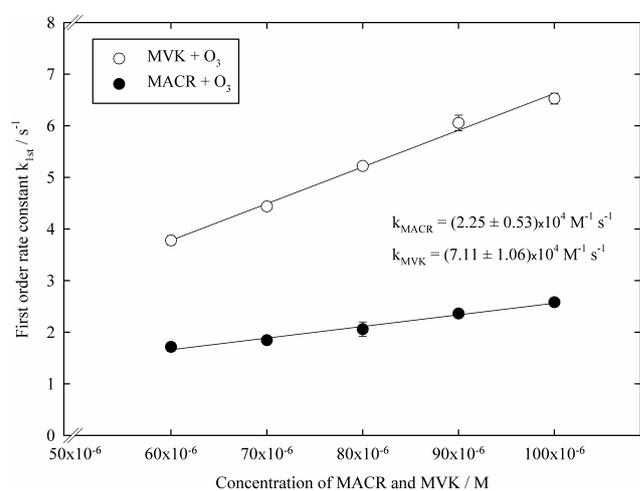


Fig. 4. Pseudo-first order rate constants k_{1st} plotted over the concentration of methacrolein and methyl vinyl ketone for the reaction with ozone at pH 2. The initial concentration of ozone was about $c(O_3) = 6 \times 10^{-6}$ M.

Since the given rate constants are first determinations (at least under these temperature conditions, namely $T = 298$ K), no appropriate comparison is possible. Ervens et al. (2004) state that glyoxal is present in the geminal diol form due to its high hydration constant in the aqueous phase ($K_{hydr} = 3 \times 10^5 M^{-1}$, Betterton and Hoffmann, 1988). The proposed mechanism in Scheme 2 was developed following the one of glyoxylic acid + ozone (Scheme 1).

At first, hydrogen abstraction at the C–H bond of the aldehyde group (3) occurs which was also proposed by Voukides et al. (2009). Subsequently, the addition of oxygen forming a peroxy radical (4) and HO₂ elimination leads to hydrated glyoxylic acid as main stable oxidation product (5). Caprio et al. (1987) have proposed the reaction of the (unhydrated) alkyl radical with ozone instead of oxygen. This pathway is not very likely because of the excess of O₂ over O₃ which they explicitly stated in their study. After another reaction of the so formed alkoxy radical with another (unhydrated)

glyoxal molecule, which appears improbable, also glyoxylic acid is formed (Caprio et al., 1987). As it has been known since the work of von Sonntag and Schuchmann (1991) that α -hydroxy-peroxy radicals likely eliminate HO₂ rather than abstract a hydrogen atom, the mechanism of Caprio et al (1987) does not appear feasible.

With regards to the reactions of methylglyoxal and glycolaldehyde with ozone, no reaction mechanism can be given due to missing analytical data since no product studies were performed in this work.

3.1.3 Unsaturated compounds + ozone

The reactions of methacrolein (MACR) and methyl vinyl ketone (MVK) with ozone were investigated using the stopped flow technique at pH 2. These more complex measurements were necessary because of the much higher reactivity of ozone towards unsaturated compounds as ozone adds to C–C double bonds. As can be seen from Fig. 4, reactions between MACR or MVK and ozone are at least 4 orders of magnitude faster than the other investigated substances (see also Table 2). The second-order rate constants determined in this study are $k_{\text{MACR}+\text{O}_3} = (2.25 \pm 0.53) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{MVK}+\text{O}_3} = (7.11 \pm 1.06) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Pedersen and Sehested (2001) also studied both reactions (pH 2) and observed quite similar rate constants. These authors obtained values of $k_{\text{MACR}+\text{O}_3} = (2.4 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{MVK}+\text{O}_3} = (4.4 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction with MACR and MVK, respectively. These values indicate good agreement with this work's measurements. For the reaction of MVK with ozone a 1.6 times larger rate constant was observed in this work.

The mechanism for the reaction of MACR and MVK with ozone is provided by Chen et al. (2008). Addition of ozone to each of the molecules builds primary ozonides which decompose rapidly to HCHO, methylglyoxal and several Criegee intermediates. These reactive intermediates get deactivated by collision, become hydrolysed and decompose to HCHO and methylglyoxal, but H₂O₂ and pyruvic acid are also formed. Ervens et al. (2004) confirm the formation of HCHO and methylglyoxal and also provide ratios for each pathway. The reaction of ozone with unsaturated compounds therefore provides an effective way to build up organic aldehydes and acids in the atmospheric aqueous phase.

3.2 H₂O₂ measurements

3.2.1 Monocarboxylic acids + H₂O₂

Reactions of pyruvic acid and glyoxylic acid (and their anions) with H₂O₂ were investigated using the capillary electrophoresis system. Hence, not only concentration-time profiles of the reacting acid were obtained, but the formation of anionic reaction products was also observed.

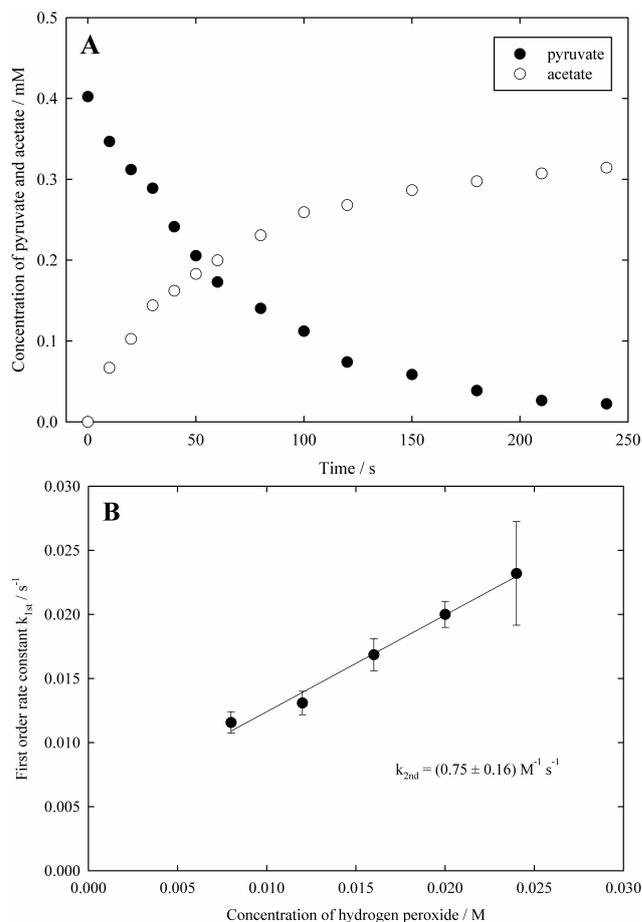


Fig. 5. (A) Concentration-time profiles of pyruvate and acetate during the reaction with H₂O₂ at pH 7 for $c(\text{pyruvate}) = 0.4 \text{ mM}$ and $c(\text{H}_2\text{O}_2) = 12 \text{ mM}$. (B) Pseudo-first order rate constants k_{1st} plotted over the concentration of hydrogen peroxide for the reaction with pyruvate at pH 7.

Figure 5 shows on the left hand side the track of the pyruvate depletion as well as the development of acetate during the reaction of pyruvate with hydrogen peroxide. Until 50 seconds reaction time, one depleted molecule of pyruvate leads to one formed molecule of acetate. In the further course of the reaction the sum of both educt and product is not constant anymore. A reason could be the formation of other products than acetic acid which cannot be detected by capillary electrophoresis.

von Sonntag and Schuchmann (1997) and Stefan and Bolton (1999) propose mechanisms which agree with our observations, thus acetate must be the main oxidation product of this reaction (see Scheme 3).

The rate constants determined in this work can only be compared with a single value by Stefan and Bolton (1999) (see Table 3). Concentrations of pyruvate and hydrogen peroxide as well as replicates undertaken exceed those from Stefan and Bolton (1999). Also, the determined rate constant is

Table 3. Comparison of this work's reaction conditions with Stefan and Bolton's (1999).

Method	This work		Stefan and Bolton (1999)
	Capillary electrophoresis		Ion exchange chromatography "mostly ionised"
pH	1	7	
c(pyruvate) / mM	5	0.4	0.25
c(H ₂ O ₂) / mM	50–150	8–24	5
c(H ₂ O ₂) / c(pyruvate)	10–30	30–60	20
no. of c(H ₂ O ₂)	5	5	1
k _{2nd} / M ⁻¹ s ⁻¹	0.12 ± 0.04	0.75 ± 0.16	0.11

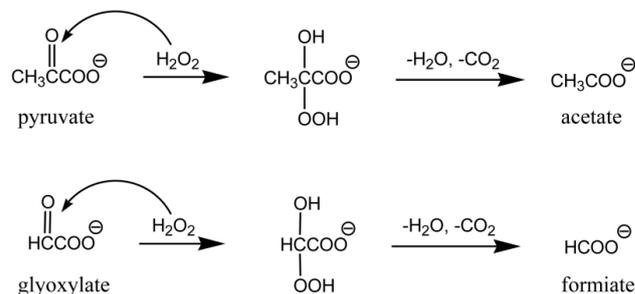
larger in this work. Furthermore, Stefan and Bolton (1999) do not specify any exact pH value; they solely write that pyruvate is "mostly present in its ionised form". Since 99.99% of the acid is ionised at pH 7, the working pH of Stefan and Bolton (1999) must be smaller than pH 7. This could be an indication for the smaller k_{2nd} value these authors observed. We used a phosphate buffer system to adjust the pH, which could be a potential source of impurities leading to a higher rate constant. However, control experiments provided evidence that the buffer system used does not disturb the measurement.

The reactivity of glyoxylic acid and glyoxylate towards H₂O₂ is about one to two orders of magnitude smaller compared to pyruvic acid/pyruvate (see Table 2). The rate constants determined are $k_{\text{glyoxylic acid}+\text{H}_2\text{O}_2} = (3.96 \pm 0.91) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{glyoxylate}+\text{H}_2\text{O}_2} = (0.11 \pm 0.01) \text{ M}^{-1} \text{ s}^{-1}$ for glyoxylic acid and glyoxylate, respectively. Scheme 3 shows the reaction pathway which occurs analogously to pyruvate. In this case, the formation of formiate is observed during the capillary electrophoresis measurements. Formiate could also be confirmed as the main oxidation product by Tan et al. (2010) and Zhao et al. (2013). Zhao et al. (2013) furthermore propose the additional formation of α -hydroxyhydroperoxides (α -HHPs) because the amount of formic acid formed was smaller than the decay of glyoxylic acid.

For glycolic acid and glycolate no kinetic investigations could be undertaken because of the insufficient recovery rate of the anion in the CE. Furthermore, the UV/Vis spectra of the two reactants also do not permit the use of UV/Vis spectroscopy because no wavelength could be identified, where the spectra differ by at least one order of magnitude.

3.2.2 Aldehydes + H₂O₂

The reactivity of aldehydes towards hydrogen peroxide is very small. The rate constants obtained for glycolaldehyde and glyoxal are $k_{\text{glycolaldehyde}} = (0.04 \pm 0.02) \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{glyoxal}+\text{H}_2\text{O}_2} = (1.67 \pm 0.80) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Patai and Zabicky (1970) state a rate constant for formaldehyde exposed to H₂O₂ of $1.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, indicating slow reactions throughout.

**Scheme 3.** Reaction mechanism of pyruvate and glyoxylate + H₂O₂.

Carlton et al. (2007) suggested the formation of two formic acid molecules in the reaction of glyoxal with H₂O₂. These authors propose a rate constant of $1 \text{ M}^{-1} \text{ s}^{-1}$ which is about four orders of magnitude larger than in this work. This value was not measured but fitted during their model studies. Zhao et al. (2013) also observed the formation of small amounts of formic acid during the reaction of glyoxal with hydrogen peroxide whereas another product might be hydroxyhydroperoxides (Zhao et al., 2008; Zhao et al. 2012; Huang et al., 2013). The formation of such species was already proposed much earlier by Satterfield and Case (1956).

For the reaction between methylglyoxal and H₂O₂ no rate constant could be determined because of the inappropriate UV/Vis spectra of both reactants. The spectra are too similar to extract a wavelength where they differ by at least one order of magnitude. Nevertheless, test measurements were undertaken which indicated a reaction even slower than with glyoxal.

3.2.3 Unsaturated compounds + H₂O₂

The rate constant for the reaction of methacrolein with H₂O₂ was determined to $k_{\text{MACR}} = (7.56 \pm 2.84) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. Zhang et al. (2009) give an upper limit as an estimate of $0.13 \text{ M}^{-1} \text{ s}^{-1}$, which is about a factor of 2 larger.

Claeys et al. (2004) propose an acid-catalysed addition of hydrogen peroxide to the molecule forming 2,3-dihydroxymethacrylic acid, whereas Zhao et al. (2013) did not observe this specified product during their

measurements. Zhao et al. (2013) furthermore confirm the small reactivity of MACR towards H₂O₂.

Due to a missing appropriate wavelength where the spectra differ by at least one order of magnitude, the reaction of MVK with H₂O₂ could not be investigated kinetically. Nevertheless, Zhao et al. (2013) state that ketones in general are relatively stable against nucleophilic addition.

3.3 Comparison to model studies

Table 2 summarises the second-order rate constants measured at 298 K. Apart from the reactions of the unsaturated compounds methacrolein and methyl vinyl ketone with ozone, the investigated monocarboxylic acids and aldehydes show only small absolute rate constants in their reactions with H₂O₂ and ozone. The second-order rate constants lie below 3 M⁻¹ s⁻¹.

A comparison with radical reaction rate constants in the aqueous phase reveals a difference of several orders of magnitude since the values are $k_{\text{OH}\cdot} \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{NO}_3\cdot} \sim 10^7\text{--}10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. From that point of view, the examined reactions do not seem to have any influence on the degradation of organics in the global aqueous environmental system. However, not only rate constants are important to be considered to judge the importance of a reaction, but also the concentration of the investigated substances, because first-order conversion rate constants $k_{1\text{st}}$ are described by the product of rate constant and reactants' concentrations. Therefore, $k_{1\text{st}} [\text{s}^{-1}]$ is calculated according to Eq. (2) multiplying the second-order rate constants [M⁻¹ s⁻¹] by the corresponding oxidant concentration $c(\text{X}) [\text{M}]$. The non-radical reaction rate constants are taken from the present work, whereas aqueous phase radical reaction rate constants are adopted from Tilgner and Herrmann (2010). Oxidant concentrations were calculated from CAPRAM3.0i. CAPRAM stands for Chemical Aqueous Phase RADical Mechanism and deals with, e.g., the radical-driven conversion of carbonyls to acids and further acid degradation in tropospheric aqueous systems (Tilgner and Herrmann, 2010). Table 4 summarises maximum concentrations of hydroxyl OH \cdot and nitrate NO₃ \cdot radicals as well as H₂O₂ and ozone at 20–44 hours reaction time occurring in a polluted (so-called ‘urban’) cloud droplet. It has to be noted that the aqueous phase concentrations given in Table 4 are maximum concentrations of one simulation day. The comparison between $c(\text{OH}\cdot)$ and $c(\text{H}_2\text{O}_2)$ shows a difference of 10 orders of magnitude, indicating much larger concentrations of non-radical oxidants than of radicals in an urban aqueous environment.

The calculated first order conversion rate constants are plotted in Fig. 6 (logarithmic scale) over the investigated compounds for each of the four oxidants H₂O₂, O₃, OH \cdot and NO₃ \cdot . On the right y axis, the lifetime in days is plotted according to $\tau = 1/k_{2\text{nd}}[\text{X}]$.

Table 4. Oxidant concentrations for an urban cloud droplet calculated from CAPRAM3.0i at 20–44 h reaction time (Tilgner and Herrmann, 2010).

Oxidant X	$c(\text{X}) / \text{M}$
OH \cdot	1.0×10^{-14}
NO ₃ \cdot	2.0×10^{-13}
H ₂ O ₂	1.0×10^{-4}
O ₃	2.0×10^{-9}

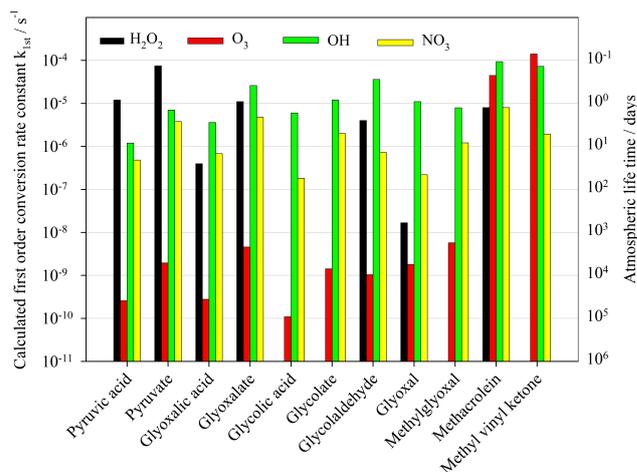


Fig. 6. Intercomparison of the calculated first-order conversion rate constants $k_{1\text{st}} [\text{s}^{-1}]$ from reactions with H₂O₂, O₃, OH \cdot and NO₃ \cdot , with the investigated carboxylic acids, aldehydes and unsaturated compounds for an urban cloud droplet.

If H₂O₂ first-order conversion rate constants are regarded, only pyruvic acid and pyruvate exceed those of the OH \cdot radicals. Glyoxalate, glycolaldehyde and glyoxylic acid can also be competitive with OH \cdot under certain circumstances. Compared with the night-time active nitrate radical, H₂O₂ first-order conversion rate constants show even more importance. From the conducted measurements, it can be pointed out that the $k_{1\text{st}}$ of glyoxalate and methacrolein with H₂O₂ are slightly higher compared to NO₃ \cdot . First-order conversion rate constants of pyruvic acid, pyruvate and glycolaldehyde with H₂O₂ exceed those of NO₃ \cdot even by one order of magnitude. However, ozone reactions only seem to be competitive with radical reaction first-order conversion rate constants if unsaturated compounds like methacrolein and methyl vinyl ketone are considered.

The aqueous phase concentrations given in Table 4 are taken from CAPRAM3.0i. They are maximum concentrations of one simulation day. The maxima do not occur simultaneously as the oxidants show different diurnal patterns. According to Calvert et al. (2000) and Monks (2005), the highest (gas phase) concentrations of OH \cdot exist at noon, whereas ozone and NO₃ \cdot dominate early in the afternoon and during the night, respectively. To accomplish a first comparison, no

specific time of day was chosen, but maximum concentrations of one entire day.

H₂O₂ is highly dependent on the sulphur oxidation capacity in an aqueous environment. Nevertheless, the present considerations are thought to provide a helpful tool to judge on the importance of non-radical reactions on the degradation of organics in the tropospheric aqueous phase.

4 Conclusions

Despite the small rate constants determined for the investigated reactions with non-radical oxidants the calculated first-order conversion rate constants indicate a potential importance of the studied non-radical reactions for the atmosphere. The reason lies in the much larger concentrations of hydrogen peroxide and ozone since these non-radical oxidants are tenfold more prevalent in the tropospheric aqueous phase than radicals like OH• and NO₃•. Therefore, radical reactions play only a minor role in the degradation of organic substances in cloud droplets and deliquescent particles under certain conditions. Considering non-radical reactions in pre-existing models like CAPRAM dealing to date mainly with the radical-driven reduction of organics (Tilgner and Herrmann, 2010) would change our understanding substantially. The mechanisms occurring during the reaction with non-radical oxidants lead to different products changing the budgets and regimes of these and corresponding compounds. Further investigations and model studies intend to improve the predictability of non-radical reaction rate constants and aim at a better assessment of such reactions in the overall degradation and conversion of organics in the tropospheric aqueous phase.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/4503/2014/acp-14-4503-2014-supplement.pdf>.

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