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Discussions

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

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Abstract

Within the aqueous atmospheric environment free radical reactions are an important degradation process for organic compounds. Nevertheless, non-radical oxidants like hydrogen peroxide and ozone also contribute to the degradation and conversion of this substance group (Tilgner und 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 of glyoxal, methylglyoxal, glycolaldehyde, glyoxylic, pyruvic and glycolic acids as well as methacrolein (MACR) and methyl vinyl ketone (MVK) towards H_2O_2 and ozone. The measurements indicate rather small rate constants at room temperature of $k_{2nd} < 3\,M^{-1}\,s^{-1}$ (except for the unsaturated compounds exposed to ozone). Compared to radical reaction rate constants the values are about 10 orders of magnitude smaller ($k_{OH\cdot} \sim 10^9\,M^{-1}\,s^{-1}$). However, when considering the much larger non-radical oxidant concentrations compared to radical concentrations in urban cloud droplets, calculated turnovers change the picture to more important H_2O_2 reactions especially when compared to the nitrate radical. For some reactions also mechanistic suggestions are given.

1 Introduction

The troposphere is a complex mixture of gases, liquid substances and particulate constituents (e.g. Herrmann et al., 2010). Some components are primarily emitted to the atmosphere; others get 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_1 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 OH· (at daytime), or NO_3· (especially at night) and other radicals for the aqueous systems. 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 show similar turnovers like OH· or NO_3·. At present, problems prevent the proper implementation of such processes into models as there are only few kinetic and mechanistic data available. Most values include thermodynamical calculations or estimates for the kinetic parameters.

The present work aims to improve the lack of kinetic (but also mechanistic) data for reactions of hydrogen peroxide and ozone with chosen 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 named species are products occurring during the oxidation of isoprene, one of the largest single sources of organic carbon (Guenther et al., 2006; Sharkey et al., 2008) in the troposphere. Especially glyoxal and methylglyoxal gained enormous importance in recent studies since it provides a large contribution to the formation of organic particulate matter (Lim et al., 2013, and references therein). Methods used for the mainly kinetic investigations are UV/Vis spectroscopy and capillary electrophoresis. At the end, a comparison to model studies debates the atmospheric relevance of the reactions studied.

2 Experimental

Most kinetic measurements were conducted according to the optical properties of the reacting substances. Therefore, specific absorption bands in the ultraviolet or visible region of the spectrum in the aqueous phase need to exist for one of the reactants.

2.1 Studies of ozone reactions

During most of the ozone investigations pseudo-first order kinetics were applied using a dual-beam UV/Vis spectrophotometer (LAMBDA 900, Perkin Elmer). As the reactants' concentrations were in excess over the ozone concentration (see Eq. 2), the depletion of ozone can be recorded with time by tracking its absorbance at $\lambda = 260\,\text{nm}$ ($\varepsilon = 3300\,\text{M}^{-1}\,\text{cm}^{-1}$, Hart et al., 1983). For faster reactions with unsaturated compounds like methacrolein and methyl vinyl ketone the Stopped Flow technique was used (SF-61DX2, HI-TECH Scientific, also UV/Vis). The advantage of this method is the immediate start of the absorbance recording in the moment of mixing. Here, also the concentration of ozone was monitored at $\lambda = 260\,\text{nm}$ during the reaction. 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 to calculate the second order rate constant $k_{2\text{nd}}$ ($\text{M}^{-1}\,\text{s}^{-1}$, Eq. 2).

$$\text{O}_3 + X \longrightarrow \text{products} \qquad \text{(R1)}$$

$$\frac{\text{d}c(\text{O}_3)}{\text{d}t} = -k_{2\text{nd}} \cdot c(\text{O}_3) \cdot c(X) \qquad (1)$$

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

$$\frac{\text{d}c(\text{O}_3)}{\text{d}t} = -k_{1\text{st}} \cdot c(\text{O}_3) \qquad (3)$$

2.2 Studies of H_2O_2 reactions

Some reactions with H_2O_2 were also investigated kinetically using UV/Vis spectroscopy where suitable UV/Vis spectra of the educts were available. Pyruvic acid/pyruvate and glyoxylic acid/glyoxylate were quantified by capillary electrophoresis (CE) after stopping the reaction by adding catalase to each sample. During CE measurements two buffer reservoirs are constantly filled with an electrolyte containing 2 mM 5-

sulfosalicylic acid, 8 mM tris(hydroxylmethyl)aminomethane and 0.001 % hexadimetrinbromide (HDB) at pH 8.2. The reservoirs are connected by a fused silica capillary (82 cm) with an inner diameter of 75 µm. A high voltage source is adjusted at −30 kV. Anionic compounds such as deprotonated organic acids move towards the cathode, the migration speed depending on their size and charge. The detection was performed indirectly at $\lambda = 208$ nm. Concentration-time-profiles of the corresponding acid can be obtained. The analysis occurs analogously to the ozone measurements. The CE also provides an indication of the products formed during the reaction.

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 (≥ 99 %, Fluka), glyoxal (40 % in water, Sigma-Aldrich), glyoxylic acid monohydrate (≥ 97 %, Fluka), hexadimethrinebromide (HDB, ≥ 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 deHaën), 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 (≥ 99.9 %, Sigma Aldrich), hydrogen peroxide (≥ 30 % in water, Fluka). All solutions were freshly prepared with MilliQ water (18 MΩ). 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 $OH\cdot$ scavenger. Especially considering aqueous solutions at non-acidic pH, hydroxide ions are formed by the reaction of water with the corresponding base. At basic pH, ozone will degrade to form hydroperoxyl radicals $HO_2\cdot$ or hydroperoxide anions HO_2^- (Reactions R2 and R3) as well as oxygen or superoxide, respectively. Since $HO_2\cdot$ is a quite reactive species it reduces ozone forming even more reactive OH· radicals (Reaction R4). These will destroy ozone leading again to $HO_2\cdot$ (Reaction R5). Taking OH off the system by addition of a scavenger (Reaction R6) means to prevent O_3 to be destroyed by the following cycle.

$$O_3 + OH^- \rightarrow O_2^- + HO_2\cdot \quad k = 210\,M^{-1}\,s^{-1} \quad \text{(Staehelin and Hoigné, 1982)} \tag{R2}$$
$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad k = 40\,M^{-1}\,s^{-1} \quad \text{(Sehested et al., 1991)} \tag{R3}$$
$$O_3 + HO_2\cdot \rightarrow 2O_2 + OH\cdot \quad k < 10^4\,M^{-1}\,s^{-1} \quad \text{(Sehested et al., 1984)} \tag{R4}$$
$$O_3 + OH\cdot \rightarrow O_2 + HO_2\cdot \quad k = 1.1 \times 10^8\,M^{-1}\,s^{-1} \quad \text{(Sehested et al., 1984)} \tag{R5}$$
$$OH\cdot + t-BuOH \rightarrow \text{products} \quad k = 6 \times 10^8\,M^{-1}\,s^{-1} \quad \text{(Buxton et al., 1988)} \tag{R6}$$

To avoid this decomposition, the pH of the aqueous solution can be adjusted to an acidic milieu (e.g. pH 2).

Hoigné and Bader tested several OH·radical scavenging substances like HCO_3^-, PrOH, BuOH, $NaHCO_3$ or methyl mercury hydroxide, respectively, but *t*-BuOH was found to be the most appropriate scavenger (Hoigné and Bader, 1983a, b, 1985). Variation of *t*-BuOH upwards the suggested concentration led to a significant 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*(glyoxylate) (right) plots for the reaction of glyoxylate with O_3 at pH 7 measured with the Perkin Elmer spectrometer. The pseudo-first order rate constant k_{1st} increases with increasing glyoxylate concentration, the slope corresponds to the second order rate constant $k_{2nd} = 2.30 \pm 0.60\,M^{-1}\,s^{-1}$.

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, white dots). The figure indicates a 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 don't give any proposal about the reaction pathway of glyoxylic acid and ozone. Scheme 1 illustrates one possible mechanism which is suggested here. In solution most of the aldehyde group in glyoxylic acid is hydrated ($K_{\mathrm{hydr}} = 1.09 \times 10^4\,\mathrm{M\,atm^{-1}}$, Ip et al., 2009). With ozone in the system, the most weakly bound H-atom at the carbon atom ($\mathrm{BDE} = 337.2\,\mathrm{kJ\,mol^{-1}}$, Dean and Lange, 1992) is abstracted leading to an OH· radical from the decomposition of HO_3, molecular oxygen and an alkyl radical (3). This step is identical with the one proposed by Caprio et al. (1987). Subsequent reaction with the released O_2 forms a peroxyl radical (4) which quickly decomposes to build oxalic acid (5) and an HO_2· radical. Caprio et al. (1987) 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).

The additional formation of OH· and HO_2· 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 $k_{\mathrm{2nd}} = (20 \pm 0.5)\,\mathrm{M^{-1}\,s^{-1}}$. Reasons for this discrepancy are the missing scavenger during their measurements and probably a different ratio of protonated and deprononated acid forms since no pH value is declared.

The reaction of glycolic acid with ozone also leads, analogously to the just proposed mechanism, to the formation of glyoxylic acid and $HO_2\cdot$. The rate constants measured here is $k_{2nd} = (5.50 \pm 1.52) \times 10^{-2}\,M^{-1}\,s^{-1}$.

For the interaction of pyruvic acid with ozone no mechanism is proposed so far in literature. The only suggestions include manganese as catalyst leading to acetic acid as well as O_2 and CO_2 (pH 2–4, Andreozzi et al., 1998). The rate constant measured in this work is $k_{2nd} = (0.13 \pm 0.03)\,M^{-1}\,s^{-1}$. Table 2 indicates a 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 neighbour 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 $k_{2nd} = (0.90 \pm 0.17)\,M^{-1}\,s^{-1}$. The other two aldehydes, methylglyoxal and glycolaldehyde, react with similar rate constants of $k_{2nd} = (2.89 \pm 0.72)\,M^{-1}\,s^{-1}$ and $k_{2nd} = (0.52 \pm 0.10)\,M^{-1}\,s^{-1}$, respectively. The reactivities of the deprotonated forms of the acids are also in the same range (see Table 2).

Since the given rate constants are first determinations (at least under these temperature conditions), 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).

After hydrogen abstraction at the weak C-H bond of the aldehyde group (3) and subsequent addition of oxygen forming a peroxyl radical (4), HO_2-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 O_2 over O_3 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 is known since the work of von Sonntag and Schuchmann (1991) that α-hydroxy-peroxyl radicals likely eliminate HO_2 rather than abstracting 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.

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 (also see Table 2). The second order rate constants determined in this study are $k_{2nd} = (2.25 \pm 0.53) \times 10^4\,M^{-1}\,s^{-1}$ for MACR and $k_{2nd} = (7.11 \pm 1.06) \times 10^4\,M^{-1}\,s^{-1}$ for MVK, respectively.

Pedersen and Sehested (2001) also studied both reactions (pH 2) and observed quite similar rate constants. These authors obtained values of $k_{2nd} = (2.4 \pm 0.1) \times 10^4\,M^{-1}\,s^{-1}$ and $k_{2nd} = (4.4 \pm 0.2) \times 10^4\,M^{-1}\,s^{-1}$ for the reaction with MACR and MVK, respectively. These values indicate a 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 also H_2O_2 and pyruvic acid are 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 H_2O_2-measurements

3.2.1 Monocarboxylic acids + H_2O_2

Reactions of pyruvic acid and glyoxylic acid (and their anions) with H_2O_2 were investigated using the capillary electrophoresis system. Hence, not only concentration-time profiles of the reacting acid were obtained but also the formation of anionic reaction products was observed.

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 s reaction time, one depleted molecule of pyruvate leads to one formed molecule of acetate. In the further course the turnover is no longer 100 %. A reason could be the volatility of acetic acid distorting a quantitative measurement of its concentration.

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 1). Concentrations of pyruvate and hydrogen peroxide as well as replicates undertaken exceed those from Stefan and Bolton (1999). Also the determined rate constant is 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 are 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 furthermore a phosphate buffer system to adjust the pH which could be an additional source of impurities leading to a higher rate constant. However, control experiments provided evidence that the puffer system used does not disturb the measurement.

The reactivity of glyoxylic acid and glyoxylate towards H_2O_2 is about one to two orders of magnitude smaller compared to pyruvic acid/pyruvate (see Table 2). The rate constants determined are $k_{2nd} = (4.0 \pm 0.9) \times 10^{-3}\,M^{-1}\,s^{-1}$ and $k_{2nd} = (0.11 \pm 0.01)\,M^{-1}\,s^{-1}$ 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 bad recovery rate of the anion in the CE. Furthermore, also the UV/Vis spectra of the two reactants do not permit to use the UV/Vis spectroscopy.

3.2.2 Aldehydes + H_2O_2

The reactivity of aldehydes towards hydrogen peroxide is very small. The rate constants obtained for glycolaldehyde and glyoxal are $k_{2nd} = (0.04 \pm 0.02)\,M^{-1}\,s^{-1}$ and $k_{2nd} = (1.67 \pm 0.80) \times 10^{-4}\,M^{-1}\,s^{-1}$, respectively. Patai and Zabicky (1970) state a rate constant for formaldehyde exposed to H_2O_2 of $k = 0.0014\,M^{-1}\,s^{-1}$ indicating slow reactions throughout.

Carlton et al. (2007) suggested the formation of two formic acid molecules in the reaction of glyoxal with H_2O_2. These authors propose a rate constant of $k_{2nd} = 1\,M^{-1}\,s^{-1}$ 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., 2012). The formation of such species was already proposed much earlier by Satterfield and Case (1956).

For the reaction between methylglyoxal and H_2O_2 no rate constant could be determined because of the inappropriate UV/Vis spectra of both reactants. Nevertheless, test measurements were undertaken which indicated an even slower reaction than with glyoxal.

3.2.3 Unsaturated compounds + H_2O_2

The rate constant for the reaction of methacrolein with H_2O_2 was determined to $k_{2nd} = (7.56 \pm 2.84) \times 10^{-2}\,M^{-1}\,s^{-1}$. Zhang et al. (2009) give an upper limit as an estimate of $k_{2nd} = 0.13\,M^{-1}\,s^{-1}$ which is about the factor 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 the named product during their measurements. Zhao et al. (2013) furthermore confirm the small reactivity of MACR towards H_2O_2.

Due to a missing appropriate wavelength the reaction of MVK with H_2O_2 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 $T = 298\,K$. 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 H_2O_2 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 $k_{\mathrm{OH\cdot}} \sim 10^9\,\mathrm{M^{-1}\,s^{-1}}$ and $k_{\mathrm{NO_3}} \sim 10^7$–$10^8\,\mathrm{M^{-1}\,s^{-1}}$, 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. But 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 reaction rates or turnovers are described by the product of rate constant and reactants' concentrations. Therefore, turnovers [$\mathrm{s^{-1}}$] are calculated according to Eq. (2) multiplying the second order rate constants [$\mathrm{M^{-1}\,s^{-1}}$] by the corresponding oxidant concentration $c(X)$ [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 e.g. with the radical-driven conversion of carbonyls to acids and further acid degradation in tropospheric aqueous systems (Tilgner and Herrmann, 2010). Table 3 summarises maximum concentrations of hydroxyl OH· and nitrate $NO_3\cdot$ radicals as well as H_2O_2 and ozone at 20–44 h reaction time occurring in a polluted (so-called "urban") cloud droplet. The comparison between c(OH·) and c(H_2O_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 turnovers are plotted in Fig. 6 (logarithmic scale) over the investigated compounds for each of the four oxidants OH·, $NO_3\cdot$, H_2O_2 and O_3.

If H_2O_2 turnovers are regarded only pyruvic acid and pyruvate exceeded those of the OH· radicals. Also glyoxylate, glycolaldehyde and glyoxylic acid can be competitive with OH· under certain circumstances. Comparing with the night-time active nitrate radical, H_2O_2 turnovers show even more importance. For the undertaken measurements glycolaldehyde, glyoxylic acid, glyoxylate, pyruvic acid and pyruvate reaction turnovers of H_2O_2 exceed those of $NO_3\cdot$ partly by far. However, ozone reactions only seem to be competitive with radical reaction turnovers if unsaturated compounds like methacrolein and methyl vinyl ketone are considered.

Since the chosen concentrations for the considerations made above are maximum values over a period of one entire day, differentiations have to be made regarding the daytime. According to Calvert et al. (2000) and Monks (2005), highest (gas phase) concentrations of OH· exist at noon whereas ozone and NO_3· dominate early in the afternoon and during the night, respectively.

H_2O_2 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 turnovers 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 prevalent in the tropospheric aqueous phase than radicals like OH· and NO_3·. Therefore, sometimes turnovers of radical reactions play only a minor role in the degradation of organic substances in cloud droplets and deliquescent particles. 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-discuss.net/13/25537/2013/acpd-13-25537-2013-supplement.pdf.

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Table 1. Comparison of this work's reaction conditions with Stefan and Bolton's (1999).

	This work		Stefan and Bolton (1999)
Method	Capillary electrophoresis		Ion exchange chromatography
pH	1	7	"mostly ionised"
c(pyruvate) / mM	5	0.4	0.25
$c(H_2O_2)$ / mM	50–150	8–24	5
$c(H_2O_2)$ / c(pyruvate)	10–30	30–60	20
No. of $c(H_2O_2)$	5	5	1
k_{2nd} / $M^{-1}\,s^{-1}$	0.12 ± 0.04	0.75 ± 0.16	0.11

Table 2. Second order rate constants for the investigated systems as well as the method used. CE = capillary electrophoresis, PE = Perkin Elmer, SF = Stopped Flow, the numbers indicate the wavelength in nm used during the spectrometer measurements.

	k_{2nd} / M^{-1} s^{-1}		Method	
Substance	H_2O_2	O_3	H_2O_2	O_3
Glyoxylic acid pH 1	$(3.96 \pm 0.91) \times 10^{-3}$	0.14 ± 0.06	CE	PE 260
Glyoxylic acid/Glyoxylate pH 3	–	0.53 ± 0.12	–	PE 260
Glyoxylate pH 7	0.11 ± 0.01	2.30 ± 0.60	CE	PE 260
Pyruvic acid pH 1	0.12 ± 0.04	0.13 ± 0.03	CE	PE 260
Pyruvate pH 7	0.75 ± 0.16	0.98 ± 0.35	CE	PE 260
Glycolic acid pH 1	–	$(5.50 \pm 1.52) \times 10^{-2}$	–	PE 260
Glycolate pH 7	–	0.71 ± 0.05	–	PE 260
Glycolaldehyde	0.04 ± 0.02	0.52 ± 0.10	PE 229	PE 260
Glyoxal	$(1.67 \pm 0.80) \times 10^{-4}$	0.90 ± 0.17	PE 233	PE 260
Methylglyoxal	–	2.89 ± 0.72	–	PE 260
Methacrolein	$(7.56 \pm 2.84) \times 10^{-2}$	$(2.25 \pm 0.53) \times 10^{4}$	SF 310	SF 260
Methyl vinyl ketone	–	$(7.11 \pm 1.06) \times 10^{4}$	–	SF 260

Table 3. Oxidant concentrations for an urban cloud droplet calculated from CAPRAM3.0i at 20–44 h reaction time (Tilgner and Herrmann, 2010).

Oxidant X	$c(X)$ / M
$OH\cdot$	1.0×10^{-14}
$NO_3\cdot$	2.0×10^{-13}
H_2O_2	1.0×10^{-4}
O_3	2.0×10^{-9}

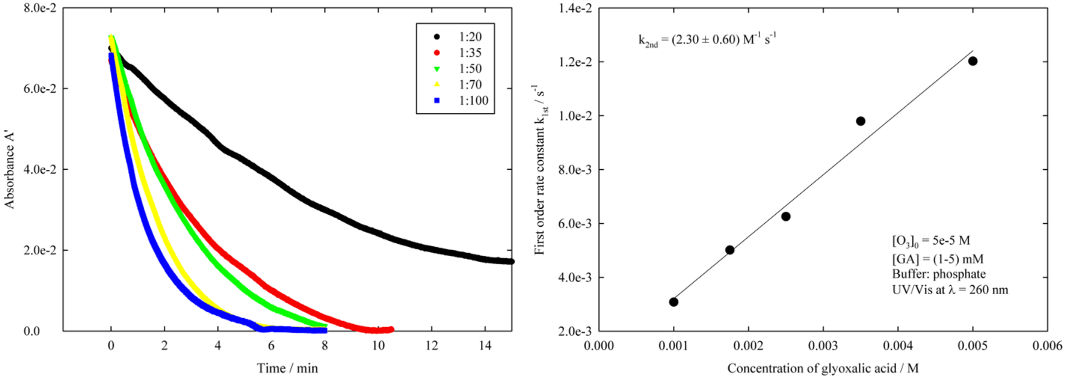


Fig. 1. Left: absorbance-time profiles of ozone during the reaction with glyoxylate at pH 7. The initial concentration of ozone was about $c(O_3) = 5 \times 10^{-5}$ M. Right: pseudo-first order rate constants k_{1st} plotted over the concentration of glyoxylate.

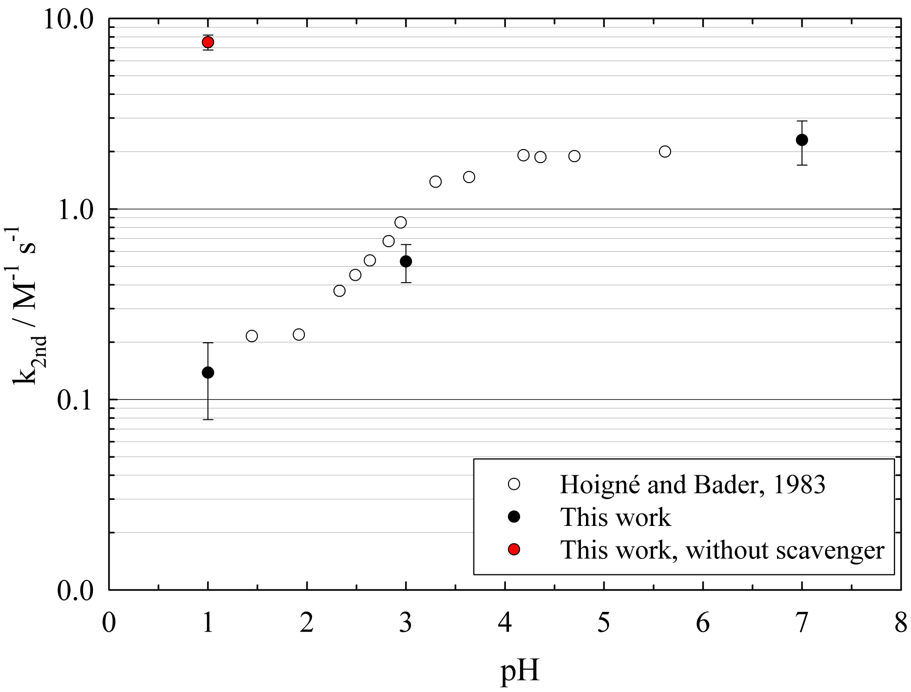


Fig. 2. Rate constants ($M^{-1}s^{-1}$) plotted as a function of pH value for the reaction of glyoxylic acid/glyoxylate with ozone. Hoigné and Bader (1983b, white dots); this work (black dots); no scavenger used in this work (red dot).

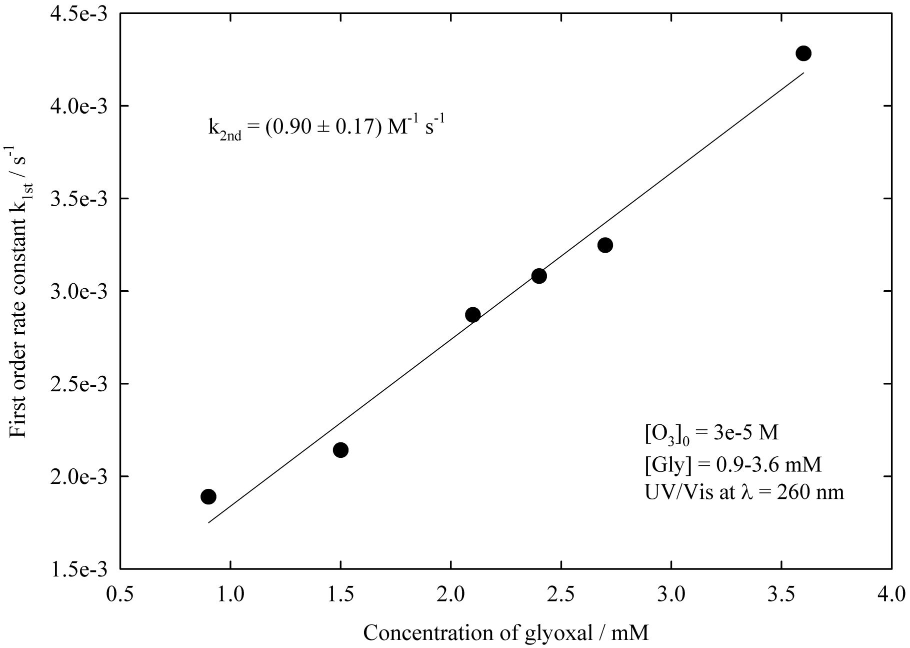


Fig. 3. Pseudo-first order rate constants k_{1st} plotted over the concentration of glyoxal during the reaction with ozone. The slope corresponds to $k_{2nd} = (0.90 \pm 0.17)\,M^{-1}\,s^{-1}$.

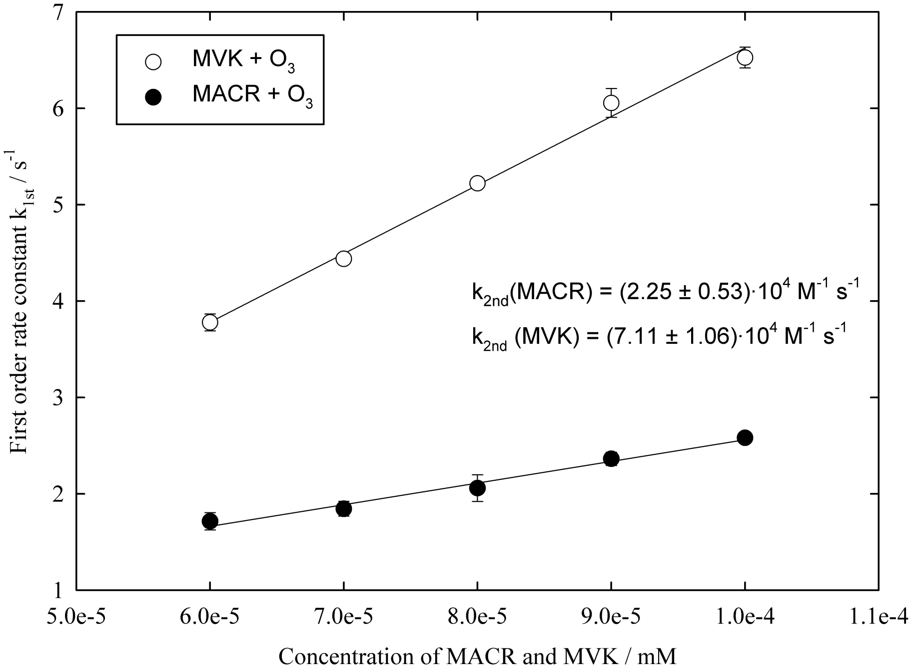


Fig. 4. Pseudo-first order rate constants k_{1st} plotted over the concentration of methacrolein and methyl vinyl ketone for the reaction with ozone.

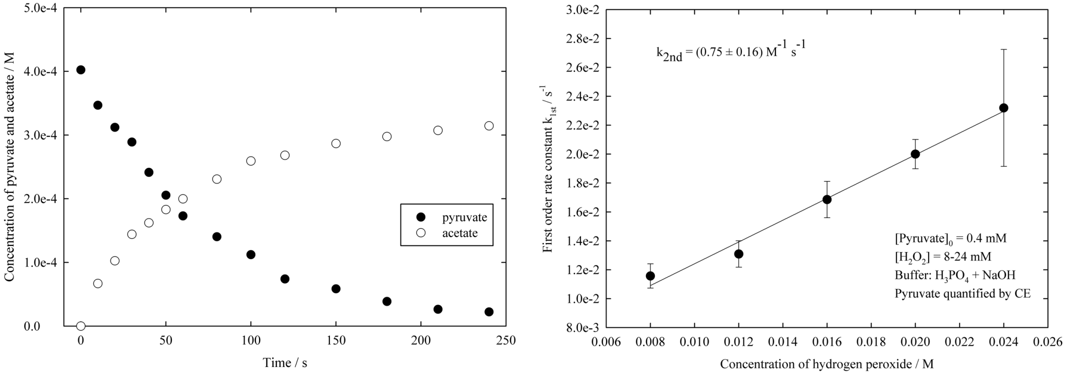


Fig. 5. Left: concentration-time profiles of pyruvate and acetate during the reaction with H_2O_2 at pH 7 for c(pyruvate) = 0.4 mM and $c(H_2O_2)$ = 12 mM. Right: pseudo-first order rate constants k_{1st} plotted over the concentration of hydrogen peroxide for the reaction with pyruvate at pH 7.

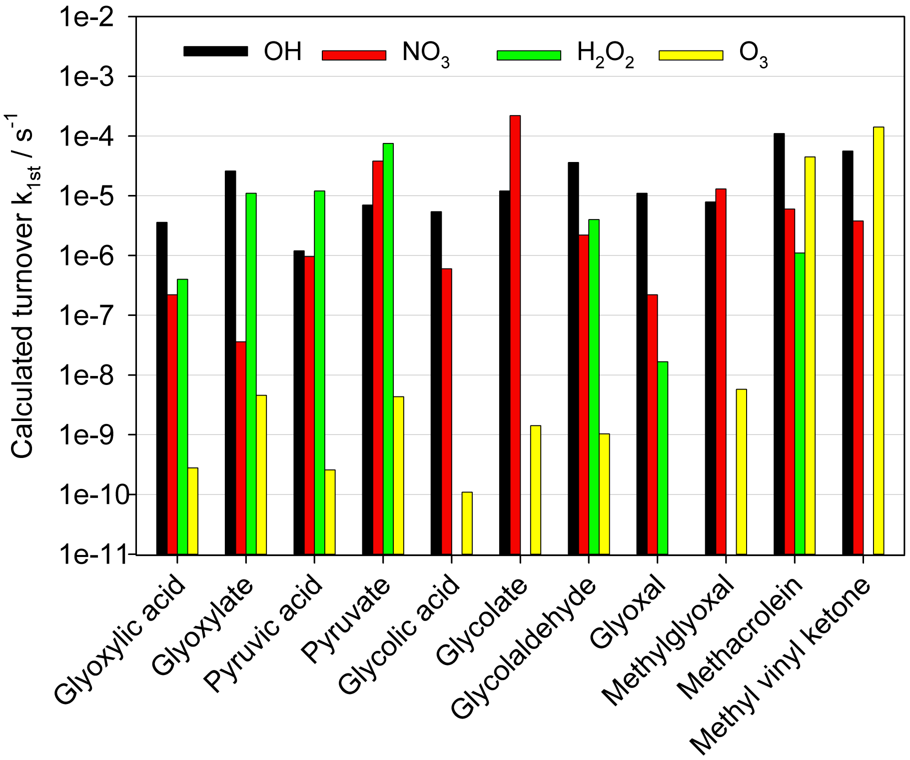
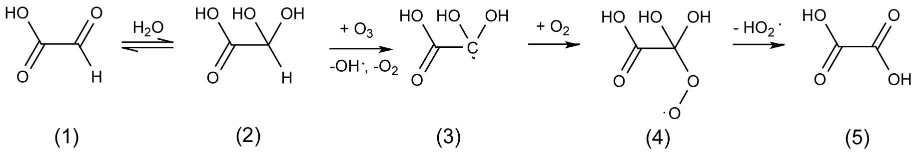
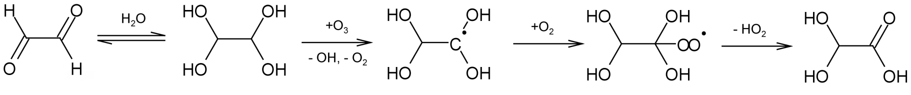


Fig. 6. Intercomparison of the calculated turnovers k_{1st} [s^{-1}] from reactions with OH·, NO_3·, H_2O_2 and O_3 with the investigated carboxylic acids, aldehydes and unsaturated compounds for an urban cloud droplet.

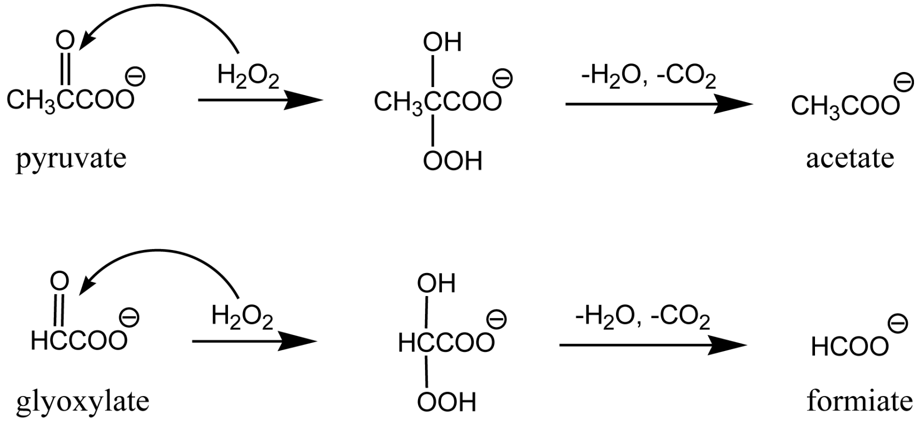


Scheme 1. Proposed oxidation mechanism of (hydrated) glyoxylic acid exposed to ozone in an aqueous environment.



(1) (2) (3) (4) (5)

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



Scheme 3. Reaction mechanism of pyruvate and glyoxylate + H_2O_2.