Answer to Reviewer 1 for “Kinetic measurements on the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solution”

by Luisa Schöne and Hartmut Herrmann

We thank the reviewers for the careful consideration and the constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the four reviewers are addressed as follows.

Referee#1 (C8529)

The paper presents the kinetic results for the reactions of H2O2 and O3, two main non-radical oxidants, with some selected small organic compounds in aqueous solution. Most of the studied compounds were found widely in the gas and aerosol phases, cloud and fog water. With the exception of methacrolein and methyl vinyl ketone, they are also well soluble in water. Thus, they are relevant for tropospheric multiphase systems. Although small rate constants for the reactions of organics (i.e. glyoxal, methylglyoxal, glycolaldehyde, glyoxylic acid, glycolic acid, pyruvic acid) with H2O2 and O3 (except for methacrolein and methyl vinyl ketone with O3) were determined, some of the calculated reaction rates (turnovers) taking into account the oxidant concentrations in urban cloud water seem to be competitive with radical (OH and NO3 radicals) reaction turnovers. The paper is of sufficient atmospheric interest to merit publication after revision; in “specific comments” some questions and/or comments are listed which should be considered. I also suggest to elaborate the experimental details and be more precise in the formulation to clarify the text.

Response:
The Henry coefficients of methacrolein and methyl vinyl ketone are $H_{MACR} = 6.5\ M\ atm^{-1}$ *and* $H_{MVK} = 41\ M\ atm^{-1}$*(Iraci et al., 1999), respectively. As the referee rightly mentioned these substances are less soluble in water than the other compounds investigated in the present study. Nevertheless, high concentrations of both compounds were detected in cloud water exceeding the concentration expected based on their Henry coefficients (van Pinxteren et al., 2005; Djikaev and Tabazadeh, 2003). Furthermore, their concentrations were found to be much higher than those of glycolaldehyde, glyoxylic acid, glycolic acid and pyruvic acid. Thus it can be concluded that they are of great atmospheric relevance.*

It would be relevant to give some numbers on concentration levels of studied organic compounds measured in atmospheric waters and aerosols. I agree that aqueous photooxidation of glyoxal and methylglyoxal has been examined most extensively and in general the reactions have been performed in a batch reactor with OH radicals generated by photolysis of H2O2. The photooxidation of the other above mentioned carbonyl compounds has been studied as well, but the kinetic data are very scarce. It would be good to give some references related to these studies.

Response:
We agree on the reviewers comment and thus several references were added. As a huge number of studies exist, the authors selected those which have the greatest impact on understanding the atmospheric photochemistry. Hence, the following papers were inserted: Carlton et al. (2007), Galloway et al. (2011), Zhao et al. (2012), Charbouillot et al. (2012), Guzman et al. (2006), Carlton et al. (2006), Beeby et al. (1987), Perri et al. (2009) and Liu et al. (2009, 2012).

The authors should describe in more details their experiments, e.g. the initial concentrations of organic compounds, oxidants, pH, temperature, volume of solution, amount of catalase, addition of t-BuOH as radical scavenger for OH radicals, etc. It is true that the information can be found in "results, figures or supplement", but it is more transparent if all important information on experiments can be found in the experimental part. For example, the temperature can be found for first time on page 12 (in section 3.3).

Response:
The manuscript was changed accordingly and a complete overview about the adjusted experimental parameters is now given in the manuscript for each experiment (Table 1).

How efficient is catalase as a reaction quencher? Did you check this?

Response:
According to the manufacturer's information one unit of the enzyme quenches two molecules of H_2O_2 in a two-step reaction. Furthermore, catalase was added in great excess to ensure a complete destruction of H_2O_2. A control experiment was conducted to proof this assumption. The usually used amount of catalase was added to the largest concentration of H_2O_2 used within the present study. Pyruvic and glyoxylic acid were added and the concentration of both acids were quantified by CE continuously over one week. No change of the acid concentration was observed, thus it was concluded that the added amount of catalase is sufficient to quench H_2O_2. This information is included in the experimental section.

How relevant are the initial concentrations of the studied organic compounds in aqueous solutions for real atmospheric liquid water?

Response:
The initial concentrations used during the laboratory work are mostly higher than those usually observed in the atmospheric liquid phase. The comparably high concentrations were necessary due to laboratory restrictions. Low initial concentrations will cause small first order conversion rate constants [k_{1st} / s^{-1}]. The detection of such small k_{1st} is challenging. To overcome this issue the reaction has to be conducted on large time scales which might lead to unwanted side reactions. Thus, to obtain rate constants the initial concentration was adjusted in a way to enable the detection of the first order conversion rate constants. The so

determined rate constants can be used to recalculate first order conversion rate constants for specific ambient conditions (i.e. the atmosphere).

3.1.1. Fig. 1: Please give a more detailed explanation of figure (experimental conditions given inside the “right” figure can be moved to the text) and also correct the graph in such a way that it can be seen that the plot goes through the origin. It is also better to mark the figures as A and B (not left, right). In the left figure it is not clear what the insert means. It is better to use the same units for the concentrations in all figures: in Fig.1 the concentration is given in M; in Fig. 3 in mM and in Fig. 4 it is as 5.0 10-5 mM; obviously, this one is wrong.

Response:
The manuscript was changed accordingly.

In Fig. 2 the pH dependence on the rate constant is shown. It is pointed out (page 7) that in the absence of a OH radical scavenger a much higher rate constant was found. But is this statement true since this was at pH 1? On page 6, it is explained that at higher pH values O3 can be destroyed in the presence of the OH- anion (R2) and through reactions R3 and R4 the OH radical is formed. So, is it reasonable that at pH 1 the higher rate constant is due to OH radicals?

Response:
The decomposition of ozone due to OH^- *anions leads to the formation of* HO_2 *radicals which react subsequently with* O_3 *yielding OH radicals (R4). We agree that low pH values* HO_2 *formation is suppressed but not fully prevented. Therefore, the formation of OH radicals cannot be excluded even if low pH values are used.*
Furthermore, as can be seen from Scheme 1, the reaction of ozone with glyoxylic acid also yields HO_2 *radicals which further react via R4 leading to OH radical formation. Therefore, the reaction of ozone with organic compounds has to be considered as source for OH radicals. This additional source might cause the much higher rate constant observed in the absence of an OH radical scavenger.*

Scheme 1: If oxalic acid is the main product (according to the proposed mechanism) it can be easily followed by ion chromatography.

Response:
The overall goal of the present study was to determine the rate constants of the non-radical reactions of atmospheric relevant compounds. Within the present study the formed products were quantified by CE but no further product characterisation using IC was conducted.

3.1.2 Page 8, line 20: At which temperature?

Response:
It is T = 298 K throughout the whole work. This information was added to the manuscript.

Fig. 3: Similar comment as for Fig. 1; please add also at which pH the rate constant was determined. It looks that the plot does not go through the origin (from Fig. 3: the intercept k1st is ca. 1x10-3 s-1). Why?

Response:
Figures, captions as well as textual description of the figures have been harmonised and expanded.
The intercept must not necessarily be zero as side reactions of the reactants with water, substances which change pH, and the OH radical scavengers occur as well. These reactions are expected (and partly kinetically investigated) to be slow and thus the intercept (k_{1st}) is not very significant but unequal zero. Such reactions occur equally for all experiments and are therefore a kind of offset that does not change the second order rate constant.

3.1.3 Fig. 4: Please give more information concerning the experimental conditions (concentration of O3, temperature, pH); the concentration and kst should start from 0. It would be good to correct all the kst vs. concentration figures (also in the supplement).

Response:
All figures have been unified to start at the origin and the reaction conditions were added to each figure.

3.2.1 p.10: Pyruvate + H2O2 (Fig. 5): The reason for a lower turnover of acetate could be in the formation of other product(s) which you probably cannot detect with capillary electrophoresis. I think that you could not lose acetate (due to its volatility) when present in aqueous solution at room temperature.

Response:
We also take the formation of other products into account (that cannot be seen by CE) during the reaction as a further explanation of the lower turnover of acetate and agree to the reviewer about acetate not evaporating. We have changed this discussion accordingly.

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