Answer to Reviewer 4 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 #4 (C9581)

General comments:
This manuscript reports the laboratory kinetic measurements of the reactivity of nonradical oxidants (ozone and hydrogen peroxide) towards a few atmospherically relevant organic species (i.e., mainly the gaseous isoprene oxidation products) in aqueous solution. Since most of the previous studies focused on the radical oxidation mechanisms, this study extends our current understanding of aqueous oxidation chemistry. On the basis of their observed kinetic data and modeling results, the authors conclude that the atmospheric significance of the non-radical oxidation pathway especially those with H2O2 are comparable to the radical oxidation (e.g. OH and NO3 radicals) pathways. This work also attempts to provide mechanistic information of non-radical oxidation pathway but their arguments are rather weak because of the incomplete product characterizations. The experimental section should be polished to meet the publication standard. Overall, this manuscript fits well in the context of Atmospheric Chemistry and Physics and can be published after addressing the following comments.

Specific comments:

1. Section 2.1, Page 25540: The authors should provide more details about their ozone experiments in this section. First, what are the range of reactant concentrations (ozone, H2O2 and organics) and the reaction temperature used in this study? Are those atmospherically relevant (e.g. aerosol or cloud conditions)? Second, the approach that used to prepare the aqueous mixtures of ozone and organics in both standard UV/Vis method and stopped flow techniques should be described in the text. Third, the wavelength at 260 nm was used to monitor the ozone decay but carbonyl compounds always give a strong absorption band at 260-300 nm. What are the potential interferences from those organic species in the experiments? Lastly, did the authors conduct any control experiments (e.g. ozone decay at different values of pH in the absence of organics)? This kind of control is particularly important to interpret their results because the observed second order rate constants between organics and ozone are very small.

Response:
We agree to the referee and included a complete overview about all adjusted experimental parameter (Table 1).
First: The temperature was T = 298 K throughout the whole work. When not stated in the manuscript, the concentrations can be found for each reaction system in Table 1. Furthermore, the used concentrations are included now to the figure captions.
The question about the initial concentrations was also raised by Referee 1 (C8529) in the fifth comment. Thus, this question was discussed in detail at this point. For more information please see the answer to question 5 of Referee 1.
Second: Ozone was produced by an ozone generator (500 M, Fischer, Germany) where pure O_2 *passes a UV-lamp to split* O_2 *and build up* O_3*. Ozone "stock solutions" were prepared as follows: The ozone-enriched gas flow was bubbled through an aqueous solution with adjusted pH (see Table 1 and 2). This proceeding was repeated prior to each experiment as ozone decomposes in aqueous solution (see R2 to R5) and thus it cannot be stored. The ozone concentration in the "stock solution" was determined spectroscopically at 260 nm using the extinction coefficient reported by Hart et al. (1983, see page 25540 line 6,* $\varepsilon = 3300\ M^{-1}\ cm^{-1}$*). The prepared stock solution was then diluted to the required concentration. The time between the end of bubbling and the start of the measurement was about one minute.*
Third: We agree to the reviewer that the reactants also absorb at 260 nm. Since pseudo-first order conditions were applied, the concentration of the reactants are in excess and should therefore be constant during the reaction. For the calculation of the rate constants, the spectral contribution of the reactants was subtracted from the measured signal to obtain "pure" ozone signals.
Last: Control experiments were conducted examining the ozone decays within an aqueous solution at different pH. Furthermore, throughout the experiments with the dual-beam spectrometer, the decay of the ozone concentration was recorded simultaneously and subtracted in order to obtain the ozone decay solely resulting from the reaction with the organic compound.

2. Section 2.2: (Page 25540, line 22): Please specify the wavelength used for different reaction system and briefly describe the potential interferences from the products. (Page 25541, line 5-6): What type of detection technique (UV/Vis absorption?) used in the CE instrument? How specific of the selected wavelength (208 nm) to the products and reactants? The meaning of this sentence is not clear to the reviewer. Why the detection "performed indirectly"?

Response:
The wavelengths chosen for the measurements are given in Table 1 and 2. For further details, we added the spectra of all reactants and oxidants to the Supplement (Figure A15 and Figure A16).
As described by Scheinhardt et al. (2013), indirect UV detection was used with a measurement wavelength of 260 nm and a reference wavelength of 208 nm. The applied method was an indirect method, because instead of the absorbance of the investigated anions (i.e. small organic mono- and dicarboxylic acids as well as inorganic ions) the absorbance of the electrolyte was recorded. Sulfosalicylic acid was used as electrolyte that absorbs strongly

at 208 nm and less at 260 nm. In the presence of an analyte, the absorbance of the electrolyte decreases because the non-absorbing analyte replaces the absorbing electrolyte. This decrease results in a negative peak which can be used to quantify the concentration of the analyte after calibration. This explanation was added to the ESM.

3. Page 25544, line 7-11: As the authors mentioned in the manuscript, ozone can degrade via Reactions R2 and R3 more efficiently at higher pH. Would it be another possibility to explain the observed pH dependence of rate constant of organic acids (i.e., faster kinetics at higher pH)?

Response:
As already mentioned, the decay of ozone was recorded simultaneously in the reference cuvette of the dual-beam spectrometer and subtracted from the overall signal to obtain the decay of ozone solely by the reactant. Therefore, the faster rate constants observed at higher pH values indeed result from faster non-radical reactions. Furthermore, organic acid anions react faster than the corresponding acid as a result of slightly differing electron densities that occur due to electron-withdrawing properties of the deprotonated group.

4. Page 25544, line 13-18: What were the pH values of those aldehyde solutions? The reviewer would expect the glyoxal and methylglyoxal solutions in mM level were slightly acidic, and this may play a role in affecting the ozone decay during the measurements.

Response:
We agree to the reviewer that the solutions were slightly acidic at about pH 5. As already described, the ozone decay was subtracted during every single measurement.

5. Page 25546, line 15-18: The authors assume all pyruvate/pyruvic acid converted to acetic acid but it may not be the case. Did the authors observe other products from this reaction system?

Response:
The formation of other products than acetic acid cannot be excluded. Nevertheless, no other products were observed during the CE measurements. Other analytical technique would be useful to detect possible side products occurring during these reactions.

6. After reading through Section 3.2, the reviewer confuses with the way to determine the second order reaction constants of the reaction between H2O2 and organics in this study. It seems that the authors used different approaches to determine the rate constants of organic acids (CE with H2O2 in excess) and aldehydes (UV/Vis with organics in excess). Please clarify carefully in the text.

Response:
The reviewer understand this correctly. In the present study, 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 + H_2O_2 *(because the acids and methacrolein were recorded), whereas the reactions of* H_2O_2 *with glycolaldehyde and glyoxal were conducted under aldehyde excess (where* H_2O_2 *was recorded). The necessary information is now added to the manuscript (Table 1).*

7. Scheme 1 and 2: Did the authors conduct any product identification in the ozone reaction studies (e.g., oxalic acid detection)? Without this information to support the arguments, the reviewer suggests to remove the proposed schemes in the manuscript.

Response:
We did not conduct any other product studies and can therefore not support the suggested mechanisms with own experimental data. Nevertheless, oxalic acid was been found to be the main reaction product of glyoxylic + ozone by Caprio et al. (1987) who analysed oxalic acid by means of a $KMnO_4$ *solution after being separated as calcium oxalate (uncertainty of <5 %). Furthermore, oxalic acid was reported as main oxidation product by Holen et al. (1998). Since all suggested mechanisms are tentatively and should be deemed as such, we suggest to not remove the schemes from the manuscript.*

8. The reviewer does not familiar with the details of CAPRAM and cannot find out the details of version 3.0i in the CAPRAM website. Dose the model include the photolysis of H2O2 in aqueous phase? This reaction can be a significant source of OH radicals in aerosol liquid water, and can reduce the concentration of aqueous H2O2. Please provide more information about this. Also, if aldehydes react with H2O2, it is possible to form a substantial amount of α-hydroxyhydroperoxides (α-HHP) as described in this manuscript. Further photolysis of α-HHP can be an additional source of OH radical.
Can the authors comment on the effects of these reactions?

Response:
In CAPRAM also photolysis processes (e.g. that of H_2O_2*) are included (http://projects.tropos.de/capram/capram30i.txt, line 271). We agree to the reviewer that this reaction is an important source for OH radicals that would surely reduce the concentration of* H_2O_2*. The concentrations taken from the model are well accepted (e.g. Tilgner et al., 2010, Herrmann et al., 2010) and were therefore judged to be appropriate for the comparison in section 3.3.*
We agree to the reviewer, that the formation of α-HHPs during the reaction of aldehydes with H_2O_2 *and subsequent photolysis may be a non-negligible source of OH radicals. However, such reactions are not yet included in CAPRAM since the model deals up to now only with radical reactions. The results from Figure 6 in section 3.3 are therefore a crude first comparison to radical reactions. A detailed modelling of the aqueous phase chemistry with CAPRAM including non-radical reactions (i.e. with α-HHPs) is still in development and thus this information is not yet available at this moment.*

Minor comments:

1. Abstract, Page 25538, line 5: The meaning of “substance group” is not clear. Does it means “organic compounds”?

Response:
“Substance group” is a hypernym for the organic compounds that were mentioned in the sentence before. To avoid confusion the phrase was changed to “these substances”.

2. Page 25541, line 20: Please correct “18 MΩ” to “18 MΩ cm”

Response:
The manuscript was changed accordingly.

3. Figure 1: The meaning of ratios shown in the legend is not clearly described.

Response:
The ratios shown in Figure 1 represent the concentration of glyoxylic acid and H_2O_2*. We changed the legend to glyoxylic acid concentrations to avoid confusion.*

4. All the rate constants are already presented in Table 2. The reviewer recommends to move Figure 3 and 4 to the supplementary information.

Response:
Figure 3 and 4 show original data and give hints to their quality. Furthermore, the figures provide k_{1st} *values that are not shown in Table 2 and we therefore suggest to keep them in the manuscript.*

5. The sequence of Table 1 and 2 should follow the main text.

Response:
We agree to the referee’s comment that the sequence should correspond to the order of appearance in the text. The manuscript was changed accordingly.

6. Page 25547, line 5: Please change “puffer” to “buffer”.

Response:
The manuscript was changed accordingly.

References

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