Atmos. Chem. Phys. Discuss., 13, C9581–C9584, 2013
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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Kinetic measurements on the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solution" *by* L. Schöne and H. Herrmann

**Anonymous Referee #4**

Received and published: 9 December 2013

General comments:

This manuscript reports the laboratory kinetic measurements of the reactivity of non-radical 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.

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”?

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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)?

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.

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?

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.

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.

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 $\alpha$-hydroxyhydroperoxides ($\alpha$-HHP) as described in this manuscript. Further photolysis of $\alpha$-HHP can be an additional source of OH radical. Can the authors comment on the effects of these reactions?

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Minor comments:

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

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

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

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

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

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

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25537, 2013.