

## ***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 #3**

Received and published: 9 December 2013

In this manuscript, L. Schöne and H. Herrmann present the results of experiments designed to measure rate constants of aqueous oxidation reactions for several relevant organic compounds. The authors use UV-vis spectroscopy, Stopped Flow techniques, and capillary electrophoresis to determine rate constants arising from the reaction between hydrogen peroxide or ozone and several water-soluble organic compounds typically found in cloud and fog droplets. Measurements were performed at various pH values. In general, they find rate constants that are consistent with published work. For the most part, these rate constants are much smaller than those of radical reactions.

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However, because concentrations of hydrogen peroxide and ozone typically exceed radical concentrations in cloud and fog droplets, their presence may have a larger effect on the depletion of these water-soluble compounds. The paper is comprehensive and presents rate constant measurements for many atmospherically relevant reactions. The paper is well-suited for publication subject to the following revisions.

#### Specific Comments:

The manuscript will greatly benefit from a careful editing of the grammar. There are a few places where the English is ambiguous and it is difficult to distinguish what the authors are trying to convey. I have identified these specific sentences in the technical corrections below.

Ozone depletion was measured with a UV-Vis at 260 nm. Many of the compounds that were studied also absorb in that range, albeit with much weaker absorption cross sections. How does this contribute to the uncertainty in the rate constant calculations? How did you treat the interference between hydrogen peroxide and the reactants in the experiments involving UV-vis measurements (H<sub>2</sub>O<sub>2</sub> + glycolaldehyde, H<sub>2</sub>O<sub>2</sub> + glyoxal, H<sub>2</sub>O<sub>2</sub> + methacrolein)? In each of these cases, the reactant and H<sub>2</sub>O<sub>2</sub> have absorption cross sections of similar magnitudes.

The experimental section is lacking a few details about the experimental setup that would be necessary for another investigator to reproduce your work.

What are the major sources of uncertainty that lead to the error-bars in the figures?

In Figure 5, the authors state that depletion of one pyruvate molecule leads to the formation of one acetate molecule in the initial stages of the experiment. During the later stages, there is less acetate than expected. The authors theorize that this is due to evaporation of acetic acid. Can you produce more evidence to back up this claim? It would seem that the increase in the evaporation rate of acetic acid as its concentration increases would be represented by a decreasing concentration of acetate after the

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reaction has come close to completion ( $> 200$  s). Is it possible that an undetected product is formed?

Line 10, Page 25545: What is the missing analytical data? Be more specific.

Line 18, Page 25547 and Line 6, Page 25548: Be more specific. What about the UV/Vis spectra of the reactants prevents use of a UV/Vis spectrometer?

It may be more helpful to the reader to compare atmospheric lifetimes (more intuitive) instead of turnovers in Figure 6.

Technical Corrections:

Figure 1 left: It is not clear what the ratios shown in the legend represent.

Table 2:  $K_{1st}$  for  $H_2O_2$  + Glyoxylic acid pH1 has a different number of significant figures than in the text on line 8, page 25547

Line 5, Page 25547: "puffer" should be "buffer"

Line 26-28, Page 25549: This sentence is unclear

Line 3-5, Page 25550: This sentence is unclear

Table A1:  $K_{1st}$  for  $H_2O_2$  + methacrolein have commas instead of periods.

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