

# **Answer to Reviewer 3 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 #3 (C9353)**

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.

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.

### *Response:*

*The authors agree on the referee comment. The revised manuscript has undergone language editing.*

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.

*Response:*

*We agree to the reviewer that the reactants also absorb at 260 nm. Thus, UV/Vis measurements were conducted for each single reactant. For the calculation of the rate constants, the spectral contribution of the reactants was subtracted from the measured signal to obtain the signal that corresponds almost solely to ozone or H<sub>2</sub>O<sub>2</sub> reduction. Furthermore, pseudo-first order conditions were applied where the reactant is in excess towards the oxidant. Thus, concentration and absorbance of the reactant change to a much lesser extent than the oxidant concentration and absorbance during the reaction and can therefore be neglected. We chose the wavelength where reactant and oxidant spectra differ most. For illustration, we added two pictures with the corresponding spectral data to the Supplement (Figure A15 and A16). To improve the experimental section in the manuscript an overview is included about the adjusted experimental parameters (Table 1).*

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

*Response:*

*The error bars in the figures correspond to the error of regression calculated by the least-squares method (error = 1 $\sigma$ ). Depending on the number of data points and their correlation the uncertainties vary. Especially for Stopped Flow measurements, a large number of data points (several hundreds) were taken which leads to comparably small error bars. Furthermore, at the Stopped Flow as a single-beam spectrometer, lamp variations cannot be excluded. For experiments with capillary electrophoresis, the number of data points is small (5-10 data points) and thus the scattering is much more pronounced. Finally, sample handling during CE measurements is more prone to errors since samples are taken at small time steps (down to 10 s), treated by catalase, two times diluted and only then quantified by CE.*

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

*Response:*

*The quantification of acetate by capillary electrophoresis has always been fraught with problems due to its ubiquity in the air of the laboratory. Acetate is soluble in water ( $k_H = 5000 \text{ M atm}^{-1}$ , Ip et al., 2009) and gets enriched in solution. We agree that the evaporation of acetic acid was a too speculative explanation for the observed discrepancy between pyruvic and acetic acid concentration. As no product characterisation was*

*conducted, the formation of oxidation products other than acetic acid cannot be excluded. This is also suggested by referee 1 (C8529). The manuscript was changed accordingly.*

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

*Response:*

*The focus of this study was on the kinetic investigation of non-radical reactions. Suggestions of possibly formed products given here mostly rely on literature data or hints from CE measurements. To give a clear and precise product distribution the application of further analytical techniques like HPLC-MS, IC or GC-MS would be necessary. The manuscript was changed accordingly.*

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?

*Response:*

*The UV/Vis spectra of the reactants methylglyoxal, methyl vinyl ketone and H<sub>2</sub>O<sub>2</sub> are too similar to extract a wavelength where they differ by at least one order of magnitude. For these two systems the method of UV/Vis is indeed unsuitable and no rate constants can be given. This issue was added to the manuscript.*

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

*Response:*

*Lifetimes for second order reactions correspond to the reciprocal of the here calculated first order conversion rate constant ( $\tau = 1/k_{2nd}[X]$ ). The values were added to the right y-axis in Figure 6, denoted in days.*

Technical Corrections:

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

*Response:*

*The ratios shown in Figure 1 represent the concentration of glyoxylic acid towards H<sub>2</sub>O<sub>2</sub>. We changed the legend to glyoxylic acid concentrations to avoid confusion.*

Table 2: K1st for H<sub>2</sub>O<sub>2</sub> + Glyoxylic acid pH1 has a different number of significant figures than in the text on line 8, page 25547

*Response:*

*We agree to harmonise this and changed the manuscript accordingly.*

Line 5, Page 25547: “puffer” should be “buffer”

*Response:*

*The manuscript was changed accordingly.*

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

*Response:*

*In Figure 6, the rate constants are shown for different reactants exposed to the oxidants OH radical, NO<sub>3</sub> radical, H<sub>2</sub>O<sub>2</sub> and ozone. Thus, a comparison can be drawn between the four oxidants to which extent they contribute to the degradation of the reactants. From the comparison it pointed out that higher first order conversion rate constants were reached with H<sub>2</sub>O<sub>2</sub> compared to NO<sub>3</sub> radicals. At night time, no photolysis of H<sub>2</sub>O<sub>2</sub> occurs, so the NO<sub>3</sub> radical is the most important radical and the non-radical reaction with H<sub>2</sub>O<sub>2</sub> seems to be able to compete with the decay of organics initialised by the attack of nitrate radicals. The manuscript was changed accordingly to clarify this issue.*

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

*Response:*

*The aqueous phase concentrations given in Table 4 are taken from CAPRAM3.0i. They are maximum concentrations of one simulation day. The maxima do not occur simultaneously as the oxidants show different diurnal patterns. To accomplish this first comparison, not one specific time of day was chosen but maximum concentrations of one entire day. The issue was clarified in the manuscript.*

Table A1: K1st for H<sub>2</sub>O<sub>2</sub> + methacrolein have commas instead of periods.

*Response:*

*The manuscript was changed accordingly.*

## *Reference*

Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, *Geophysical Research Letters*, 36, L01802, 2009.