

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 #1

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General comments

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,

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methylglyoxal, glycolaldehyde, glyoxilic 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.

Specific comments

Introduction:

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.

Experimental:

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).

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

How relevant are the initial concentrations of the studied organic compounds in aque-

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ous solutions for real atmospheric liquid water?

Results:

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 $5.0 \cdot 10^{-5}$ mM; obviously, this one is wrong.

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?

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

3.1.2 Page 8, line 20: At which temperature?

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 k_{1st} is ca. $1 \cdot 10^{-3}$ s⁻¹). Why?

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

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

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capillary electrophoresis. I think that you could not lose acetate (due to its volatility) when present in aqueous solution at room temperature.

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

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