Answer to Reviewer 2 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#2 (C9299)

Understanding multiphase processes in the troposphere is clearly key to a thorough understanding of the fate of organic matter. This manuscript addresses part of this problem through a series of kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes i.e., ketones and organic acids in aqueous solution. The scientific motivation is sound as non-radical oxidants like hydrogen peroxide and ozone may contribute to the degradation and conversion of this kind of compounds.
The experiments were performed using UV/Vis spectroscopy (dual-beam spectrophotometer and Stopped Flow technique) and a capillary electrophoresis system applying pseudo-first order kinetics of glyoxal, methylglyoxal, glycolaldehyde, glyoxylic, pyruvic and glycolic acids as well as methacrolein (MACR) and methyl vinyl ketone (MVK) towards H2O2 and ozone.
Despite the fact that the measurements indicate rather small rate constants, this chemistry is discussed to play a significant role as H2O2 and ozone may be abundant. Overall I do find this paper very interesting and recommend its publication after some changes to strengthen its content. The experimental section starts with underlying the need for spectroscopic information about at least for one reactant. But the manuscript does give any spectroscopic information. Maybe it would be useful to add.

Response:
The referee rightly mentioned that the spectroscopy data is essential for this work. Therefore, it is necessary to give at least some spectral information about the reactants and oxidants. Hence, the missing information is now included in the Supplement (Figure A15 and Figure A16). The chosen wavelength and extinction coefficients are listed in Table 1 and 2.

Also, there is no indication on how the ozone solutions were prepared and stored. This could be important as some ozone generators do produce NOx and once transferred into an aqueous solution this may alter its ionic strength and therefore the measured kinetics. Therefore, adding some practical information here would be useful to the reader.

Response:

Ozone was produced using 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 by introducing this ozone-enriched gas flow to an aqueous solution with adjusted pH value. Ozone "stock solutions" were prepared freshly prior to each experiment as it decomposes in aqueous solution (see R2 to R5). The ozone concentration in the "stock solution" was determined spectroscopically at 260 nm using the extinction coefficient by Hart et al. (1983, see page 25540 line 6,* $\varepsilon = 3300\ M^{-1}\ cm^{-1}$*). Subsequently, the stock solution was diluted to the requested concentration. The time between the end of bubbling and the start of the measurement was about one minute. It cannot be excluded that the ozone generator does produce* NO_x*.*

The procedure of the ozone preparation was added to the manuscript.

Also, I did miss some information about the mixing times in both approaches (dualbeam spectrophotometer and Stopped Flow technique). Please add this information just to make sure that the mixing times was indeed very short compared to the observed lifetimes. This may be also important in assessing the linearity of the observed decays.

Response:

The mixing time of the Stopped Flow technique is about 1 ms. Since the measurement of an ozone reaction with an unsaturated compound lasted minimum 1 s, only the first data point (t = 1.48 ms) was discarded a priori. There was no deviation in linearity observed at the beginning of recording.

Measurements with the dual-beam spectrometer lasted minimum 5 min to several hours with a mixing times of about 5 s. However, also here, no deviation from linearity due to mixing were observed.

The information was added to the manuscript in the experimental section.

Concerning the H2O2 measurements, how was the catalase acting? How fast was its reaction? Did this introduce some uncertainties in the reported reaction advancement times?

Response:

According to the product information catalase acts as catalyst in the following two-step reaction: $2\,H_2O_2 \rightarrow O_2 + 2\,H_2O$ *(Ogura, 1955). In the first step,* H_2O_2 *is reduced und the enzyme is oxidised yielding water as product. In the second step,* H_2O_2 *as well as the previously oxidised enzyme get reduced leading to water and* O_2 *as products. How fast the reaction occurs, depends on the concentration of catalase and* H_2O_2*, being highest at high concentrations (Michaelis-Menten theory). During the conducted experiments both concentrations were comparably high (see Table 1), thus the reaction of* H_2O_2 *with catalase is much faster than with the reactant. Rate constants are rare, but are estimated to be about* $2\times10^{7}\ M^{-1}\ s^{-1}$ *(Beers and Sizer, 1951). Tests revealed that the amount of catalase was sufficient to destroy* H_2O_2 *and stop the reaction with the organic acid (= reactant). This was concluded as no change in the concentration of the formed organic acids was observed after the reaction was stopped.*

To what are the reported uncertainties referring to? Just the uncertainties in the fitted slopes or do they convey more parameters?

Response:
The reported uncertainties refer to the fitted slopes with an error of 1σ and do not convey any other parameters.

After reading the result section, I'm still confused about the possible reaction mechanism, especially for aldehydes for which two distinct reaction schemes are provided. Is there a way from your data to rationalize this into a single reaction mechanism?

Response:
The present study was focused on kinetic investigations in the aqueous phase. The suggested mechanisms are only tentatively as no product characterisation was conducted. Due to this lack of information no single reaction mechanism can be recommended. Nevertheless, some propositions were furthermore taken from the literature where product studies have been conducted to underline the suggested mechanisms.
If there is an unhydrated carbonyl function in the molecule, H_2O_2 would probably add to the molecule forming an alpha-hydroxyhydroperoxide which has been stated several times in literature (Huang et al., 2013, Zhao et al, 2008, 2012, 2013). Reactions with ozone are suggested to react generally via H-atom abstraction (e.g. Voukides et al., 2009; apart from unsaturated compounds).
We think the different results of this study cannot be summarized into one single reaction scheme but mechanisms always only refer to one substrate.

In chemistry, the terminology turnover has a precise definition and refers to catalytic processes (including enzymology). Therefore, its use in the context of this paper may be misleading or leading to confusion. Best would be to avoid its use or if not to give a precise definition. The units given to it corresponds rather to a rate constant. . . So some clarification would be welcome.

Response:
We agree to the reviewer that "turnover" is usual in enzymatic notation. We changed the term to "first order conversion rate constant k_{1st}".

Specific comments

Title: Wouldn't "Kinetic measurements of. . ." be nicer?

Response:
Yes, the manuscript was changed accordingly.

The engineering notation should be avoided in the figures.

Response:
We agree to the reviewer and changed the manuscript accordingly.

Abstract: what is meant by “substance group”? Also referencing papers in an abstract is unusual. . .

Response:
The term “substance group” is a hypernym for the organic compounds that were mentioned in the sentence before. To avoid repetitions, we decided to change to an alternative word. We changed the manuscript to “these substances”. We agree to the referee and deleted the citation in the abstract.

References

Hart, E. J., Sehested, K., and Holoman, J.: Molar absorptivities of ultraviolet and visible bands of ozone in aqueous solutions, Analytical Chemistry, 55, 46-49, 10.1021/ac00252a015, 1983.

Huang, D., Chen, Z. M., Zhao, Y., and Liang, H.: Newly observed peroxides and the water effect on the formation and removal of hydroxyalkyl hydroperoxides in the ozonolysis of isoprene, ACP, 13, 5671-5683, 2013.

Voukides, A. C., Konrad, K. M., and Johnson, R. P.: Competing mechanistic channels in the oxidation of aldehydes by ozone, The Journal of organic chemistry, 74, 2108-2113, 2009.

Zhao, R., Lee, A. K. Y., and Abbatt, J. P. D.: Investigation of Aqueous-Phase Photooxidation of Glyoxal and Methylglyoxal by Aerosol Chemical Ionization Mass Spectrometry: Observation of Hydroxyhydroperoxide Formation, The Journal of Physical Chemistry A, 116, 6253-6263, 10.1021/jp211528d, 2012.

Zhao, R., Lee, A. K. Y., Soong, R., Simpson, A. J., and Abbatt, J. P. D.: Formation of aqueous-phase α-hydroxyhydroperoxides (α-HHP): potential atmospheric impacts, Atmospheric Chemistry and Physics Discussions, 13, 10.5194/acpd-13-5509-2013, 2013.

Zhao, X., Zhang, T., Zhou, Y., and Liu, D.: Preparation of Peracetic Acid from Acetic Acid and Hydrogen Peroxide: Experimentation and Modeling, The Chinese Journal of Process Engineering, 8, 35-41, 2008.