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Comment

Interactive comment on “Formation of aqueous-phase α -hydroxyhydroperoxides (α -HHP): potential atmospheric impacts” by R. Zhao et al.

Anonymous Referee #1

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The manuscript discusses results and implications of studies of the formation of alpha-hydroxy hydroperoxides (alpha-HHPs). Although previous results on this class of compounds exist they are quite limited. The work is very thorough and clearly presented and the authors make a strong case for the role of this compound class in tropospheric chemistry, primarily with respect to condensed phase (aerosol and cloud) processes but also the gas-phase, and they also point out the potential role of these compounds for human health. The topic is well suited to ACP. Although the atmospheric implication section is a little speculative, this section is important as I hope it will stimulate future work into this class of compounds, which, as this paper clearly demonstrates, is of high importance. I recommend the manuscript for publication after addressing the

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fairly minor comments below.

1. p. 5511 line 1: To my knowledge only hydroxy methyl hydroperoxide has been measured in the gas-phase. If this is the case I recommend stating it as such, in order to not give the impression that a whole range of alpha-HHPs have been observed in the gas-phase. (It is possible that the methyl case is unusual).

2. p. 5512 line 24-26: Could you clarify a little what exactly is meant with processing, what are the products and are they different than “regular” processing? This is a general comment also for the summary: A very interesting aspect of this work is in how far the alpha-HHPs present different reaction pathways and products. I am not sure how much more can be said at this point, but it clearly is an important future research direction.

3. p. 5513 line 3: If I understood correctly the solvent was H₂O and D₂O was only added for locking etc. Did you consider conducting the experiments in D₂O to reduce the problem of the water peak in the NMR. This could have helped with a number of assignments.

4. 5515 line 20: Is the problem with salt common to all NMR instruments or is it specific to the one used here? Such experiments would be very interesting.

5. 5517 line 22 quantification: Where the NMR experiments conducted quantitatively by making sure that the delay between pulses was long enough for small molecules to fully relax? It should be ensured that the used pulse delay time was appropriate.

6. 5519 line 9-10: “Thus the use of K_{app} negates the need for unambiguous quantification of all the peaks.” Could you clarify this. Do you need to be quantitative with respect to relative peak heights.

7. 5519 line 21-26 just for completeness: Was pH affected by addition of H₂O₂ and could this affect the hydration / HHP equilibria or rates? Also was the pH of all solutions the same. A brief statement whether pH can affect the experiments or not would be

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helpful.

8. 5521 line 15-16 I know it is labeled in the figure, but it would be clearer to use “methylene proton peaks of the hydrated formaldehyde”; as written hydrated formaldehyde protons could also refer to the OH group protons as they are on the molecule as well.

9. 5528 line 9-14. Although the following equations clarify this, it would be helpful to phrase more clearly whether effective KH or KH is discussed as KH (not effective) of formaldehyde is much smaller than effective KH.

10. A general comment with respect to the hydration equilibria: The Taft equation (linear free energy relationships J. Am. Chem. Soc. 74, 2729, (1952)), especially the polar substituent constant, have been used very successfully before for carbonyl hydration equilibria, e.g., R.P. Bell *Advances in Physical Organic Chemistry* 4, 1-29 (1966); Greenzaid et al. *JACS* 89, 749-756 (1967). It could be interesting to incorporate it into this work also as this aspect could be useful for modeling efforts and section 4.2 as it might provide a pathway to structure reactivity aspects of Kapp. However the Taft equation does not explain the effect of sulfate (Yu et al. *Environ. Sci. Technol.*, 45, 6336–6342, 2011)

11. P. 5531: “increase of solubility”. I assume this is with respect to an aqueous phase or is this true also for organic phases? Please clarify.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 5509, 2013.

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