

Interactive comment on “Organic peroxide and OH formation in aerosol and cloud water: laboratory evidence for this aqueous chemistry” by Y. B. Lim and B. J. Turpin

Anonymous Referee #1

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The authors present mass spectral evidence for the formation of peroxyhemiacetals forming in aqueous solution when methylglyoxal is either mixed with a commercial organic hydroperoxide or when a methylglyoxal/hydrogen peroxide solution is photolyzed at 254 nm. The mass spectral approach is to use electrospray ionization coupled to an FT-ICR mass spectrometer, so that very high mass spectral resolution is obtained along with MS-MS spectra. To my knowledge, this is the first evidence for the formation of peroxyhemiacetals forming in the aqueous phase via reactions of organic hydroperoxides formed also in the aqueous phase. Ziemann has shown that peroxyhemiacetals may form via uptake of gas phase peroxides. This is an interesting observation but I

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have a few comments that need to be addressed before it can be published.

1. Title. I find the title a little bit baffling because it does not include the word peroxyhemiacetal. This class of compounds is what is observed in the experiments and will likely lead to SOA. As written, the focus of the title is on peroxides and OH but I don't think that the novelty of the paper lies in the experimental inference of peroxide or OH formation occurring in the aqueous phase, i.e. it is not surprising that they form and the authors have no direct evidence that they do. I suggest the title be changed to: "Laboratory evidence for peroxyhemiacetal formation in the aqueous phase".
2. First sentence of Abstract: I don't agree that aqueous phase chemistry in aerosols is well accepted as an important SOA formation mechanism. This is still a hypothesis lacking compelling evidence from the field that can place it quantitatively on a scale with other SOA formation mechanisms. This is not to say that it is not interesting and does not occur, just that our understanding is not at this level as yet.
3. The reference to Ehn et al, Nature, 2014 is lacking in the Introduction, as a motivation for the likely presence of organic hydroperoxides in aerosol and cloud water.
4. Page 17370, Line 23 – The Henry's Law constants for the organic hydroperoxides will be very highly dependent on their structure, and will not all fall in the range of 100 to 1000 M/atm.
5. Page 17371, Line 10 – The use of high concentrations of 20 mM of hydrogen peroxide will lead to the formation of hydroxyhydroperoxides of methylglyoxal in solution (see Liu et al., ACP, 2102; Zhao et al., ACP, 2013). How will this class of compounds affect the chemistry? Will they photolyze to form OH, for example? Will they react with methylglyoxal to form peroxyhemiacetals?
6. Perhaps I missed it, but I do not recall seeing the pH of the solutions described.
7. Figures: It would be helpful to the reader if all the key peaks were labelled on the Figures. This is done in some cases but not others.

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8. Figure 1: It is not clear what is meant for the products formed from the second reaction (i.e. that with three consecutive arrows).
9. Control Experiments: What is the spectrum of a solution of methylglyoxal with hydrogen peroxide present and no illumination? What is the spectrum of methylglyoxal with illumination and no hydrogen peroxide? These need to be provided in the Supplementary Information.
10. I find the wording in the modeling section confusing. In particular, is the HO₂ in the condensed phase arising mostly via uptake from the gas phase or via production in the condensed phase?
11. In the modeling, a 1 M concentration of methylglyoxal is quite high. Could the authors provide a modeling scenario with smaller values, or at least address how the results would scale with the concentration?
12. Page 17378, Section 5.3. Note that Badali et al., ACP, 2015 have recently demonstrated that OH radicals are formed photolytically in SOA solutions. This should be referenced here and probably in the Introduction too.

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