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Atmospheric Chemistry and Physics Discussions

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 #2

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The manuscript describes formation of hydroperoxides via aqueous processing of H2O2 with methylglyoxal. Evidence for the formation of these peroxides is proposed via mass spectrometric detection of m/z assigned to peroxy hemiacetals. This finding of hydroperoxide formation via aqueous processing has not been previously considered, to my knowledge; partitioning of hydroperoxides produced in the gas-phase has been considered as the main source of condensed phase peroxides. There is much current interest in peroxides and this work presents an interesting and important contribution, especially as peroxides in aerosol may play an important role with respect to reactivity and health effects of aerosol. The work addresses a topic that fits well in the scope

of ACP and generally should be published. The high O/C ratio with low unsaturation supports the formation of hydroperoxides in these experiments. The hydroperoxides themselves were however not observed, and I have some reservations whether the methods used are able to identify the peroxy hemiacetals unambiguously raising some questions whether peroxides were in fact formed. Thus, I recommend publication after my main comments below can be clearly addressed and resolved.

Main comments

1. A novel and very interesting finding is the production of hydroperoxides in the condensed phase. The mechanism proposed in the manuscript is reasonable. However, the potential for formation of (hydro)peroxy compounds from non-radical reactions of H2O2 with either MGL via formation of alpha-hydroxy hydroperoxides, or formation of peroxy carboxylic acids via reaction of H2O2 with carboxylic acids, may contribute. This would not change the fact that peroxide containing compounds are made, but it does affect the mechanism and implications with respect to radical chemistry.

2. My main concern is that the instrumental setup used in this work is poorly suited for detection and quantification of peroxides. This is reflected in the fact that the hydroperoxides themselves were not observed, a substantial drawback. Even techniques that use components at lower temperatures than the 300C capillary (P. 17372 L.6), such as PTR-MS have been shown to destroy hydroperoxides (Liu et al. ACP, 13, 5715-5730 2013 and others). For this work a technique that can directly observe the proposed hydroperoxides is critical or use of a method that can resolve isomeric compounds, as explained in the following: Generally, there can be substantial uncertainties in assignment of chemical structures to m/z observed in ESI-MS, in particular without the use of a LC separation method. Depending on conditions, the method can produce spectra that contain large amounts of clusters of molecular species. For example, using methanol and water as a solvent it is not unexpected to see these solvents cluster with other species. This could explain the loss of methanol observed in the most of the MS/MS spectra. Another example is that there is no difference in mass between a hy-

droperoxide and geminal diol or between PHAstd and a cluster of MGLY and t-BuOOH (see 2b and also 2a). Given these concerns a more detailed analysis is required before the proposed m/z from the ESI spectra can be identified unambiguously as peroxy hemiacetals, i.e., the MS/MS spectra have to clearly highlight how they cannot arise from clusters or other species. This is critical as the evidence of hydroperoxide formation resides in the observation of PHA1 and PHA2.

2(a) For example, in Figure 4 can the authors prove that m/z 159.06278 does not (in part) correspond to a cluster of two methanol molecules with MGLY rather than a double hemi acetal of methanol with MGLY. It would be extremely helpful and important to discuss this. Using liquid chromatography (LC) this should be easily feasible as that should separate the double hemiacetal from unreacted MGLY that merely clustered with methanol (or water) in the ESI source.

2(b) P. 17374 discussion of PHAstd and figure 5. It would be important and helpful for the authors to disprove the possibility that the observed m/z = 185.07802 could (in part) correspond to a cluster (in contrast to a chemically bonded peroxy hemiacetal) of t-BuOOH, MGLY and Na+, which has the same exact mass. This could also explain the observation of the intense peak at 95.01041 as it would correspond to fragmentation via loss of t-BuOOH, which would be expected for the proposed cluster. One of the keys to this and discussion of the other PHAs would be a mechanism for the fragmentation with loss of methanol from PHAs, which the authors do not discuss. If I understand correctly the authors propose that Na+ stays attached but MeOH or O2 are being eliminated. Both of these would require complex arrangements from PAHstd, without loosing the fairly weakly bound Na+ (compared to a chemical bond). The authors state that HO2 and O2 loss are expected but do not comment on this MeOH loss, which is the second most intense m/z after the MGLY peak. Given the experimental setup and used mixture, loss of methanol from a cluster is a very straightforward explanation. The authors reference O2 loss from soft ionization/IRMPD without any detail of whether this was for a Na+ cluster. It would be very helpful to reference literature for such a

process or give more detail and concrete experimental results. For example, one could also propose a pathway were the t-BuOOH in the cluster eliminates methanol forming acetone, a process found in both the NO+ and H+ mode by Liu et al. ACP 13, 5715–5730, 2013. Using a separation technique before ESI detection would obviate the possible confusion between clusters and chemical bonded species. Also, elimination of methanol as a solvent would be a useful approach.

Also, regarding the discussion of PHAstd, p. 17374 line 29. Loss of O2 from t-BuOOH. This requires some clarification. I was under the impression that the parent m/z for the MS/MS was PHAstd and not t-BuOOH. How can there be loss of anything from t-BuOOH in the MS/MS if the m/z of the PHAstd, in which the t-BuOOH has reacted to a different chemical species, was selected unless the parent is the cluster of t-BuOOH, MGLY and Na+ proposed above. In addition, the signal at 81.06971 is small and it would be useful to discuss the role of all the other m/z compared to m/z = 81.06971 one.

Lastly, t-BuOOH is not the best compound to use for peroxyhemiacetal work. It is sterically hindered which hinders formation. Also, it only has a t-Butyl group which may cause its nucleophilicity to be completely different from the nucleophilicity of hydroperoxids formed in atmospheric water, which are highly functionalized.

2(c) Section 4.2 would benefit from more extensive discussion. The discussed m/z do match the chemical formulae of PHA1 and PHA2. However, it would be useful to find stronger evidence how the MS/MS spectra can actually prove that they structurally correspond to PHA1 and PHA2. Observation of MGLY Na+ could for example result from MGLY Na+ clustering with one of the many other compounds in the mixture (see next point). Like for the m/z 81.06971 discussed above, the statement that 59.01377 results from loss of O2 from R1OOH is rather confusing as R1OOH is not present, unless the parent ion corresponds to a cluster with R1OOH. Observation of the m/z = 59.01377 fragment only shows that acetate is formed but the process is unclear. It cannot result from O2 elimination from R1OOH as the corresponding negative ion, m/z

= 91.00316, was not selected as the parent ion for fragmentation.

Contrary to the discussion, in Fig. 7b, 159.02946 results from loss of CH3OH from the parent mass, 191.05540, not loss of O2 from PHA2. It appears a parent mass different from PHA2 was selected for fragmentation again highlighting the possibility of formation of methanol clusters from the solvent. I believe the authors were referring to m/z = 87.00832 when discussing m/z of 59.01377 for PHA2, which results from loss of C4H8O3 from the parent m/z of 191.05540, the latter corresponding to C7H12O6 (a cluster of methanol with C6H8O5?).

Similarly, the discussion of the positive mode in figure 8 could indicate cluster of MGL Na+ with some other compounds existing in the solution.

3. Figure 6: It would be helpful to discuss the role of the peroxy hemiacetals in context of this figure. There are a large number of m/z observed in the boxed region. In fact, the proposed peroxy hemiacetal m/z do not correspond to the most intense peaks and they represent a very small fraction of the signals. It would be helpful to discuss the importance of the proposed peroxy hemiacetals if they only are a minor component.

Minor comments:

(a). Chemical nomenclature: With respect to point 2 above the authors on p. 17374 line 2 and 5 mention "solvation of methylglyoxal" with methanol. Solvation describes formation of a complex via intermolecular forces and not formation of a chemically-bonded hemiacetal. I don't think the authors mean to imply that m/z 159.02678 corresponds to a cluster species and not the double hemiacetal or related species. In addition, and related to Figure 9: The nomenclature in figure 9 is unconventional: "DeMGLY" is in fact what should be referred to as MGLY (methylglyoxal) and not dehydrated methylglyoxal, and "MGLY" is in fact hydrated methylglyoxal. I would encourage the authors not to redefine organic nomenclature. However, it makes the statement at the beginning of this point confusing as I am not sure which form of methylglyoxal is meant. I would also encourage the authors to refer to ROOH compounds as organic hydroperoxides

to distinguish them from ROOR type peroxides.

(b) Abstract: The whole first paragraph is more suitable for an introduction to a paper than to an abstract presenting new findings. The paragraph describing the work and new findings is shorter than the intro paragraph. However, this is a style aspect. I would encourage the authors to be more specific about the actual experimental findings in the abstract.

(c) P. 17368 first sentence and abstract. I do not believe that the role of aqueous SOA formation is clearly proven or well accepted. It certainly represents a strong hypothesis based on lab experiments. In fact, a little later on P. 17369 Line 3 the authors state "potentially". Hence, I encourage the authors to weaken this statement.

(d) P. 17368 L. 17 Which peroxides form epoxides. As plural is used this statement is going beyond IEPOX and some references for these would be very helpful.

(e) P. 17369 L. 11. As the aqueous SOA is a hypothesis I recommend phrasing as "may explain . . .".

(f) P. 17369 line 13-15. In the first sentence an oxidant is mentioned (OH). In the second sentence reactions are mentioned. These cannot really be directly compared as they are not the same thing. I think the authors are implying that oxidants other than OH and non-radical reactions play a role in aerosol. It would be helpful to clarify what is meant here.

(g) P. 17370 Line 13. Do the authors mean flux or emission. They are clearly related but not really the same. I also assume that they are referring to non-methane VOCs?

(h) P. 17370 Line 18. The authors are correct that ROOH can be an OH source. However, I recommend weakening the statement, as this is only true for functionalized peroxides. For example CH3OOH has a very slow photolysis rates and does not contribute as an OH source because of this (in fact this is why 250nm lamps and not solar radiation is used to photolyze H2O2). In contrast, the abstraction of the hydroperoxy H

can make hydroperoxides even act as catalytic HOx sinks. Ditto for the statements on line 20-22.

(i) P. 17370 Line 22-23. The Henry's law constants of organic peroxides can be very low, e.g., with a large organic rest, or for ROOR with unpolar R groups. The Henry's law constants of hydroperoxides can be higher but that will greatly depend on structure. I recommend weakening the statement.

(j) It would be helpful to show the mass spectra of blank solutions and those after processing of MGLY without H2O2 as well as those of MGLY that has been equilibrated with H2O2 without photochemical processing. The authors mention these but there is no harm in adding a comparison in the supplement.

(k) P. 17374 line 26. I would have thought there must be some literature on the fact that hydroperoxides decompose on heated surface and not just a personal communication.

(l) P. 17374 line 26: I believe many of the current CI-API-TOF MS methods are able to ionize hydroperoxides without much problem, e.g., using I- as a reagent ion.

(m) How was the rate constants for peroxihemiacetal formation that was used in the model determined?

(n) P. 13747 line 28029. I am not sure that "much more stable" compounds correspond to "(less volatile)" compounds. For example CH4 is much more stable but also much more volatile. Do the authors mean stability (decomposition) or vapour pressure (volatility). It would in fact be useful to see vapour pressure estimates based on structure activity relationships. Some of the peroxy hemiacetals may not be very low volatility as they have few OH groups.

(o) Title: OH formation seems to have no relationship with this manuscript, as there is no experimental work on OH formation from (hydro)peroxides.

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