**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Yields of hydrogen peroxide from the reaction of hydroxyl radical with organic compounds in solution and ice" *by* T. Hullar and C. Anastasio

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Author Response to Interactive Comments

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1. Interactive Comment from D. Kieber :

The Hullar and Anastasio paper is very interesting. However, they are missing a key reference to a paper that contained results that are directly relevant to their study, and which showed the same result that they observed-namely the OH together with OM were an important source of peroxide. Zhou et al. 2008. Geophys. res. Lett.

(doi:10.1029/2008GL035418) showed that the OH radical (as formed from nitrate) along with organic matter were an important source of peroxide in newly formed marine aerosol extracts.

Response:

We thank the reviewer for directing us to this paper. We have added a mention of the results in our revised paper.

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2. Interactive comment from anonymous referee #1:

The manuscript of Hullar and Anastasio describes experiments aimed at investigating photolytic production of HOOH from a variety of model organic compounds in both aqueous and ice systems. The results of this study are important to help the atmospheric community better model fundamental atmospheric processes, understand the unique properties of water/ice and potentially help explain the preservation of HOOH in polar ice (given one would expect depletion of this particular species due to its lifetime on the order of hours).

Although previous work has looked at the HOOH yields from organics, those experiments were conducted using radiolysis techniques, which itself can produce the intermediates responsible for HOOH production. This extraneous source of HOOH thus confounds the experimental results previously obtained. This work aims to improve the experimental techniques, making the results more applicable to 1) environmentally relevant sources of oxidants (nitrate) and 2) environmentally relevant concentrations/production rates of oxidants responsible for the chemistry. This work thus provides an important improvement over previous laboratory based work done using radiolysis. This manuscript results in several key findings that will be important for the atmospheric and glaciology communities to consider:

1) HOOH yields obtained using nitrate as the source of OH radical were about 50%

smaller than those obtained using radiolysis methods. This means current models using HOOH yields established previously may be overpredicting HOOH generation.

2) The authors observed a pH dependence in HOOH yields that are not currently taken into account in current atmospheric models.

3) HOOH yields in ice are (sometimes) comparable to liquid, but often HOOH yields in ice are indistinguishable from zero. These results thus show that recycling of HOOH via OH reaction with organics is not able to explain the preservation of HOOH in ice cores.

Overall the manuscript is very well written, clear and concise. I have a few questions that likely could be addressed with a few small revisions of the current manuscript. The current work is interesting and timely and certainly of interest to the broad readership of ACP.

Comment:

1) Was there any particular reason for the two amino acids chosen? I could imagine a host of reasons to choose these or others – was it mainly because the pKas were similar but one was aliphatic and the other aromatic?

Response:

We chose glycine because it is the simplest amino acid, so that we could examine the chemistry of the amino acid functionality without a side chain. In addition, it has good solubility. Yes, we chose phenylalanine because it is the simplest aromatic amino acid. We have added a mention of this in the text.

Comment:

2) In section 2.6 it states regarding dark controls: "With some exceptions, these samples did not show HOOH production rates greater than zero ... consequently we did not include a correction factor for dark samples..." In the case of the exceptions (where

I presume there was some significant dark reactivity) was there a dark correction then? Were the deviations even in the case of the exceptions much smaller than the illuminated samples, or did you have a few cases where there was some significant dark reactivity? This statement needs some clarification.

Response:

We did not include a dark correction in our determination of HOOH yields; we have clarified this in the text. This is because only a small percent (14%) of dark control production rates were statistically different from zero and because the rate of HOOH production in dark samples was small (and noisy) compared to the production in the illuminated sample. To assess the impact of including a dark correction, we re-analyzed the experimental results by including a dark correction for samples with statistically significant HOOH production in the dark control. This evaluation found only minor changes to the calculated HOOH production rates and yields.

Comment:

3) It appears for the ice experiments, not all model compounds were tested (e.g.glycine, 2-butoxyethanol, octanol), was there a reasoning for this? It appears (generally speaking) that the compounds tested where you still observe significant HOOH yields in ice are also the more soluble species (formaldehyde, formate) while the ones where HOOH yields become zero in ice (octanal, phenylalanine, etc) are much more insoluble. Perhaps this has some link to the partitioning of the solute within the ice matrix and whether it is in proximity to the photochemical source of OH. i.e. if nitrate and the solute partition differently to the bulk ice vs surface liquid layers, could that in part explain some of the difference between ice/liquid HOOH yields? Obviously more targets would need to be tested to say this with any certainly, but it may be worth mentioning as part of section 3.5.

Response:

We tested seven of the ten model compounds in ice; the remaining three were not tested in ice exactly because of their low solubilities. This is because, in general, the reviewer's observation is correct: HOOH production in our ice experiments did not occur for the organic compounds that have low aqueous solubilities. We have revised the text in section 3.5 to include this observation.

Comment:

4) Section 3.4 invokes the idea of metal contaminants as a potential explanation for the observed pH dependence. This brought up an interesting point that perhaps could be incorporated into the introduction or discussion. How would the HOOH production rates studied here compare to other sources in, say, a typical urban aerosol? The introduction doesn't really discuss the overall "magnitude" of how important these reactions might be in comparison to other (inorganic) processes.

Response:

Thank you for your insight. We have included an additional paragraph in Section 4 (Implications and Conclusions) discussing this point.

Comment:

5) A few typos/grammar items: Introduction line 5: "...two sources of HOOH in cloud and fog drops" (suggest changing "to" to "in") Section 2.2 line 15: should that be 8 cmЁĘ3 volume? (the cube is missing from cm) Section 3.1 line 14: "...that have either been found..." (have is written twice in sentence) Figure 6: The caption does not indicate what the horizontal dashed lines represent. Is this just the linear regression?

Supplemental: In some cases there is a negative yield listed. Presumably this would be due to overall consumption of HOOH, but if you start with zero HOOH at the initiation of the experiment, how is any consumed? Is this just an artifact of the data fit over the experiment? In most (but not all) cases the standard error is larger, so it would be good if these (and any others that aren't statistically significantly different from zero)

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be somehow "tagged" in the table to point out they aren't significant (perhaps have the ones that are significant in bold)? It may visually help a reader pull out the conditions where significant HOOH production occurred.

Response:

We have corrected the typographical errors and clarified the figure caption.

Yields are calculated by correcting the production in the presence of nitrate for any production without nitrate. In some cases, the production without nitrate is higher, giving a negative yield. We have changed the supplemental table to bold those positive yields greater than the propagated standard error, indicating there is likely net production of HOOH due to interaction with the model organic compound.

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3. Interactive comment from anonymous referee #2:

The manuscript provides the chemical insight of HOOH formation via aqueous chemistry in atmospheric waters (e.g., cloud droplets, wet aerosols and snow). HOOH is important in atmospheric waters because it can potentially oxidize organic/inorganic constituents and produce OH radical via photolysis. The authors explore reaction mechanisms including peroxy radical formation, and then discuss HOOH formation based on experimental results. They also measure HOOH yields, which are useful for atmospheric aqueous chemistry models like CAPRAM (Herrmann et al., 2005). They estimate that the lifetime of HOOH formation via OH reaction with organic compounds is 179 h and conclude this HOOH recycling is not likely to be the major process that preserves the HOOH in polar snowpacks for months. The paper is interesting, well-written, and suitable for publication in ACP, but following comments are provided for the authors' consideration.

Comment:

- Introduction, Page 6459, Line 3-5: HOOH also oxidizes organic compounds. For ex-

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ample, it converts pyruvic acid into acetic acid (Carlton et al., 2006), and glyoxylic acid into formic acid (Tan et al., 2009). Those organic compounds are potentially important in atmospheric waters because they are photochemical products from glyoxal and methylglyoxal.

Response:

Thank you for your observation. We have updated the introduction to include this information.

Comment:

- Introduction, Page 6460, Line 16, 18: In addition to R8 and R9, HOOH also reforms by bimolecular reactions of two OH radicals with the rate constant of 5.5e9 $M^{-1}s^{-1}$ (Buxton et al., 1988).

OH + OH -> HOOH (k = 5.5e9 $M^{-1}s^{-1}$)
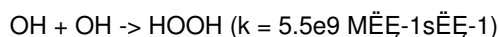
Apparently, this relates to pH dependent HOOH formation in Section 3.4.

Response:

Although the rate constant for self-reaction of OH is very fast, the steady-state concentration of OH is so low as to make the rate of this reaction insignificant as a mechanism for reforming HOOH. We have updated the text to include this point.

Comment:

- Section 2.7, Page 6468, Line 22-24: The production rates of HOOH and OH were normalized by j(2NB). But the OH production rate (R3) seems too small. The j(2NB)-normalized value is 1.8e-5 s^{-1}/s^{-1}. Since j(2NB) = 0.019 s^{-1} for aqueous solutions and 0.017s^{-1} for ice samples (Page 6466, Line 22-23), the rate constants should be 3.42e-7 s^{-1} for aqueous solutions and 3.06e-7 s^{-1} for ice samples. But Bock and Jacobi (2010) suggest 2.3e-4 s^{-1} for the same reaction under snow conditions.

Response:

The Bock and Jacobi (2010) nitrate photolysis rate constant is much higher than ours because they did not filter their light source to conform to tropospheric sunlight. Thus they have large fluxes of photons with wavelengths below 280 nm, wavelengths that are essentially absent in the troposphere, which leads to much faster production of hydroxyl radical from nitrate. Jacobi and Hilker (2007) give a reaction rate constant (Table 2) normalized to Summit, Greenland of 8.3 x 10-7 s-1, comparable to the rate constant we used in this paper. Anastasio and McGregor (2001) also measured a nitrate photolysis rate constant in simulated sunlight that is comparable to the value we measured in this paper.

Comment:

- Section 3.3, Page 6470, Line 20-27: The experimental results indicate HOOH formation even in the absence of nitrate. HOOH formation was even observed in UV Milli-Q water. Is this due to OH radical? Or does it imply pathways other than OH radical?

Response:

Small amounts of HOOH are formed by illumination of UV treated Milli-Q water. We do not know if this production represents OH radical reactions, or other pathways. Either mechanism is possible but we have no way of determining the pathway. It should be noted that our rates of production in the UV-MQ are very low and are only observable because of the very low detection limit of our HOOH analytical system.

Comment:

- Section 3.3, Page 6471, Line 3-17: The HOOH yield for glycine is very small (around 1% according to Fig 3). Does that imply HOOH formation from R13 is insignificant? In other words, is the contribution of RO2-RO2 reactions to the HOOH formation insignificant? How does this compare with the yield of 0.17 from non HO2 pathways (Stemmler and von Gunten, 2000) mentioned in Introduction?

Response:

The relative importance of HO2 versus non-HO2 pathways (such as reaction R13) will depend on the chemical characteristics of each model compound. Glycine has little overall production, so the R13 pathway and hydroperoxyl pathways are both small; we are not able to determine the relative importance of each pathway from our current work.

Comment:

- Section 3.4, Page 6474 Line 6-10. pH should affect OH formation according to R3. Do your experimental results support the more OH formation at the lower pH? Could this be the evidence of self-reactions of OH radicals to form HOOH (OH + OH -> H2O2)? HO2 formation from R6 (decomposition of peroxy radicals) is expected to be insensitive to pH.

Response:

There is no pH-dependence to OH formation from nitrate photolysis in solution over the range we tested, pH 1.9 to 8.3 (Anastasio and McGregor, 2001). In ice samples, Anastasio and Chu (2003) found decreased quantum yield for OH production from nitrate at lower pH values. This effect, however, should decrease OH production at lower pH in ice samples, not increase it. Note that the proton (H+) in R3 is only there to balance the reaction and it occurs – very rapidly – in the next step. We have modified the text to make this clear.

References to Referee comment #2:

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Bock, J., and Jacobi, H. W.: Development of a Mechanism for Nitrate Photochemistry in Snow, J Phys Chem A, 114, 1790-1796, 10.1021/jp909205e, 2010.

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