

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

Anonymous Referee #1

Received and published: 11 April 2011

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 inter-

C1679

mediates 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.

- 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?
- 2) In section 2.6 it states regarding dark controls: "With some exceptions, these sam-

C1680

ples 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.

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 certainty, but it may be worth mentioning as part of section 3.5.

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.

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 cm^3 volume? (the cube is missing from cm) Section 3.1 line 14: "...that have either been found..." (have is written twice

C1681

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) 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6457, 2011.

C1682