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***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 #2

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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-

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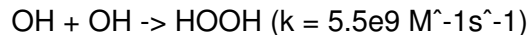
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written, and suitable for publication in ACP, but following comments are provided for the authors' consideration.

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

- 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 $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988).



Apparently, this relates to pH dependent HOOH formation in Section 3.4.

- Section 2.7, Page 6468, Line 22-24: The production rates of HOOH and OH were normalized by $j(2\text{NB})$. But the OH production rate (R_3) seems too small. The $j(2\text{NB})$ -normalized value is $1.8 \times 10^{-5} \text{ s}^{-1} / \text{s}^{-1}$. Since $j(2\text{NB}) = 0.019 \text{ s}^{-1}$ for aqueous solutions and 0.017 s^{-1} for ice samples (Page 6466, Line 22-23), the rate constants should be $3.42 \times 10^{-7} \text{ s}^{-1}$ for aqueous solutions and $3.06 \times 10^{-7} \text{ s}^{-1}$ for ice samples. But Bock and Jacobi (2010) suggest $2.3 \times 10^{-4} \text{ s}^{-1}$ for the same reaction under snow conditions.

- 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?

- 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 $\text{RO}_2\text{-RO}_2$ reactions to the HOOH formation insignificant? How does this compare with the yield of 0.17 from non HO_2 pathways (Stemmler and von Gunten, 2000) mentioned in Introduction?

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- 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 ($\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$)? HO₂ formation from R6 (decomposition of peroxy radicals) is expected to be insensitive to pH.

References

Bock, J. and Jacobi, H.: Development of a mechanism for nitrate photochemistry in snow, *J. Phys. Chem. A*, 114, 1790-1796, 2010.

Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B.: Critical review of rate constants of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O⁻) in aqueous solution, *J. Phys. Chem. Ref. Data*, 17, 513-886, 1988.

Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, doi:10.1029/2005GL025374, 2006.

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Stemmler, K. and von Gunten, U.: OH radical-initiated oxidation of organic compounds in atmospheric water phases: part 1. Reactions of peroxy radicals derived from 2-butoxyethanol in water, *Atmos. Environ.*, 34, 4241-4252, 2000.

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