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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Synthesis and characterization of peroxypinic acids as proxies for highly oxygenated molecules (HOMs) in secondary organic aerosol" *by* Sarah S. Steimer et al.

Anonymous Referee #3

Received and published: 12 February 2018

General Comments

In this manuscript the authors describe results of an experimental study in which they synthesized 3 peroxyacid compounds expected to be formed in the ozonolysis of a-pinene, characterized their mass spectra, and then used this information with liquid chromatography to search for them in secondary organic aerosol formed from this reaction. One of the peroxyacids was detected in the SOA and its yield quantified. The authors also show that peroxyacids decompose in SOA on timescales of hours, and so are difficult to measure in long filter samples. The method development and evalu-

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ation, and SOA experiment were well done and demonstrate that this approach could be used for analyzing these compounds and other peroxyacids in SOA systems. This approach represents an advance in the area of molecular analysis of SOA, especially for organic peroxides, which are of growing importance because of new understanding regarding autoxidation chemistry. The manuscript is well written, and I recommend it be published after the following minor comments are addressed.

Specific Comments

1. Page 3, lines 23–25: The concentrations of a-pinene and ozone used in these experiments were extremely high. Is it possible that a-pinene partitions to particles, walls, or the filter and that some of the reaction occurs there? Some discussion of the differences between reactions conducted under these conditions and at more typical atmospheric concentrations seems warranted.

2. Page 3, line 26: For these reactant concentrations the ozone should be gone in a few seconds, so the statement that the reaction time is 6.25 min could be clarified. This may give the time for particle-phase reactions, but these will then continue after collection on the filter.

3. Because of the unstable nature of peroxides it seems that some of the conditions in the HPLC-MS/MS analysis could impact the analysis. For example, the use of 0.1% formic acid, and heater and capillary temperatures of 250 C and 275 C. Please comment on this.

4. Did the authors consider measuring the total peroxide content of their SOA so that they could estimate the fraction of total peroxides that their molecular analysis detects?

5. Might it be possible to collect particles in a cooled filter apparatus in order to reduce the decomposition of peroxides?

Technical Comments

None

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