

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 #1

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This manuscript describes the synthesis of two monoperoxy pinic acid isomers (designated I and II) along with the diperoxy acid in a one-pot procedure. The peroxy acids are characterized by HPLC/ESI-MS, including MS2 analysis, but pure compounds were not isolated. Dimer species observed at the retention times of the monoperoxy acids were shown to be artifacts generated in the ESI source. SOA was generated from alpha pinene and analysis demonstrated the presence of the monoperoxy isomers, with isomer II predominating. The effect of RH on SOA formation was investigated and found to be insignificant. Stability of the monoperoxy isomers in SOA collected on filters was

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also investigated and rapid decomposition was observed, indicating that even rapid work-up will likely result in significant underestimation of peroxyacid concentration.

This manuscript is important as an illustration of the need for synthesis of authentic standards for verification and quantitation of SOA components. Furthermore, the flow tube experiments support the growing realization that peroxyacids, among other highly oxidized species may be significant contributors to SOA and its biological effects. The manuscript is clearly written and work logically developed. Eventual publication is therefore strongly recommended. However, the report has several shortcomings that must be addressed prior to publication.

1. In general, synthetic standards should be isolated and characterized as pure compounds. While the mass spectrometric analysis presented in this manuscript is convincing that the structures proposed for the synthetic targets are correct, additional physicochemical data, for example, ^1H NMR, is desirable for definitive proof. The authors report that the monoperoxy acids could not be well resolved, but effort directed towards achieving resolution is not clear. For example, a promising possibility would be the use of a HILIC column, such as recently reported for separation of carboxylic acids in SOA (J. Chromatogr. A 2011, 1218, 4417–4425). The column used in this citation was also a 3 mm column, which would be adequate for collection of sufficient sample for NMR analysis. If the authors did investigate the separation more thoroughly, this information should be included.
2. Why was the LC/ESI-MS analysis not performed using a UPLC column? A UPLC version of the same column would likely provide significant improvement in resolution. It would be surprising if the authors did not have access to UPLC. Mass spectrometric data on better-resolved peaks could have acquired even though resolution on the semi-preparative scale column was difficult to achieve.
3. The observation of different MS₂ spectra for isomers I and II indicates that 1-electron reduction in the ESI source did not make an important contribution to the mass spec-



tra of the monoperoxy acids and that the anions of the more acidic carboxylic acids were the parent species. The fragmentation patterns provide sufficient information to distinguish between the two proposed structures, and the authors should be able to tentatively assign structures to isomers I and II. Although the literature on EIS-MS of carboxylic acids is sparse, there is sufficient precedent to propose plausible pathways to the observed product ions which are unique to each structure.

4. Graphic presentation of the actual MS and the MS₂ data would be helpful to the readers. The mass spectra could be presented as supporting information.
5. The investigation of the effects of RH rules out the formation of the peroxyacids via a hydrolytic pathway, but does not preclude an oxidative pathway in the condensed phase. In the gas phase, peroxyacids can form via HO₂ chemistry (e.g., *Atmos. Chem. Phys.* 2012, 12, 6489–6504) without the participation of H₂O. Therefore insensitivity of yield to RH is not surprising, and the discussion might be amended to reflect this. The order of magnitude discrepancy between the observed and predicted relative yields of monoperoxydicarboxylic acids is probably not explicable entirely by peroxyacid degradation during work-up, and illustrates the importance of quantitation using authentic standards to improve models.

An experiment that would be informative with regard to whether the peroxyacids form in the gas or condensed phases would be to monitor the gas phase species by CIMS if the authors have access to such instrumentation. Although interesting, this experiment would not be a prerequisite to publication since access to CIMS instrumentation is required.

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