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Interactive comment on "Chamber-based insights into the factors controlling IEPOX SOA yield, composition, and volatility" *by* Emma L. D'Ambro et al.

Anonymous Referee #1

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General comments

This manuscript describes laboratory experiments using the Filter Inlet for Gases and Aerosols/Chemical Ionization Mass Spectrometry (FIGAERO-CIMS) technique that aim to investigate the nature of the components of IEPOX-derived secondary organic aerosol (IEPOX-SOA). Specifically, the work addresses the inconsistency between GC-MS approaches that have identified semi-volatile molecular components and volatility measurements that have indicated that the bulk of IEPOX-SOA must be made up of much lower volatility molecular components. The main claim is that a desorption signal that corresponds to C5H12O4 has two maxima, one that arises from a semi-volatile

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source (presumably from 2-methyl tetrols directly evaporating) and one that arises from the thermal decomposition of a low volatility source and a desorption signal that corresponds to C5H10O3, which also arises from the thermal decomposition of a low volatility source. Because knowledge of the molecular composition of IEPOX-SOA is critical to the development of accurate SOA mechanistic models, this work will be of great interest to readers of Atmospheric Chemistry and Physics. However, I believe that a number of uncertainties remain in the interpretation of both the present work and past studies, and that a revised manuscript should more directly address these issues.

Specific comments

Because of a lack of authentic standards, there continues to be no proof whatsoever that either the GC/MS signals previously attributed to C5-alkene triols or the present CIMS signals attributed to C5-alkene triols actually correspond to these species. Indeed, Watanabe et al. 2018 showed that these species are among the least thermodynamically favored among a variety of possible C5H10O3 isomers. I suggest that the manuscript be revised to simply refer to a C5H10O3 thermal decomposition product and refrain from associating this product with any particular molecular form.

Similarly, while I find the argument fairly convincing that the semi-volatile C5H12O4 component is probably the 2-methyl tetrols themselves, I don't think the low volatility thermal decomposition product can be assumed to be the 2-methyl tetrols.

The proposed oligomerization mechanism given in Figure 7 would benefit from more detailed discussion. Rather than a more obvious mechanism directly involving IEPOX, the authors are proposing two types of reactions: 1) acid-catalyzed etherification reactions of organosulfates to form ether-linked oligomers and 2) acid-catalyzed sulfate esterification reactions to form sulfate-linked oligomers. The authors don't provide any literature precedents for these types of reactions. Therefore, I think the authors should provide a rationale for these somewhat unusual reaction types.

Along the same lines, the overall interpretation would benefit from estimates of the thermal desorption behavior of the proposed oligomer components. Did the authors suggest two isomers of a monosulfate dimer as their major proposed molecular species because $C_{10}H_{22}SO_{10}$ is expected to have roughly the observed thermal desorption behavior?

Technical comments

Line 87: There should be a reference to Hu et al. 2016 ACP 16, 11563-11580 here.

Line 128: There is something wrong with the grammar in this sentence. Please revise.

Line 464: I'm not sure why there is a reference to Atkinson, 1987 here. There are two measurements of IEPOX + OH rate constants: Bates et al. 2014 and Jacobs et al. 2013, ES&T 47, 12868-12876, which differ by a factor of two. The choice of rate constant should be explicitly discussed.

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