

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 #2

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Overview:

This study sheds new light on the question of volatility and chemical composition of secondary organic aerosol derived from IEPOX, a ubiquitous biogenic aerosol component. IEPOX is known to react in aqueous aerosol to form commonly observed products such as methyltetrols and organosulfates, and compounds with the molecular formula C₅H₁₀O₃ (C₅ alkene triols, methyl-tetrahydrofuran-diols, or both) have also been observed in IEPOX SOA. The total reactivity of IEPOX in the aerosol phase and its uptake are known to be highly dependent on aerosol acidity, sulfate content, organic coating, and other parameters, but a detailed chemical understanding of the

C1

composition of the resulting organic aerosol is still lacking. Most observations of ambient IEPOX-derived SOA suggest that the majority of the SOA is of lower volatility than the individual species described above, suggesting a greater presence of oligomers and organosulfates and relatively small contributions from methyltetrols, alkene triols, or MeTHF-diols. This work bridges that apparent gap by showing that observed alkene triols or MeTHF-diols are artifacts formed during the thermal decomposition of lower-volatility material, as is a portion of the signal observed at the same mass as methyltetrols, while another portion that likely arises from the methyltetrols themselves is volatile and undergoes evaporation from the particle phase on the timescale of 1 hour.

The authors reach these conclusions by observing the uptake of trans-*b*-IEPOX onto acidified ammonium bisulfate seed aerosol in a series of controlled chamber experiments. They evaluate the evolution of particle chemical composition and component volatility using a high-resolution time-of-flight I- chemical ionization mass spectrometer outfitted with a filter inlet for gases and aerosols, which enables the separation of isobaric compounds by thermal desorption. Thermograms taken at varying humidities and timepoints during the experiments support the assertion that methyltetrols form quickly via direct hydrolysis following IEPOX uptake, and are then both transformed to lower-volatility species and evaporated into the gas phase, where they can be lost to walls or further photooxidation. The remaining IEPOX-derived SOA is therefore of very low volatility, likely including oligomers of the tetrols and organosulfates. Finally, the authors use a simple box model to illustrate how these results might play out under ambient conditions, and show that models using either aqueous uptake or volatility basis set schemes should be modified to account for the high uptake probability of IEPOX followed by revolatilization of methyltetrols.

While the description of the experiments performed herein and the conclusions drawn from thermal desorption measurements is straightforward and represents a valuable contribution to our understanding of the volatility and chemical composition of IEPOX-derived SOA, the extrapolation to ambient conditions remains tenuous and deserves

C2

further attention. Additional comparison to ambient results (e.g. Hu et al 2016) would help convince the reader that the results from these chamber studies are borne out in the atmosphere and are relevant to processes that occur in isoprene- and sulfate-rich settings. The brief comparison on lines 221-232 is not sufficient, and if anything brings up more questions than it answers as to the validity of comparing field to laboratory results. Does Lopez-Hilfiker et al. suggest that a further 50% of IEPOX SOA observed in ambient consists of tracers that don't even correlate with those identified here, in addition to the fraction that correlates with them but isn't explicitly C₅H₁₂O₄ or C₅H₁₀O₃? What are those other tracers and what could explain their absence in these experiments? Ambient particles likely contain much more variability in organic compounds in the condensed phase with which tetrols and other IEPOX-derived species might oligomerize or otherwise interact. How would that affect the conclusions here and our ability to put simple parameterizations into models? Is there any evidence that products of such cross-reactions result in similar observed compounds upon thermal decomposition?

Technical comments:

L 136: Is it possible that ethyl acetate interferes at all?

L 141-143: How does this uncertainty carry through to the conclusions you draw in this study? Since most of your analysis is independent of IEPOX mass, these uncertainties may not affect any major conclusions, but greater discussion of the uncertainties associated with the I-CIMS measurements is warranted. What is the potential for differences in sensitivities to the various compounds measured herein? Is the sensitivity to any given compound known to be constant over the course of a thermogram?

L 144: What were the concentrations of ammonium bisulfate and sulfuric acid, and what size particles did their atomization generate?

L 211-214: This sentence is confusing and may be missing a verb or clause.

C3

L 216: Speaking of vapor wall losses, how might the wall loss of the re-evaporated 2-methyltetrols affect the results of this study? If you have a large sink to the walls, might Henry's law equilibrium effectively pull more tetrol out of the particles that would otherwise occur?

Figure 4: Should there be units on UHP N₂?

L 335: Is the assumption of no particle-phase diffusion limitations a safe one? How might phase separation or organic coatings change these estimates?

L 339-342: How close do you expect these estimates of the Henry's law constant to be? A variation of two orders of magnitude seems strikingly large.

L 460: Since other reported values (e.g. Figure 8) are in ug/m³, it would be helpful to report the same units for the starting IEPOX concentration

L 460-461: Why were 90% and 10% chosen? How certain are these branchings, and how wide a range might they span in ambient conditions? How sensitive are the simulation results to changes in these numbers, and in the other parameters used?

L 463-464: What rates are used for the gas-phase reactions with OH?

L 499: Hyphen in the wrong place on "2 methyl-tetrol"?

Reference:

Hu, W., Palm, B. B., Day, D. A., Campuzano-Jost, P., Krechmer, J. E., Peng, Z., de Sá, S. S., Martin, S. T., Alexander, M. L., Baumann, K., Hacker, L., Kiendler-Scharr, A., Koss, A. R., de Gouw, J. A., Goldstein, A. H., Seco, R., Sjostedt, S. J., Park, J.-H., Guenther, A. B., Kim, S., Canonaco, F., Prévôt, A. S. H., Brune, W. H., and Jimenez, J. L.: Volatility and lifetime against OH heterogeneous reaction of ambient isoprene-epoxydiols-derived secondary organic aerosol (IEPOX-SOA), *Atmos. Chem. Phys.*, 16, 11563-11580, <https://doi.org/10.5194/acp-16-11563-2016>, 2016.

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Iyer, S., Zhang, Z., Gold, A., Surratt, J. D., Lee, B. H., Kurten, T., Hu, W. W., Jimenez, J., Hallquist, M., and Thornton, J. A.: Molecular composition and volatility of organic aerosol in the southeastern US: Implications for IEPOX derived SOA, Environ. Sci. Technol., 50, 2200-2209, doi: 10.1021/acs.est.5b04769, 2016.

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