

Interactive comment on “Phase, composition and growth mechanism for secondary organic aerosol from the ozonolysis of α -cedrene” by Y. Zhao et al.

Anonymous Referee #1

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Review of Zhao et al. “Phase, composition, and growth mechanism for secondary organic aerosol from the ozonolysis of α -cedrene”.

Synopsis: The study reported in this manuscript examines the ozonolysis of α -cedrene (a sesquiterpene having an empirical formula of C₁₅H₂₄) and the formation of secondary organic aerosol (i.e., SOA) following the reaction. The compound contains a double bond, two planar rings and a bridge structure. The single double bond helps to limit the complexity of the process since only a single ozonolysis reaction occurs. Thus, the flow tube and chamber reactions and product distribution should be reasonably connected in time. Among the several analysis methods used for measuring O₃+ α -cedrene SOA products are ATR-FTIR, ESI-MS, AMS, and DART-MS. These techniques are used together to give a comprehensive characterization of the physical

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and chemical properties of the O₃+ α -cedrene SOA. The phase and viscosity of SOA from the systems shows that it is a highly viscous semisolid for which the diffusion rate was measured. The products of SOA were primarily measured using electrospray-MS and were classified into four product groups, P1 – P4, of successively higher molecular weight. Individual products were rationalized from the mass spectrum from which an ozonolysis mechanism was proposed. A final Physico-chemical property, nucleation mechanism, was also examined using a uniquely interpretative approach. Some comparison with other alkene systems were then given.

Overview comments: The manuscript provides a comprehensive examination of the ozonolysis of α -cedrene. There are many strengths and few weaknesses in this work. The experimental design has been well thought-out and address a reasonable complete set of initial conditions. The references are extensive (110), if not exhaustive. There appear to be no flaws in the sampling, measurements, and calibrations. The primary measurement techniques were the ATR-MS and the ESI-MS. The other two techniques, AMS and DART-MS, were only used incidentally which simply detracts from the focus of the paper. Both should have been handled in the Supplementary Information (SI). Similarly, negative-ion ESI-MS was used in an incidental fashion. In some cases, I believe there were a few missed opportunities for adding to the body of information on this reaction and SOA formation system. (See below.) Regardless, the manuscript should be quickly advanced to ACP following a revision that considers these and other discussion comments.

Specific review comments:

Within the Introduction in the last paragraph, a better case should be made as to why α -cedrene was used for study particularly from a mechanistic perspective.

Experimental section:

- p 34498, L 9, the sentence is unclear; are the authors' referring to SOA mass? If not, how was the AMS analysis used in SOA characterization?

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- p 34498, L 11, was the SOA mass measured by micro gravimetric analysis of the PTFE filter or was the filter extract used solely for ESI-MS analysis? For example, for the sampling conditions reported ($v=360$ L), the CH 3–5 reported concentrations would be sufficient and the density could be measured directly without the need for any assumptions for the SMPS measurements.

- ESI is highly prone to multiple ionization of analyte compound; was this an issue during the analysis or what was done to account for this? I believe this at least deserves a sentence in Sec 2.3.2.

- Were there any corrections for bounce of the semi-solid aerosol or the application of a collection efficiency for the HR-ToF-AMS?

- p 34990, L 21, Since the AMS uses a chopper approach to correct the aerosol spectrum for gas-phase components, it is not clear to me why there would be an interference from 15NN.

Results and Discussion

- Are there any substantive changes in the mass spectrum of the aerosol between the first appearance of the particles (earliest FR port) and chamber samples collected after a 1 h reaction time?

- Is there any possibility that P3 and P4 from ESI result from multiply charged products? Assuming not, some qualitative statement regarding P3 and P4 should be made in the text.

- Please comment on the relative contributions to particle growth of P1 vs. P2. It is a bit confusing to me in that p 34997 L 1 suggests P1 contributes mainly to particle growth compared to P2 and then later in L 10 it is stated that P2 contributes most to particle growth. Some clarification would be helpful.

- The authors' might consider a Section 3.3.3 entitled P3 and P4 products. Even though the concentrations are to be at low levels, might they also contribute substantially to

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nucleation?

- As an introduction to the mechanism section, since the experiments were conducted without an OH scavenger, information as to the OH yield from the ozonolysis reaction would be valuable.

- With respect to Section 3.5, is there any information from the study that might suggest the competitive rate for RO₂+HO₂ vs. RO₂+RO₂ recognizing that there are many different RO₂ radicals present in the system.

- Does the O:C ratio change during the reactive process, especially in going from the FR to the CH systems.

- The authors' might consider including possible mechanisms for particle growth assuming it is not outside the scope of the paper.

Summary

- I believe the authors are missing an opportunity to discuss differences between monoterpene and α -cedrene particularly with respect to the physical form of the molecule. The text now covers this only superficially.

- The atmospheric implications of this work might also be addressed in greater detail, particularly with respect to new particle formation under pristine conditions.

Figures and Tables.

Table 1. It seems unlikely that the RH in CH1, CH 3–5 is below 1% for a Teflon film chamber. I would suggest a more conservative value that better represents the accuracy of such probes which are notoriously inaccurate at these low levels of humidity.

Fig 2. The caption is high ambiguous, especially for Panels (b) and (c). The inclusion of the word "respectively" should help resolve the problem.

Fig. 5. Since a quantitative value is being derived from this plot, the error bars for the

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individual points should be included, especially when examining the 1280 cm⁻¹ peak in Fig. 4.

Fig 9 and 10. Are all possible isomers included among the structures? If not, make a statement to this effect in the caption.

Fig 11. The size distribution would be better depicted using the volume distribution, $dV/d(\log)D_p$, rather than the number distribution. It would also help in illustrating the particle masses given in Table 1.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 34981, 2015.