

Response to Reviewer #1

We thank the reviewer for the helpful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer comments are in black, and author responses are in blue).

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.

Response: We thank the reviewer for the overall positive evaluation of the manuscript. In this study, although most of the data presented are from the measurements by ATR-FTIR and ESI-MS, we believe that the data from AMS and DART-MS provide unique and/or complementary information that makes the discussion and conclusions of the manuscript clearer and more readily comparable to other studies.

For example, the O:C ratio of the chamber SOA examined by AMS aids in the discussion of the mechanisms of particle formation and growth and the potential role of ELVOCs in this system. In addition, AMS spectra of SOA formed under dry and wet conditions are complementary to the ESI-MS data and support the conclusion that SOA composition is not significantly impacted by the presence of water. DART-MS data support that the high molecular weight products observed by ESI-MS are real components of SOA, rather than artifacts from the ion-molecule reactions in the ion source, which can be an issue during ESI-MS analysis. In addition, DART-MS provides complementary information on the newly observed P1 products.

We have included AMS and DART-MS spectra in the SI, but prefer to have the brief description of the techniques and the discussion of the data in the main text, especially given that DART-MS is not very well-explored in the literature.

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.

Response: To illustrate why α -cedrene was used for the study, we have added a description to the first sentence in the fourth paragraph of the Introduction. The first sentence of that paragraph now reads:

“ α -Cedrene (Fig.1) is found in air, reacts rapidly with O_3 , and is also an ideal compound for the study of sesquiterpene oxidation because (1) the single C=C bond in its structure helps to simplify the oxidation chemistry and the product distribution, and (2) its resemblance to other sesquiterpenes such as β -caryophyllene and α -humulene in the endocyclic double bond structure (with a methyl group at one end) may enable, to some degree, the generalization of SOA formation mechanisms for this class of compounds.”

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?

Response: We believe the reviewer is referring to p 34988, L9. To clarify this, we have changed the first sentence of that paragraph to the following:

“For experiments CH1-CH3 (Table 1), SOA composition was examined online by a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.), or by collection onto a PTFE filter at a flow rate of 12 L min^{-1} .”

We have also changed the first sentence in the AMS section (2.3.3) to the following: “An Aerodyne HR-ToF-AMS was used to analyze the chemical composition and to examine O:C ratios of polydisperse SOA formed in the chamber. Due to the small sizes of the SOA formed in the flow reactor, it was impossible to measure them with the AMS, and thus all AMS results presented hereafter are exclusively from the chamber studies.”

- 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 ($v=360 \text{ L}$), 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.

Response: We did not measure the SOA mass collected onto the PTFE filter, so the particle density could not be derived directly. To obtain the mass concentrations of SOA formed in the flow reactor and chamber, we used particle volume size distributions measured by SMPS and the density of α -cedrene SOA (1.1 g cm^{-3}) reported in the literature.

The filter extract was used solely for ESI-MS analysis in this study.

- 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.

Response: This was not an issue during the analysis in this study. The major peaks observed in the ESI mass spectrum are in the form of singly charged ions as indicated by the spacing between the isotopes of individual peaks (that is one). We have added a statement “Although ESI often forms multiply charged ions, the major ions observed throughout the mass spectra are in the singly charged state, as indicated by the unity spacing of the isotope peaks (Greaves and Roboz, 2013).” to Section 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?

Response: Corrections were not made for collection efficiency or particle bounce on the vaporizer in these measurements. Mass loading comparisons were not made using AMS measurements, so these corrections were not necessary.

- 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 ^{15}N .

Response: It is true that the chopper approach corrects the aerosol spectrum for gas phase species. This is carried out by subtraction of gas phase mass spectra from gas+particle mass spectra. However, subtraction of gas phase $^{15}\text{N}^{14}\text{N}^+$ (m/z 29.0032) is handled using the natural isotopic abundance multiplied by the signal for $^{14}\text{N}_2^+$, which is saturated and thus not well quantified. This can result in an over-subtraction which often causes a negative peak for $^{15}\text{N}^{14}\text{N}^+$. This peak is not resolved from CHO^+ (m/z 29.0027) and thus a negative peak often results for CHO^+ . This issue and a solution for it are discussed in the work by Canagaratna et al. (2015) which we have referenced.

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?

Response: Yes, as seen in Figs. 6 and 8 that show the ESI mass spectra of the SOA formed in the flow reactor (30 s reaction time) and chamber (30 min reaction time), respectively, high molecular weight oligomeric products account for a greater fraction of the total for the flow reactor SOA. Conversely, low molecular weight P1 products contribute more to the chamber SOA. We have included a discussion about this difference in the manuscript.

- 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.

Response: As mentioned in a previous comment, we observed no evidence for multiply charged ions in our ESI spectra, including P3 and P4 products. We have added a statement to the end of the first paragraph in Section 3.3: “As discussed above, there is no evidence that any of these peaks arise from multiple charging of higher molecular weight species.”

- 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.

Response: As shown in ESI mass spectra (Figs. 6-8), the typical P2 products appear in the mass range of 450-620 Da. Those at m/z 481–543 are the most abundant P2 products in the flow reactor SOA and they have a greater contribution to smaller particles than to the larger particles (Fig 7). Therefore, these P2 products (i.e., m/z 481–543) likely play an important role in initial particle formation. Further, the subset of P2 products with $m/z > 543$ account for a greater fraction of total P2 products in the *chamber* SOA (Fig. 8a) than in the flow reactor SOA (Figs. 6a and 7). This suggests that these larger P2 products (i.e., $m/z > 543$) are mainly formed at longer reaction times in the chamber and contribute mainly to particle growth.

To clarify this, we have modified the second and third paragraphs in Section 3.3 to read (changes underlined):

“Figure 7 shows the ESI mass spectra of polydisperse α -cedrene SOA (size distributions are given in Fig. S1a) with geometric mean diameters of 15 and 23 nm formed in the flow reactor at the same concentrations of α -cedrene and O_3 but different reaction times (27 s and 44 s) under dry conditions (Table 1, experiments FR1-FR2). Among P2 products, those at m/z 481-543 are the most abundant ones in the flow reactor SOA and they have a greater contribution to the smaller particles formed at shorter reaction times (Fig. 7a). Conversely, P1 products contribute more to larger particles formed at longer reaction times (Fig. 7b). Figure S4 shows additional ESI mass spectra of polydisperse α -cedrene SOA particles of different geometric mean diameters (13, 18, and 26 nm) formed in the flow reactor at the same reaction time (30 s) but different concentrations of α -cedrene under dry conditions (Table 1, experiments FR3-FR5). A similar size-dependent distribution of P1 and P2 products is observed. These results suggest that P2 products at m/z 481–543 may play an important role in initial particle formation, while P1 products contribute significantly to particle growth.

Figure 8 shows typical ESI+ and ESI– mass spectra of α -cedrene SOA formed in the chamber. The chamber SOA has a geometric mean diameter of 66 nm, larger than those formed in the flow reactor (13–26 nm, depending on the experimental conditions) due to the longer reaction times and hence greater extents of reaction. Figure 8 shows that the chamber particles also have relatively more P1 products, in agreement with the important role of P1 products in particle growth. In addition, the subset of P2 products with $m/z > 543$ in the positive ion mode account for a greater fraction of total P2 products in the chamber SOA than in the flow reactor SOA (Figs. 6a and 7). This suggests that these larger P2 products (i.e., $m/z > 543$) are mainly formed at longer reaction times in the chamber and contribute mainly to particle growth.”

- 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 nucleation?

Response: It is likely that P3 and P4 are also involved in the nucleation. This is supported by our data and is stated on p35004, L12. However, because of the lack of data on their chemical composition and formation mechanisms, we cannot draw any definitive conclusions about their specific role in SOA formation and growth. We have added to Section 3.5 the following sentences:

" This is also expected to be the case for the HMW P3 and P4 products. However, without information on their chemical composition and structures, data on P3 and P4 could not be included in Fig. 13. "

- 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.

Response: In Section 3.5, the discussion focused on the mechanisms of particle formation and growth, rather than the specific mechanism of oxidation. But to include the information regarding the OH yield from ozonolysis of α -cedrene, we have added the following paragraph before the P1 products section (3.3.1).

“Previous studies have reported an OH yield of 62-67% from ozonolysis of α -cedrene (Shu and Atkinson, 1994; Yao et al., 2014). Therefore, reaction with OH could play a role in α -cedrene oxidation in the absence of an OH scavenger. We reported in a previous study (Zhao et al., 2015) ESI-MS spectra in the absence and presence of cyclohexane, which showed that the relative intensity of P2-P4 peaks in the presence of cyclohexane is smaller. This suggests that OH oxidation may contribute to the formation of higher molecular weight species.”

- With respect to Section 3.5, is there any information from the study that might suggest the competitive rate for RO_2+HO_2 vs. RO_2+RO_2 recognizing that there are many different RO_2 radicals present in the system.

Response: The data from this study does not enable a quantitative examination of the competitive rate of RO_2+HO_2 vs. RO_2+RO_2 , but they do suggest an important role for both reactions in SOA formation. For example, a number of multi-functional P1 products were observed and identified in the SOA. The RO_2+RO_2 reactions that lead to RO radicals, and the subsequent isomerization of RO radicals, are the key steps to form those multi-functional products. As shown in Fig. S9, formation of the newly observed P1 products that contain 5-6 oxygens requires 2-4 steps of RO_2+RO_2 reactions. The RO_2+HO_2 reaction leads mainly to the formation of ROOH. Although ROOHs were not detected by ESI-MS in this study, probably because of their decomposition during SOA collection and analysis, their formation in the SOA from α -cedrene ozonolysis without an OH scavenger has been observed by on-line analysis using APCI-MS by Reinnig et al. (2009). In addition, the present study identified the peroxyhemiacetal as one of the major

types of potential structures for P2 products, the formation of which indicates precursor ROOHs are produced during ozonolysis.

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

Response: We were also interested in the possibility of changes in composition or O:C ratio during the reaction. Unfortunately AMS measurements cannot be made in the FR system as the particle sizes generated are too small for the AMS. However, in the chamber system, the O:C ratio is fairly constant over the course of the reaction.

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

Response: The data from this study show that particle growth occurs mainly via the condensation of smaller, more volatile P1 products, as well as the production of larger P2 products with $m/z > 543$ Da. We have included this information in several places (e.g., the first three paragraphs) in the mechanism section.

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.

Response: When relevant, we have noted in the text that possible structures and formation mechanisms of typical P1 and P2 products observed in α -cedrene SOA were based in part on previous studies on monoterpene and sesquiterpene ozonolysis, and these studies are cited throughout. The aim of this work is to show that SCI and the subsequent high molecular weight (HMW) products play an important role in new particle formation during ozonolysis of α -cedrene as a representative sesquiterpene. We have compared with other systems, including monoterpenes, with respect to the formation of HMW products and their role in particle formation. Finally, in the Summary we have tried to compare the general mechanisms of particle formation from different alkenes, which is directly related to the structure of the precursor alkene. However, more work needs to be carried out to discuss in greater detail the differences of particle formation mechanisms between monoterpenes and α -cedrene.

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

Response: We have added a discussion regarding the potentially important role of sesquiterpenes in atmospheric new particle formation to the summary section.

“Bonn and Moortgat (2003) have suggested that sesquiterpene ozonolysis could be one source of new particle formation in the boreal forest. Evidence for the role of sesquiterpenes in

atmospheric new particle formation has been recently presented by field observations in the boreal forest in Finland (Bonn et al., 2008) and in the Front Range of the Colorado Rocky Mountains (Boy et al., 2008). These studies have proposed possible nucleation mechanisms involving low-volatility products such as intermolecularly formed SOZ and organosulfates from sesquiterpene oxidation. The results of the present study suggest that the formation of HMW products during ozonolysis may serve as an important mechanism for such new particle formation.”

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.

Response: We did not measure the RH in the chamber for these experiments. As no water vapor was added to the chamber, the RH is expected to be the same as that of commercial ultra zero air (Praxair), which is significantly less than 1% initially. However, the RH in the chamber may increase slightly over the 30 or 60 min reaction due to diffusion through the Teflon film, which has been observed in previous experiments in this laboratory. To account for this, we have used a more conservative value (< 5% RH) for these experiments.

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

Response: We have modified the figure caption to read (changes underlined):

“Figure 2 (a) A typical ATR-FTIR spectrum of SOA from ozonolysis of α -cedrene in the chamber (experiment CH4, Table1). This spectrum is obtained from $\log_{10}(S_0/S_1)$ where S_0 is the single beam spectrum of the clean crystal and S_1 is that of the SOA covered crystal recorded immediately following impaction. (b) and (c) Typical difference spectra of SOA after 20 hours of exposure to a flow of clean and, 8 ppm O₃-containing dry air, respectively. These spectra are $\log_{10}(S_1/S_{20})$ where S_1 is the single beam spectrum of SOA covered crystal collected immediately following impaction and S_{20} is that after 20 hours of air or O₃ exposure. The positive and negative peaks in the difference spectra represent an increase and decrease, respectively, of the functional groups in SOA over 20 hours of exposure.”

Fig. 5. Since a quantitative value is being derived from this plot, the error bars for the individual points should be included, especially when examining the 1280 cm⁻¹ peak in Fig. 4.

Response: We have included the 1 σ error bars for the data points in Fig.5.

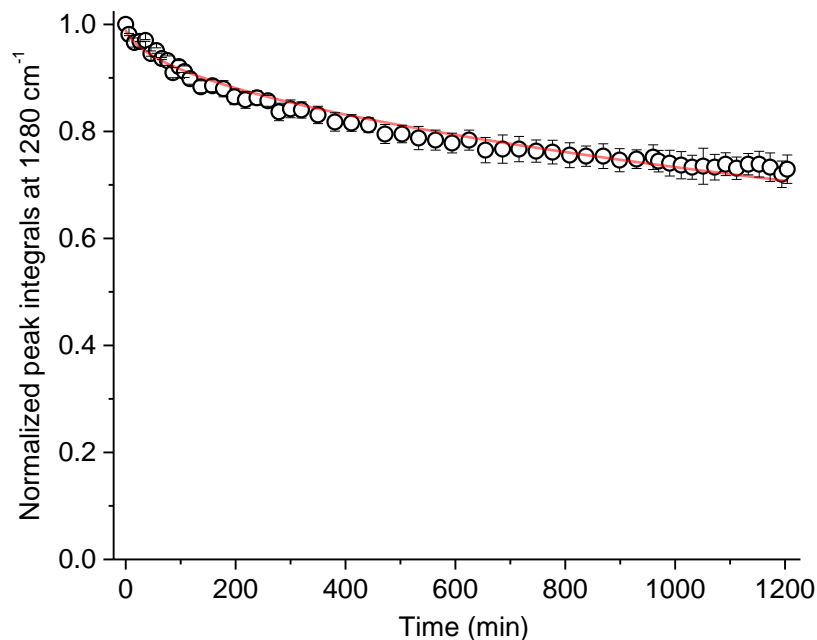


Figure 5 The normalized integrated area of $-\text{ONO}_2$ peak at 1280 cm^{-1} as a function of time over 20 hours of clean, dry air exposure. The red line is a best fit ($R^2 = 0.976$) of the evaporation data to eq. (1). Error bars represent $\pm 1\sigma$.

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

Response: Figs. 9 and 10 show likely structures for these products, but there certainly may be additional isomers. We have added the statement “note that there may be additional isomeric structures for these products” to the figure captions.

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.

Response: Fig.11 shows the effects of water vapor and SCI scavenger on particle formation. The changes in particle number concentration upon addition of water vapor and SCI scavenger, in combination with the changes in their ESI mass spectra, provide important information as to the particle formation mechanism, that is, high molecular weight products must be important in new particle formation. We think the number size distribution shown in Fig. 11 is essential for elucidating the mechanisms of particle formation.

References:

- Bonn, B., and Moortgat, G. K.: Sesquiterpene ozonolysis: origin of atmospheric new particle formation from biogenic hydrocarbons, *Geophys. Res. Lett.*, 30, 1585, doi:10.1029/2003GL017000, 2003.
- Bonn, B., Kulmala, M., Riipinen, I., Sihto, S. L., and Ruuskanen, T. M.: How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation, *J. Geophys. Res.*, 113, D12209, doi:10.1029/2007jd009327, 2008.
- Boy et al.: New particle formation in the Front Range of the Colorado Rocky Mountains, *Atmos. Chem. Phys.*, 8, 1577–1590, doi:10.5194/acp-8-1577-2008, 2008.
- Canagaratna et al.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15, 253–272, doi:10.5194/acp-15-253-2015, 2015.
- Greaves, J., and Roboz, J.: *Mass spectrometry for the novice*, CRC Press, Boca Raton, F. L., USA, 2013.
- Reinmig, M. C., Warnke, J., and Hoffmann, T.: Identification of organic hydroperoxides and hydroperoxy acids in secondary organic aerosol formed during the ozonolysis of different monoterpenes and sesquiterpenes by on-line analysis using atmospheric pressure chemical ionization ion trap mass spectrometry, *Rapid Commun. Mass Sp.*, 23, 1735–1741, doi:10.1002/Rcm.4065, 2009.
- Shu, Y. G., and Atkinson, R.: Rate constants for the gas-phase reactions of O₃ with a series of terpenes and OH radical formation from the O₃ reactions with sesquiterpenes at 296±2 K, *Int. J. Chem. Kinet.*, 26, 1193-1205, 1994.
- Yao et al.: Role of stabilized Criegee intermediate in secondary organic aerosol formation from the ozonolysis of alpha-cedrene, *Atmos. Environ.*, 94, 448–457, 2014.
- Zhao, Y., Wingen, L. M., Perraud, V., Greaves, J., and Finlayson-Pitts, B. J.: Role of the reaction of stabilized Criegee intermediates with peroxy radicals in particle formation and growth in air, *Phys. Chem. Chem. Phys.*, 17, 12500–12514, doi:10.1039/C5cp01171j, 2015.