Response to Reviewers

Referee 1

The manuscript by Luo et al. characterizes the formation of HOMs from Δ3-carene ozonolysis in two different chamber environments, with and without OH scavenger and at different temperatures and relative humidities. It also includes a box modeling of the formation process of various HOMs from Δ3-carene oxidation.

The paper is well written, nicely structured and provides a good overview over the chemical mechanisms involved and the experimental results. It fits the scope of ACP and I thus recommend publication after addressing the following minor comments.

Minor comments:

1. line 123: you mention “other untypical reactions”, but you do not give an example or reference. Can you add an example and/or reference to shed more light on these untypical reactions?

Response: An example and the corresponding reference have been added in Lines 126-127.

2. line 180: You use the acronym PRAM already two times before defining it. Can you define it at the first occurrence in line 173?

Response: Revised.

3. line 212: do you have an explanation, why the there are much more C5 molecules formed for α-pinene ozonolysis, compared to Δ3-carene?

Response: C_5 molecules are likely fragments resulting from specific reaction pathways in the ozonolysis of α-pinene but we unfortunately still lack a good enough mechanistic understanding of the reaction steps in Δ^3-carene and α-pinene to be able to pinpoint exactly how the C_5 molecules form. Given that our study has already demonstrated distinct differences in HOM formation between these two systems, this finding further highlights the unique chemical behaviours of each monoterpene in similar oxidation conditions.

4. line 243/Figure 4: Can you briefly discuss the much earlier flattening of the RO2 curve compared to the traces for the closed shell products?

Response: RO_2 radicals are more reactive and consequently have shorter lifetimes. Due to their high reactivity, they will stabilize sooner since they cannot accumulate for as long as closed-shell species can. This rapid stabilization is a direct result of their inability to persist over extended periods, unlike the more stable closed-shell species.

5. line 246/Figure 4: You state that “C10H14O9 began to rise immediately once C10H15O10 was formed” and that C9H12,14O9 and C10H16O9 “started to increase ~3 min later”. Can you indicate either in text and/or in the figure, how you did determine these rise-times. Is it a 50% rise like in the cutoff estimation for CPCs, or 10 %, or another method?

Response: To determine the appearance time in this study, we first calculate the average value and standard deviation of the background for each species. Following the addition of precursors, if the signal difference at time t (X_t) compared to the background level (X_b) was significantly greater than the standard deviation and average value during the background measurement (X_t-X_b > std & X_b), we designated the time point before (t-1) as the appearance time for that species. We chose not to use a 50% or 10% rise like a cutoff estimation for CPCs in our estimations because increases in RO_2 and HOM are influenced by volatilities in addition to formation rates. Therefore, some species may form more rapidly and start increasing at an earlier stage; however, if they are semi-volatile, they might require more time to stabilize or may not stabilize at all during the experimental period. Our objective was to gain insights into the formation pathways based on the appearance time; thus, using a cut-off method would indeed complicate the interpretation. We appreciate this point being raised, as it has prompted us to clarify our definition of appearance time in the manuscript. We have now added explanation on determining appearance time in Lines 245-246 of the discussion section.

6. Figure 4: Does normalized signal mean normalized to the reagent ions? You use a variety of normalizations throughout the paper (be it to certain species or time steps), so I would recommend to always clearly stat to what you normalize to. You might also add the unit ncps to indicate normalization to reagent ions.

Response: Yes, in most cases, the normalized signal refers to normalization relative to the reagent ions. However, you raised a valid point regarding the variety of normalization methods employed in specific analyses. To clarify this, we have added an explanation in Section 2.1, Lines 84-86. Additionally, we have specified the normalization methods used in Figures 4, 5 and S8, which are the figures that employ different normalization techniques.

7. line 293: You write "Assuming all dimers are ELVOCs at 20 ºC,…". As it is currently formulated, you assume all dimers are ELVOCs in order to prove that the seven dimers that are not C20H32O11 are ELVOCs, which doesn't make sense to me. To my understanding you would only need to assume that C20H32O11 is an ELVOC at 20°C and then you can use your method of normalized ratios to show that all seven other considered dimers do behave similarly and can thus also be considered ELVOCs, which would then be the conclusion and not an assumption.

Response: It appears there was a misunderstanding in our initial expression. We assumed that all dimers are ELVOCs and have calculated the normalized ratio of each dimer to $C_{20}H_{32}O_{11}$. The range determined by those dimers provides a reference when evaluating the relative volatilities of other HOM monomers, because it includes uncertainties associated with this method and the potential differences in formation pathways. To avoid misunderstanding, we rephrased the explanation on the determined range resulting from those dimers in Lines 303-304. Our objective was not to prove that the all dimers are ELVOCs, but rather to illustrate that many of the monomers exhibit higher volatility. Even if some dimers were not ELVOCs, it would not substantially impact this analysis.

8. line 293: For this paragraph I would again recommend to more clearly discuss what "normalized" means, since there are several different normalizations involved, which are not properly separated in the text. Especially in the formulation "the normalized ratios of the eight largest dimers to C20H32O11" normalized could be interpreted as normalized to C20H32O11,

but in the caption to figure 5 it means normalized to the 10 minute timestamp, which is not mentioned in the main text. Please reformulate this in order to avoid confusion.

Response: We have provided additional explanation regarding the normalized ratios in the main text of the manuscript (Lines 299-301, Page 13).

9. Figure 5: Panel a is rather squeezed a bit in the y-axis direction. Can you reduce the y axis range a bit, so that the change in the traces becomes more visible?

Response: Revised.

10. Figure 5: In the caption you state that “Larger normalized ratios indicate accumulation in the chamber over time, i.e. a higher volatility”, however in the main text you also mention that “it is crucial to recognize that also differences in the formation pathways can influence the ratios.” So the “i.e” in the caption is a bit too strong of a statement, as it neglects the formation side of things.

Response: We have replaced ‘i.e.’ with ‘which is likely indicative of higher volatility’ in the text. This change allows for extra discussion of other potential factors in the main text.

11. Figure 6: These three different shades of red are barely distinguishable. I would recommend to use different colors, like red, orange and blue for the three different temperatures.

Additionally, the colorscale in panel d is confusing, as it is unclear how it relates to fraction and temperature. I would suggest to use red, orange and blue again in panel d, but indicate the fraction with color saturation, so that the three different temperatures are visually distinguished by base color.

Response: Revised.

12. line 400: Thank you for also adding data that might not lead to a final conclusion yet, or might be ambiguous. As you wrote, it might stimulate further research into the specific question and is thus important to report.

Response: Thanks for your positive feedback on including preliminary and ambiguous data. We agree that it's essential to present such information, as it not only provides a complete view of our research but also invites further investigation within the scientific community.

13. Figure 9: Add units for Δ3-carene VMR.

Response: Added.

14. line 447: Your results are different to Quéléver et al., 2019, but similar to Simon et al. 2020, who also report an increase in C20/C10 ratio with falling temperatures for the T-range in question. I would add this in the discussion.

Response: We have added the discussion in Section 3.3 (Lines 353-355) and Section 4 (Lines 460-461).

SI part:

15. line ~109: Can you clarify that in batch mode you did not add any flow during the experiment to the teflon bag, but due to sampling flows the volume of the teflon bag gets smaller over the curse of the experiment. Can you give an estimate of shrinkage over the duration of the experiment?

Response: We have added the clarification in Lines 108 and 110-111. The estimated volume fraction used in the chamber bag was 50% for each experiment, which has also been added into the text.

16. line 133: "species" instead of "specie"

Response: Revised.

17. line 137: Can you clarify a bit more how you estimated the 1e10 number for C in this study? (via the reaction time with 1/kt and the reaction rate constants estimated in Ehn et al. 2014?)

Response: In this study, we only estimate the calibration factor based on previous studies. To clarify this, we have added an explanation in the text as 'in this study, a value of $C=1\times10^{10}$ cm^{-3} was used based on typical values reported earlier (Ehn et al., 2014; Jokinen et al., 2012; Jokinen et al., 2014).'. For this reason, we provide only a tentative approximation of HOM concentrations, acknowledging a substantial degree of uncertainty—by at least a factor 3—as highlighted in the SI (Page 8, Lines 137-139) and also in the main text (Page 17, Lines 386-387). However, our conclusions are based primarily on results where we compare changes in concentrations/yields between different experimental conditions while sampling with the same instrument and same instrumental settings. For example, we estimated the relative HOM yields from carene and α-pinene ozonolysis (for which many more HOM yield estimates are available) under identical conditions and using the same instrumentation. This principle similarly applies to yield comparisons at different temperatures; despite absolute values' uncertainties, we believe that the relative variations in yields still offer meaningful insights.

18. line 152: Can you briefly describe what exactly was modeled here in order to get kloss and what input parameters were used for the model?

Response: The concentrations of VOC, oxidants, and HOM were monitored continuously. The concentration of HOM in the chamber is determined by their formation and loss rates. HOM formation primarily results from the oxidation of VOC, for which we know the reaction rates. However, the loss rate to the wall (k_{loss}) is unknown. We used a series of k_{loss} values as inputs to the model. By comparing the modelled HOM concentrations with the measured HOM concentrations, we can determine the optimal k_{loss} value.

19. line 164: How does the d(HOM)/dt term compare to the kloss*HOM term for your yield estimations? Can you indicate the time periods that you used to estimate the yield in the experiments and give a range of d(HOM)/dt vs kloss*HOM. It looks like the importance of the d(HOM)/dt term goes down over time.

Response: We estimated the HOM yield using data from approximately 20 minutes to 3h for each experiment. The range of d(HOM)/dt versus kloss*HOM was within the range from e−2 to e−4. Over time, the d(HOM)/dt term decreased as the sinks for HOMs increased and the sources decreased dramatically. Thus, the loss term was the primary factor in our estimation of HOM yields.

20. Figure S5: I would change the y-axis label to "Intensity change due to CO addition" as this describes more directly what is shown in the figure.

Response: Changed.

21. Figure S8: Here the word normalized is a bit confusing again: the data “looks” like being normalized to reagent ions, but as there is no mention of normalizing to the reagent ions, but instead mentioning of a “reference dimer”, the text somehow suggests that the data was normalized to said reference dimer. So I would change the y-axis label from “Normalized signal” to “Signal normalized to reagent ions” or something similar if this is what you are showing. Since this affects multiple figures, maybe you can also just write “Intensity (ncps)” and explain that ncps means normalized to reagent ions in the corresponding figure captions. The main point is that there is no confusion potential as to what you normalize to.

Response: Similar to the response to Comment 5, we have now included an explanation in Section 2.1, Lines 84-86, to clarify the general meaning of 'normalized signal' in our manuscript. For analyses where different normalization methods were employed, we have specified these methods in the corresponding figure captions or within the text itself.

22. Figure S10: Can you add the RH values in the axis labels for panels d and e so that the reader directly knows which RH values are compared. It might be clear for the authors which experiment name corresponds to which conditions, but much less clear to the reader.

Response: Added.

23. Figure S13: You do not discuss this figure in the main or SI text. Can you either add some discussion or remove the figure? You mention SOA yields in your introduction, but do not come back to them later in the text, although you have a figure of modelled SOA yields in the SI. You write in line 97 in the SI that your study “exclusively” focusses on HOM formation in the gas phase, while other studies focus on particle phase properties of the Δ3 carene system, but Figure S13 (and also Figure S12) somewhat contradicts that. You could exchange the “exclusively” for “mostly” and also briefly discuss Figure S13 in a similar fashion as you discuss Figure S12. Can you compare the modelled SOA yields to measured ones, or is this the focus of one of the other studies? (It would be perfectly fine if the main SOA yield discussion is part of another study, however, with Figure S13 you make the reader curious also about SOA yields and the corresponding measurements, so you should at least mention where the reader can find this discussion)

Response: Thanks for pointing this out. We have removed the Figure S13 to not cause any confusion.

24. Figure S14: You do not mention what the color of the bars mean. (C number, but could you add that to the caption?)

Response: Added.

Referee 2

General comments:

This paper presents new experimental results elucidating the product distribution of highly oxygenated molecules from ozonolysis of d-carene, combined with a box model to help determine oxidation mechanisms and interpret changing yields with temperature. Particularly because of its differences to the more widely studied a-pinene ozonolysis, this study can add valuable new experimental constraints to our understanding of mechanistic reasons for varying biogenic SOA formation. There are some opportunities to improve the figures and language, which I elaborate below. I recommend publications after minor corrections.

Specific comments:

1. p.3 line 86-87: suggest to reword the phrase "meaning the sources and sinks ... each experiment", current phrasing is a bit confusing. Here you are explaining the different between batch mode and continuous chamber operation. How about something like, "meaning all reagents are injected in a single batch at the start of the experiment and products accumulate progressively" or similar? It's the idea of sources and sinks "accumulating" that doesn't feel clear to me.

Response: We have now rephrased the sentence as 'meaning that all reagents are injected in a single batch at the start of the experiment and products accumulate progressively'.

2. p. 4 line 91: do you mean that the same instruments were used as in the COALA chamber? Specify, or briefly discuss key differences, maybe refer to SI.

Response: The same instrument types were used, but they were not the exact same instrument. We have clarified this distinction in Lines 93-94 of the manuscript.

3. Line 94: Briefly describe the Bianchi 2019 criteria. Does this mean >6 O atoms?

Response: There are three criteria in Bianchi at al., 2019: (1) HOM Are Formed via Autoxidation Involving Peroxy Radicals; (2) HOM Are Formed in the Gas Phase under Atmospherically Relevant Conditions; (3) HOM Typically Contain Six or More Oxygen Atoms. We have now added the brief description in the text.

4. Line 120: "two of the RO can recombine" – is this really a recombination process, or does the ROOR just persist rather than cleaving the O-O bond?

Response: There was never an ROOR that could "persist". Instead, these compounds typically form an ROOOOR, which subsequently decomposes into RO + O_2 + RO (Valiev et al., 2019). The subsequent dimer formation process likely involves a recombination reaction that includes an intersystem crossing from the triplet to the singlet surface within the complex of two alkoxy radicals (RO···OR′).

5. p. 7 discussion around lines 160-165: I think it would be helpful if you show & label SOZs and 3-caronic acid in your Scheme 1. Also maybe include branching ratios / yields used in the model on the figure

Response: Our aim with Scheme 1 was to illustrate the primary steps in the formation mechanism of RO_2 radicals from ozone and OH-initiated oxidation of Δ^3-carene, as this step is crucial for subsequent HOM formation. While the suggestion from the reviewer is valid, we opted not to do this for a few reasons. Firstly, the model lumps certain pathways together, meaning that not all the explicit steps in Scheme 1 are included. Second, the model branching ratios includes both steps and yields that are assumptions, and if we include them in the figure, they may be perceived as results from this study, which we prefer to avoid.

6. p.8 around line 194: Maybe it's a good idea to mention the key relevant conditions from Li 2019, e.g. O3 concentration, temperature, RH?

Response: We have updated the manuscript by adding the necessary information and rephrasing relevant sentences for readability.

7. p. 9 around line 198: does this mean more auto-oxidation steps are possible in d-carene than in a-pinene? Or just different product distribution?

Response: Based on our current findings, we cannot conclusively determine the underlying reasons. Further studies, both experimental and computational, are essential to thoroughly investigate the observed differences in HOM distribution.

8. Line 199: “exclusively abundant” -> “only found” : if this is indeed what you mean here, this phrase would be clearer to me

Response: We detected C_9 species in the α-pinene ozonolysis system as well; however, they constituted only a minor fraction of the detected HOM. In contrast, these C_9 species were among the most dominant peaks in the Δ^3-carene system. Therefore, the term 'only found' does not accurately describe the difference. We changed the term to “were only abundant in”.

9. Line 200-201: explain m and n notation.

Response: Added.

10. Around line 210: Suggest to add some discussion of Figs 2b – 2e here before moving on?

Response: Thank you for your comment. The other panels were discussed in detail later in the manuscript. We structured the discussion to ensure a clear and logical progression of the information, addressing each panel at the appropriate point.

11. p.10 around line 217: why would ring-opening not be dominant in OH oxidation also?

Response: OH oxidation can also lead to ring-opening, but this requires bimolecular reactions to take place and is not the initial step as in ozonolysis. Consequently, ring opening does not sufficiently explain the larger contribution of C_9 compounds in the NO_3 and O_3 oxidation processes. Therefore, we have removed this hypothesis from our discussion and stated as ‘The reason why the larger concentration of C_9 species in Δ^3-carene ozonolysis remains unexplained based on our results.’ instead. Dam et al., 2022, suggest that the significant presence of C_9 compounds in the NO_3-carene system may be due to a pathway involving the generation of a secondary double bond followed by NO_3 addition. Unfortunately, due to the absence of quantum calculations in this study, we are unable to propose a definitive hypothesis for the ozonolysis system.

12. p.12 Fig. 4: Mention what the red dashed line is, I guess the only signal attributed to a radical?

Response: The red line is dashed to highlight that it is a radical species while other solid lines are closed-shell HOM. We have included the reason in the caption.

13. p.13 line 305: what does “transition from semi-volatile to low volatility” mean? a certain gas to particle ratio?

Response: With this we referred to the shift in behaviour of molecules from behaving like SVOCs to behaving like LVOCs. In our study, this would mean that the curves in Figure 5 (b) decrease from higher values down to nearly 1.

14. p.14, Figure 5: blue and yellow lines are not visible on panels b, c, and d. In caption, list panel label before each description, not at end.

Response: The panel labels have been adjusted, and also in other figures. It should be noted that we didn’t inlcude the yellow and blue lines in panels (b)-(d); we have included only the purple and red lines, as these correspond to the two specific species highlighted in the main text.

15. p.15 around line 342: Does any in this list of papers have any information about the stability of different ROORs for different MT precursors? How much do they range? I could imagine not much, because the R chain lengths are ~ the same, but does a different degree of oxidation matter to how stable the ROOR product channel is? Or are these differences more likely to be driven by the exact arrangement of the closest few atoms to the O-O bridge?

Response: None of the referenced papers provide information on the stability of different ROOR products derived from various MT precursors. As they are closed shell species, and we expect them all to be stable in the gas phase under the times relevant for these experiments, though in particle phase that might be different. The stability of these ROOR products in peroxy radical self- and cross-reactions largely depends on their oxidation degree, which influences the reaction pathways leading to various stable intermediates (Hasan et al., 2020). Furthermore, the stability and electronic properties of peroxides are significantly affected by the specific atomic arrangement around the O-O bond, where orbital interactions play a crucial role. The local geometrical configurations are essential in determining their stability (Khursan & Antonovsky, 2003).

16. Around line 343: List the key differences between your and Quelever's experimental and instrument settings

Response: The experimental differences include variations in VOC loadings and O_3 levels. Regarding instrumentation, to the best of our knowledge, our setup included an L-TOF with higher resolution, while the Quelever's study utilized an H-TOF with lower resolution. The specific settings, particularly voltages, were not provided in Quelever's paper, preventing a direct comparison. We have included these potential differences as examples in the text, although we could not detail all of them explicitly.

17. p.18 Figure 8: Recommend to make model lines thicker in panels d, e, f. I didn't see at first until reading further than the C10H16O7 model line goes down after CO injection, because it's buried behind the pink and blue measurements points. Also suggest to add a vertical line indicating CO injection, or mention the time in the caption

Response: Revised and the time of CO injection has been added in the caption.

18. p.19 around line 414: Can you speculate another reason that C10H16O7 does not decrease? Is there another source? It does seems to "react" to the injection, dipping in concentration before climbing back up.

Response: Volatility may explain these observations. As concluded in Section 3.2, HOM monomers with fewer than 9 oxygen atoms are likely semi-volatile. Additionally, the temporal behaviour of $C_{10}H_{16}O_7$, which continued to increase even 5 hours after the experiment's start when most HOM had already stabilized, exemplifies typical semi-volatile species behaviour in the chamber. The introduction of CO, which inhibits OH oxidation (the main source of $C_{10}H_{16}O_7$), led to an immediate decrease in its levels. However, due to its semi-volatility, $C_{10}H_{16}O_7$ could gradually be emitted from the chamber walls, subsequently accumulating in the gas phase.

19. Figure 9: Observed molar yields seem to be missing on this plot. Should definitely include

Response: Added.

20. p.20 line 434: absence -> absence and presence, right?

Response: Yes. We have reformulated the sentence.

21. Line 443: yes, warrants further investigation, but your observed decrease at lower temps matches your model well, right? Say something about this

Response: We have added a sentence in Lines 455-457 indicating the good agreement between the observed and modeled trends concerning temperature decreases.

Technical corrections:

22. p.2 line 33: hydroxyl radical (OH), or nitrate radical (NO3)

Response: Revised.

23. line 38: suggest to remove “a vital class of BVOCs”

Response: Removed.

24. p.3 line 75: suggest to change “set-ups” to “chambers”

Response: Revised.

25. p.5 line 124: suggest “unique to particular RO structures”

Response: Revised.

26. line 130: “both” -> “either”; line 131: “and” -> “or” & suggest to omit “as well”

Response: Revised.

27. p.7 line 153: researches -> research

Response: Revised.

28. line 167-169: “ The first-generation ... that is assumed to be ... and three other isomers, all C10 RO2, that ...”

Response: Reformulated.

29. line 172: reacting -> reacts

Response: Revised.

30. Line 182: Zenodo link missing?

Response: Uploading to zenodo are typically done once papers are accepted, so the link will be added in the end.

31. p.9 line 208: (0A) should probably be (20A)?

Response: Indeed, it is 0A.

32. p.11 line 235: “they have” -> “the product has”

Response: $C_9H_{12,14}O_9$ are two HOM, so the pronoun should be ‘they’.

33. line 239: “undetermined” -> “unclear”

Response: Revised.

34. p.13 line 29: identity condense behavior -> identical condensation behavior?

Response: Revised.

35. p.15 line 334: spell out CS

Response: The abbreviation CS is now defined at its first occurrence in Line 287.

36. line 353: omit “could”

Response: Omitted.

37. p.20 line 452: oxidation -> ozonolysis

Response: Revised.