

We thank the reviewer for the helpful comments on our manuscript. The comments are greatly appreciated. We have addressed all the comments and believe that the revisions based on the comments help improve the quality of our manuscript. Below please find our responses to the comments one by one and the corresponding revisions made to the manuscript. The original comments are in italics. The revised parts of the manuscript are in blue.

Revision comment:

In the revision, the authors have addressed some of my comments and improved the manuscript quality overall. However, there are a few remaining issues that were insufficiently explained or discussed, as detailed below.

Initial comment #1:

The Hyttinen et al. (2017) study was to explain why less oxidized HOMs are not well detected with NO₃-ionization. Thus, it is inappropriate to use this study to debate whether underestimation of HOM yields is possible. HOMs with high oxygen numbers from both alpha-pinene ozonolysis and alpha-pinene + OH oxidation have more than two hydrogen bond donor functional groups. Though, the sensitivities are dramatically different. The author further argued that the underestimation of HOMs from alpha-pinene + OH was mainly attributed to the steric hinderance in forming HOM-nitrate cluster for HOM with bicyclic structures and thus not common for all HOMs. First of all, is there a reference study for this point?

Response:

This steric hinderance for nitrate ionization was mentioned on the 6th paragraph of Section 3.2 in the Supplement of Berndt et al (2016). In the revised manuscript, although we have cited this paper in the same sentence, we have further clarified this as follows in **line 503**:

“Second, although underestimation of certain HOM RO₂ formed from α-pinene+OH reaction has been reported (Berndt et al., 2016), such underestimation was mainly attributed to the steric hinderance in forming HOM-nitrate cluster for HOM with bicyclic structures (C₁₀H₁₇O₇•) ((Berndt et al., 2016), **Section 3.2 of the Supplement therein**) and thus **such underestimation is** not common for all HOM.”

Why is there a steric hinderance for nitrate ionization, but not acetate ionization?

Response:

As mentioned on 7th paragraph of Section 3.2 in the Supplement of Berndt et al (2016), the original interpretation of the reason is as follows: “The RO₂·CH₃COO⁻ clusters are all more strongly bound than the corresponding RO₂·NO₃⁻ clusters, both in an absolute sense, and relative to the neutral acid-ion cluster. Even the presence of a single peroxide or carboxylic acid group is enough to make the binding of a RO₂ radical to acetate competitive with that of acetic acid. This explains why acetate CIMS is highly effective at detecting products of both OH- and O₃-initiated autoxidation. The binding of RO₂ radicals with two H-bond donating functional groups to CH₃COO⁻ is more than 10 kcal/mol stronger than the binding of acetic acid to CH₃COO⁻. Thus, acetic acid is not able to compete with the multiply substituted RO₂ at any reasonable concentration ratio, explaining the lack of dependence of the detection efficiency of autoxidation products on the acetic acid concentration, see results in Fig. 3. As expected, the relative sensitivity of acetate CIMS to carboxylic acid groups compared to OH or OOH groups is also much

larger than that of nitrate CIMS. If OH – initiated autoxidation has a larger probability of forming carboxylic acid groups than O₃ – initiated autoxidation, this may also help explain the differences in relative sensitivities toward the two groups of products.”.

More importantly, the authors stated that bicyclic structures are not common for all HOMs. But in Schemes 1 and 2 in this manuscript, I see a lot of bicyclic structures.

Response:

We apologized for the ambiguity of this sentence. In fact, we would like to state that underestimation attributed to the steric hinderance in forming HOM-nitrate cluster for HOM with bicyclic structures (C₁₀H₁₇O₇•) is not common. We revised this sentence in [line 505](#) in revised main text:

“...with bicyclic structures (C₁₀H₁₇O₇•) ((Berndt et al., 2016), Section 3.2 of the Supplement therein) and thus [such underestimation is](#) not common for all HOM.”

Although some HOM contain bicyclic structures in Scheme 1 or Scheme 2, most bicyclic products contain less than 6 oxygen atoms. They are not HOM RO₂, and as early generation RO₂, they can undergo further autoxidation to form HOM. Also, even if C₁₀H₁₇O₇• in Scheme 1 has bicyclic structures, the C₁₀H₁₇O₇• RO₂ are less intensity and not dominant in total C₁₀H₁₇O_x family as shown in Fig. S9.

Overall, we agree that some HOM from both α-pinene ozonolysis and α-pinene + OH oxidation have different sensitivities in NO₃⁻-CIMS as reported by Berndt et al. (2016). However, the difference was mostly attributed to bicyclic structures of some HOM e.g. C₁₀H₁₇O₇• formed in OH oxidation. Such difference is not applicable to HOM from OH-addition and HOM from OH H-abstraction. It is reasonable to expect a generally similar sensitivity for HOM in this study by given three reasons in our last response.

In the revised manuscript, we have further added a note in the “HOM yield” section in [line 562](#).

“We further note that these HOM yields may be subject to uncertainties due to the assumption that HOM have the same sensitivity as H₂SO₄ as we discussed in Sect. 3.3.3. As mentioned above, our previous study showed that using an unified sensitivity of H₂SO₄ only leads to a maximum uncertainty of a factor of two by comparing the condensation HOM and corresponding increase of aerosol mass (Pullinen et al., 2020).”

Initial comment #2:

With the amended chemical reactions, it should be realized that the yields of different functional groups (ROH, R=O, and ROOH) are highly structure dependent. Carbonyl yield + alcohol yield does not necessarily equal to 1; the values of alpha and beta largely vary with structure; alkoxy radical fate also largely affects the yields. My whole point is, with such complexity, deriving these equations (Eq. 2-8) is not very meaningful.

Response:

We agree that the yields of different functional groups (ROH, R=O, and ROOH) are highly structure dependent. As HOM in this study is likely formed via a 6-membered carbon ring opening as discussed below, most HOM RO₂ are likely primary or secondary RO₂ as shown in Scheme 1 and Scheme 2 and RO₂ distribution in Fig. S9. For primary and secondary HOM RO₂, although carbonyl yield and alcohol yield does not necessarily equal to 1, they are most likely to be 1 according to Jenkin et al (2019). With these equations, we can estimate carbonyl fractions formed via C₁₀H₁₇O_x• under reasonable assumption. At the same time, we have estimated the uncertainty of the value.

We added discussion in [line 206](#) of the revised main text:

“As HOM in this study is likely formed via a 6-membered carbon ring opening as discussed below, most HOM RO₂ are likely primary or secondary RO₂ as shown in Scheme 1 and Scheme 2 and RO₂ distribution in Fig. S9. For primary and secondary HOM RO₂, although carbonyl yield and alcohol yield does not necessarily equal to 1, they are most likely to be 1 according to Jenkin et al (2019). With these equations, we can estimate carbonyl fractions formed via C₁₀H₁₇O_x• under reasonable assumption.”

Initial comment #4:

Part of the response is confusing. I thought that the authors suggested that the HOMs from the OH abstraction channel is through RO isomerization, not RO₂. Then, “Y1 is the fraction of primary RO₂ undergoing autoxidation to form highly oxygenated C₁₀H₁₅O_x” means that Y1 is nearly zero?

Response:

Y1 refers to the fraction of primary RO₂ undergoing auto-oxidation to form highly oxygenated C₁₀H₁₅O_x•, no matter whether they undergo direct auto-oxidation or via RO isomerization and further auto-oxidation. In the revised manuscript, we have added a note to avoid potential confusion as follows:

“Y₁ is fraction of primary RO₂ undergoing auto-oxidation to form highly oxygenated C₁₀H₁₅O_x•, **no matter whether they undergo direct auto-oxidation or via RO isomerization and further auto-oxidation.**”

Considering the additional step to form RO from RO₂+RO₂, Eq. R1 is wrong. What are the ranges of k_{nu1_1}, k_{nu1_2}, and k[NO] anyway?

Response:

In this study, the dominant consumption of RO₂ is mainly through RO₂ with NO channel (Fig. S3 in Supplement). Therefore, Eq. R1 is tenable even if considering the reactions of RO₂+RO₂ to form RO. Unfortunately, both k_{nu1_1} and k_{nu1_2} are unknown. That's why we assume them in the calculation. When k_{nu1_1} is higher than k_{nu1_2}, one can get the ratio of [C₁₀H₁₅O_x•] to [C₁₀H₁₇O_x•] increases with increasing NO concentration. k[NO] are in the range 2 s⁻¹ to 3 × 10⁻² s⁻¹.

“From this, we infer that the average reactive rate of C₁₀H₁₇O_x• at high NO is higher than that at low NO, which finally result in the increases of C₁₀H₁₇O_x• consumption. This inference is supported by the higher relative contribution of C₁₀H₁₇NO_x at high NO (36.3%) than at low NO (16.1%) in Fig. 2.”

Wouldn't this statement work the same way for C₁₀H₁₅O_x•?

Response:

We realize that this sentence did not provide extra support to the discussion, so we decide to delete this sentence. At the same time, we move the discussion of NO dependence of the original manuscript to Sect. 3.3.3 the **line 436** of revised main text:

“The NO_x dependence for C₁₀H₁₅O_x•/C₁₀H₁₇O_x• may be attributed to the differences in their reactivity. One explanation for the NO_x dependence is that the autooxidation of C₁₀H₁₅O_x• RO₂ radicals may be faster than that of C₁₀H₁₇O_x• RO₂ radicals, which leads to the lower concentration of C₁₀H₁₅O_x• **at high NO** and **thus** higher sensitivity to NO concentrations. Ratios of C₁₀H₁₆O_x(R-OH/OOH)/C₁₀H₁₅O_x• can be derived of 0.47 and 0.02 at low and high NO, respectively. The decrease of C₁₀H₁₆O_x(R-OH/OOH)/C₁₀H₁₅O_x• at high NO compared to low NO was more evident than the decrease of C₁₀H₁₈O_x/C₁₀H₁₇O_x•. Theoretically, though, they should be similar. The difference may be attributed to the shift in C₁₀H₁₅O_x• distribution with different number of O, as evident in Fig. S6, and different isomers at high NO compared to low NO. At high NO there might thus be more C₁₀H₁₅O_x• that react slower with HO₂ or have a lower branching ratio forming ROOH in RO₂+HO₂, which depends on the explicit RO₂

structure, or have a lower yield forming ROH in RO_2+RO_2 .”

Initial comment #5:

Thanks for the analysis regarding secondary chemistry. It appears that secondary chemistry has increased significantly after ~ 5 min. I wonder if the same analysis is performed comparing first 5-min vs. 15-min, what contributions would be for the OH-abstraction chemistry in limonene+OH oxidation. With the 15-min analysis, the authors suggest that $C_{10}H_{15}O_x$ -derived HOMs contribute 41-42% of total C_{10} -HOMs. Would this number be lower within the first 5 min?

Response:

We guess that the reviewer refer to Fig. S9b, where the significant change at ~5 min at high NO (Fig. S9b) is attributed to the uncertainty of measured limonene consumption. Actually, as shown in Fig. S9, the importance of secondary chemistry within the first 15 min did not change significantly based on both the experiment data or MCM simulation.

We have clearly shown that secondary chemistry is not important in the first 15 min. At the first 5 min, the contribution of $C_{10}H_{15}O_x$ -derived HOMs in total C_{10} -HOMs are 41.1% at low NO, and 48.3% at high NO. Note that there would be higher uncertainty in the very earlier stage of the experiments. Considering the uncertainty, the contribution of $C_{10}H_{15}O_x$ -derived HOMs in total C_{10} -HOM in the first 5 min is similar to the contribution of the first 15 min.

The caption of the Fig. S9 has been revised as follows:

“The large change in panel (b) **at ~5 min** results from the large measurement uncertainty of low accumulated limonene consumption measured by PTR-ToF-MS in the first few minutes.”