

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.

Overall comment:

This work by Luo et al. examined HOM formation from limonene + OH and highlighted the importance of the H-abstraction pathways, in addition to the well-known OH-addition pathways. The main conclusion is well supported by the observations of C₁₀H₁₅O_x-RO₂ as well as their termination products. These results are also in line with the authors' recent publication on H-abstraction derived HOM for alpha-pinene + OH chemistry (Shen et al., 2022 Sci. Adv.). Therefore, I believe that the underscored H-abstraction pathways for monoterpene + OH chemistry are important and should be considered in future chemical mechanisms. However, there are a number of major issues that need to be addressed before consideration for publication, as discussed below.

Detailed comments:

1. Estimation of HOM yields. This work used NO₃-CIMS to estimate HOM yields and relative contributions of the H-abstraction vs. OH-addition pathways, assuming unified sensitivity for all the HOMs products. However, this approach may have large uncertainties. For example, Berndt et al. (Nature Comm. 2016, 7, 13677) demonstrated that NO₃-CIMS could underestimate HOM formation from OH-addition pathways for alpha-pinene and beta-pinene. This might also be the case for limonene. If this is true, then the contribution of OH-addition to limonene HOMs as well as the total HOM yields could be underestimated. Better constraints on these aspects are needed.

Response:

We thank the reviewer for the supportive remarks. Regarding the sensitivity, admittedly, using unified sensitivity may lead to uncertainties. Currently, an absolute calibration using HOM standards is not possible mainly due to the difficulty to synthesize pure HOM and unclear chemical structures of many HOM.

However, we think that it is reasonable to expect a generally similar sensitivity for HOM in this study for the following reasons. First, Hyttinen et al. (2017) found that the increase in binding energy with NO₃⁻ for molecules with an additional hydroxyperoxy group to two hydrogen bond donor functional groups is small for HOM formed in cyclohexene ozonolysis. As HOM in this study generally contain more than two hydrogen bond donor functional groups, their sensitivity is expected to be similar. We used a unified H₂SO₄-based calibration coefficient for HOM, which is commonly used to calibrate NO₃⁻-CIMS (Kirkby et al., 2016; Jokinen et al., 2015; Rissanen et al., 2014; Ehn et al., 2014). Second, the underestimation of total HOM RO₂ concentrations from the OH radical reaction using nitrate ionization while not for HOM formed by ozonolysis reported by Berndt et al. (2016) is mostly contributed by a single HOM-RO₂ C₁₀H₁₇O₇•. The reason for the difference in sensitivity between HOM formed in two oxidation scheme was attributed mainly to the steric hinderance in forming HOM nitrate cluster for HOM with bicyclic structure (C₁₀H₁₇O₇•). In our study, we found the significance of C₁₀H₁₅O_x•-related product at all oxygen content and most of them were contributed by closed-shell products with number of oxygen atom great than 8, indicative of more H-donating functional groups (Fig. S6 in revised Supplement). And the presence of NO particularly at high NO leads to ring-opening reactions as shown in Scheme 1.

45 Therefore, the HOM products from OH addition in this study are likely to form stable clusters with nitrate and thus have similar sensitivity with HOM formed via H-abstraction in nitrate CIMS. Third, our previous study showed that using an unified sensitivity of H₂SO₄ only leads to an uncertainty of a factor of two by comparing the condensation HOM and corresponding increase of aerosol mass (Pullinen et al., 2020).

50 Nevertheless, in the revised manuscript, we added discussion regarding the influence of the sensitivity in **line 486** in the revised main text:

“Currently, an absolute calibration using HOM standards is not possible mainly due to the difficulty to synthesize pure HOM and unclear chemical structures of many HOM. However, we think that it is reasonable to expect a generally similar sensitivity for HOM in this study for the following reasons. First, Hyttinen et al. (2017) found that the increase in binding energy with NO₃⁻ for molecules with an additional hydroxyperoxy group to two hydrogen bond donor functional groups is small for HOM formed in cyclohexene ozonolysis. As HOM in this study generally contain more than two hydrogen bond donor functional groups, their sensitivity is expected to be similar. We used a unified H₂SO₄-based calibration coefficient for HOM, which is commonly used to calibrate NO₃⁻-CIMS (Kirkby et al., 2016; Jokinen et al., 2015; Rissanen et al., 2014; Ehn et al., 2014). 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•) and thus not common for all HOM. In our study, we found the significance of C₁₀H₁₅O_x•-related product at all oxygen contents, particularly for closed-shell products with number of oxygen atom great than 8, indicative of more H-donating functional groups (Fig. S6 in revised Supplement). This indicates that the significance of C₁₀H₁₅O_x• related products is not affected by the detection sensitivity, which would mostly affect the sensitivity of less oxygenated compounds. And the presence of NO particularly at high NO leads to ring-opening reactions as shown in Scheme 1. Therefore, the HOM products from OH addition in this study are likely to form stable clusters with nitrate and thus have similar sensitivity with HOM formed via H-abstraction in nitrate CIMS. Third, 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). If for some currently unknown reason C₁₀H₁₇O_x•-related products had higher sensitivity than C₁₀H₁₅O_x•-related products, this would lead to under-estimate of the significance of OH H-abstraction pathway. This will not change our conclusion that the C₁₀H₁₅O_x• related products contribute significantly to HOM formation.”

2. RO₂ chemistry. In Page 2, the RO₂ reactions are listed. However, there are a few missing pathways. First, the RO₂ + HO₂ reaction may only partially form ROOH and could also produce RO (Kurten et al., JPCL, 2017, 8, 2826). The branching ratios of the two pathways likely depend on the RO₂ structure. In addition, RO unimolecular isomerization could produce RO₂ in the same CHO family. For example, C₁₀H₁₅O_x RO could form C₁₀H₁₅O_(x+2) RO₂. Therefore, this pathway needs to be included in the data analysis. Lastly, the RO₂ + RO₂ reaction described in (R2) is only correct for primary and secondary RO₂. For tertiary RO₂s, carbonyls cannot be formed. Without considering these above-mentioned pathways, the estimation of contributions from C₁₀H₁₅O_x vs. C₁₀H₁₇O_x to C₁₀H₁₆O_x (i.e., Eq. 2 – Eq. 8) is wrong.

Response:

We agree with the comment. In the revised manuscript, we have added the reaction of RO₂ + HO₂ forming RO, the unimolecular reaction of RO forming carbonyl and clarified the validity of RO₂ + RO₂ (R2). We have revised pathways in page 2 in the main text and Eq. 3 in **line 185** in the revised main text:

“R1a, which forms ROOH with a yield β, where β is close to 1 for most RO₂ (Jenkin et al., 2019).

$$\frac{d[ROOH]}{dt} = k_{RO_2+HO_2}[RO_2][HO_2]\beta \quad (\text{Eq.3})”$$

Also, we added more detail description in **line 75** in the revised main text:

“Note that RO₂ reaction in R2 is considered for primary and secondary RO₂. For tertiary RO₂, carbonyls cannot be formed. In addition, the unimolecular isomerization of RO (from R1b and R3-4) could produce RO₂ in the same RO₂ family.”

We moved a description from Scheme 2 to **line 385** in the revised main text, as shown below:

“Direct autoxidation of the nascent RO₂ is slow, $k \sim 10^{-2} \text{ s}^{-1}$, and formation of an alkoxy radical is to be expected immediately or after very few autoxidation steps, especially in high NO conditions. Once the ring structure is broken, fast autoxidation steps are accessible. All RO₂ intermediates have competing reactions (not shown) under current conditions with HO₂ (forming hydroperoxides) and NO (forming alkoxy radicals and nitrates). Alkoxy radicals formed thus can fragment, or continue autoxidation after ring breaking or fast migration of an hydroperoxide H-atom, forming a wider variety of HOM.”

We have further estimated the uncertainty of fraction of C₁₀H₁₅O_x•-related products in C₁₀-HOM resulted from the allocation of carbonyls and alcohols in C₁₀H₁₆O_x in Eq. 2-8. The contributions of C₁₀H₁₅O_x•-related products range from 39.5% to 41.4% at low NO and 42.2% to 42.6% at high NO, respectively. We found that fraction of C₁₀H₁₅O_x• related products in C₁₀-HOM was not much affected by how carbonyls and alcohols in C₁₀H₁₆O_x is allocated. We expanded our discussion in **line 507** in the revised main text:

“We have further estimated the uncertainty of fraction of C₁₀H₁₅O_x•-related products in C₁₀-HOM resulted from the allocation of carbonyls and alcohols in C₁₀H₁₆O_x in Eq.2-8. The contributions of C₁₀H₁₅O_x•-related products range from 39.5% to 41.4% at low NO and 42.2% to 42.6% at high NO, respectively. We found that fraction of C₁₀H₁₅O_x• related products in C₁₀-HOM was not much affected by how carbonyls and alcohols in C₁₀H₁₆O_x is allocated.”

3. Products in the low-NO conditions. A range of NO concentration was reported (0.1 ppt – 0.2 ppb) for the low-NO conditions. So, I assume there were multiple experiments performed under low-NO conditions with varied NO concentrations from as low as 0.1 ppt up to 0.2 ppb. Then, I would expect the product distributions under varied NO concentrations to be reported. However, in Figures 2 and 3, only one set of results were shown for low-NO. What is the NO concentration for the low-NO conditions shown? It is even more confusing that the fractions of C6-C9 fragmentation products (Figure 2) and organic nitrates (Figure 3) are not significantly lower for the low-NO experiments in comparison to the high-NO experiments. Even at 0.2 ppb for low-NO, it is ~ 100 times lower than the high-NO condition. But the fragmentation products are only different by 7%, and organic nitrates are 34% vs. 73%. More thorough analysis is needed to verify the difference.

Response:

We thank the reviewer for the helpful comment.

“0.1 ppt” is a typo, which was corrected in **line 139** in the revised main text:

“0.06 - 0.1 ppb”

RO₂+NO is the dominant pathway of RO₂ loss at both low and high NO (Figure S3).

To avoid the effects of second generation chemistry, we focus on the first 15min in our revised manuscript. After we updated the data, the ratio of fraction of fragmentation product at low NO to that at high NO is similar to the ratio of the fraction of organic nitrates. During the first 15 min of the experiments, at low and high NO the fraction of fragmentation products (C6-9 HOM) in total HOM are 24.1% and 45.5%, respectively. This is consistent with the fraction of C10 organic nitrates in C10 monomers of (28.1% and 55.4% at low and high NO, respectively), which indicates that high NO concentration is conducive to the generation of organic nitrates and fragment products.

We updated the ratios and added more discussion in **line 98** in the revised supplement:

“Within the first 15 min of the experiments, at low and high NO the ratios of $\frac{C_{6-9} \text{ monomers}}{\text{total HOM products}}$ are 0.24 and 0.46, respectively. This is consistent with the ratios of $\frac{C_{10}H_{15}NO_x + C_{10}H_{17}NO_x}{C_{10} \text{ monomers}}$ (0.28 and 0.55 at low and high NO, respectively), which indicates that high NO concentration is conducive to the generation of organic nitrates and fragment products.”

4. Product distributions. In Figure 3, what is there a strong NO_x dependence for the $C_{10}H_{15}O_x/C_{10}H_{17}O_x$ ratio?

Response:

We guess that the reviewer meant “why” by “what”. The NO_x dependence for $C_{10}H_{15}O_x/C_{10}H_{17}O_x$ may be attributed to the differences in reactivity of them. One explanation to the NO_x dependence is that the autooxidation of $C_{10}H_{15}O_x \cdot RO_2$ radicals may be faster than that of $C_{10}H_{17}O_x \cdot RO_2$ radicals, which lead to the lower concentration of $C_{10}H_{15}O_x \cdot$ observed in this study and higher sensitivity to NO concentrations. Assuming a steady state for highly oxygenated $C_{10}H_{15}O_x \cdot RO_2$ and $C_{10}H_{17}O_x \cdot RO_2$. Based on the production rate and loss rate, one can get the following equation for $C_{10}H_{15}O_x \cdot$.

$$k[LIM][OH]Y_1\alpha = k_{uni_1}[C_{10}H_{15}O_x \cdot] + k_1[C_{10}H_{15}O_x \cdot][NO] \quad \text{Eq. R1}$$

where k is the reaction rate constant for the reaction of limonene+OH, k_{uni_1} is the average unimolecular reaction rate constant of $[C_{10}H_{15}O_x \cdot]$ as a whole, k_1 is the rate constant for the reaction of $C_{10}H_{15}O_x \cdot + NO$. α is the branching ratio of OH abstraction and Y_1 is fraction of primary RO_2 undergoing auto-oxidation to form highly oxygenated $C_{10}H_{15}O_x \cdot$.

From Eq. R1, one can get

$$[C_{10}H_{15}O_x \cdot] = k[LIM][OH]Y_1\alpha / (k_{uni_1} + k_1[NO]) \quad \text{Eq. R2}$$

Similarly, one can get the following equation for $C_{10}H_{17}O_x \cdot$.

$$k[LIM][OH]Y_2(1-\alpha) = k_{uni_2}[C_{10}H_{17}O_x \cdot] + k_2[C_{10}H_{17}O_x \cdot][NO] \quad \text{Eq. R3}$$

where k_{uni_2} is the average unimolecular reaction rate constant of $[C_{10}H_{17}O_x \cdot]$ as a whole, k_2 is the rate constant for the reaction of $C_{10}H_{17}O_x \cdot + NO$. α is the branching ratio of OH abstraction and Y_2 is fraction of primary RO_2 undergoing auto-oxidation to form highly oxygenated $C_{10}H_{17}O_x \cdot$.

$$[C_{10}H_{17}O_x \cdot] = k[LIM][OH]Y_2(1-\alpha) / (k_{uni_2} + k_2[NO]) \quad \text{Eq. R4}$$

k_1 and k_2 can be considered equal (Ziemann and Atkinson, 2012).

From Eq. R2 and R4, one can get the ratio

$$\frac{[C_{10}H_{15}O_x \cdot]}{[C_{10}H_{17}O_x \cdot]} = \frac{\alpha Y_1}{(1-\alpha)Y_2} \left(1 + \frac{k_{uni_2} - k_{uni_1}}{k_1[NO] + k_{uni_1}}\right)$$

When $k_{uni_1} > k_{uni_2}$, the ratio of $[C_{10}H_{15}O_x \cdot]$ to $[C_{10}H_{17}O_x \cdot]$ increases with increasing NO concentration. In the revised manuscript, we have added the following text in **line 305** in the revised main text:

“The NO_x dependence for $C_{10}H_{15}O_x \cdot / C_{10}H_{17}O_x \cdot$ may be attributed to the differences in their

175 reactivity. One explanation to the NO_x dependence is that the autooxidation of C₁₀H₁₅O_x• RO₂ radicals may be faster than that of C₁₀H₁₇O_x• RO₂ radicals, which lead to the lower concentration of C₁₀H₁₅O_x• observed in this study and higher sensitivity to NO concentrations.”

Why are the ratios of C₁₀H₁₈O_x/C₁₀H₁₇O_x fairly constant (28% vs. 19%) between the two NO conditions, but C₁₀H₁₆O_x(R-OH/OOH)/C₁₀H₁₅O_x ratios are very different (51% vs. 0%)?

Response:

180 It is an error, and C₁₀H₁₆O_x(R-OH/OOH) accounts for 0.2% of C₁₀ HOMs at high NO in the first 15 min. We correct it and update [Figure 3](#), and also added a description in [line 312](#) in the revised main text:

185 “When we focus on the first 15 min of experiments to avoid the influence of secondary chemistry, 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 ratio of C₁₀H₁₈O_x/C₁₀H₁₇O_x• at low NO (0.38) is higher than at high NO (0.1).”

The relationships between different families under different NO conditions need to be discussed in-depth.

Response:

190 In our revised manuscript, we focus on the first 15 min of experiments to avoid the influence of secondary chemistry. Then one can get the ratios of C₁₀H₁₆O_x(R-OH/OOH)/C₁₀H₁₅O_x• are 0.47 and 0.02 at low and high NO, respectively. The ratio of C₁₀H₁₈O_x/C₁₀H₁₇O_x• at low NO (0.38) is higher than that at high NO (0.1). 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, they should be similar. Such a difference may be attributed to the shift in C₁₀H₁₅O_x• distribution with different number of O and isomers at high NO compared to low NO. The shift of in C₁₀H₁₅O_x• distribution with different number of O is evident in [Fig. S6](#). At high NO there might be more C₁₀H₁₅O_x• that react slower with HO₂ or have a lower branching ratio forming ROOH in RO₂+HO₂, which depends on detailed RO₂ structure as mentioned by the reviewer or have a lower yield forming ROH in RO₂+RO₂.

200 In the revised manuscript, we have discussed this issue as follows.

We expanded our discussion in [line 305](#) in the revised main text:

205 “The NO_x dependence for C₁₀H₁₅O_x•/C₁₀H₁₇O_x• may be attributed to the differences in their reactivity. One explanation to the NO_x dependence is that the autooxidation of C₁₀H₁₅O_x• RO₂ radicals may be faster than that of C₁₀H₁₇O_x• RO₂ radicals, which lead to the lower concentration of C₁₀H₁₅O_x• observed in this study and higher sensitivity to NO concentrations. Based on the measured concentrations of RO₂•, HO₂•, and NO, an average bimolecular RO₂• loss rate of ~0.02 s⁻¹ (low NO) and ~3.5 s⁻¹ (high NO) was estimated in our previous study (Zhao et al., 2018), which is predominately due to the reaction with NO. 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. When we focus on the first 15 min of experiments to avoid the influence of secondary chemistry, 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 ratio of C₁₀H₁₈O_x/C₁₀H₁₇O_x• at low NO (0.38) is higher than at high NO (0.1). 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

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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 RO₂+RO₂.”

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5. The authors suggest that some C₁₀H₁₇O_x and related products may be from secondary-generation reactions. For example, the first-generation product limonaldehyde (C₁₀H₁₆O₂) could react with OH and form C₁₀H₁₇O_x. In the same way, H-abstraction in limonaldehyde reacting with OH to form C₁₀H₁₅O_x RO₂ and further products. In MCM, H-abstraction in this reaction has a branching ratio of ~28.8%. Could this reaction explain some or a major fraction of total C₁₀H₁₅O_x products?

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Response:

In the revised manuscript, we focus on the early stages of the experiments (first 15 min), when secondary chemistry is not important. This can be demonstrated by the comparison of the chemistry of the limonene and limonaldehyde. In this study, C₁₀H₁₅O_x• peroxy radicals can also form through C₁₀ first-generation oxidation products in limonene+OH reaction. The limonaldehyde (C₁₀H₁₆O₂) is considered as the most competitive candidate, which is one of the main products in limonene+OH reaction and the most abundant first-generation C₁₀ product reported (Hakola et al., 1994; Larsen et al., 2001). H-abstraction in limonaldehyde+OH and subsequent O₂ addition could lead to C₁₀H₁₅O₄•, which would also be an initial step to form the C₁₀H₁₅O_x• family by further autoxidation. While the time length was 60 min in our original manuscript, in the revised manuscript we focus on the early stage of reaction (the first 15 min) in order to minimize the possible contribution from the second-generation reactions. Similarly, in this early stage, second-generation chemistry of OH with the first-generation products is negligible compared to the reaction of limonene (Fig. S9). This can be quantified using the following comparison of the respective reaction rate of OH via hydrogen abstraction with limonene and limonaldehyde, which is the dominant first-generation C₁₀ product (99% among C₁₀ products). We calculated the relative reaction rate of hydrogen abstraction from limonene to that from limonaldehyde by OH radicals, as shown below:

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$$\frac{R[LIM + OH]_{H\ abstraction}}{R[LIMAL + OH]_{H\ abstraction}} = \frac{k[LIM + OH] \times [LIM] \times [OH] \times BR_{LIM}[H\ abstraction]}{k[LIMAL + OH] \times [LIMAL] \times [OH] \times BR_{LIMAL}[H\ abstraction]}$$

$$= \frac{k[LIM+OH] \times [LIM] \times BR_{LIM}[H\ abstraction]}{k[LIMAL+OH] \times [LIMAL] \times BR_{LIMAL}[H\ abstraction]} \quad \text{Eq. S4}$$

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where k[LIM+OH] and k[LIMAL+OH] are reaction rate constants (Atkinson, 1997). Here, BR_{LIM}[H-abstraction] and BR_{LIMAL}[H-abstraction] are the branching ratios for limonene + OH and limonaldehyde + OH reactions to undergo H-abstraction channel, respectively. A branching ratio of 0.34 for limonene + OH was used (Rio et al., 2010) and a ratio of 0.29 for limonaldehyde + OH was used based on MCM v3.3.1 (<http://mcm.york.ac.uk/>). The concentrations of limonene were directly measured while concentrations of limonaldehyde were estimated according to their NO-dependent yields (Y[LIMAL] in Equation 1), with a value of 0.29 at low NO and 0.28 at high NO (Hakola et al., 1994). The uncertainties

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of $\frac{R[LIM+OH]_{H\ abstraction}}{R[LIMAL+OH]_{H\ abstraction}}$ was estimated to be -41%/+141% at low NO and high NO, from the uncertainty of limonene concentration (~15%), k[LIM+OH] ($\Delta \log k = \pm 0.08$), and Y[LIMAL] (± 0.06 at low NO and high NO (Hakola et al., 1994)) using error propagation. Hydrogen abstraction from limonene is 19-1600 times faster than that from limonaldehyde at low NO and 29-87 times faster at high NO. Note that the concentrations of limonaldehyde were estimated from consumed limonene and yields of limonaldehyde, thus reflecting only the production. As limonaldehyde is continuously consumed by OH, its true

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concentration should be lower, and thus its relative importance is even overestimated using this method.

Moreover, we ran MCM model with H abstraction of OH from limonene and obtained similar results
260 of the relative reaction rates of OH abstraction from limonene and from limonaldehyde (Figure S9).

Overall, we thus conclude that even the dominant product limonaldehyde likely has only negligible contribution to HOM formation at early stages of the experiments. Therefore, second-generation reactions are unlikely to contribute the C₁₀H₁₅O_x-related HOM observed in our study at those time scales. In the revised manuscript, we expanded the discussion in line 379 in the revised main text:

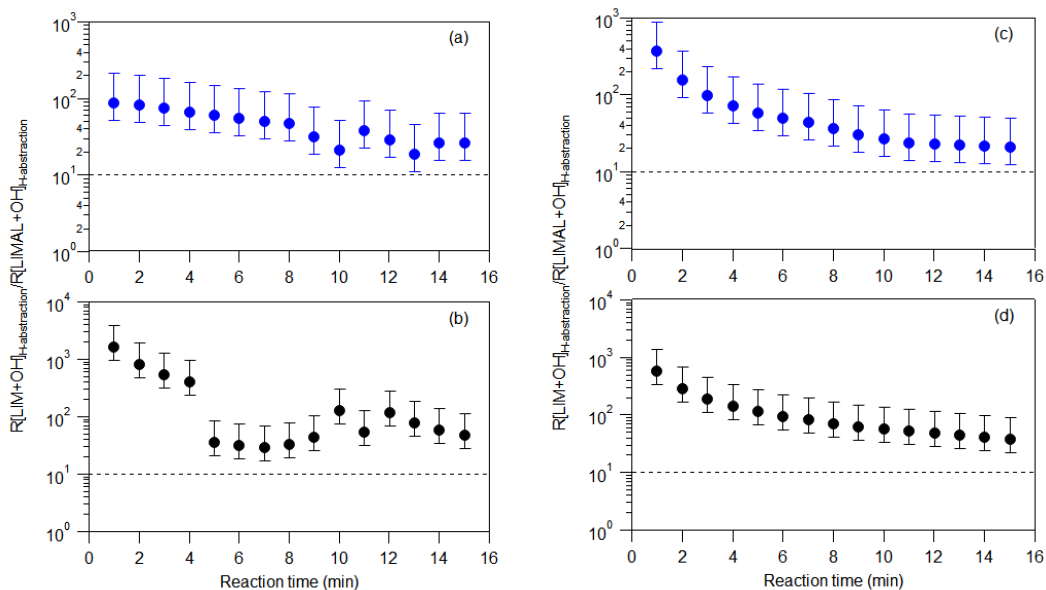
265 “In principle, C₁₀H₁₅O_x• peroxy radicals might also formed through secondary chemistry of first-generation C₁₀ oxidation products of the limonene+OH reaction. The limonaldehyde (C₁₀H₁₆O₂) is the most abundant (99%) first-generation C₁₀ product reported in limonene+OH reaction (Hakola et al., 1994; Larsen et al., 2001), which can form C₁₀H₁₅O₄• and the C₁₀H₁₅O_x• family by further autoxidation through H-abstraction and subsequent O₂ addition. Therefore, we take limonaldehyde into account as the most
270 competitive candidate. For the early stages of our experiments (first 15 min), however, we find that secondary chemistry is not important (Section S2 and Fig. S9 in Supplement).”

We added the comparison of limonene+OH and limonaldehyde+OH in the Section S2 and Figure S9 in the revised supplement:

275 “The importance of secondary chemistry is not important in this studythe C₁₀H₁₅O_x-related HOM formation. This can be demonstrated by the following comparison of the chemistry of the limonene and limonaldehyde, which is the dominant first-generation C₁₀ product (>99%). To quantify the relative importance of these two pathways, the relative reaction rates of hydrogen abstraction from limonene+OH to that from limonaldehyde+OH were calculated as below:

$$\begin{aligned} \frac{R[LIM + OH]_{H\ abstraction}}{R[LIMAL + OH]_{H\ abstraction}} &= \frac{k[LIM + OH] \times [LIM] \times [OH] \times BR_{LIM}[H\ abstraction]}{k[LIMAL + OH] \times [LIMAL] \times [OH] \times BR_{LIMAL}[H\ abstraction]} \\ &= \frac{k[LIM+OH] \times [LIM] \times BR_{LIM}[H\ abstraction]}{k[LIMAL+OH] \times [LIMAL] \times Y[LIMAL] \times BR_{LIMAL}[H\ abstraction]} \quad (\text{Eq. S4}) \end{aligned}$$

280 where k[LIM+OH] and k[LIMAL+OH] are reaction rate constants based on MCM v3.3.1 (Atkinson, 1997). [LIM], [LIMAL], and [OH] are the concentrations of limonene, limonaldehyde, and OH radicals, while limonene and OH radicals concentrations were measured and concentrations of limonaldehyde were estimated on the basis of their NO-dependent yields (0.29 at low NO and 0.28 at high NO)
285 (Y[LIMAL] in Equation S4) (Hakola et al., 1994). BR_{LIM}[H abstraction] and BR_{LIMAL}[H abstraction] are the branching ratio of H-abstraction channel from limonene + OH and limonaldehyde + OH, respectively. The branching ratio is 0.34 for the reaction limonene + OH (Rio et al., 2010) and 0.29 for limonaldehyde + OH based on MCM v3.3.1 (<http://mcm.york.ac.uk/>). The uncertainties of the relative reaction rates were estimated to be -41%/+141% at low NO and high NO, from the uncertainty of limonene
290 concentration (~15%), k[LIM+OH] (Δlogk=±0.08), and Y[LIMAL] (±0.06 at low NO and high NO) using error propagation. As a result, hydrogen abstraction from limonene is 19-1600 times faster than that from limonaldehyde at low NO and 29-87 times at high NO (Fig. S9). Note that the concentrations of limonaldehyde were estimated from consumed limonene, which only reflect the production and neglect consumption. Therefore, the relative importance of limonaldehyde was even overestimated using
295 this method. Based on this evidence, the contribution of limonaldehyde to HOM formation was likely negligible at early stages of the experiments. Therefore, the second-generation reactions are unlikely to contribute the C₁₀H₁₅O_x-related HOM observed in our study.”



300 **Figure S9.** The relative ratio of hydrogen abstraction rate of the reaction limonene+OH to that of the reaction
 limonaldehyde+OH within the first 15 min reaction time obtained from measured at low NO (a, c) and high NO (b,
 305 d). Panels a-b and c-d show the results obtained from measured limonene concentration and limonaldehyde yield
 and from MCM modeling, respectively. The dashed lines are at the value of 10 (i.e., ~10% contribution of secondary
 chemistry). Note that different scales of y axes between panel (a, c) and (b, d). The large change in panel (b)
 results from the large measurement uncertainty of low accumulated limonene consumption measured by PTR-ToF-MS in
 the first few minutes.

Minor comments:

1. The concentration of limonene used in the experiments are not mentioned in the main text.

310 **Response:**

To make it clear, we added a description to the revised main text in line 140:

315 “OH radicals were generated from the photolysis of HONO in both low and high NO experiments
 and the HONO was formed from the Teflon chamber wall via a photolytic process. The details have been
 described by Rohrer et al. (2005). HO₂ was produced from the reaction of O₂ with RO, which can be
 formed in the reaction of RO₂+NO in photo-oxidation during the experiments. The concentration of
 limonene was 7 ppb. The reaction time after the roof opened was 8 hours.”

2. Suggested references:

Line 72. For HOM dimers: Zhao et al. PNAS, 2018, 115, 12142.

320 Line 89. For limonene + NO₃: Mayorga et al., ES&T, 2022, 56, 15337.

Response:

Accepted. We have added in the line 75 and line 95 in the main text.

3. Line 84. Should be C₁₀H₁₄-18O7-11.

325 **Response:**

Accepted. We have corrected this typo in the main text.

4. Line 93. Here the actual HOM yield from Jokinen et al. should be mentioned.

Response:

330 We have added the actual HOM yields from Jokinen et al. (2015). In **line 101** in the revised main text as follow:

“...without OH scavenger (HOM yields: 5.3% (limonene+O₃); 0.93% (limonene+OH)) (Jokinen et al., 2015).”

335 5. Nox analyzer. What is the detection limit of the Nox analyzer? The manuscript says low-NO has NO concentration of 0.1 ppt – 0.2 ppb but did not clearly say that the Nox analyzer measured the NO concentration.

Response:

The detection limit of the NO_x analyzer is 5 and 10 pptv for NO and NO₂, respectively. “0.1 ppt” is a typo and we corrected it in **line 139** in the revised main text:

“0.06 - 0.1 ppb”.

To classify, we have revised in **line 127** in the revised main text:

“... the concentrations of NO₂, NO and O₃, respectively.”

345 6. Line 146-147. This sentence should move to the results section.

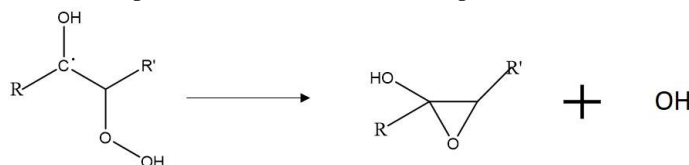
Response:

Accepted. We move this sentence to Section 3.4 in **line 550** in the revised main text.

7. Line 163. How are epoxides formed?

350 **Response:**

Generally, epoxides can be form from H-abstraction in β-hydroperoxy alkyl radicals and then cyclisation with elimination of OH (See a possible scheme as below, adapted from Bianchi et al. (2019)).



355 8. In the equations, sometimes R-H=O is used for carbonyls and sometimes R=O is used. They need to be the same.

Response:

Accepted. We have unified the expression in the manuscript.

360 9. Line 394. Carbonyls may also be formed from RO + O₂ if the RO is primary or secondary.

Response:

We agree with the reviewer. However, for large RO (C₁₀ in this study), the RO+O₂ is generally slower than unimolecular reactions including the isomerization (H-shift) and decomposition (See e.g. Vereecken and Peeters (2010, 2009)). Therefore, we think that RO + O₂ is not a major source of carbonyl in this study. Nevertheless, we have added discussion of this point in **line 442** in the revised main text as follows.

“The much higher abundance of carbonyl than alcohol is unlikely to be explained by the RO+O₂ forming carbonyl as for large RO (C₁₀ in this study), the RO+O₂ is generally slower than unimolecular reactions including the isomerization (H-shift, i.e., alkoxy-peroxy pathway) and decomposition.”

In addition, the original sentence in **line 445** was not clear and we have re-formulated the sentence

370 as follows.

“The higher **abundance** of carbonyl products **compared to alcohol products** indicates that that here **a large portion of** carbonyls are not formed from $\text{RO}_2 + \text{RO}_2$ reactions (see also **Figure S3**), but rather from termination reactions in $\text{HOOQOO}\cdot$ radicals eliminating an OH radical after an α -OOH H-atom migration, forming $\text{O}=\text{QOOH}$.”

375

10. Line 503. Molar yields? Line 505. SOA mass yields?

Response:

Yes. Thanks for the comment. We added the clarification in **line 583** of the revised main text:

“The **molar yields...**”

380

and in **line 585** in the revised main text:

“...SOA **mass yields...**”

11. Line 522. Significant contribution of $\text{RO}_2 + \text{HO}_2$ after 2 h at low NO. But this study only focused on within 1 h after oxidation, correct?

385

Response:

Yes. In our original manuscript, we focus on the oxidation within 1 hour. However, we now focus on the first 15 min of the experiments in discussion to minimize the effects of secondary chemistry.

In the revised manuscript, we have modified this sentence in **line 608** in the revised main text as follows:

390

“The major RO_2 loss rate in all experiments is via RO_2+NO .”

Reference

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