

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.

Review of Luo et al. ACP submission: Formation of highly oxygenated organic molecules from the oxidation of limonene by OH radical: significant contribution of H- abstraction pathway

Significance:

This is a well-motivated study about an important general process that is currently neglected in atmospheric chemistry models. The common chemistry models assume that an OH radical will always find its way to a double bond although several well-known facile H-abstractions would be available in the same molecule; the same double bond catalyzes the H-abstraction adjacent to it forming an allylic alkyl radical. This is quite well understood effect, but practically completely neglected in the current models describing atmospheric processes. This lack is likely most severe for secondary aerosol modelling, in which the condensing vapors are generated in-situ by rapid chain like oxidation chemistry, which likelihood is controlled by the oxidizing hydrocarbon structure. Only a fraction of the overall pathways leads to low volatile, condensable products, and thus describing the correct paths becomes critically important. Thus the study and analysis are timely and well-motivated.

While I find the topic worthwhile and certainly interesting for the readers of ACP, I am poorly convinced that such a parameter could be derived in a setup like SAPHIR. By reading the work through, I am sadly not much more convinced. Several crucial approximations have to be made to get started with the analysis, and with such a long processing times it becomes a tedious task to fill in the gap between the first reaction step (i.e., the reaction that is studied), and the chain like chemistry progressing to observed products through a complex and convoluted mechanism. I want to emphasize that the whole mechanism is littered with uncertainty, and with longer time scale this uncertainty only grows. Additionally, there seems to be some confusion with the presentation and some worrying observations about NOx have been made that put the final result in doubt. I'll detail my concerns below.

Major comments:

So first of all: Can you estimate such a quantity with this platform and experimental setup? Ideally this sort of work should be performed with techniques capable of seeing the primary radical products at short reaction times (e.g., resonance fluorescence, photoionization mass spectrometry, IR-spectrometry, etc.), and not deduce the value from a very complex mechanism at very long reaction times (note that it seems the reaction time is not given in the manuscript text), with several assumptions about the mechanism and the detection. Such long residence times are arguably poorly suited to study details of chemical mechanisms, and are far more better equipped to study, for example, SOA forming potential. A large volume implies long time-scales, which leaves open the possibility for even slow processes to make a dent. The bare minimum is that the caveats of this approach should be discussed.

Response:

We assume that the reviewer mentioned “quantity” refers to the importance of the OH H-abstraction in HOM formation. We agree that some slow processes may confound the deduction of the importance of OH H-abstraction over long reaction time, for example, the second-generation reactions, and prior to the

45 experiments we did not anticipate that this aspect would be so important and hence did not particularly
 design for it. However, as seen in Figure 4, the dominance in the HOM formation of $C_{10}H_{15}O_x\bullet$ formed
 from H-abstraction is clear already in the very first few minutes of the experiments, where long term
 effects or chamber influences are virtually absent. Specifically, the large volume guarantees that the
 influence of wall reactions is negligible relative to the chemistry time scales as determined by the reactant
 50 concentrations. 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
 55 abstraction with limonene and limonaldehyde, which is the dominant first-generation C_{10} product (99%
 among C_{10} products). We calculated the relative reaction rate of hydrogen abstraction from limonene to
 that from limonaldehyde by OH radicals, as shown below:

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

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

60 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
 65 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
 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
 70 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
 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
 75 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 a negligible
 contribution to HOM formation at early stages of the experiments. Therefore, second-generation
 reactions are unlikely to contribute the $C_{10}H_{15}O_x$ -related HOM observed in our study at those time scales.

In the revised manuscript, we added the reaction time in line 121 in the revised main text:

80 “To avoid possible interference due to long reaction time, the subsequent discussion focuses on the
 early stage (15 min) of the experiment. The initial experimental conditions are shown in Table S1.”

And expended the discussion in line 379 in the revised main text:

85 “In principle, $C_{10}H_{15}O_x\bullet$ peroxy radicals might also formed through secondary chemistry of first-
 generation C_{10} oxidation products of the limonene+OH reaction. The limonaldehyde ($C_{10}H_{16}O_2$) is the
 most abundant (99%) first-generation C_{10} 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 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).”

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

“The importance of secondary chemistry is not important in this study the 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
95 to that from limonaldehyde+OH were calculated as below:

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

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

100 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) (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.
105 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 concentration (~15%), k[LIM+OH] (Δlogk=±0.08), and Y[LIMAL] (±0.06 at low NO and high NO)
110 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 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
115 contribute the C₁₀H₁₅O_x-related HOM observed in our study.”

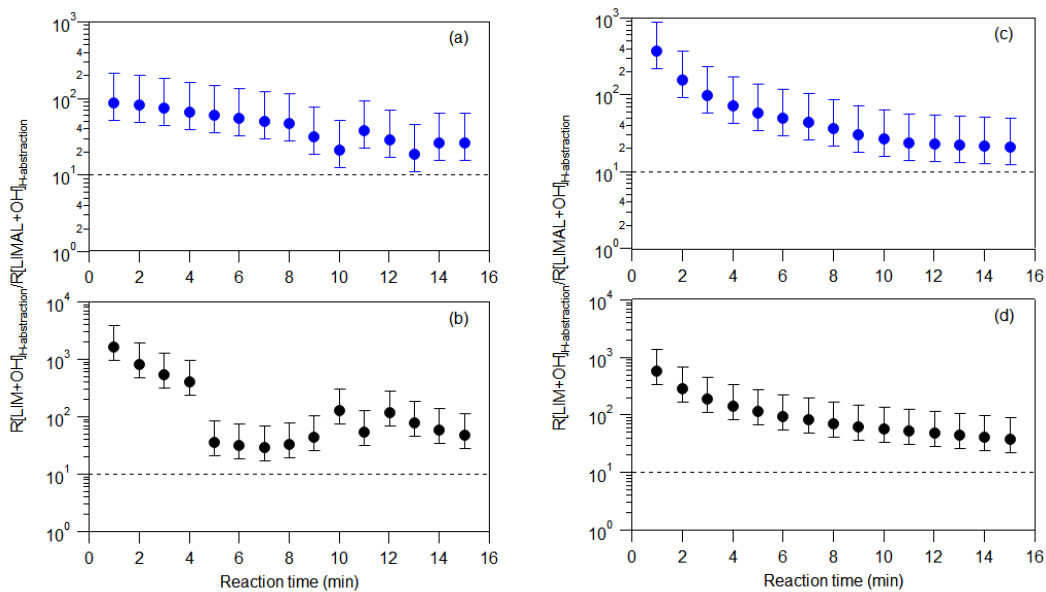


Figure S9. The relative ratio of hydrogen abstraction rate of the reaction limonene+OH to that of the reaction limonaldehyde+OH within the first 15 min reaction time obtained from measured at low NO (a, c) and high NO (b, d). Panels a-b and c-d show the results obtained from measured limonene concentration 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.

Several details seem to be missing which prevent understanding how the work was performed and analyzed. First of all, what was the OH source? You are reporting OH oxidation experiments but it appears you do not even mention the OH source in the main text. The method of OH production should be discussed extensively especially if you claim the current work was done better than the previous. Also, what was the source of HO₂? How was it controlled? Was it? What were the used limonene concentrations? What was the time-scale of the experiment? Where is the HONO originating from? Does it prevent making such a study as apparently the chamber has always appreciable NO_x present. To clarify, it is really difficult to put the results into any context when the most important parameters are left out. I hope you remember that the study should be reproducible with the given information, and that the ACP format does not require for a shorter length. Also, please remember that the supplemental material is for adding information that is not pertinent for understanding the work, but is a place to add additional information supporting the claims.

Response:

We thank the reviewer for the helpful comment. We clarify these details below and in the revised manuscript.

Regarding OH source, in low and high NO experiments, OH radicals were generated from the photolysis of HONO. HONO were produced from a well-characterized photolytic source related to the Teflon wall, which we have mentioned in [line 138](#) of our original manuscript. Besides this OH source, OH was further formed via the photolysis of O₃ formed during the photo-oxidation of limonene.

Regarding HO₂ sources, HO₂ was produced during the photo-oxidation of limonene, i.e., RO₂+NO→RO+NO and the reaction of RO with O₂ during the experiments. There is no extra HO₂ source,

and we did not control its concentration in our experiments.

150 The concentrations of limonene are 7 ppb. The initial experimental conditions are now shown in Table S1. We focus on the first 15 minutes in this study, although the duration of the experiments lasts for several hours. Meanwhile, the time resolution of the CIMS instrument is 4 seconds.

We added a detailed description to the revised main text **in line 140**:

155 “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.”

160 *How well does the “HOM measured under 17 ppb of NO_x in a one chamber setup” represent the general “high NO_x” yield of limonene HOM? Is this realistic to use for atmospheric modelling? Would some sort of fit between the conditions be better, or is it sufficient to use a one value for all the environments?*

Response:

165 At 17 ppb NO the RO₂ fate is exclusively dominated by its reaction with NO. The HOM yield at 17 ppb NO represents the environment where RO₂ mainly react with NO. Such environments include urban regions and sub-urban regions, especially in developing countries such as East Asia and South Asia. Therefore, it is realistic to use the HOM yield to model these areas.

It is certainly not sufficient to use one value for all environment. Here we also measured the HOM yield at low NO to represent the rural and remote continental environment (Rohrer et al., 1998; Lelieveld et al., 2008; Whalley et al., 2011; Moiseenko et al., 2021; Wei et al., 2019).

170 In the revised manuscript, we discussed the atmospheric relevance of the HOM yield obtained in this study as follows and extend the discussion in **line 589** in the revised main text:

175 “At 17 ppb NO the RO₂ fate is exclusively reaction with NO, and is representative for all environment where RO₂ loss is dominated by the reaction with NO. Such environment includes urban regions and sub-urban regions, especially in developing countries such as East Asia and South Asia, where our HOM yield can be used to model these areas. In contrast, our HOM yield at low NO is representative for rural and remote continental environment (Rohrer et al., 1998; Lelieveld et al., 2008; Whalley et al., 2011; Moiseenko et al., 2021; Wei et al., 2019).”

180 *On the same lines: What does “a HOM yield of a single molecule” actually signify? Can you apply it for an air quality study, or how is it a useful quantity? How much does it depend on the individual configuration of the experiment and the instruments? When you consider that individual HOM measurement is affected by the transmission and fragmentation of the instrument, the detection sensitivity due to changes in diffusion of bulky HOM, detection (=charging) probability that depends on the exact molecular structure, and so on... So to sum it up: how realistic is any given HOM yield, and how useful it is for others to utilize? This should be discussed.*

185 **Response:**

190 The HOM yield refers to a class of compounds, not just a single molecule. HOM have low to extremely low volatility due to its high oxygenation and exists in the gas phase, and have an important contribution to SOA. Obtaining HOM yields allows one to estimate SOA yield contributed by HOM. It can be used in atmospheric chemical transport models to simulate the HOM concentrations (Pye et al., 2019; Xu et al., 2022) and assess its importance in new particle formation and particle growth (Zhao et al., 2020). If

the reactions to form HOM and their contribution to SOA formation are incorporated into models, the accuracy of SOA concentration simulation in models can be further improved.

In the revised manuscript, we discussed the atmospheric relevance of the HOM yield as follows and extend the discussion in [line 593](#) in the main text:

195 “Combined, our results can thus be used directly in atmospheric chemical transport models to simulate the HOM concentrations in many atmospheric regimes (Pye et al., 2019; Xu et al., 2022) and help refine the simulations to assess its importance in new particle formation and particle growth (Zhao et al., 2020).”

200 *The given range for “low NO” spans over 3 orders of magnitude(!), whereas the “high NO” is only about 80 times higher than highest low. This seems a bit strange. Even more strange is that you obtain 33% yield for the nitrates even with the low NO conditions – to me it would imply that your low and high conditions were far closer that what you assume here. Also it raises the question that is it possible to deduce the OH reaction influence with such a high persistent background levels of NO_x? A sensitivity analysis based on the model chemistry would improve the credibility.*

Response:

The range of NO concentration is a typo. We apologize for this error. The range of NO at low NO was 0.06 - 0.1 ppb in the first 15 min. In our study, the difference of the low and high NO concentrations is about two orders of magnitude. As mentioned above, low and high NO concentrations represent rural and most remote continental regions and urban regions, respectively. We would like to note that in our study, low NO mostly referred to the clean continental environment with low NO concentrations of 0.1 - ~0.2 ppb (Rohrer et al., 1998; Lelieveld et al., 2008; Whalley et al., 2011; Moiseenko et al., 2021; Wei et al., 2019) and does not refer to the case where RO₂ loss is dominated by the reaction with HO₂, e.g., in remote oceanic environment. In our study at low NO the dominant RO₂ loss reaction is still RO₂+NO, which has been stated clearly in our original manuscript and noted again in the revised manuscript ([Figure S3](#)). This explains why there is considerable formation of organic nitrate under low NO conditions.

The NO_x level does not affect how we deduce the contribution of OH abstraction in HOM formation as we have clearly specified the NO_x level. We are not sure why a sensitivity analysis is necessary here. We have revised in [line 139](#) in the main text:

220 “0.06 - 0.1 ppb”

And we have noted the meaning of low NO as follows in [line 147](#) in the main text:

“We would like to note that the low NO does not refer to the case where RO₂ loss is dominated by the reaction with HO₂, e.g., in remote ocean environment.”

225 *I generally find the discussion around this NO influence confusing. For example you state that “to estimate the impact of ozone oxidation during photooxidation, we calculated the reaction rates of VOC+OH and VOC+O₃ in low and high NO conditions of this study..” without explaining where this difference comes from. Obviously the NO has nothing to do with the VOC + OH and VOC + O₃ rates unless you consider the secondary chemistry. This can be very misleading to a reader without a prior good grasp on the ongoing processes. Please connect these statements to the chemical phenomenon you’re describing.*

Response:

We did not intent to indicate that NO influences VOC+OH or VOC+ O₃. We would like to state that in both conditions OH oxidation is the dominant reaction pathway of VOC. In our original manuscript, the

235 slightly higher contribution of O₃ at high NO is attributed to higher O₃ formed in the photo-oxidation of limonene compared to low NO. In the revised manuscript, as we only focus on the first 15 min, the difference is not noticeable (Figure S2 in the revised Supplement).

In the revised manuscript, we have clarified the point as follows and revised in line 145 in the main text:

240 “To estimate the impact of ozone oxidation during photo-oxidation, we calculated the reaction rates of VOC+ OH and VOC+O₃ in the experiments of this study (Fig. S2).”

To consider:

*Do you consider the $RO_2 + HO_2 \rightarrow RO + O_2 + OH$ pathway for any of the RO₂ in the mechanism?

245 This should be possible as you follow the structures explicitly.

Response:

This pathway is possible in principle. However, according to the RO₂ loss in Figure S3, RO₂ + HO₂ is not important at both low and high NO (less than 1% proportion of RO₂ loss) in our study.

In the revised manuscript, we added this reaction in the introduction in line 79.

250

*Why can't the C₁₀H₁₇O_x produce an C₁₀H₁₆O_y alcohol by RO₂ + RO₂?

Response:

By RO₂ + RO₂ pathway, C₁₀H₁₇O_x produce C₁₀H₁₈O_x alcohol and C₁₀H₁₆O_x carbonyl (Barbara J. Finlayson-Pitts).

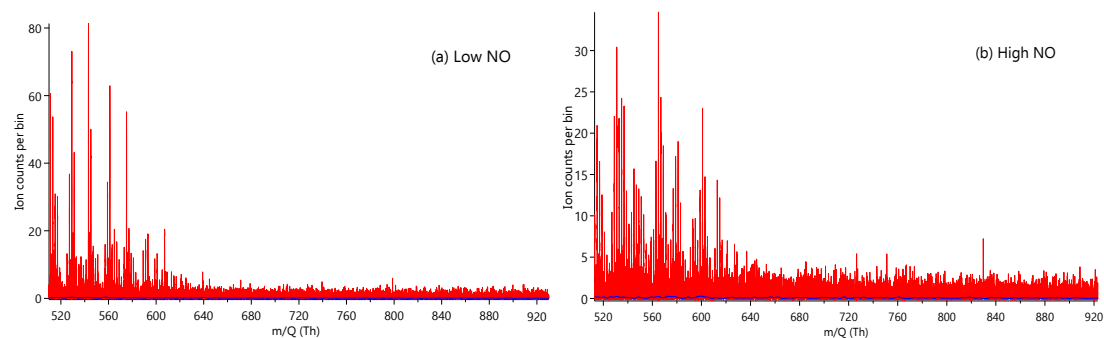
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*Is it really the case you saw no trimer species? By looking at the Figure 1, it appears that dimers are high, and for a two double bond systems trimers have been reported (e.g., Molteni et al. <https://acp.copernicus.org/articles/18/1909/2018/>). So if you would provide me a Zoom of the 700-900 Th – are there no apparent bands of peaks present?

260

Response:

We did not observe trimers in our limonene+OH system. We would like to note that the results of Molteni et al. (2018) were observed in the oxidation of aromatic hydrocarbons. The oxidation pathways and products can be quite different from that of limonene+OH in this study. We have added a zoom of 520-920 Th (Figure S4) in the revised Supplement.



265

Figure S4. The average mass spectrum in the range of 520-920 Th at low and high NO over the first 15 min.

*The method (Fuchs et al. 2012) used to determine [RO₂] and [HO₂] has been debated to be prone to artefacts from different RO₂ propagation reactions. For example, a tertiary RO₂ will not lead into HO₂ and is thus miscounted, especially here when your most facile reaction advances through a tertiary RO₂.

270

Was any correction applied to the values of [RO₂] and [HO₂]? If not, the caveat of not doing so should be the very least discussed.

Response:

275 Concerning HO₂, we assume that the reviewer refers to the work by Fuchs et al. (2011), in which the potential artefact in HO₂ measurements from the concurrent chemical conversion of RO₂ in the instrument making use of chemical conversion of HO₂ by the reaction with NO is described. As shown in that work, the artefact can be avoided, if only a small NO concentration used. This was done in all experiments in this study, so that no corrections of HO₂ concentration measurements are required. Therefore, the method to determine HO₂ concentration is not affected by the artefact.

280 RO₂ radicals are detected as sum of HO₂+RO₂ and the contribution from HO₂ radicals is subtracted from the signal to derive RO₂ radical concentrations. The method relies on the conversion of RO₂ to HO₂ in their reaction with NO that is achieved in a conversion reactor of the instrument. The reviewer is correct that RO₂ species that do not yield HO₂ cannot be detected. For example, Novelli et al. (2021) found that the decomposition of beta-nitrate alkoxy radicals (formed in the reaction of nitrate RO₂+NO) form NO₂ instead of HO₂. However, such a reaction is only found for nitrate RO₂ up to now. Even tertiary RO₂ can still form HO₂ in the reaction with NO via the further decomposition of RO forming a new primary or secondary RO₂ (Ziemann and Atkinson, 2012; J. et al., 1997). In photochemistry experiments, there is no significant fraction of nitrate RO₂ formed. In this study, we do not expect that there were a large contribution of nitrate RO₂ to the sum of all RO₂. The large contribution of nitrate RO₂ would only be the case in experiments, in which the VOC is mainly oxidized by NO₃. We only make use of the RO₂ measurements to calculate the lifetime of RO₂ with respect to the different reaction channels. Therefore, this should not matter for the RO₂ lifetime calculation in photochemistry experiments, when RO₂ is mainly from the OH oxidation.

290 We did apply a correction to RO₂ concentrations. To make it clear, we added some description in **line 128** in the revised main text:

300 “Note that the potential artefact in HO₂ measurements from the concurrent chemical conversion of RO₂ in instrument making use of chemical conversion of HO₂ by the reaction with NO can be avoided in this study through NO used, so that no corrections of HO₂ concentration measurements are required. The detection of RO₂ radicals relies on the conversion of RO₂ to HO₂ in their reactions with NO. We applied a correction to RO₂ concentrations (Fuchs et al., 2011). We would like to note that only a few nitrated RO₂ were observed to not form HO₂ in the reaction with NO. In this study, we do not expect that there were a large contribution of nitrate RO₂ to the sum of all RO₂ as in photochemistry experiments, as there is no significant fraction of nitrate RO₂ formed.”

305 **Line 348: Yes, the alkoxy-peroxy step removes the geometrical constraint, but it also imposes a limitation on the efficiency of this path, as the bimolecular step is needed to allow for autoxidation, whereas losses by wet and dry scavenging, photolysis and reactions with other trace gases might as well happen. Postulating several alkoxy-peroxy sequences will impose even greater limitations, as the radicals may be lost in each step and the OH is mainly lost with the high [VOC]. This caveat on the way to HOM should be clearly stated.*

Response:

Losses of the RO₂ radicals by scavenging, photolysis and other trace gasses also occurs during HOM formation that does not proceed through an alkoxy-peroxy step, and thus are not an unusual limitation for autoxidation efficiency; the limonene alkoxy radicals are too short-lived to be affected by these

315 processes. During the experiments, the bimolecular step RO_2+NO was fast ($\sim 0.01 \text{ s}^{-1}$ at low NO and 4 s^{-1} at high NO, respectively), and was the dominant loss of the cyclic RO_2 in our study, such that the alkoxy-peroxy step is not limiting under those conditions. In the atmosphere, HOM yields always depend on the reaction conditions due to competition, but for limonene the yields may be peak at higher NO concentrations than for non-cyclic VOCs due to the alkoxy-peroxy step. However, neither the alkoxy-peroxy step or fragmentation of the alkoxy steps breaks the radical chain, and autoxidation can proceed without further OH reactions.

We have extended this section in the revised manuscript, emphasizing that the need for one alkoxy-peroxy step probably leads to peak HOM formation at somewhat higher NO conditions than non-cyclic VOCs, and stating explicitly that multiple alkoxy-peroxy steps are not necessary for HOM formation.

325 In **line 400** in the revised manuscript:

“Though further alkoxy-peroxy steps are not necessary for HOM formation from limonene, subsequent autoxidation steps will compete against bimolecular reactions with NO, suggesting that more alkoxy-peroxy steps may occur even when the unimolecular lifetime of these later non-cyclic RO_2 radicals is typically shorter than that of the early-stage cyclic RO_2 .”

330 In **line 410** in the revised manuscript:

“The need of a ring-breaking alkoxy-peroxy step in the proposed HOM formation mechanism does suggest that the highest yields of limonene HOM formation may occur at slightly higher NO concentrations than for non-cyclic VOCs who autoxidize even without alkoxy steps.”

335 **How good is the assumption to use “the same k_{uni} , $k_{\text{RO}_2+\text{RO}_2}$, $k_{\text{RO}_2+\text{HO}_2}$, and α for a given $\text{C}_{10}\text{H}_{15}\text{O}_x\cdot$ and $\text{C}_{10}\text{H}_{17}\text{O}_x\cdot$ family.”? Easy examples where this does not hold are: H-shift across the ring vs H-shift in a linear chain after ring breaking. $\text{RO}_2 + \text{RO}_2$ for a primary RO_2 vs oxygenated RO_2 . How big of an uncertainties these assumption generate?*

Response:

340 We agree the assumption can lead to uncertainties. Both the $\text{C}_{10}\text{H}_{15}\text{O}_x\cdot$ and $\text{C}_{10}\text{H}_{17}\text{O}_x\cdot$ families include primary or oxygenated RO_2 . The k of RO_2 reaction cannot be determined directly by experiment at present.

As mentioned in the manuscript, $\text{C}_{10}\text{H}_{16}\text{O}_x$ can be divided into carbonyls ($\text{RC}=\text{O}$) and alcohols (ROH) or hydroperoxides (ROOH) from $\text{C}_{10}\text{H}_{17}\text{O}_x\cdot$ reactions. When k_{uni} , $k_{\text{RO}_2+\text{RO}_2}$, $k_{\text{RO}_2+\text{HO}_2}$, and α were assigned of $(0.01-1)\cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Crouse et al., 2013), $(0.001-1)\cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Berndt et al., 2018), and $(0.5-2)\cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ziemann and Atkinson, 2012), respectively, one can get the yield of carbonyl according to Eq. 6 and Eq. 7, which ranged from 90%-96% at low NO and 97%-100% at high NO. This indicated that the yields of carbonyl are not sensitive to these assumption k and α .

350 We revised the equations and expanded our discussion in **line 206** in the revised main text:

“We did a sensitivity analysis to test the influence of varying the k_{uni} , $k_{\text{RO}_2+\text{RO}_2}$, $k_{\text{RO}_2+\text{HO}_2}$, and α using the ranges of these parameters reported in the literature on the fraction of carbonyl in $\text{C}_{10}\text{H}_{16}\text{O}_x$ and on the importance of H-abstraction channel in HOM formation. When k_{uni} , $k_{\text{RO}_2+\text{RO}_2}$, $k_{\text{RO}_2+\text{HO}_2}$, and α were varied in the range of $(0.01-1)\cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(0.001-1)\cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(0.5-2)\cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the values in the literature (Crouse et al., 2013; Berndt et al., 2018; Ziemann and Atkinson, 2012), and 0.5, respectively, one can get the yield of carbonyl according to Eq. 6 and Eq. 7, which ranged from 90%-96% at low NO and 97%-100% at high NO. This indicated that the yields of carbonyl are not sensitive to these assumption of k and α .”

360 We have further estimated the uncertainty of fraction of $C_{10}H_{15}O_x$ -related products in C10-HOM resulted from the allocation of carbonyls and alcohols in $C_{10}H_{16}O_x$ in Eq.2-8. The contributions of $C_{10}H_{15}O_x$ -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 $C_{10}H_{15}O_x$ related products in C10-HOM was not much affected by how carbonyls and alcohols in $C_{10}H_{16}O_x$ is allocated. We expanded our discussion in [line 507](#) in the revised main text:

365 “We have further estimated the uncertainty of fraction of $C_{10}H_{15}O_x$ -related products in C10-HOM resulted from the allocation of carbonyls and alcohols in $C_{10}H_{16}O_x$ in Eq.2-8. The contributions of $C_{10}H_{15}O_x$ -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 $C_{10}H_{15}O_x$ related products in C10-HOM was not much affected by how carbonyls and alcohols in $C_{10}H_{16}O_x$ is allocated.”

370

**How does the shifting detection sensitivity of CIMS affect your conclusions (e.g. Hyttinen et al. <https://pubs.acs.org/doi/10.1021/acs.jpca.7b10015>), as the C10H17Ox is likely detected better than the C10H15Ox products, especially at the lower end of the oxygen content?*

Response:

375 To our knowledge, there is no evidence that the $C_{10}H_{17}O_x$ is detected better than the $C_{10}H_{15}O_x$ products. Currently the sensitivity of individual HOM cannot be obtained. We assume the similar detection sensitivity to $C_{10}H_{15}O_x$ related HOM and $C_{10}H_{17}O_x$ related HOM. The basis of this premise is that $C_{10}H_{15}O_x$ and $C_{10}H_{17}O_x$ related HOM with six and more oxygen atoms from autooxidation (Bianchi et al., 2019; Mentel et al., 2015) have two or more hydrogen bond donors (-OOH or -OH), which allows
380 HOM to form strong clusters with NO_3^- . These clusters need be competitive to the very stable $(HNO_3)NO_3^-$ to be detected, and has the similar rates near the collision limit to that of H_2SO_4 , resulting the same high sensitivity (Hyttinen et al., 2015). Moreover, counterparts of $C_{10}H_{15}O_x$ related HOM and $C_{10}H_{17}O_x$ related HOM with the same oxygen number, either radicals, or termination products (carbonyls or organic nitrates), only differ in the chemical structures by one C=C bond or an endocyclic
385 peroxide ring. Therefore, the multiple H bonding based sensitivities of $C_{10}H_{15}O_x$ related- and $C_{10}H_{17}O_x$ related families are supposed to be similar (Hyttinen et al., 2017). Besides, no dependence of sensitivity on the functional groups of HOM within a maximum uncertainty of a factor of 2 was detected by using the same NO_3^- -CIMS with the same setting in our previous study (Pullinen et al., 2020).

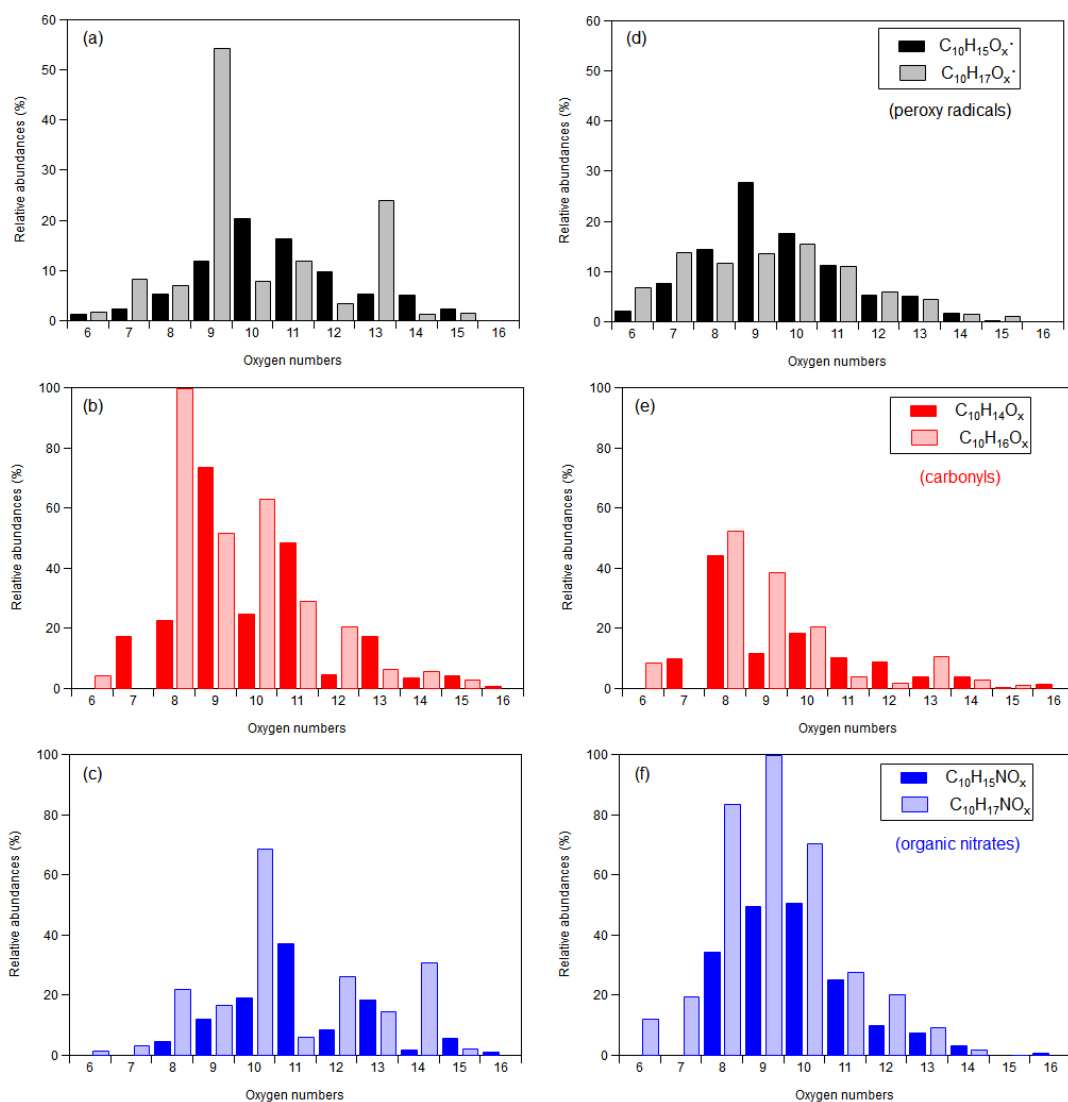
390 Additionally, we observed that $C_{10}H_{15}O_x$ related products are comparable to $C_{10}H_{17}O_x$ related products at all oxygen numbers ([Fig. S6](#)). This indicates that the significance of $C_{10}H_{15}O_x$ related products is not affected by the detection sensitivity, which would mostly affect the sensitivity of less oxygenated compounds as the reviewer pointed out. Therefore, we conclude that the sensitivity of NO_3^- -CIMS to $C_{10}H_{15}O_x$ and $C_{10}H_{17}O_x$ related HOM is the same and near the collision limit.

395 If the sensitivity of $C_{10}H_{17}O_x$ related products were indeed higher than $C_{10}H_{15}O_x$ related products, the $C_{10}H_{15}O_x$ related products would be underestimated and they would be even more important than the current estimate. This will not change our conclusion that the $C_{10}H_{15}O_x$ related products contribute significantly to HOM formation.

In the revised manuscript, we discussed extend the discussion in [line 486](#) in the revised main text:

400 “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 NO_3^-

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.”



425

Figure S6. Relative abundances of individual products at low NO (0.06 - 0.1 ppb, panel a-c) and high NO (~17 ppb, panel d-f) at the first 15 min with the panels (a, d) showing $C_{10}H_{15}O_x\bullet$ (peroxy radicals, $x=6-15$) and $C_{10}H_{17}O_x\bullet$ (peroxy radicals, $x=6-15$) in black, the panels (b, e) showing $C_{10}H_{14}O_x$ (carbonyls, $x=7-16$) and $C_{10}H_{16}O_x$ (carbonyls, $x=6, 8-15$) in red, and the panels (c, f) showing $C_{10}H_{15}NO_x$ (organic nitrates, $x=8-16$) and $C_{10}H_{17}NO_x$ (organic nitrates, $x=6-15$) in blue. $C_{10}H_{15}O_x\bullet$ and their related products are in solid bars and $C_{10}H_{17}O_x\bullet$ and their related products are in transparent bars. The individual products are normalized to the signals the most abundant individual product respectively ($C_{10}H_{16}O_8$ at low NO and $C_{10}H_{17}NO_9$ at high NO).

430

**It seems unlikely that the SAR will reproduce the rates of the highly oxygenated molecule Hshift rates. This is due to intramolecular interactions (mainly H-bonding) that influences the thermochemistry; a favorable interaction on the reactant side will increase the barrier to reaction, and can significantly decrease the H-shift rate. Looking at the schemes of the paper with the given SAR rates can leave a very wrong picture for the reader. This influence is hinted in the manuscript but, still the uncertain numbers are presented in the schemes. Is this reasonable?*

440

Response:

It is clearly stated throughout the manuscript that these numbers, and the mechanism itself, is not a quantitative model for various reasons: the uncertainties on the numbers, the selection of only one starting

RO₂, the selection of only one pathway from each intermediate etc. Still, the numbers given by the SAR reflect the current knowledge available for such reactions, and these best-available estimates suggest that
445 the rates are of the correct order of magnitude to sustain autoxidation without the need to make adjustments or artificially increasing rates. We feel it is reasonable, even required, to provide readers with these current-knowledge estimates to show that the proposed reaction steps are at least viable, as far as anyone can tell at the moment.

In this class of reaction, it is often the case that both reactant, TS, and products have similar number
450 and strengths of H-bonds, especially when there are multiple combinations of H-bonds possible; the most favorable H-bonding combination need not be the same in reactant and TS. Also, H-migration can occur even if the peroxy moiety is H-bonded. Furthermore, H-bonded structures, while energetically more favorable, are entropically less favorable such that both more and less H-bonded conformers contribute significantly to the population of both reactant and TS. In some cases, H-bonding can indeed hamper the
455 H-migrations, but in other cases it can promote H-migration (e.g., by increasing the population contribution of conformers with the radical site near an abstractable H-atom, or favoring a cyclic TS that is best for H-migration). Overall, the complexity of H-bonding in multi-functionalized species definitely leads to larger uncertainty margins on the rate estimates, but does not imply that the SAR predictions are fundamentally biased towards too-high values and would mislead the reader.

460

**The secondary OH reaction is generally inherently less likely in lab systems, as I would expect to be here as well (i.e., how much would you need to accumulate the product before it'll find the second OH at a rate sufficient for measurable product formation?). Yet, with the missing documentation about the used concentration ranges it is not possible to even roughly estimate this fraction.*

465

Response:

We agree that in our study, particularly in the first 15 min, the secondary OH reaction is unlikely. We have addressed this comment in our response to the comment #1 (line 42-78 of this document). We added the concentrations in the main text (see [Table S1](#) in the Supplement and [line 143](#) in the main text).

470

**Line 323: "However, this extra bimolecular OH reaction takes time, and can delay formation of HOM. An analysis of the secondary chemistry is outside the scope of this work, ..." As mentioned above, not all pathways lead to HOM, and the whole paper is an analysis of secondary chemistry if you are studying OH abstraction vs OH addition through a complex mechanism. Please sharpen your words and thinking.*

Response:

475

As we explained above ([line 42-78](#) of this document), now we focus on the early stages of the experiments (first 15 min), and thus secondary chemistry is not important in this study. This can be quantified by the comparison of the chemistry of the limonene and limonaldehyde referring to the response to comment #1.

In the revised manuscript, we expanded the discussion in [line 379](#) in the main text:

480

"In principle, C₁₀H₁₅O_x• peroxy radicals might also form 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
485 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.

490 **Line 328: Here you imply that the low NO is actually the highest of your reported range (0.2 ppb) and quote a value of 29% for RONO2 which is not in line with the previously given 33%. At these conditions this seems like a very high value. Have you considered, for example, that your CIMS could be more sensitive to nitrates than to HOM devoid of -ONO2? There are some hints in the recent literature about this.*

495 **Response:**

We have corrected the error of NO concentration and the inconsistent ON fraction. ONs account for ~31% at low NO in this study. According to the RO₂ loss rate (Figure S2), RO₂+NO was the dominant RO₂ loss pathway at both low and high NO, although there is a very small amount (<1%) RO₂ loss through RO₂+HO₂ pathway at low NO. Therefore, it is not surprising that the fraction of ON in the products can reach 31% at low NO. To our knowledge, there's no direct measurement evidence yet that the CIMS could be more sensitive to nitrates than to HOM devoid of -ONO₂. Even if the sensitivity were different, as we compared both the C₁₀H₁₅O_x related HOM-ON and non-nitrate HOM with their counterparts related to C₁₀H₁₅O_x, it would not affect our conclusion regarding the importance of OH abstraction.

In the revised manuscript, we correct the ON fraction in **line 616**:

505 "Even at ~0.2 ppb NO, ONs account for a large part (31%) of HOM ONs."

**Finally, it is very difficult for me to see why higher NO can lead to higher abstraction vs addition rates. These issues seem uncoupled (i.e., no amount NO can increase an OH abstraction rate) and rather point into being misunderstood RO₂ + NO (or indeed RO + NO) chemistry connected to the long processing time-scales.*

510 **Response:**

We agree with the reviewer that NO does not directly affect the H abstraction rate and we did not state that higher NO can lead to higher abstraction vs addition rates in our manuscript. What NO affects in this study is the HOM formation via H abstraction versus OH addition, which involves RO₂ auto-oxidation. The reaction of NO with RO₂ promotes alkoxy radical formation which can affect the autoxidation pathway in both H abstraction channel and OH addition channel. In order to avoid potential misunderstanding, we have revised the sentence regarding the NO influence in **line 533** in the revised manuscript as follows:

520 "...we speculate that an NO dependence of ratio of HOM formed via H-abstraction versus OH addition might become apparent even in the limonene system at strongly reduced NO levels."

Minor comments:

**Consider changing the "dimer" into "accretion product".*

Response:

525 Dimers can be the accretion products between two monomers. Both words represent the product in our study. Considering contrasting with "monomer", we prefer to use "dimer".

**Line 66: "Biomolecular" is an error. (Other places as well).*

Response:

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

*Line 150: What “organic” are you referring to? The identity matters a lot, as has been shown in this chamber setup previously.

Response:

535 To classify, we added a description in **line 168** in the revised main text:

“...organic vapor (such as $C_{10}H_{15}NO_{9-12}$ (nitrated compounds) and $C_{10}H_{14}O_{8-11}$ (non-nitrated compounds) in the reaction of limonene with OH in the presence of NO) concentrations in the dark (Guo et al., 2022).”

540 *Line 158: delta symbol is usually reserved for a changing quantity.

Response:

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

545 *Line 210: How should one understand the statement: “Briefly, we only consider a limited oxidation network by considering all possible reaction channels, ...”

Response:

We have modified this sentence in **line 235** in the revised main text:

“Briefly, we only **take into account** a limited oxidation network by **considering** all possible reaction channels and select **only the** dominant channels, **based on their rate as predicted by SARs.**”

550

*Don’t mix -y and -yl endings, i.e., if you choose to use “peroxyl” then use “alkoxyl” as well.

Response:

Accepted. We have unified the expression in the main text.

555 *Line 394: Didn’t catch why you presume the disproportionation of $RO_2 + RO_2$ would favor carbonyls over alcohols.

Response:

We did not mean that the disproportionation of $RO_2 + RO_2$ would favor carbonyls over alcohols. We apologize for the ambiguous sentence. In the revised manuscript, we modified this sentence in **line 442** in the revised main text as follows:

560

“The higher **abundance** of carbonyl products **compared to alcohol products** indicates that here a **large fraction of the** carbonyls is not formed from $RO_2 + RO_2$ reactions (see also Fig. S3), but rather from termination reactions in $HOOQOO\cdot$ radicals eliminating an OH radical after an α -OOH H-atom migration, forming $O=QOOH$.”

565

*Plural of formula is formulae.

Response:

We looked up the dictionary and found that both formulas and formulae can be used as the plural form of formula. Therefore, we kept the usage of “formulas”.

570

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