RC2

We thank the reviewer for the helpful comments and responded to all comments. The reviewer comments are type set in italics while our reponses are type set in plain Times New Roman fonts. In case of changes line numbers refer to the revised manuscript. In case of “no changes” line numbers refer to the submitted manuscript.

With chamber oxidation experiments, Kang et al. show that bimolecular reactions of alpha-pinene + OH derived peroxy radicals with RO2 and NO enhance the formation HOM by alkoxy-peroxy steps instead of inhibiting it as previously thought. RO2 + NO reactions appear to be particularly important in this regard, leading to products with up to 15 oxygen atoms, three oxygens higher than experiments without NO. As they highlight in their conclusion, this would imply that the formation of HOM is more favorable under polluted conditions than clean, opposite to what is widely accepted in the community. This work is important, timely and highly relevant to the work of others in the field. I recommend its publication. I have the following comments that I request be addressed.

We thank reviewer 2 for the positive words.

1. One concern I have is the scarce measurement of the C10H17Ox family of peroxy radicals. These first-generation peroxy radicals from OH addition to alpha-pinene are completely unmeasured, except for C10H17O10, while first-generation peroxy radicals from H-abstraction, a minor channel in comparison, are measured.

We will respond in the following point by point.

- *It is clear from Xu et al. 2019 and Berndt 2021 that OH addition to alpha-pinene initiates autoxidation and the formation of peroxy radicals at least up to C10H17O7. Further reactions of some of these are likely the source of the C10H17O10 measured here. Insensitivity of the NO3-CIMS method toward these products is unlikely to be the reason as Figure S5 in this paper shows that C10H15O6-9 are measured above the detection limit.*

$C_{10}H_{17}O_X$ (X<10) are surely formed, but in our system apparently their concentrations remained below the detection limit, though a potential role of $C_{10}H_{17}O_X$ becomes evident as we find substantial amounts $C_{20}H_{34}O_Y$ accretion products. Why our system behaves differently is less obvious. Differences to Berndt’s experiments are longer reaction times which would allow a larger contribution to $C_{10}H_{15}O_X$ by oxidation of first-generation products. Another difference is the presence of O_3. However, Shen et al. (2021) found dominance of $C_{10}H_{15}O_X$ chemistry in absence of O_3. In any case, an assumed significant O_3 contribution to $C_{10}H_{15}O_X$ should not suppress $C_{10}H_{17}O_X$ chemistry. Our explanation would be: a) Autoxidation of $C_{10}H_{17}O_X$ does not efficiently lead to HOM products with high oxygen number (O > 7, 8). (We are able to detect $C_{10}H_{17}O_X$ (Figure 6) and $C_{10}H_{18}O_X$ in the NO_X experiments and monomer termination products $C_{10}H_{18}O_X$ in the OH reference experiments (Figure S7)). b) Autoxidation of $C_{10}H_{15}O_X$ (X>7) can be more efficient than autoxidation of $C_{10}H_{17}O_X$(X>7). c) $C_{10}H_{17}O_X$ (X<=7) are at the edge of what we can detect with our Eisele style CIMS set up.

No action.

- *The authors attribute their low detection of C10H17Ox compounds partly to their measurement conditions. While some secondary oxidation of pinonaldehyde could explain the C10H15Ox compounds, the authors find primary products from OH H-abstraction to also be at least equally important (Figure S6). This necessitates a more detailed discussion regarding why primary OH-addition products, which should dominate a-pinene + OH reactions, are not measured or measured minimally. Perhaps* *the additional -OH group in the latter leads more efficiently to termination during autoxidation, and these are then candidates for secondary oxidation by OH?*

We were apparently unable to express the intended conclusions clearly. In Figure S6 we show the turnover of α-pinene by the different routes. We only show that, based on MCMv3.3.1 level chemistry, oxidation of $C_{10}H_{16}O_Y$ compounds by OH is fast enough to explain in principle a part of the observed $C_{10}H_{15}O_X$ chemistry. We do not claim it is pinonaldehyde. In the same sense also the channel of H-abtraction by OH has sufficient potential to explain (a part of) the observed $C_{10}H_{15}O_X$ chemistry. That H-abstraction by OH exists as a minor oxidation channel for α-pinene is well known. Here we would like to refer to the article by Shen et al. (2021) where it is shown that a minor channel of α-pinene oxidation can be still a main path to HOM. A reason is that α-pinene HOM, despite their importance for SOA, still have small chemical yields (<10%!). We cannot discriminate which routes are taken by measurement as this would require speciation.

No action.

- *Figure S5 shows multiple C10H18Ox measured. As the authors state in line 257 of the manuscript, these products can only from bimolecular reactions of C10H17Ox and C10H17Ox+1 (correct the typo in the manuscript, you have two instances of C10H17Ox+1). So, the C10H17Ox peroxy radical precursors of C10H18Ox clearly form during these experiments.*

We agree that $C_{10}H_{17}O_X$ (X>7) radicals must be of some importance as we see resulting products. Besides the $C_{10}H_{34}O_Y$ accretion products, which result from recombination of two $C_{10}H_{17}O_X$, also some $C_{10}H_{18}O_X$ compounds are observed as result from the alcohol channel of HOM-$C_{10}H_{17}O_X$ + RO_2 (or from HOM-$C_{10}H_{17}O_X$ + HO_2). However, the $C_{10}H_{18}O_X$ family contributes only a small fraction of about 5% to the HOM-C_{10} monomers in OH reference experiment and of about 10% in the NO_X experiment. $C_{10}H_{17}O_X$ contribute also to $C_{20}H_{32}O_Y$ accretion products, but here it is not clear in how far these result from the recombination of HOM-$C_{10}H_{15}O_X$ and conventional $C_{10}H_{17}O_3$, or form in the recombination of HOM-$C_{10}H_{15}O_X$ and HOM-$C_{10}H_{17}O_X$.

Nevertheless, a low contribution of $C_{10}H_{17}O_X$ chemistry to HOM formation compared to $C_{10}H_{15}O_X$ chemistry is a finding, whereby “low” refers to primary oxidation chemistry where $C_{10}H_{17}O_3$ dominate to > 80%. We stated clearer that we cannot finally clarify what the detailed reasons are, based on the data presented:

Action:

Typo corrected.

In manuscript we added to Section 3.1, line 411 - 413:

“Despite the line of arguments above, we are not able to finally clarify why we observe only a minor contribution of $C_{10}H_{17}O_X$ chemistry to HOM formation in our experiments. It had at least some significance as indicated by the observed termination products $C_{10}H_{18}O_Y$ and $C_{10}H_{32,34}O_Y$.”

We would prefer not to go deeper into this mechanistic discussion in the present manuscript. For the main topic of the paper - the role of alkoxy-peroxy steps in the autoxidation chain – the question why the contribution of $C_{10}H_{17}O_X$ is minor is not so important. In Figure 6 we show that the $C_{10}H_{17}O_X$ peroxy radical family shows a similar behavior as a function of NO_X as the $C_{10}H_{15}O_X$ peroxy radical family. Hence, alkoxy-peroxy steps may keep also $C_{10}H_{17}O_X$ on a high level at high NO_X (in accordance with Berndt et al. (2015)).

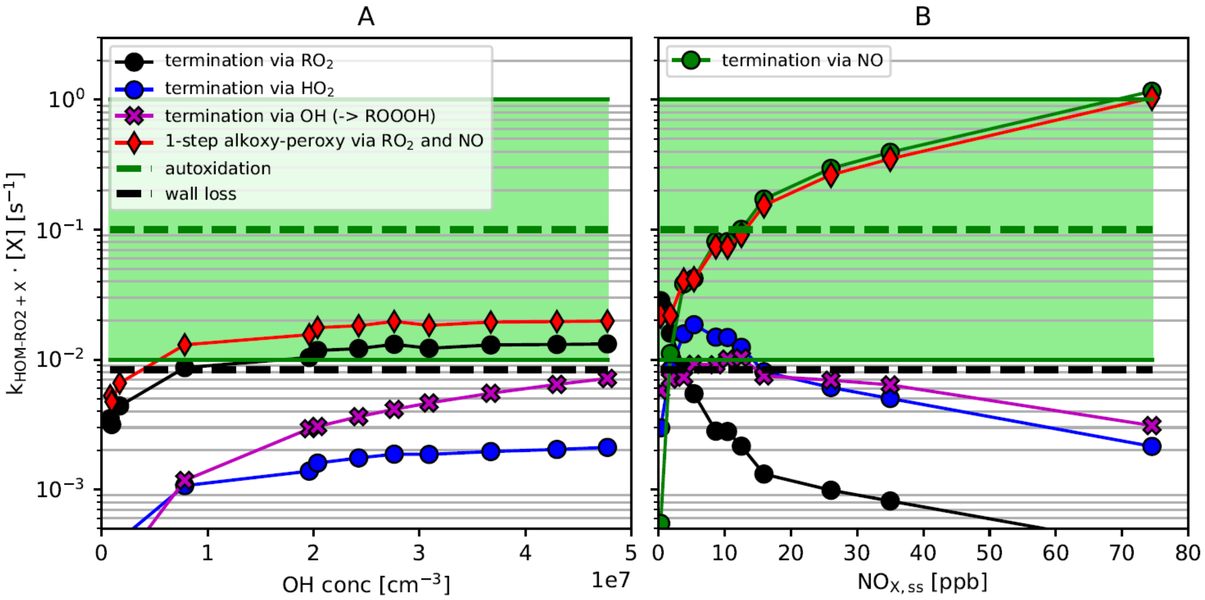
2. In addition to the reaction classes described by the authors, some of the products could form from RO2 + OH reaction producing trioxides (ROOOH) (Assaf et al.). This reaction could be *particularly important under the elevated OH conditions of the experiments carried out here. The importance of this reaction should perhaps be modelled out.*

Yes, we agree that RO_2 + OH should be mentioned in the manuscript.

- *Related, could the increase in C10H15O2n+1 signals at elevated levels of OH (line 420) be attributed in some part to the RO2 + OH => ROOOH => RO + HO2 (and not just HOM-*RO2 + RO2 as currently stated)?

The rate coefficient of the RO_2 + OH reaction was determined to about 1.5 10^{-11} cm^{-3} s^{-1} (see summary paper by Fittschen in ChemPhysLett (2019)). For larger molecules it was theoretically calculated that >>90% form the ROOOH adduct (Assaf et al. 2018). From these numbers it follows that $k_{RO2+OH}\cdot[OH]_{SS}$ is of the order of 7.5 10^{-3} s^{-1} for $[OH]_{SS} = 5\cdot10^{7}$ cm^{-3} in the OH reference experiments and $1.1\cdot10^{-2}$ s^{-1} for $[OH]_{SS} = 7\cdot10^{7}$ cm^{-3} in the NO_X experiments.

A comparison of RO_2 + OH (magenta crosses) to all other channels is demonstrated in the following Figure in style of Figure 9.



For the JO1D experiments this means that ROOOH adduct formation could be probably more important than RO_2 + HO_2, therefore it could contribute to $C_{10}H_{16}O_X$. But even at the highest $[OH]_{SS}$ applied during these experiments RO_2 + RO_2 is still about a factor of two faster. In the NO_X case RO_2 + OH could be more important than RO_2 + RO_2. However, it is still about a factor of two slower than RO_2 + HO_2 at $[NO_X]_{SS}$ < 8 ppb. At $[NO_X]_{SS}$ > 8 ppb, RO_2 + NO is dominant. Lifetime of ROOOH with respect to unimolecular decay is estimated to about 5000-10000 s. From these numbers it could be indeed true that RO_2 + OH has some influence. If all findings for small molecules are applicable to highly functionalized HOM-RO_2, the reaction RO_2 + OH can contribute to formation of molecules of the $C_{10}H_{16}O_X$ and the $C_{10}H_{18}O_X$ families.

For the topic of our paper the minor path alkoxy-radical formation, RO_2 + OH -> RO + HO_2, would be more interesting, but this is obviously unimportant for larger molecules. Although RO_2 + OH should be investigated as a potential path to $C_{10}H_{16}O_X$ in mechanistic oriented papers, for our purpose to make aware of the alkoxy isomerization as carrier of the autoxidation/radical chain it is not so interesting. We would strongly prefer not to discuss the potential issues of RO_2 + OH = ROOOH for HOM formation in general here, because it is beyond the scope of this already lengthy paper.

We will mention the RO_2 + OH reaction and stable trioxide formation in the Introduction (line 75 - 77):

“Recent studies indicate that RO_2· could also react with OH· radicals (summarized in Fittschen, 2019). Theoretical calculations suggest that larger peroxy radicals could form stable trioxides under atmospheric conditions, while formation of alkoxy radicals is negligible (Assaf et al., 2018).”

and in Method section 2.4 (line 24 - 242):

“Reaction of HOM-RO_2· with OH· (Assaf et al., 2018; Fittschen, 2019) could contribute somewhat to the HOM-termination products at our reaction conditions but it will not be considered, since it cannot compete with the particular major termination pathways in the experiments.”

- *This mechanism could also explain in part the CO experiments. In the absence of CO, higher OH concentrations can lead to C10H15O2n+1 products via the ROOOH pathway above, which switches in the presence of CO when OH concentrations are lower. The trioxide does get more stable against decomposition with the increase in carbon chain length, so the contribution of the channel is perhaps minimal.*

A similar consideration as in the previous response shows that in the CO case at $[OH] = 1\cdot10^7$ cm^{-3}, RO_2 + OH cannot significantly compete with HOM-RO_2 + HO_2 and HOM-RO_2 + RO_2.

No action.

3. About the C10H16O7 signal in page 10 which dominates the C10H16Ox family in their measurements, the authors state that the contribution to this signal from C10H17Ox is low (line 351). Does the majority of the C10H16O7 signal measured then come from reactions of C10H15Ox? Maybe provide additional details regarding the reactions that are likely involved, whether R2 or R3b or something else. If it’s R2, does [HO2] explain the measured intensity?

The purpose of these lines was to make it plausible that $C_{10}H_{17}O_X$ peroxy radicals likely did not end up in $C_{10}H_{16}O_7$, so they are not trapped specifically in this compound. As a consequence, $C_{10}H_{16}O_7$ must arise from $C_{10}H_{15}O_8$ + RO_2 or $C_{10}H_{15}O_7$ + HO_2. Both, HOM peroxy radicals have large abundances. The high concentration and the fast increase with turnover by OH indicate an efficient termination reaction. For the latter a missing HO_2 source in the model calculations would help, as discussed in the supplement. (To continue the discussion on comment 2: the contribution of the reaction HOM-RO_2 + OH -> HOM-ROOOH is small since $C_{10}H_{15}O_6$ is relatively small.)

Action:

We will add to the manuscript, Section 3.1, line 370 -372):

“$C_{10}H_{16}O_7$ is thus likely formed from $C_{10}H_{15}O_8$ or $C_{10}H_{15}O_7$ which show high abundances (Fig. S5). The large contribution of $C_{10}H_{16}O_7$ to the $C_{10}H_{16}O_X$ family indicates specifically efficient termination reactions of $C_{10}H_{15}O_8$ + RO_2 or $C_{10}H_{15}O_7$ + HO_2.”

4. Lines 415-419: C10H15O6 can form from a-pinene ozonolysis. In fact, Meder et al. 2025 cited here measure multiple isomers of this peroxy radical. Also, consider a different word than “unimportant” in line 419. C10H15O6 is crucial to formation of the next peroxy radical in the autoxidation chain, C10H15O8. It can also react bimolecularly to form the closed-shell C10H14O5 species, as reported in Meder et al.

We agree with the reviewer, our formulations are unlucky and misleading.

First, we would like to state that the concentration of $C_{10}H_{15}O_6$ is low in our dark case (60% ozonolysis / 40% OH) but not zero. It increases with OH, which means at least one $C_{10}H_{15}O_6$ isomer must have a strong OH related source, as stated in the manuscript.

However, a low concentration of an intermediate is indeed not equivalent to being unimportant. Iyers et al. (2021) suggested that $C_{10}H_{15}O_6$ is rapidly converted to $C_{10}H_{15}O_8$, which would explain the small concentration and relatively high $C_{10}H_{15}O_8$ concentrations at the same time. Meder et al. (2025) discuss the relative importance of different abstraction pathways. Meder et al. supported the mechanism proposed by Iyers et al. (2021) as it can explain a part of the observed H-abstraction behavior leading to $C_{10}H_{15}O_6$. However, Meder et al. also state that Iyers' mechanism cannot explain all H-abstraction pathways they observe, which indicates involvement of different $C_{10}H_{15}O_6$ isomers. In our opinion, $C_{10}H_{15}O_6$ isomers could also arise in Meder's experiments from (dark) OH, as they did, like us, not quench OH in their experiments. Insofar we agree with Iyers and Meder, however, in different aspects.

Action:

We modified the sentence in Section 3.2.1 (line 441 – 444) and avoided the notation "unimportant".

"This observation is consistent with the HOM pathways in α-pinene ozonolysis proposed by Iyer et al. (2021) wherein an efficient 1,4 shift to $C_{10}H_{15}O_8$ should lead to a small concentration of $C_{10}H_{15}O_6$ in bare ozonolysis. The fraction of $C_{10}H_{15}O_6$, which in Meder's et al. (2023, 2025) experiments could not be explained by the Iyer mechanism, could arise in parts from dark OH as in our experiments."

5. Regarding the effect of CO on the formation of HOM RO, the authors cite Jenkin et al. 2019 to say that the branching to alkoxy radicals from RO2 + HO2 reactions should be low (line 464). However, this is highly dependent on the structure of the R. According to Jenkin et al., there is an almost 50:50 branching towards ROOH and RO for beta-oxo peroxy radicals (Table 8 in Jenkin et al 2019). The authors should discuss the importance of the RO2 + HO2 reaction in the context of the structures of the Rs in their system.

We agree with the reviewer that the result of the CO experiment looks a bit more complex than simply replacing RO_2 by HO_2, although the overall trend is suppression of the alkoxy-peroxy paths (parity change). If HOM-RO_2 + HO_2 would be an important source of HOM-RO, the oxygen parity should behave like in the OH reference experiment or like in the NO_X experiments. This is, however, not the case. Parity change is reduced in the presence of enhanced HO_2, which indicates that HOM-RO is suppressed compared to reaction with RO_2. Secondly, we agree with the reviewer that the structure of R is key for (the rate of) isomerization. Regarding the structure of R in HOM-RO_2 and potential HOM-RO formation by HO_2, we agree that there may be isomers with significant tendency to form alkoxy radicals. However, we have no direct handle on the structure R of isomers in this study, since we applied HR mass spectrometry, which provides only chemical formulas. The advantage of HR-MS is that we can observe the time evolution or here the steady state abundance of several HOM-RO_2 simultaneously. Therefore we probably capture a variation of Rs. Our approach assumes that there are structure isomers represented in the pool of intermediates with the reactant formula that have the ability to form the hydroperoxide in reaction with HO_2. While there may be also isomers that are able to form a significant fraction HOM-RO, which we don't know. This would overall mostly shift the chemistry somewhat between termination and autoxidation within a rather large uncertainty envelope.

Action:

We added a remark to the Introduction (line 89 - 90):

"For specific peroxy radicals even reaction with HO_2 can lead to significant branching into alkoxy formation (Jenkins et al. 2019)."

and made clearer in section 3.2.2. (line 507 - 509) that we do not exclude contribution of RO from HO_2:

"Regarding the reaction HOM-$RO_2\cdot$ + $HO_2\cdot$ (R9) a production of HOM-RO· cannot be excluded; it seems to be less efficient than HOM-ROOH formation (R2), though."

6. How does the decrease in [OH] from CO addition affect the RO2 intensities and distribution? In line 494 the authors put the onus of HOM-RO2 suppression completely on HOM-RO2 + HO2 reactions, but how much of the suppression is due to lower [OH]?

We choose for this comparison experiments with a similar turnover with and without CO, therefore the primary production of RO_2 is about the same. We do therefore not expect a large effect on the distribution of R of the RO_2 radicals starting the autoxidation. Since production is about the same it must be the enhanced sink by HO_2 that leads to overall reduction of HOM-RO_2. (Further, we did not claim in line 494f that the suppression is *completely* due to enhanced [HO2].)

In summary, the enhanced importance of HOM-RO_2· + HO_2· reactions compared to HOM-RO2· + RO2· reactions in the CO experiment led to suppression in the abundance of HOM-RO_2· radicals as well as fragmented compounds related to alkoxy steps.

Action:

We modified the sentence (Section 3.2.2. line 521 -523):

“In summary, the enhanced importance of HOM-RO_2· + HO_2· reactions compared to HOM-RO_2· + RO_2· reactions in the CO experiment led to a general suppression of the abundance of HOM-RO_2·. Hereby concentrations of HOM-$C_{10}H_{15}O_{2n+1}$ and fragmented compounds which are related to alkoxy steps were disproportionally stronger suppressed.”

7. The increase in C10H15Ox signals with the increase in NOx: is there a possibility that some ozone is forming from NO2 photolysis? If I understand the method section correctly, UV-A lights are on during these experiments, so won’t NO2 photolysis increase O3 concentrations, explaining at least partly, the observed increase in C10H15Ox signals?

Yes, we agree that NO_X chemistry affects the O_3 steady state concentrations. In our experiments, we observed net destruction as well as production of O_3 depending on $[NO_X]_{SS}$. For our calculations, we used always the steady state concentration of O_3 as measured (Table S1), insofar NO_X related changes in O_3 are already considered. In the NO_X experiments, turnover is dominated by 90% by OH despite high $[O_3]_{SS}$; even in the experiment with the highest NO_X, it is still 86%. Moreover, RO_2 production is much more efficient in OH photochemistry compared to RO_2 production from O_3 (vinylhydroperoxide path). In any case, for the measured NO concentration >8 ppb, reaction by NO is the dominant fate of peroxy radicals. So, a little stronger RO_2 source from O_3 cannot explain the relatively high levels of $C_{10}H_{15}O_X$ with increasing NO_X. Moreover, O_3 related HOM-RO_2 would react with NO in the same way as OH generated HOM-RO_2. Of course O_3 related peroxy radicals will also undergo the alkoxy-peroxy steps (Mentel et al. 2015). In addition, as shown in Figure 9, $C_{10}H_{17}O_X$, which are not formed by O_3, also survive at high NO_X. All this indicates that for HOM-RO_2 an extra source must exist compared to conventional RO_2. And our suggestion is that it is alkoxy-isomerization under preservation of the carbon backbone.

No action

Assaf, E., Schoemaecker, C., Vereecken, L. and Fittschen, C., 2018. Experimental and theoretical investigation of the reaction of RO2 radicals with OH radicals: Dependence of the HO2 yield on the size of the alkyl group. International journal of chemical kinetics, 50(9), pp.670-680

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