RC1

We thank the reviewer for the helpful comments and responded to all comments. The reviewer comments are type set in italics while our responses 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.

Kang et al. uses high resolution NO_3^- ToF mass spectrometry to investigate the peroxy alkoxy pathway to highly oxygenated organic molecules (HOMs). Since the alkoxy radical cannot be detected using CIMS, they infer alkoxy reactions occurring by the parity of oxygen and hydrogen number, where odd oxygen $C_{10}H_{15}O_x$ peroxy radicals are assumed to have formed via an alkoxy radical intermediate. There are some limitations to this method (e.g. oxygen parity only works through one generation of peroxy-alkoxy isomerization and NO_3^- CIMS is only sensitive to HOM RO_2) and many assumptions about complex RO_2 and RO chemistry. Nevertheless, the story of this paper, summarized in Figure 8, is sound and may fundamentally shift how we think about HOM formation. I find this study interesting and believe the audience of ACP will too. Before being published I request the following comments to be addressed.

We thank the reviewer for the positive statement. Addressing the upcoming comments helped us to make the manuscript clearer.

Specific comments:

1. *My main concern is that the discussion often neglects the importance of R structure for the peroxy-alkoxy pathway. This includes RO formation and RO isomerization, both of which are broadly parameterized here. While there are instances where structure is addressed (e.g. Figure 1), below are a few places where I would like to see a deeper discussion,*

First, we would like to make two general statements regarding the structure of R. Firstly, we only refer to HOM-RO and HOM-RO_2 and not to alkoxy and peroxy radicals in general. Limiting to HOM-RO and HOM-RO_2 already provides a preselection of potential R that are able to isomerize and grow into HOMs. Secondly, we agree with the reviewer that the structure of R is key for (the rate of) isomerization. However, we have no direct handle on the structure R of isomers in this study, since we applied mass spectrometric data. Nevertheless HR-MS provides sufficient resolution to resolve CHON molecular formulas. The advantage of HR-MS is that we can observe time evolution or steady state abundance of 100's of compounds simultaneously, so we capture quite a large wealth of R's. Nevertheless, our approach is limited to relations between formulas, which e.g. represent radicals. We must assume that at least one of the structure isomers represented by the reactant formula has the right structure for a fast isomerization step to react to a compound represented by the product formula. Our suggestions/conclusions are thus not to read as "10% of compounds do that step" but as "there must be one or more isomers" with the given formula which are able to provide 10% of the turnover to the product formula.

Action:

We clarified the limits of the approach to prevent misinterpretations of our results by adding the following to section 2.4, line 291-302:

"However, multifunctional HOM-RO· should have quite a potential for hydrogen rearrangement since they are highly functionalized, and functionalization facilitates isomerization (Vereecken and Peeters, 2010). Note that we are using HR-MS data, which allow for determining the compounds formulas but not the speciation. As a consequence, more than one structure isomer can contribute to the signal for one formula. We have thus no direct handle on the structure of R. The advantage of HR-MS is that we can observe the steady state abundance of 100's of compounds simultaneously, so that we capture

quite a large wealth of R's. Nevertheless, our approach is limited to relations between formulas, which e.g. represent HOM-RO2· and their termination products. We assume that at least one of the structure isomers represented by the reactant formula has the right structure of R for a fast isomerization step to react to an isomer represented by the product formula. Our suggestions/conclusions are thus not to interpret in a statistical sense but in terms of "there must be one or more isomers" with the given formula that are able to provide the observed conversion to the product formula. Using this approach, we will show that isomerization can become dominant in cases of large, highly functionalized molecules, such as α-pinene derived HOM-RO· radicals."

A deeper investigation of which isomers could do the isomerization is beyond the scope of the present manuscript but could be a good starting point for further studies. Here, we *try to raise attention* to insight that alkoxy radicals play an important role in HOM formation and how that could happen as a general principle.

- *Figure 1 is a great illustration of how a step of alkoxy chemistry changes the RO_2 hydrogen parity, in this case from an even to odd number. However, mechanism ABE produces a less oxygenated RO_2. This contradicts the paper conclusion that the peroxy alkoxy pathway leads to more oxygenated organic compounds. A discussion on R here would help clarify branching between mechanisms ABCD and ABE.*

We agree with the reviewer that ABE produces a less oxidized alkoxy radical. However, the gain in O/C for HOMs is not so much in getting higher oxidized alkoxy radicals, but in that isomerization of alkoxy radicals does not stop the autoxidation chain but rather regenerates peroxy radicals that can then continue the autoxidation in competition to fragmentation or to termination of the radical chain. That is why we coined the notation "alkoxy peroxy" steps. If peroxy radical E continues with one autoxidation step, we will have gained still one O atom, and more in any subsequent steps. Regarding the structure of R, for our level of approach it is sufficient that an R exists, that enables isomerization of HOM-RO resulting in an HOM-RO_2 and that is able to continue the autoxidation…(See our response to comment 1.)

We stated that already in paragraph 3.4 line 682-689 and in the Conclusions line 780 in the originally submitted manuscript.

No action.

- *It is difficult to interpret changes in the RO_2 and RO branching chemistry when the ratio of OH:O_3 oxidation changes. Peroxy and alkoxy branching is sensitive to R, and so it matters whether the peroxy radical you make is coming from OH addition, OH abstraction, or ozonolysis. Please address how the ozonolysis rate is accounted for in the AP turnover when you adjust O_3, NO_x, CO, or light aperture.*

In the manuscript we used only the turnover of α-pinene with OH as a parameter and this is explicitly noted in the text and in x-axis labels in all figures where it applies.

Within the JO1D experiments we kept the O_3 input constant and increased JO1D and thus the [OH]. That leads to an increasing importance of OH, which became ≥ 90% at OH turnover of about $4 \cdot 10^7$ cm^{-3} s^{-1}. In the JO1D related plots we show the whole range of turnover by OH, but we considered only the latter data for analysis and comparison (Fig. S3, Fig. S9, Fig. 9b). The OH pathway was thus the dominant channel for HOM formation. If, conversely, O_3 would be dominant, O_3 effects should decrease with increasing OH, but we mainly observe the OH effects increasing. Note that OH

photochemistry produces peroxy radicals for HOM formation more efficient than O_3 chemistry (via the vinylhydroperoxide path).

In the CO and NO_X experiments, there are only two exceptions where OH contributed little less than 90% to the α-pinene turnover, but even there the OH contribution is still high: in the CO experiment, OH contributed about 86% to the α-pinene turnover, and in the NO_X experiment at the highest NO_X OH contributed 86%. In the NO_X cases it was necessary to vary the O_3 input in order to increase the OH source for compensating the OH loss with NO_2. Otherwise, such experiments maintaining a roughly constant α-pinene turnover by OH would not have been possible.

Thus, we compare only chemically similar systems regarding the OH vs. O_3 turnover (fraction of turnover by O_3 < 10%), with the two exceptions mentioned and the primary chemistry very likely generating similar sets of Rs. For our investigation on the role of alkoxy isomerization in HOM formation, it does not so much matter how exactly the HOM-RO are formed, as long as the isomeric distribution remains similar.

Action:

We added the information about the O_3 contribution for CO in paragraph 3.2.2, line 493:

"Turnover by O_3 contributed 14% in case of CO and 3% in case of the OH reference experiment."

and for NOX in section 3.2.3, line 552:

"Despite increasing $[O_3]_{SS}$ with increasing $[NO_X]_{SS}$ (Table S1), the turnover of α-pinene by OH contributed more than 90% with exception of the highest $[NO_X]$ where it still contributed 86%."

- *Line 84: ROO-OOR -> 2RO₂ + O₂ branching ratio seems to be largely parameterized and probably varies much more. Please clarify if using structure activity relationships.*

We do not exactly understand this question. We assume the reviewer refers to the reaction $RO_2 + RO_2 -> 2\ RO + O_2$. From structure-activity relationships we know there is high variability in the rate coefficients for these processes, spanning many orders of magnitude. However, processes that are too slow will not lead to HOMs in our experiments, leaving a strongly reduced rate range allowed for the observable chemistry. The rate coefficients used were averaged from reactions included in literature data and models, e.g. MCMv3.1.1 or Jenkin et al. (2019), and represent reasonable estimates for the subset of viable reactions. While this still leaves a high variability around the selected rate coefficients for each individual reaction, the conclusions are derived from the average change over the pool of intermediates and are not critically dependent on these exact values. Specifically, modifying the rate values doesn't change the interpretation, but merely the estimated ratios between the competing effective processes.

Action:

We expressed that clearer in the Introduction, line 87 - 91:

"The branching ratio of alkoxy radical formation from peroxy radicals varies strongly depending on their structure; for example, for primary and secondary RO_2· 60% are given for R7 by Jenkins et al. (2019). For R8 branching ratios supposedly vary between 70%-90% (MCMv3.1.1). For specific peroxy radicals even reaction with HO_2 can lead to significant branching into alkoxy formation (Jenkins et al. 2019). Alkoxy intermediates play an important role in the atmospheric degradation of VOCs (Färber et al., 2024; Jaoui et al., 2021; Yang et al., 2025)."

- *Line 427: I don't agree that RO isomerization will be a statistical probability as you make it out here. It will be extremely dependent on R structure. RO isomerization will create new functionalized R backbones that may favor or inhibit future isomerization steps. Please clarify if using structure activity relationships and also their applicability.*

The reviewer is correct; it is not a simple statistical probability for any given intermediate. However, there are hundreds of organic radicals involved, and a fraction of these will undergo one type of reaction, another fraction another type, and these fractions within the population are reflected in the rate ratios of the competing processes. In the sense of our general statements above, for the level of our interpretation it is thus sufficient that isomers exist that can do the reaction, not that each isomer has competing pathways. Since we have no structural information, we cannot apply SARS to individual isomers. Instead, we are tentatively applying an average branching ratio to the whole group of structure isomers. Like RO_2 autoxidation, RO isomerization may also produce intermediates with backbones that cannot undergo autoxidation (besides fragmentation). However, our results suggest that sufficient RO_2 with suitable backbones are produced, which can carry on the autoxidation. Our approach is clearly limited, as pointed out correctly by the reviewer, but interestingly the observed concentrations for the sum of structure isomers (with the same formula) treated with lumped and averaged rate constants and branching ratios, as applied also in MCM, produced results which are compatible with the observation. This serves here only for qualitative demonstration of the possibility.

Action:

We clarified this limitation by modifying the paragraph (line 454 - 457) in section 3.2.1.:

"Note, that the applied branching ratios of 0.6 (Jenkins et al. 2019 for primary and secondary RO_2·) and 0.5 for HOM-RO isomerization (see below and Suppl. Section 6) comprise a certain degree of lumping and serve here to demonstrate the possibility of alkoxy-peroxy steps. Individual branching ratios and thus alkoxy-peroxy steps for specific HOM-RO_2· and HOM-RO· are strongly dependent on the structure of R and can deviate quite far from the chosen values."

- *Line 798: Please clarify what you mean by the alkoxy-peroxy step does not rely on specific chemistry of alpha-pinene. I agree these results are applicable (and important!) for large, functionalized VOCs, but would this statement hold true for alkanes, especially those with 5 or fewer carbon atoms?*

We meant to express that alkoxy peroxy steps are not limited to α-pinene as a precursor. It will also apply to many atmospherically important VOC, in general to all that have structures to allow autoxidation and formation of HOM. This implies having a backbone of a certain minimum length since H-shifts are largely determined by formation of cyclic structures in the transition states. The smallest alkane with observable H-migration would thus be butane (i.e., forming 1-butoxy allowing a 1,5-H-shift with rate $\sim 1 \cdot 10^5\ s^{-1}$)

Action:

We modified the paragraph in the Conclusions (line 831 - 835):

"The analysis of the contribution of alkoxy-peroxy steps in this work, however, does not rely on specific chemistry of α-pinene, but also holds for a variety of atmospheric VOC. Prerequisite is a backbone of a certain minimum length since H-shift are largely determined by formation of cyclic structures in the transition states. Consideration of alkoxy-peroxy steps enables to derive a consistent interpretation across a wide variety of reaction conditions based solely on the reactivity trends captured in generalized Structure-Activity Relationships applicable to all peroxy- and alkoxy radicals (e.g. Jenkin et al. 2019, Vereecken and Peeters, 2009, 2010)."

2. Although it is pointed out that NO_3^- CIMS is selective towards measuring HOMs, there is little discussion as to what it cannot efficiently detect. Including more information on this is important for readers to interpret what's shown in the plots and also what's not shown (e.g. less oxygenated RO_2 that precede HOM RO_2).

Our experiments were performed under steady state conditions. The HOMs will react at the steady state concentrations. In this specific situation it is for our purposes not so important to measure all HOM precursors.

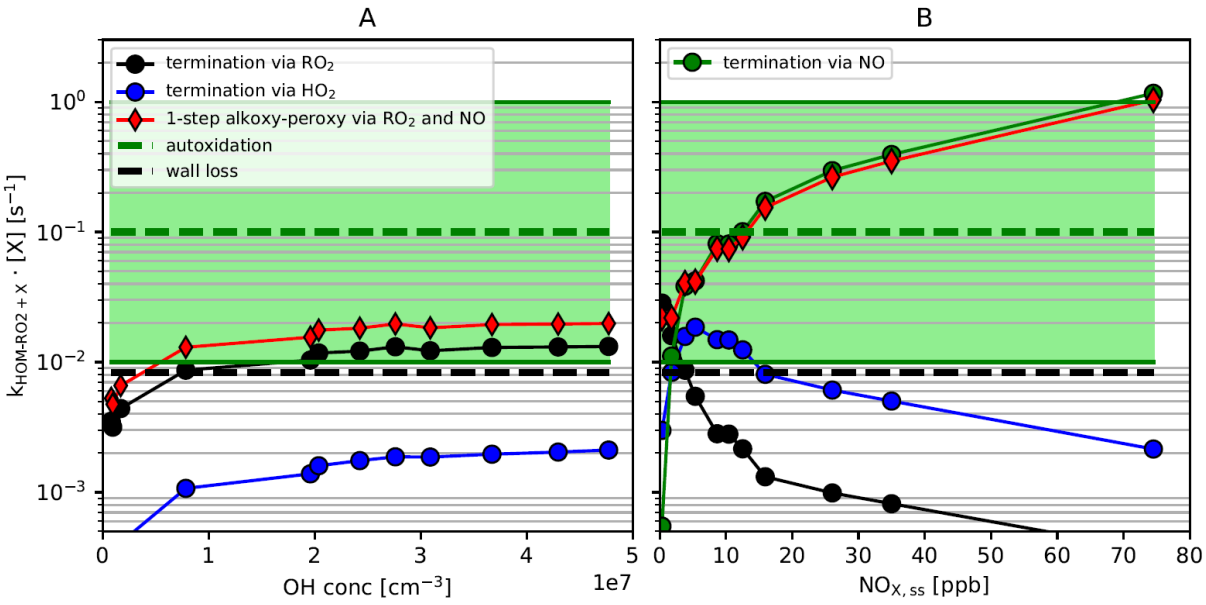
Action:

We added to the manuscript (section 2.3, line 206 - 210):

"As a consequence, compounds with less oxygen atoms cannot be detected with the same sensitivity. For example, the first generation of conventional peroxy radicals cannot be detected at all. Currently, absolute calibration for HOMs does not exist. Assuming clustering of HOMs with NO_3^- takes place at the kinetic limit it is common to apply the sensitivity towards sulfuric acid. This sensitivity was determined to be $3.7(\pm1.2)\cdot10^{10}$ molecules cm^{-3} $ncps^{-1}$ and applied to convert the MS signal to a concentration (see Pullinen et al. 2020)."

3. For the NO_x experiments, your aim is to increase [NO_x] to produce RO from RO_2+NO reactions. There is a good discussion in the main text and SI about how NO_x affects OH and thus the alpha pinene turnover rate. Have you calculated/modeled how additional NO_x affects OH:HO_2? The previous CO experiments show that increased HO_2 shuts down peroxy alkoxy pathways, which could also explain your data in the NO_x experiments.

Regarding modelling, we don't have a good handle on [HO_2] in the NO_X experiments as described in the supplement. NO, OH, and HO_2 are given in Table S1 and Table S2, respectively. In the presence of more than 8 ppb of NO_X, RO_2 + HO_2 cannot compete with RO_2 + NO, independent if we assume an HO_2 source in the model or not (see Figure B below, the termination is dominated by NO for NO_X > 8 ppb). Thus, while HO_2 shuts down alkoxy peroxy pathways, NO opens alkoxy-peroxy pathways more efficiently.



No action.

4. In Figure 5, the x-axis is plotted as the NO_x concentration. Table S1 indicates almost all of NO_x is NO_2. Can this be changed to NO concentration since it is RO_2+NO reactions that produce alkoxy radicals?

This is a good point, but we did not find a better plotting solution as the one presented; note that NO and NO_X are highly correlated and yield similar plots. We have considered plotting against NO, and the plots give the same information as the NO_X plots, however the data points at low NO_X become even more compressed as they are already now. A way out could be a logarithmic NO scale, which we also tested. Log scale axis is counter-intuitive in our case. Moreover, in atmospheric chemistry people often think in NO_X regimes. We would therefore prefer not to change the plot as it would not bring more clarity.

No action.

5. Figure 6 is interesting but may be better suited for the SI. The text points out that signal is changing due to [OH] which is not corrected for. The comparison to MCM does not fit in with this specific study since autoxidation is not implemented and therefore it is without a single path to HOM RO2 (with or without considering the peroxy alkoxy pathway).

Here we don't agree with the reviewer: the MCM results were not intended to fit the data. They are supposed to illustrate how $[RO_2] = f([NO_X])$ will look like in the absence of alkoxy isomerization, since MCM does not consider it. On top, in MCMv3.1.1 a prerequisite for alkoxy isomerization, i.e., autoxidation as source for highly functionalized compounds, is also missing, but this is not so important here.

Figure 6 shows that HOM-RO_2 behave different as $f([NO_X])$ than conventional RO_2, and we suggest that this is the case because HOM-RO can isomerize. We believe that this plot pretty well illustrates our findings and suggestions about the role of alkoxy isomerization. We would prefer to leave the plot where it is.

No action.

6. The branching ratios you derive for both RO formation and subsequent isomerization are important and really jumped out to me in the abstract. However, the discussion in the text comes late and was not clear. I would recommend putting more of a focus on this in the main text.

We do not quite agree with the reviewer. We put a lot of effort in deriving an idea of a value for *branching of HOM-RO into isomerization* based on our data. All steps are described in the manuscript, eventually referring to the supplement. Lacking better approaches at this time, we tried to distill, as good as we could, branching ratios for HOM-RO_2 into RO in analogy to conventional RO_2 from the literature; these are our choices but not our findings. They are momentarily assumptions. As explained before, it is not our intention to claim certain values as best ones, but to show that assuming alkoxy isomerization is indeed feasible for a not unreasonable choice of "numbers" documented in the literature.

In any case, we are using mass spectrometric data without speciation. Thus, we are treating strongly lumped systems with all their limits. Kinetic data derived from lumped systems are in any case of limited transferability. On the other hand, we based as much as possible on our observed data (including those published in Pullinen et al. 2020), which are at least self-consistent in a certain way. We think of our results as more of a starting point than a final result.. Every step of derivation and assumption is clearly described, and as soon as there will be better data available the branching ratio can be recalculated by everyone who is interested.

Action:

We removed the values for branching ratios into alkoxy radicals from the abstract. We had given them because their values were used for the calculation of the branching into isomerization, which we determined in this study (Supplement section 6).

We underlined the preliminary character of our results and the limits of our kinetic data in Section 3.4, line 739 -741:

"Note, we are dealing here with mass spectrometric data, and several isomers are possibly lumped under the same formula. The values for rate coefficients and branching ratios we derived and chose for the following calculations are suited for the intended *plausibility considerations* and should be handled with care when transferred to other systems or used for the purpose of *strict* quantification."

Minor comments:

Line 70: Should alcohol product have a radical dot?

A typo, fixed.

Line 90: Add NO_2 as product

"NO_2" added

Line 97: Clarify RO_2+NO produces RO or $RONO_2$ as products

The reaction scheme is split into termination reactions generating closed shell products (R1-R5) and chain continuing reactions generating radicals (R7-R9). The formation of $RONO_2$ is covered by R4. We do not see a need to change this; the desired information is given by R4.

Line 201: You mention using SA calibration factor for HOMs and specify a value. But no concentrations are reported in the paper. Why is that?

As described in line 195

"In this work, the observed MS signals, normalized to the total signal, were used for the interpretation of the data since the *relative changes* of the HOM product distribution for the different reaction conditions were more relevant than the absolute concentrations."

We rely on the precision of our data. We could have also used concentrations, which means in our case multiplication with the calibration factor for sulfuric acid of $3.7(\pm1.2)\cdot10^{10}$ molecules cm^{-3} $ncps^{-1}$. This will not help the precision and may pretend an accuracy which we don't have. For kinetic considerations signals must be converted into concentrations, though.

Line 258: You specify the same formula, $C_{10}H_{17}O_{x+1}$, twice. Please clarify.

Accepted, should be "$C_{10}H_{17}O_{X+1}$ or $C_{10}H_{17}O_X$"

Line 264-267: This paragraph is generally confusing to read. Please clarify. You point out 3 products coming from 2 precursors and then say respectively. It is not clear what products are from which precursors.

Accepted, we will change the text in section 2.4, line 274 – 276:

"Still, classifying C_{10} and C_{20} molecules by family may help to understand which HOM-$RO_2\cdot$ were involved in their formation, especially in case of $C_{10}H_{14}O_Y$ and $C_{10}H_{15}$-HOM-NO_3, which are exclusively produced by $C_{10}H_{15}O_X$, and for $C_{10}H_{18}O_Y$ and $C_{10}H_{17}$-HOM-NO_3, which are exclusively formed from $C_{10}H_{17}O_X$."

Line 268: What is sufficient NO? Even low NO will be important to peroxy-alkoxy chemistry (Nie, W., et al, Nature Comm, 2023)

Accepted, we removed "sufficient amounts of"

Line 417: "Different from $C_{10}H_{15}O_8$ and $C_{10}H_{15}O_{10}$, formation of $C_{10}H_{15}O_6$ is obviously exclusively initialized by OH oxidation." I would remove obviously. Could $C_{10}H_{15}O_6$ not been formed from AP + O_3 -> $C_{10}H_{15}O_4$ -> $C_{10}H_{15}O_6$ through one generation of autoxidation?

Accepted, we will replace "obviously exclusively" by "efficiently"

Line 495: "The CO experiment resulted in a clear suppression in the abundance of HOM-RO_2 radicals" This is not clear from the data presented in Figure 4 which is normalized. Please show unnormalized data to make this point.

Accepted, this sentence is misleading: We wanted to repeat the **result** stated in the text (line 472), that enhanced HO_2 decreased HOM-RO_2 by a factor of two (from $\approx 6 \cdot 10^6$ to $\approx 3 \cdot 10^6$ cm^{-3}) since HO_2 is in general an RO_2 sink. This information is a measurement result and independent from Figure 4. Since the abundance of HOM-RO_2 decreased, normalization makes the results clearer as it just removes the effect of different concentrations, therefore we would not like to change Figure 4.

We rephrased that sentence in 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."

Line 655: "...strong increase in O:C caused by NOx addition is only explainable by impacts of HOM-RO..." I agree that your data supports this conclusion, but I would caution against saying this is the only explanation since there are not measurements for how the less oxygenated RO_2 were affected

Accepted: We discarded "only"

Additionally, please reread the manuscript to minor typos (extra word in line 491, missing word in line 638, subscripts in line 726)

We are sorry about too many surviving mistakes and eliminated as many of them as possible.

Citation: https://doi.org/10.5194/egusphere-2025-2772-RC1