

Referee response

Ether and ester formation from peroxy radical recombination: A qualitative reaction channel analysis

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Referee 1

This paper discusses an analysis of the formation of accretion products from the cross-reactions of peroxy (RO₂) radicals formed in atmospheric reactions of several representative compounds using a modified version of the Gecko-A atmospheric chemical mechanism generation system. Previously it was thought that the major pathways for such cross-reactions was either dissociation forming alkoxy radicals or H-shifts (when possible) forming an alcohol and carbonyl, but addition forming peroxides + O₂ has also been considered. More recently, experimental and theoretical studies indicated that accretion reactions forming more stable (yet lower molecular weight) ethers and esters may also occur in some cases. This is investigated in this work, where the Gecko-A system is modified to include estimates of these accretion reactions for peroxy radicals formed from representative compounds. A number of the estimates are uncertain and approximations had to be used in this analysis because it is not possible in practice to represent all the possible peroxy + peroxy combinations in explicit mechanisms, and because the levels and distributions of peroxy radicals formed, depend significantly on the environment where they react. Therefore, as the authors admit, the results are largely qualitative, and do not necessarily represent any particular environment. However, this appears to be the first attempt to estimate the distributions formation of accretion products in reactions of organics in atmospheric systems, which are potentially important sources of secondary organic aerosol in the atmosphere that are not represented in current models. For this reason, I consider this work to be of high scientific significance and appropriate for publication in this journal.

Answer: Thank you sincerely!

Although the methods they used to estimate the branching ratios for the peroxy + peroxy reactions have uncertainties, especially for the larger radicals where accretion reactions may be more significant, I believe their chemical mechanism estimation methods represent the current state of the science and are probably as good as can reasonably be done given our current state of knowledge. Unfortunately, the Gecko-A tool that they used was not ideally suited for this study because it did not consider

H-shift auto-oxidation isomerization reactions of peroxy radicals, which will affect predictions of distributions of peroxy radicals formed and which last long enough to react with other peroxy radicals. The authors recognize this limitation and attempts are made to deal with it by removing at least one type of radical where this is known to be fast from their analysis (acyl peroxy radicals with -OOH groups). However, this isomerization is either fast or at least non-negligible for radicals with -CHO groups or with allylic hydrogens, and these are formed from many compounds, including some examined in this study. Fortunately, structure and reactivity (SAR) methods now exist for H-shift reactions of a wide variety of peroxy radicals (e.g., Vereecken and Nozière, 2020, <https://doi.org/10.5194/acp-20-7429-2020>), and those could be incorporated in mechanism generation systems to account for this type of reaction. It would have been better, and certainly within our current state of knowledge, had they also modified Gecko-A to include these auto-oxidation reactions as well as the accretion reactions. As it is, a study like this would need to be repeated once this modification is made.

Answer: We are well aware of this limitation. The RO₂ H-shifts pose difficult technical problems for the implementation in GECKO-A due to the competition between unimolecular and bimolecular RO₂ chemistry, as H-shift rates range from 'maybe competitive in some conditions', through 'out-competes all bimolecular chemistry in low NO_x but not in high NO_x' all the way to 'out-competes everything, even H-scrambling'. We do plan on dedicating a future article on how to include unimolecular RO₂ reactions (including RO₂ ring closure reactions, since referee 2 brought these up) in GECKO-A and other atmospheric automated reaction mechanism generators, but we consider the problem to be beyond the scope of this work. Moreover, we disagree somewhat on the need to repeat this study once said autoxidation code exists, as we already discussed this issue in the paragraph starting from line 540. The inclusion of autoxidation reactions certainly changes the distribution of RO₂ generated by the code, but we do not expect it to change the conclusions drawn in this work regarding the importance of endocyclic beta-scissions and RO₂ with rapid recombination rates (most importantly RC(O)O₂ and beta-substituted RCH₂O₂) for accretion product formation.

The greatest problem I have with this work is that it did not provide any indication of the overall importance of these peroxy + peroxy reactions in atmospheric systems, or how the estimated accretion product yields and distributions might depend on environmental conditions. Environmental conditions are important in affecting both the importance of peroxy + peroxy reactions compared to competing reactions with NO_x and HO₂, and also the distribution of peroxy radicals present. Peroxy + peroxy reactions can be important in laboratory systems in experiments with high concentrations and no NO_x, but are negligible at high or moderate NO_x levels characteristic of urban daytime scenarios, and tend to be much less important than reactions with HO₂ under lower NO_x conditions in the atmosphere. Therefore, the significance of these reactions as a source of low-volatility compounds in the real atmosphere is uncertain. Unfortunately, this work provided no useful information in this regard, which yields given only relative to the total amounts of peroxy + peroxy reactions.

A better approach for this study would be to define a set of standard environments where levels of NO_x, HO_x, O₃, peroxy radicals, light intensity and spectrum and reaction times are specified, so that total yields of accretion and all other products,

relative to the amount of compound reacted, can be unambiguously determined. This gives information not only on product yields and distributions, but also how they depend on the environment if more than one standard environment is used. For the purpose of this study, it is also necessary to specify a distribution of peroxy radicals that serve as co-reactants for the peroxy radicals formed from the compound of interest, unless the scenario being simulated has only one organic reactant initially present. That may be a good representation of laboratory experiments carried out to determine product yields, but is a poor representation of the atmospheric environment where a wide variety of compounds are reacting, most being lower the molecular weight compounds than compounds of interest for SOA formation. However, if a peroxy radical distribution that is reasonably representative of the environment is specified as an input, with Gecko calculating only the peroxy radicals formed from individual compounds of interest, then the modified Gecko simulations could give quantitative predictions of types of accretion products formed from the compounds in various environments. It may not be practical to use Gecko to simulate complex atmospheric mixtures, but the MCM mechanism, which explicitly represents many of the most important types of radicals formed, should be sufficient for this purpose.

However, the use of scenarios with simple mixtures, as employed in two of the three sets of calculations presented in this study, is not a good representation of either the atmosphere or of the types of laboratory experiments generally used to study product formation from individual compounds. The other set of calculations used beta-caryophyllene alone, which may be a good representation of product yield experiments with that compound, but is a very poor representation of real atmospheres.

Answer: As a general comment on the environment-dependence of $\text{RO}_2 + \text{RO}_2$ reactions, we fully agree that the environment has a large impact on which of our generated $\text{RO}_2 + \text{RO}_2$ pairs actually end up reacting in non-negligible numbers. However, this effect is difficult to quantify without performing a large number of box model simulations under different atmospheric conditions. In this work we only set out to generate a representative sample of all $\text{RO}_2 + \text{RO}_2$ reactions which are theoretically possible in atmospheric conditions in order to gain a better mechanistic understanding of the new in-complex RO decomposition channel. For this purpose, the GECKO-A reaction mechanism generator is a very good tool, as it in principle generates all the known possible atmospheric reaction channels for arbitrary organic compounds and radicals. Finally, considering the interest shown in accretion product formation from $\text{RO}_2 + \text{RO}_2$ during the last decade (Ehn et.al., 2014) <https://www.nature.com/articles/nature13032>, we also believe that exploring the different channels of this reaction are likely to be interesting in itself for the atmospheric chemistry & aerosol physics communities.

Nevertheless, in order to quantify the importance of these $\text{RO}_2 + \text{RO}_2$ reactions under environmental conditions, we calculated concentrations for a subset of the radicals, using the GECKO-A mechanism for 'realistic but $\text{RO}_2 + \text{RO}_2$ -relevant' daytime and nighttime conditions. This calculations are described in the new sections 2.3 and 3.5, with additional details given in section S8 in the Supplement. We hope this addresses the issue you brought up about the importance of these reactions.

I found their discussion of how they estimated product yields in the approach they employed to be unclear and questionable. The discussion of how yields are determined for the purpose of determining which radical pairs can be neglected, and for the purpose of reporting relative yields in the various figures, is unclear and needs to be improved. On lines 110-115 they suggested that a maximum yield of 100 % was used for competitive bimolecular reactions, while in Section 2.1.2 they discuss calculating relative yields based on rate constants and levels of co-reactants. I'm not sure the approach they discuss in Section 2.1.2 is valid for acyl peroxy radicals, since reaction with NO₂ is not a final sink for these radicals, since the PAN compounds formed in the acyl peroxy + NO₂ reaction can decompose and re-form these radicals. What is needed is presentation of simple examples in the SI for exactly what calculations are used to judge whether reactions of a peroxy pair should be neglected, and for how the relative yields that are presented in the figures are derived. However, if they used actual yields in calculations with standard environments, as suggested above, then all this complexity and questionable treatments regarding estimated yields can be eliminated.

Answer: The theoretical maximum yield, an already existing parameter in the GECKO-A mechanism generator, was used to identify the RO₂ that are not formed at large amounts under any atmospheric environment, and to judge which reactive pairs to neglect. We realize now that this was not made clear enough in the manuscript. Section 1.2 was modified to clarify this, and to make it clearer how the theoretical maximum yield is calculated in practise. We agree that this theoretical maximum yield is not representative of atmospheric RO₂ concentrations. The figures showing the relative yields have thus been removed from the manuscript, and we also took up your suggestion to calculate actual yields in standard environments to re-examine some of our results.

I could not locate a discussion of how they handle cases where both of the reacting peroxy radicals form alkoxy radicals with rapid decompositions. If they both form alkoxy radicals with rapid β-scission reactions that form alkyl radicals, could they react together and form accretion products with new C-C bonds, rather than ethers or esters?

Answer: This could indeed occur, and masses corresponding to these kinds of reactions have been observed experimentally, according to personal communications. However, these 'double RO decomposition reactions' are purposefully neglected in GECKO-AP because we have no mechanistic information on how these reactions occur. In Peräkylä et.al (2023) it was suggested that the ester formation after the alkoxy scission requires an ISC to occur, and the ISC rate was calculated to be 10¹¹ s⁻¹ in this case. Presumably thus the 'double RO decomposition' reaction is possible if the decomposition rates of both RO not only outspeed the ISC of the ³(RO...OR) system, but also the recombination of the radicals in the ³(RO...R system, for which the 10¹¹ s⁻¹ ISC rate may or may not be generally representative. This is purely speculation, of course. More experiments and computational studies are needed before we can properly understand when 'double RO decomposition' reaction occur, let alone how to handle them in automatized reaction mechanism generation.

There are several other concerns or issues I have with this paper. These are summarized below, in approximate order they appear in the manuscript and supplement.

130 Main Manuscript:

I do not understand why the fact that several reaction channels may form the same accretion products, mentioned in Section 2.2.3, is a problem. Certainly Gecko-A must have the code needed to tell whether a molecule formed in one reaction is the same as that formed in another. For the purpose of this paper, I think this should be sufficient for the code to compute the number of products formed without double counting. Or am misunderstanding something in this section?

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Answer: It is indeed not a problem per se. This section exists because the first author wanted one version of the data with all the generated reaction channels present, and one with only the unique product molecules. This led to some exploration of where all the duplicates are coming from, and subsequently to a short section on the topic. However, section 2.2.3 is maybe not of interest for the readers, and has been removed from the manuscript.

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In Table 3 in the "Statistics" section, it indicates that the first generation n-decane reactions could form an acyl peroxy radical in one generation. I don't understand how this could be the case. In addition, the column headers on Table 3 need to be improved. How are the numbers in the "yield" column computed and what are they relative to? It can't be relative to the amounts of compounds reacted because the yields of peroxy radicals on OH or NO₃ reactions should be close to 100 %, or higher in cases where consecutive reactions are important. If they are relative to the amount of reactant present, then they would depend on the reaction time and the levels OH, O₃, or NO₃ present.

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Answer: The first of these questions may require a bit of explanation. From Section 2.2.2: *To each RO₂ in the accretion product datasets was assigned a required combination of atmospheric oxidants based on the RO₂ list resulting from these mechanisms. Similarly, for the DTA and Terpene datasets a GECKO-A mechanism was generated for each product generation leading up to the final one to assign a generation to each of the RO₂ in the dataset. Finally, for each precursor molecule in the DTA and Terpene datasets a mechanism was generated with only one precursor in to label which of the precursors each of the RO₂ is derived from.* This labelling of the radicals is done with all the precursor molecules present, and Table 3 is based on these labels. This may result in some confusion if the same radical is formed by multiple channels from several precursors.

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Case in point: You are indeed correct that CH₃C(O)O₂ is not present among the 1st generation radicals of n-decane, but it does show up in the 2nd generation. On the other hand, CH₃C(O)O₂ is a 1st generation radical of alpha-pinene, and this is why it gets labelled as a 1st generation radical when both n-decane and alpha-pinene are present as precursors. To avoid this source of confusion, Tables 3 and 4 were redone from a new set of radical lists where only a single precursor molecule was present. On the question regarding the yield column: These are the average theoretical maximum yields. The other referee was confused by this column as well, so we removed it, as the theoretical maximum yields do not really mean anything when

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compared over generations like this.

165 I am assuming that the yields shown plots shown on Figures 2-5 are relative to the total amount of accretion products formed from a given compound, since it looks like they may sum up to 100 %. If so, this should be stated explicitly. If not, the meaning of yields in these figures, and what they are relative to, need to be clarified. Note that as mentioned above these relative yields give no useful information on how important these products may actually be in the atmospheric environment, which might be very low or negligible for many conditions.

170 **Answer:** It is stated in the captions that the yield-weighted plots are scaled such that each pair of generations n+m has an equal areas. This choice was originally made because the theoretical maximum yield are (at best) quantitatively comparable only within a generation. However, as you have already correctly criticized, these theoretical maximum yields don't really provide any information. Thus these figures were removed from the updated version of the manuscript. In a few figures (4b and 5b) the yield-weighted plot has been replaced with a similar $k_{RO_2RO_2}$ · Branching plot.

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Figures 2b, 2d, 5b, 5d, and perhaps others seem to have more colors on the bar graphs than there are in the legends. If lighter and darker shades of the same color on the bar graphs have significance, then this needs to be mentioned.

180 **Answer:** Each histogram was made transparent to enhance readability of the histograms that are behind. This results in some color mixing, which may add confusion. Unfortunately we don't see a better way to visualize the data while still grouping the products by generation like this.

185 In figure 3, it is very difficult to determine which structures are being plotted because the font of the group designations on the X axis is so small it is unreadable without greatly expanding the screen. This figure needs to be redone so that the main information, the type of group, can be more clearly seen. In addition, the plot labels should have "terpene and beta-caryophyllene peroxy radicals", not "terpene peroxy radicals".

Answer: The suggested changes were made.

190 Line 424 in section 3.3 states that "the code insures that peroxy radicals with an NO₂ group in the alpha position never forms accretion products". This should be corrected to state that the NO₂ is in the beta position. It may be in the alpha position of the alkyl radical formed in the decomposition, but it is in the beta position in the peroxy radical.

195 **Answer:** To avoid confusion we changed the formulation to the more unambiguous 'peroxy radicals with a geminal NO₂ group', as this by definition means the NO₂ and peroxy groups are attached to the same carbon.

Why are the product yields shown on the volatility distribution plots on Figures 9b and 9d be almost an order of magnitude lower than on the analogous plots of carbon or oxygen number distributions on Figures 2-5? Are they relative to a different quantity? Note that the volatility distributions seem to include compounds of all volatilities, so the total amounts should be the same as in the atom number plots on the earlier figures.

Answer: These figures include only the data for the 1st generation accretion products in the Terpene dataset, and this means the yields are scaled such that the sum of all 1st gen Terpene accretion products is 1. These plots are however removed in the revised manuscript along with the other yield-weighted plots.

Supplement:

As indicated above, there needs to be a section giving a more complete description of the algorithm(s) used to derive yields for various purposes, and it should include examples of such calculations. The examples would need to as simple as possible while incorporating all the types of situations that may need to be considered. With an adequate discussion of yields in the supplement, some of the complexity in sections 2.1.2 and 2.1.5 could well be moved to the supplement, so the main paper focuses more on the chemistry.

Answer: A short explanation was added on how exactly the theoretical maximum yields of the RO_2 are determined in Section 1.2, and all the yield-related parameters in Sections 2.1.2 and 2.1.5. are directly derived from these. A page's worth of details related to the RC(O)O_2 corrections was moved from Section 2.1.2 to the Supplementary, which hopefully makes the text flow better.

We found that 'simple' examples of yield determination easily balloon in size once one starts to consider the combinatorial nature of $\text{RO}_2 + \text{RO}_2$ recombinations. Take six well-known primary RO_2 products from Isoprene + OH. The theoretical maximum yields of these are simply the IUPAC-recommended yields for each radical. Combinatorially we have 21 RO_2 pairs for which the recombinations yields are determined from equation 2. All of these six radicals have a competitive RO decomposition reaction, half of which result in delocalized alkyl radical products that can recombine with the other RO in the complex in two different ways. Taken together, this means that we have a total of 84 potential $\text{RO}_2 + \text{RO}_2$ accretion products from the original six Isoprene + OH radicals, of which some might be filtered out due to low branching ratios and some of which might be duplicates. The y_{Prod} values are determined by equation 7. All of these calculations are simple if you have the rates and parameters in front of you, but demonstrating it would take up so much space that we hardly see it as a fruitful addition to the article. In principle all of the data is already available in the Zenodo archive with the analysed datasets, with radicals labelled consistently across the files.

Section S1 is useful, and is sufficiently important that it may be appropriate to include some of this discussion in the main text. This includes possibly Figure S3, which I found to be interesting. However, I think Figure S3 could be improved by using

only one plot with different symbols for the complexes with multiple stereoisomers, and also include the 35 kJ/mole cutoff. The line fit should only consider the points below or near that cutoff.

235 **Answer:** A new plot was made with the suggested changes. We did not move it to the main text, however, as Table S1 is required to give context to the binding energies. As a sidenote, we also noticed an error in our reference calculations for the HBN parameter: The hydroxy-substituted alpha-pinene radicals had one H-bond acceptor too many, and thus too high HBN numbers in the table. This may partially explain why removing the optical isomers improved the fit in the previous version. In any case, in the new figure we were able to include the optical isomers and still get a good fit by simply taking the average over
240 the isomer energies. Fortunately for us, the HBN cutoff received from this new fit was within 0.01 of the previous value, so we were able to keep the cutoff value 1.75 that our data was generated with.

I found the bubble plots on Figure S19 sufficiently interesting that maybe this figure should also be promoted to the main text. Similar bubble plots comparing C and O numbers would also be interesting.

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Answer: Why not. For consistency the yield parameter was replaced with the branching ratio as the parameter determining the bubble yields.

Referee 2

This study analyzes to possible contribution of alkoxy radical chemistry in the triplet RO/RO complexes formed in $RO_2 + RO_2$
250 bimolecular reactions, as a source of accretion products for atmospherically relevant molecules. They do this by generating a large number of RO_2 intermediates potentially formed in the atmosphere and looking at the likelihood that such accretion reaction occur. The research topic is timely, as the formation of HOMs, accretion products, and other contributors to SOA formation are of high interest at the moment, and our understanding of the formation of these precursors and their chemistry is evolving rapidly. The methodology used to show the importance of these reactions is mostly good (see comments below), and
255 shows that the title reactions are likely to play a role in RO_2 -driven atmospheric chemistry. The manuscript itself is well-written and clear, and of the appropriate length for the topics discussed. The results are relevant for modeling SOA formation, even if the manuscripts does not provide any direct information under which reactions conditions / regions the reactions are expected to be important.

260 I support publication of this work. The authors may wish to consider the comments below.

Answer: Thank you sincerely!

General comments:

265 The methodology used to generate the datasets of RO₂ intermediates of interest is rather elaborate. Using a mechanism generator like Gecko-A is much better than just randomly generating substituted RO₂, as the RO₂ produced can be assumed to be formed in the atmosphere to some extent. However, using the Gecko-A generator without modeling does not yield any quantitative data; this is acknowledged by the authors not only in the title but explicitly in several places in the manuscript. In that respect, it is awkward that the authors provide statistics weighted by a theoretical maximum yield. This latter quantity
270 is unrelated to atmospheric concentrations nor does it provide any sensible ranking, and should only be used for filtering out reactions. By using maximum yield in a weighting process, it is implied that there is quantitative meaning to both the number of distinct species as well as their theoretical maximum yield, facilitating erroneous interpretation as providing relative proportions that are atmospherically meaningful. This is even more so because several processes are not included in the generation process (autoxidation, CH₃O₂, RO₂ ring closure, scrambling,...), and there is little guarantee that including them would not
275 drastically change the RO₂ dataset size and content, and/or the theoretical maximum yields.

I propose that the results weighted by maximum generated yield are removed from the paper as being more confusing/misleading than enlightening. If the authors wanted to provide (semi)quantitative information, they might have set the (lumped) concentrations of all co-reactants to a representative value relevant for a specific environment (HO₂RO₂NOOHNO₃O₃ hν, ...),
280 as then the reaction selection becomes based on fluxes even for bimolecular reactions, and a better estimate of the real RO₂ concentrations can be made. I recognize that the Gecko-A software was not designed for such a selection process.

Answer: You are probably right. The theoretical maximum yield was used in the manuscript as a weighting function to (crudely) estimate the extent to which abundantly produced RO₂ differ from typical RO₂ in our datasets. The yield-weighted
285 figures have been removed from both the main article and the Supplement. Regarding the (semi)quantitative results, both referees gave some version of this suggestion, so we calculated concentrations for a subset of the radicals, using the GECKO-A mechanism for 'realistic but RO₂ + RO₂-relevant' daytime and nighttime conditions. This calculations are described in the new sections 2.3 and 3.5, with additional details given in section S8 in the Supplement.

290 Section 2.1.2 feels like an overly complex presentation. Overall, it appears the authors just set the concentrations of the 5 co-reactants, and assume an autoxidation rate, which leads to a lumped pseudo-first-order loss rate that can be compared to the bimolecular rate of interest.

Answer: Admittedly this description is largely correct. We moved a lot of the text discussing why these correction factors
295 were chosen to Section S2 in the Supplementary.

The use of the "effective H-bond number $HBN = nD\alpha * nA\beta + nD\beta * nA\alpha$ " seems incorrect to me. That formula calculates the number of distinct H-bonds possible, e.g. with 1 donor and 16 acceptors you get HBN=16. What is needed conceptually

in this context is the maximum number of H-bonds possible, i.e. " $\text{HBN} = \min(nD\alpha, nA\beta) + \min(nD\beta, nA\alpha)$ ", e.g. if only 1
300 donor is available only 1 H-bond can be present ($\text{HBN}=1$) irrespective of the number of acceptors (≥ 1). This then correlates to
the best possible complex bonding strength and hence the complex lifetime. Overestimating HBN will result in selecting too
many "viable" RO_2 molecules, and thus artificially increasing the apparent impact of the title chemistry. The cut-off used by
the authors is fairly low (1.75), so perhaps the impact of this is limited.

305 **Answer:** The suggested $\min(nD\alpha, nA\beta) + \min(nD\beta, nA\alpha)$ formula is certainly more consistent with the classical definition
of a Hydrogen bond, and a better formula to use if one is only interested in counting the H-bonds between the two radicals.
However, the purpose of the formula in the code is to act as a proxy for the intermolecular binding energy, which does not
exclusively depend on H-bonds, but also on dipole-dipole, dispersion, and Pauli interactions. From this point of view, the fact
that the $nD\alpha * nA\beta + nD\beta * nA\alpha$ value increases linearly with the addition of polar groups is a good feature. Note that the
310 alpha-pinene ozonolysis derived RO_2 pair, from which these ester-forming reactions were first observed (Peräkylä et.al. 2023),
has a strong binding energy despite lacking traditional H-bond donor groups. This was our reasoning behind treating the C-H
bonds as partial H-bond donors in the parametrization, and a good example of why adhering to the strict definition of a 'Hy-
drogen bond count' results in a less quantitative and less useful parameter.

315 However, you do have a point that this approach may grossly overestimate the intermolecular interactions for $^3(\text{RO} \dots \text{OR})$
complexes where one of the radicals is a small and the other is monoterpene-sized or above. Unfortunately, we don't have any
computational data on such complexes, so we will simply have to revisit the problem in the future when the reference data
exists. The discussion around the H-bonding parameter in the article was adjusted to clarify that the H-bond counting is only a
proxy for the strength of the intermolecular interactions. The discussion in the Supplement was also extended.

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As a sidenote, we also noticed an error in our reference calculations for the HBN parameter: The hydroxy-substituted alpha-
pinene radicals had one H-bond acceptor too many, and thus too high HBN numbers in the table. This may partially explain
why removing the optical isomers improved the fit in the previous version. In any case, in the new figure we were able to
include the optical isomers and still get a good fit by simply taking the average over the isomer energies. Fortunately for us,
325 the HBN cutoff received from this new fit was within 0.01 of the previous value, so we kept the cutoff value 1.75 that our data
was generated with.

Minor comments:

$\text{MetC}(\text{O})\text{O}_2$ notation seems inconsistent as all other instances of the CH_3 group which are written as " CH_3 ".

330 **Answer:** This was changed.

p. 3, line 67: The Novelli et al. 2021 update to the RO decomposition SAR is mentioned later in the paper, but could already be mentioned here. In this work the update mostly affects nitrated intermediates.

335 **Answer:** Added.

p. 10, line 250: "In the Supplementary of Peräkylä et al. (2023) this assumption was tested for a small model system, where it turned out that this recombination required an ISC." Perhaps rephrase this, as one does not need a small model to know a triplet to singlet transition requires an ISC.

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Answer: The ISC rate estimate was mentioned. It was also added that RO beta-scission reactions are typically endothermic (mentioned with a citation to Orlando & Tyndall elsewhere in the article), which further strengthens the argument.

p. 15, line 388: "RO₂ punch above their weight". This phrasing may not be understandable to non-native English speakers. I propose e.g. "contribute more than expected from their concentration"

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Answer: None of us are native English speakers, but you may have a point. Reformulated.

p. 11, line 270: "as we lack the ability to estimate them adequately.". add "... during the mechanism generation" (they can be estimated by modeling).

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Answer: Changed.

Table 3: I'm a bit weary of using "yield", as that has a specific meaning in kinetics, and what is listed here is not a yield. Alternatives: Fraction, Contribution, Subset size,...

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Answer: The columns actually refers to the theoretical maximum yield along with the parameters. For consistency with other revisions this column was removed completely. For the similar tables in the Supplementary, the theoretical maximum yields of the accretion products were replaced with average in-complex branching ratios whenever applicable, and removed completely when they are not.