



EGUsphere, author comment AC3
<https://doi.org/10.5194/egusphere-2022-587-AC3>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Reply on RC2

Philip T. M. Carlsson et al.

Author comment on "Comparison of isoprene chemical mechanisms at atmospheric night-time conditions in chamber experiments: Evidence of hydroperoxy aldehydes and epoxy products from NO₃ oxidation" by Philip T. M. Carlsson et al., EGU sphere,
<https://doi.org/10.5194/egusphere-2022-587-AC3>, 2022

We thank the reviewer for the comments. Find below our responses to the comments.

Comment: There are many sections of text (such as Section 3) which go into great detail about the chemical mechanism – describing different reactants, pathways, and products – but with little to no reference to a graphical mechanism (which is far easier to follow). Sometimes reference is made to the two mechanistic figures (Figs. 1 and 6), but these are quite large. I would recommend assigning reaction numbers to each reaction in the mechanism for easier reference, and possibly adding more mechanistic figures for sub-components of the overall mechanism. I would definitely recommend a mechanistic figure to show the chemistry of the first-generation products – parts of section 5.9 are hard to follow without structures or reactions given.

Response: We numbered reaction in Fig 6 and added references to the specific reactions in the text. Concerning the chemistry of the first-generation products, we do not aim for giving details of the chemical reaction, because we did not identify specific products but quantified the loss rate with different oxidants, most of which are too slow to be relevant for the timescale of a night for atmospheric conditions. We numbered loss reactions in Table 2 and added references to the reactions in text instead of adding mechanistic figures.

Comment: Comparison of measurements with mechanistic predictions is done by reference to figures 4 and/or 5. But those figures each have 16 panels! These panels need to be labelled, and the specific panel (not just the whole figure) should be referenced.

Response: We added labels and references to the specific panels in the manuscript, as appropriate.

Comment: At the same time, these are just 16 ions out of (presumably) many hundreds measured. How were these chosen? Are they the 16 main products predicted by the mechanism? Or the most abundant ions from the various mass spectrometers? I ask because if there are major species measured that are not predicted by the mechanism(s),

or that are present in far higher concentrations than predicted, this also provides information about the completeness of the mechanisms. More discussion of the importance of these 16 (e.g., fraction of total ion signal), and the abundance and characteristics of all the others, would be helpful.

Response: The ion signals were chosen because they correspond to masses of products that are expected to be formed. They also correspond to the highest ion signals in the mass spectrum except for the ion signal corresponding to a C₄H₇NO₅ compound observed by the Br⁻ and I⁻ CIMS instruments. This is now mentioned in the Methods section. This was mentioned in the Conclusions (p34 L843) and discussed in detail in Tsiligiannis et al. 2022. We added in the section "Results": "Ion signals shown in Fig. 4, 5, A5, A6 were the highest signals observed in the mass spectrometer instruments except for the ion signal corresponding to a C₄H₇NO₅ compound observed by the I⁻ and Br⁻ CIMS instruments. A species with this sum formula cannot be attributed to a major product species expected from the chemical mechanism. This is discussed in detail in Tsiligiannis et al. (2022)." We feel that a detailed discussion about fractions of total ion signals for all compounds mentioned in this work is beyond the scope of this work and can be also found in Wu et al. (2021) for the Br⁻ CIMS instrument and in Tsiligiannis et al. (2022) for the I⁻ instrument.

Comment: Comparison with previous results (e.g., papers by Kwan and Schwantes) are extensive and made throughout the results section, sometime repeating themselves (e.g., the formation of HPALD). It may be clearer to have a compiled "comparison with previous results" section.

Response: As suggested by the reviewer, we moved the comparison to other studies into a separate section.

Comment: Throughout: "Caltech" is typically spelled with a lowercase "t".

Response: We corrected this throughout the manuscript.

Comment: Throughout: I think assigning names (and not dates like "09 August 2018") to the 4 different experiments would be helpful for readability. They could be "Experiment 1", "Experiment 2", etc., or even better, something more descriptive ("Scavenger", "Low isoprene", etc.).

Response: In our opinion, there is no ideal referencing of experiments. We chose the date because this retains the link between the experiments and the database with experimental data. We do not think that numbering experiments is more helpful for the reader. A short descriptor is also difficult as the experiments vary in more than one way, and which variation is important depends on which aspect is discussed. Hence, we see the challenge for the reader to keep differences between the experiments in mind. On many occasions, we thus remind the reader of the key difference and added this in the text at various further occasions. As suggested by the reviewer we also numbered the experiments.

Comment: Figure 1: 2 of the RO₂ radicals in the middle have only 4 carbon atoms.

Response: We corrected the structure of RO₂ radicals in figures 1.

Comment: line 217: should this be ppt?

Response: It should indeed be ppt. This sentence, however, is cancelled in the revised version because of comments from other reviewers.

Comment: lines 240-245: what might be the cause of this error in the HO₂ concentration? This would seem to suggest some sort of shortcoming in the organic mechanism used; this is worth some discussion.

Response: As mentioned in the text, the difference between modelled and measured HO₂ concentrations are discussed in the paper by Vereecken et al. (2021) for the same experiments. At this point, there is no solid speculation what the reason behind this discrepancy is, which could be due to shortcomings of the model, but could also be measurement artefacts. Further experiments will be needed to investigate this specific point. As we could only repeat what is already published in Vereecken et al. (2021) we refer to this study for additional discussions on the HO₂ measurement/model discrepancy.

Comment: Figure 6 (and accompanying text): ring-closure to form a three-membered ring (epoxide) is shown and discussed, but there is no discussion of the possible ring-closure to form a four-membered ring (oxetane). This would have a lower ring strain, so would likely have a lower barrier, and would form a more stable alkyl radical. This of course cannot be distinguished mass spectrometrically from the epoxide but may have different chemistry.

Response: Ring-closure reaction forming oxetane is not competitive with the ring-closure reactions forming epoxides. We did additional theoretical calculations to estimate the energy barrier for the ring-closure reaction forming oxetane of the E-1-NO₃-isoprene-4-OO RO₂ and found a value of 30 kcal/mol, which is a factor of 3 higher than the value for the competing epoxidation reaction and 1,5-H-shift reaction. Results are transferable to all other nitrate RO₂ from the isoprene + NO₃ reaction.

We added in L209: "In contrast, 4-membered ring closure (barrier ~30 kcal/mol) requires breaking the planar double bond to bring the radical O-atom in an appropriate position for bonding. 5- to 6-membered ring closure (barriers ~13-29 kcal/mol, Vereecken et al. (2021)) are also less favorable."

Comment: lines 264-266: I don't understand this sentence; the concentrations of co-reactants (NO, HO₂, RO₂) and the product yields matter too for production rate.

Response: The sentence is indeed misleading. We rephrased the text: "They are formed from the same pool of nitrate RO₂ radicals from the reaction of isoprene with NO₃, which is the rate limiting step for their production. The temporal evaluation of their concentrations at later times of the experiment when isoprene had been consumed is determined by the rate of loss processes, which can be chemical loss and dilution and these experiments."

Comment: lines 273-274: by doing this scaling to one model (out of three being compared), visually the measurement-mechanism agreement will naturally look best for that one model. It would be useful to show (in the SI) similar versions of Figs 4 or 5 with scaling to the Caltech mechanism or MCM.

Response: It is certainly correct that the model-measurement comparison looks best if the traces are scaled to match results of a specific model run. However, we only point to differences between model-measurement agreement in the context of the loss rates of product species later in the discussion. We believe that these few differences are obvious also if traces are scaled to the results of the FZJ-NO₃ mechanism. We think that it might be rather confusing to include 8 more plots with several panels, all of which would essentially show the same. We therefore only added one plot in the Appendix with the VOCUS PTR measurements scaled to the 3 models for the experiment on 13 August 2018.

Comment: para starting at line 275: this is hard to follow without reference to a figure.

Response: We added references to figures in the text.

Comment: line 288 (and elsewhere): these are isomers, not isobars. Isobars refer to compounds with different formulas but the same nominal (unit) mass: see <https://www.degruyter.com/document/doi/10.1351/PAC-REC-06-04-06/html>

Response: We corrected this throughout the manuscript.

Comment: line 334: is ROOR formation observed, or considered in any mechanisms?

Response: We added in L337: "Formation of peroxides (ROOR) is considered in the Caltech and FZJ-NO₃ mechanisms with a small yield of 3.5%."

Comment: line 455: this is the only time "counts" is given as a unit, so it's not clear that this is a low value.

Response: We put the low value into context in L455: "Only the I- CIMS instrument detected a very small signal (less than 30 cnts) at the corresponding mass, which is at least a factor of 100 smaller than ion signals at masses of other products shown in Fig. A9."

Comment: line 605: this discussion of RO₂ from the 09 August 2018 experiment is very repetitive from the previous paragraph.

Response: We cancelled the sentence in this paragraph.

Comment: Section 5.9-5.10: there are many discussions of some reactions being “irrelevant” over the course of one night. But what is the cutoff for “irrelevant”? I assume it’s not just a comparison with the oxidation timescale (τ , last column of Table 2); even a loss of 10% of a given compound overnight could be viewed as “relevant”.

Response: The term “irrelevant” can indeed be misleading. Here, we mean that the loss rate cannot be determined from the measured time series of product concentrations and is therefore much lower than the dilution rate of trace gases in the chamber. We rephrased statements in the text accordingly.

Comment: Section 5.10: the relationship between reactivity and the loss of a given product in a single night is unclear to me – one is $k[\text{VOC}]$, the other is $k[\text{OH}]$ – in what way do these two quantities provide the same information?

Response: The calculation of the fraction of OH reactivity from organic compound from measured OH reactivity is explained in the instrumental section. This is now referenced in Section 5.10. In Section 5.10, we compare if the temporal behaviour of the measured reactivity is consistent with the modelled reactivity. The consistency supports small reaction rate constants derived from the temporal behaviour of product concentrations. They are part of the calculation of the OH reactivity from an OH reactant, because OH reactivity is the product of the OH reactant concentration and its reaction rate constant. We modified the text to emphasize that the comparison of modelled and measured OH reactivity from organic compounds can only be a consistency check.

Comment: Typos: line 256 (incomplete sentence), 283 (reference), 376 (“NO, MVK”), 652 (units), 50 (“product s”).

Response: We corrected the typos accordingly.