



EGUsphere, referee comment RC2
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Comment on egusphere-2022-587

Anonymous Referee #2

Referee 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-RC2>, 2022

This manuscript describes a series of experiments and mechanistic modeling simulations of the detailed chemistry of the NO₃ + isoprene reaction. The reaction was run under a range of conditions in the SAPHIR chamber, using a very large array of analytical instruments to characterize the chemistry, and simulated with three major mechanisms describing isoprene oxidation (MCM, the Caltech mechanism, and FZJ-NO₃). Comparisons are done for a range of radicals and organic intermediates, and the mechanistic implications (e.g., rates and products of individual steps) are broken down in detail.

This is an impressive study, on both the experimental and modeling sides, and provides a good deal of new information on the isoprene+NO₃ reaction; it advances our understanding of this mechanism, and will likely be used to improve reaction mechanisms. My main concern is the presentation of the work – the manuscript is extremely dense, extremely long, and often hard-to-follow. It breaks down the complex mechanism into many parts, each one of which is discussed in detail, making comparisons between: experiments and mechanisms, different mechanisms, and present work and past studies. While the level of detail is commendable, the key points of the work are often lost, and not always clear. I would recommend the paper be reorganized and condensed so that the work is easier to follow. Specific suggestions, and other comments, are below.

General comments:

- 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.

- 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 labeled, and the specific panel (not just the whole figure) should be referenced.

- 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.

- 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.

Other comments:

- Throughout: “Caltech” is typically spelled with a lowercase “t”.

- 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.).

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

- line 217: should this be ppt?

- 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.

- 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.

- 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.

- 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.

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

-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>

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

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

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

- 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 (tau, last column of Table 2); even a loss of 10% of a given compound overnight could be viewed as "relevant".

- 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?

- Typos: line 256 (incomplete sentence), 283 (reference), 376 ("NO, MVK"), 652 (units), 750 ("product s").