



EGUsphere, author comment AC1
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Reply on RC1

Philip T. M. Carlsson et al.

Author comment on "Comparison of isoprene chemical mechanisms under 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-AC1>, 2022

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

Comment: Could the relative humidity (RH) in the experiments be mentioned in Table 1? The text indicates that the effects of RH on the detection of isoprene were taken into account, but the value of RH is not specified.

Response: All experiments analysed in this work were performed in dry air as mentioned in L. 92. This is now also stated in the caption of Table 1. As relative humidity did not change during the experiment, the calibration factor for isoprene valid for RH=0% was applied.

Comment: The O₃ and NO₃ levels shown in Fig. 2 and 3 suggest that more than the 10 % of isoprene indicated in the text might react with O₃, especially in the experiment of 09/08/18. 60 ppb of O₃ or more correspond to a consumption of isoprene of at least $2 \times 10^{-5} \text{ s}^{-1}$ ($k \sim 1.3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$) while 2 ppb of NO₃ corresponds to $3.5 \times 10^{-5} \text{ s}^{-1}$ ($k \sim 7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$). This suggests that 40 % of isoprene reacted with O₃ in this experiment?

Response: Isoprene was not only consumed by NO₃ and ozone, but also was lost due to dilution and potentially OH (discussed in Section 5.7). It is correct that the fraction of isoprene that reacted with ozone was between 25 and 30% in the experiment on 9 August 2018 but was around 10% in the other experiments if all loss processes are considered. We changed the text in L 222 (moved to the section "Methods"): "Approximately 10% of the total isoprene consumed in the experiments reacted with ozone except for the experiment on 09 August 2018, when 25 to 30% of isoprene was lost in the reaction with ozone due to the low NO₃ and high ozone concentration. ... Overall, the dominant loss for isoprene was due to the reaction with NO₃ radicals (80 to 90% of the total loss in most of the experiments)." It is worth noting that the fraction of ozonolysis reaction to the total loss of isoprene does not impact the interpretation of results of the model calculations, because ozonolysis reactions are included in the chemical model.

Comment: What is the order of the rate of H-abstraction by NO₃? Is it truly negligible,

even compared to the minor channels discussed here?

Response: To our knowledge, the H-abstraction channel of isoprene has not been investigated so far. However, abstraction of vinylic, aliphatic and allylic H-atoms is generally considered to be negligible. We added in L175: "H-atom abstraction from isoprene by NO₃ is estimated to be at least 2 orders of magnitude slower than NO₃ addition, based on the available literature data on aliphatic and allylic H-abstraction reactions (Canosa-Mas et al., 1991, Atkinson et al., 2006) and therefore not further considered in this work." We would like to emphasize that we do not discuss reaction channels that are supposed to be minor. For example, we only consider pathways of the NO₃ addition to isoprene and the RO₂ reaction channels that are expected to be of main importance for the conditions of our experiments.

Comment: Although this might be beyond the point of the present paper, could there be more connections made with the Brownwood et al., 2021 study on the particulate phase? For instance, could some of the products expected in the mechanism not be detected because they partition into the condensed phase? Was some SOA produced in the experiments presented in this work? If so, how much of the carbon balance did they account for?

Response: Experiments analysed in this work were performed without seed aerosol and as discussed in Brownwood et al., 2021, no measurable SOA was produced in these experiments. In addition, the loss rates of products determined from their time series specifically for the last part of experiments, when their production rate was small (isoprene consumed), are consistent with dilution and/or further gas-phase oxidation as discussed in Section 5.9. Only one organic nitrate species (C₄H₅NO₄) that would be expected from the mechanism was not detected in our experiments, but this species was also not observed in previous experiments in other chambers (Section 5.4). As mentioned in L. 453, there is no obvious reason, why this species would behave differently from the other organic nitrates that were detected.

For these reasons, we do not believe that heterogeneous loss on aerosol surface and/or the chamber wall surface were significantly impacting the concentrations of products discussed in this work. Further analysis of the experiments with seed aerosol would be of interest but is indeed beyond the scope of this work.

We added in L. 92: "In the experiments in this work, no measurable secondary organic aerosol was formed, so that loss of products species on aerosol did not play a role (Brownwood et al., 2021)."

Comment: "conformer" vs "isomers" IUPAC defines "conformers" as isomers differing only by free rotation around a chemical bond or other "soft" rearrangement of the carbon chain not involving the breaking of a bond (for instance, the "chair" and "boat" conformers of cyclohexane). Here, the text uses "conformer" to refer to different isomers that do not differ only by rotation around a bond. In all cases, a bond would need to be broken to transform these isomers into each other, thus the name "conformer" needs to be replaced by "isomer".

Response: We corrected this throughout the manuscript.

Comment: "isobar" vs "isomer" IUPAC defines "isomers" as compounds having the same brut formula but differing in their detailed structure. In several occurrences the text mentions exactly this situation (for instance p. 13 Li. 257; p.20. Li. 435...) yet refer to the compounds as "isobars". Isobars are something else, they have different brut formula (thus different molecular masses) but close enough that they cannot be separated by mass spectrometry due to insufficient resolution. This obviously is not what is discussed in the text, thus "isobar" should be replaced by "isomer". Perhaps the resolution of the VOCUS instrument used in this study should be given, as it has direct implication for the identification of compounds. But the resolution of current VOCUS is large enough (> 5000) that the one used in this study should be able to distinguish most "isobar" compounds

Response: We corrected this throughout the manuscript.

Comment: a few other terms are also used improperly such as "RO₂ recombination" instead of "self-reaction" (p. 3 Li. 53; recombination would suggest that the RO₂ were once combined, which is not true), and "mass detected by PTR-MS" instead of "ion signal" (everywhere in the discussion of the observed products).

Response: We corrected this throughout the manuscript.

Comment: All the following information, currently in the "Result" section, needs to be moved to "Methods": experimental conditions, such as p.10 Li. 214-219, "In the experiments in this work, NO₃ was produced by the gas phase reaction of NO₂ and O₃. NO₃ production rates ranged between 0.9 and 11 ppbv/215 hour..." - methodological information, such as p.10/11 Li. 227-232, "Experimental conditions were varied among the experiments to explore the different fates of nitrate RO₂ radicals initially generated." (this should also be the first sentence of the paragraph).

Response: The information how NO₃ was produced is already given in the section "Methods" (L 92). We deleted the sentence in the section "Results". Numbers of production rates are moved to the section "Methods" L93. The information that experimental conditions were varied to explore different fates of nitrate RO₂ radicals is already given in L 98 in the section "Methods". We deleted the sentence in the section "Results". In addition, we moved most of the first 3 paragraphs of the section "Results" to the section "Methods" (L 104).

Comment: The "Methods" section should have a sub-section for the detection of organic products, including

- the description of the instruments used, how they work, how they were calibrated, their general performances...:

- 12/13 Li. 251-255, "With respect to organic products, the VOCUS PTR-MS instrument was only calibrated to quantify the sum of methyl vinyl ketone (MVK) and methacrolein (MACR)..."
- 14 Li. 270-273, "Br--CIMS and I--CIMS instruments also recorded signals from oxygenated organic compounds in the experiments. Compared to the CIMS instruments, the sensitivity of the VOCUS PTR-MS instrument was higher for organic compounds that contain few oxygens. The CIMS instruments were not calibrated for the organic nitrate species, so that only relative signals can be compared."

- 15 Li. 287-290, "In general, the sensitivity of CIMS instruments can be different for different isomers and functional groups, so that a change in the distribution of isobaric compounds could partly explain the observed differences between instruments (Lee et al., 2014a; Xiong et al., 2015, 2016). In addition, changes in the operational conditions of the instrument such as the temperature of the ionization region can lead to a variability of the instrument's sensitivity (Robinson et al., 2022)."

Response: We added a subsection header at L104 "Instrumentation". We think this subsection should also include the description of instruments not detecting organic compounds as done in L 123-149. Information mentioned by the reviewer was moved to the section "Methods" (L114), if not already given such as the calibration of the mass spectrometer instruments. We believe that all relevant information about the mass spectrometer instruments is now included. A more detailed description of the working principle is beyond the scope of this work and are already described elsewhere. For example, detailed description of the Br- and I- CIMS instruments are given in the work of Tsiligiannis et al. 2022 and Wu et al. 2021 which are referenced. We now cite the paper by Krechmer et al. 2018 for a description of the VOCUS PTR. No specific operational conditions were applied in the experiments in this work.

Comment: The "Results" section needs to present the detection of the organic products, which is currently in the Discussion. This should considerably improve the clarity of the manuscript. In addition, these results should be justified by giving, for each compound, the exact ion mass (m/z).

Response: We moved several paragraphs within the section "Results" and moved parts from the section "Discussion" to this section to address this comment. However, we want to emphasize that this study is not limited to the detection of organic products. We added a table in the Appendix giving the ion mass (m/z) of organic products in the 3 mass spectrometer instruments.

In addition, the molecular weight of all organic products (now also for MVK) is shown in Fig. 6. Their sum formulas were identified in the ion signals in spectrometer instruments at the expected ion mass (m/z). We added in the subsection "Instrumentation": "The high resolution of the mass spectrometer instruments allowed to attribute the ion mass signals (m/z) to sum formulas of organic compounds (Table A1)."

Comment: The "Discussion" section should focus on the mechanism only. Its clarity would be greatly improved if the text focused first (and mostly) on the results of the present study, rather than giving lengthy descriptions of previous studies from the literature. Right now, half of the discussion seems to focus on studies rather than on the present one, underlining the lack of results of the present study.

Response: As suggested by reviewer #2, we moved the comparison of results of this study with previous studies in a separate subsection. We shortened the text, where possible. We think that this part of the discussion remains valuable, because it shows the consistency of our results with previous studies, which may not be obvious without discussing their results in the context of the updated mechanism presented in this work.

Comment: The "Conclusion" should not repeat the features of the models ("The MCM simplifies the oxidation of isoprene by NO₃ by forming only one RO₂ conformer, whereas

the other 2 chemical mechanisms differentiate between nitrate-RO₂ conformers due to the different positions at which NO₃ and O₂ can add ...” or “Another critical difference between the three chemical mechanisms is the fate of nitrate alkoxy radicals formed in the radical reaction chain. Nitrate carbonyl products are exclusively formed in the MCM, whereas abundant RO₂ conformers are assumed to decompose to MVK or MACR together with HCHO and OH in the CalTech mechanism....”). All this should have been made clear in Section 3. However, the Conclusion should present the main results and needs for future improvement in a clearer and more synthetic way, so that the reader gets the “take home message”.

Response: We shortened the section “Conclusion” and reduced repetitions. By rearranging and shortening we tried to better summarize a “take home message:

“Overall, results from experiments in this work highlight how the FZJ-NO₃ mechanism for isoprene (Vereecken et al., 2021) is currently the most complete mechanism to describe the nocturnal oxidation of isoprene. New reaction pathways in Vereecken et al. (2021) can have consequences for the nocturnal loss of reactive nitrogen and formation of secondary organic aerosol. However, large uncertainties still exist in the exact distribution of the different RO₂ isomers formed in the reaction of isoprene with NO₂ and their fate. Specifically, the yield of alkoxy radicals from the reaction of nitrate-RO₂ with HO₂ is uncertain. Calibration of instruments detecting organic nitrate products for specific reaction pathways is urgently needed in future experiments to determine the absolute importance of these reaction pathways for atmospheric conditions.”

Comment: Many sentences are very complicated, making the text difficult to follow. Typical examples are:

- p. 18/19 li. 386-389 “The good model-measurement agreement for MVK+MACR concentrations obtained using the FZJ-NO₃ and MCM mechanisms demonstrates that production of MVK and MACR from the decomposition of nitrate alkoxy radicals from isoprene (as implemented in the CalTech mechanism) does not play a role as calculated by Vereecken et al. (2021).” This sentence is so complicated that it almost says the opposite of what is intended: that the results agree with the Caltech mechanisms and contradict Vereecken et al., 2021! Why not write something simpler such as “the agreement of the MCM and FZJ-NO₃ mechanisms with the measured concentrations of MVK and MACR confirms that the decomposition of the nitrate alkoxy radicals is negligible, as predicted by Vereecken et al. 2021 and unlike the predictions of the Caltech mechanism.”

- Li. 667-670: “Nitrate hydroperoxides, NISOPOOH, are expected to react with OH with a fast reaction rate constant of 10–10 s⁻¹cm³ in the MCM. A 3 times lower reaction rate constant is implemented in the CalTech and FZJ-NO₃ mechanisms. Differences in the OH reaction rate constants explain the faster decay of NISOPOOH predicted by the MCM compared to the CalTech and FZJ-NO₃ mechanisms for the experiment on 13 August 2018.” These sentences are nearly understandable but give an example of the low quality of the language in this paper. They could be replaced by clearer sentences such as: “in the MCM the reaction of nitrate hydroperoxides, NISOPOOH, is assumed to be fast, with a rate coefficient of... By contrast, the CalTech and FZJ-NO₃ mechanisms assume a smaller rate coefficient for this reaction, by a factor 3, which can account for the faster decay of NISOPOOH in the MCM mechanism than in the CalTech and FZJ-NO₃ mechanisms” (note that referring to an experiment date is here irrelevant since only mechanisms are discussed).

-p. 35, Li. 866-867, “Differences between the chemical models with respect to product

concentrations were qualitatively like differences discussed in this work but results were additionally impacted by complex chemical and meteorological conditions at the field site.” I am not even sure of what this sentence means ...

In addition, the use of “like” should be avoided in a scientific text (replaced by “such as” or equivalent): Li. 168, p.8 legend of Fig. 1, 228, 536, 627, 632, 705, 728, 888.

In many occurrences, the expression “faster/slower/higher... compared to...” needs to be replaced by “faster/slower/higher than...” which would substantially simplify the sentences: Li. 107, 278, 280, 282/283, 340, 347, 359, 366, 447, 448, 454, legend of Fig. 6 p 25, Li. 599, 600/601, 627, 669, 679, 692, 706, 709, 750, and 788.

In conclusion, the entire text needs to be proof-read and improved.

Response: We rephrased sentences as suggested by the reviewer and went through the entire text to improve the language.

4) Product identification and validation of the mechanism

Comment: The concentration of MVK and MCAR supporting the formation of epoxy compounds instead of the decomposition of nitrate alkoxy radicals seems to be one of the main results. The abstract claims that epoxy products were identified but the presentation of the results (currently misplaced in the Discussion) is not as convincing: hydroxy nitrate epoxides were potentially observed as $C_5H_9NO_5$, but not conclusively as they are isomers of nitrate hydroperoxides (anyway this brut formula corresponds to over 1000 isomers. Cf. MOLGEN, <https://www.molgen.de/>). Compounds with brut formula of $C_5H_7NO_5$ and $C_5H_9NO_6$ were also observed and tentatively attributed to epoxide compounds but not more conclusively and at low signal intensities. If I understand the text correctly, $C_5H_8O_3$, an isomer of HPALD, and $C_5H_8O_4$ were also observed and tentatively attributed to epoxide compounds but not conclusively. The identification of epoxide products in this study is therefore not very convincing. One way to identify such epoxide products unambiguously would be to use GC/MS. The abstract should thus probably be tone down the identification of these compounds.

Response: We rephrased L13 of the abstract: “In addition, ion signals at masses that can be attributed to epoxy compounds, which are specific for the epoxidation reaction of nitrate alkoxy radicals, were detected.” Overall, we emphasize throughout the text that mass spectrometer instruments cannot unambiguously identify specific products and discuss different isomers expected to be formed that could be included in the ion signals.

Comment: “negative” results such as the discrepancies in modeling the concentration of HO₂ and the lack of detection of the expected product C₄H₅NO₄ are also important to explain for the understanding of the mechanism. However, the problems with modeling HO₂ give little confidence in the modeling of RO₂ and RO radicals in this study (sections 5.1 and 5.3 in particular).

Response: We discuss uncertainties in the theoretical calculations that could make the reaction pathway leading to the C₄H₅NO₄ compound negligible on p 21 (L456 to L462) and on p 33 (L803 to 809). At this point, no further conclusion can be drawn from experiments in this work. We agree that there are large uncertainties in the modelling, and measurement of radicals. The comparison between measured and modelled values gives at least estimates about the uncertainties. Radical concentrations used in other

studies often rely only on model calculations and / or assumptions of radical production / destruction rates. There are clearly more studies needed to improve the predictions of HO₂ and RO₂ concentrations by models.

Comment: Although not related to the present study, the intense detection of hydroperoxides (NISOP₂OOH) in the present work is very interesting because it directly contradict a recent paper claiming the inability of VOCUS PTR-MS to detect such compounds (Li et al., *Atmos. Meas. Tech.*, 15, 1811–1827, 2022).

Response: The work by Li et al. (2022) does not investigate the ability of the VOCUS PTR-MS to detect nitrate hydroperoxides and the authors do not deny the ability of this instrument to detect ion mass signals for hydroperoxides in general. Li et al. (2022) emphasize that fragmentation of oxygenated organic compounds is more likely in the VOCUS PTR-MS instrument than in CIMS instruments using different reagent ions. In our work, ion signals at the mass of NISOP₂OOH was not only observed by an VOCUS PTR-MS instrument, but also by 2 other CIMS instrument giving reasonable agreement of the relative time series indicating that all instruments detected the same species. This does not exclude that part of the NISOP₂OOH fragments in inlet of the VOCUS PTR-MS. We therefore do not see any contradiction with the work with Li et al. (2022).