Review on the manuscript
"Comparison of isoprene chemical mechanisms at atmospheric night-time conditions in chamber experiments: Evidence of hydroperoxy aldehydes and epoxy products from NO3 oxidation"
by Carlsson et al. (egusphere-2022-587)

General comments

This manuscript presents an investigation of the mechanism of the NO_3-initiated oxidation of isoprene comparing three chemical models (MCM, "CalTech mechanism" and FZJ-NO3) and chamber experiments. It is directly complementary to the study of Vereecken et al., 2021, presenting theoretical calculations of the initial steps of isoprene +NO3 and proposing the formation epoxide-nitrate radicals in some pathways. The main objectives appear to be A) to validate the reactions proposed in Vereecken et al., 2021 with experimental measurements; B) to determine if these new reactions make significant differences in the product mixtures and radical budget compared to simplified mechanisms and, C) to determine the impact of the overall mechanism on night-time isoprene chemistry under realistic (atmospheric) conditions.

This study involves a large amount of work and seems to report a few interesting results: detection of epoxy organic nitrates (although not entirely conclusive, see below), observation of HPALD in the absence of OH; yields for MCAR, MVK in agreement with epoxidation over decomposition of the alcoxy, etc… In addition, "negative" results such as the difficulties in modeling HO2 levels and the lack of observation of expected products such as C4H5NO4 are also important for the understanding of the mechanism. On another topic, the intense detection of hydroperoxides (NISOPOOH) in this study is also very interesting, as it contributes to the recent debate on the ability of the VOCUS PTR-MS to detect such compounds (see details below).

However, my main concerns are that

- A) the paper is not well written and overall difficult to follow. Half of the information in "Results" should be in the "Methods" section and the detection of the organic products should be presented in "Results" instead of the "Discussion". This should substantially improve clarity. The main objectives of the study, results, and future areas of improvement are currently lost in the large amount of information presented and need to be better emphasized in the Discussion and Conclusion. The Discussion itself needs to focus more on the results of the present work than on those of other groups. In many occurrences, literature results are discussed much more extensively than those of the present work, which underlines the lack of results in the present work (see next paragraph) and questions its relevance. The language itself needs substantial improvement as the text contains many complicated sentences, difficult to understand. Last but not least, some key terms are systematically referred to with incorrect names according to their IUPAC definition: "conformer" needs to be replaced by "isomer" and "isobar" by "isomer" (see below).

- B) the experimental efforts in identifying and quantifying key products of the mechanism appear to be limited, which defeats the purpose of this work. What is the point of trying to validate a sophisticated mechanism if its main features can not be tested experimentally ? For nearly all products, the discussion states "the VOCUS PTR-MS was not calibrated for this compound" (sentence occurring about 10 times in the text). Why is that ? Why were reference standards not synthesized (at least for a few key compounds) and why was GC-MS not used to identify the key products unambiguously ? In addition, the few compounds that are tentatively reported can not be conclusively identified as they correspond to a large number of isomers (> 1000 for most of them). Given the complexity of the chemical system, the ambitious objective of this work, and the large number of people involved, this is not acceptable. A more robust analytical strategy could have easily been put together. As a result, the discussion has often much less to say on the present results than on those reported in the literature, which is disturbing !

In conclusion, while the objectives of this study are interesting, the new results reported, especially experimental ones, are at the bare minimum to justify publication. Because these experimental shortcomings can not be fixed rapidly, I am willing to recommend publication but only after a substantial work is made to improve the text, as explained above and below.

Detailed comments

1) Experimental conditions, competing reactions/processes

Although this is not critical for the study, a few points concerning the experimental conditions and potentially competing reactions might be useful to address in the text:

- 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.

- 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 x 10^{-5} s^{-1} (k ~ 1.3 x 10^{-17} cm^3 s^{-1}) while 2 ppb of NO3 corresponds to 3.5 x10^{-5} s^{-1} (k ~ 7 x 10^{-13} cm3 s-1). This suggests that 40 % of isoprene reacted with O3 in this experiment ?

- what is the order of the rate of H-abstraction by NO3 ? Is it truly negligible, even compared to the minor channels discussed here ?

- 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 ?

2) Improper terms/ IUPAC definitions

Some terms in the text are wrongly used according to the IUPAC definitions, and need to be corrected:

- "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".

- "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 can not 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.

- 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).

3) Clarity of the text

A) Structure

As mentioned above, some substantial rearrangement needs to be made between the "Methods", "Results" and "Discussion" sections, to improve the clarity of the paper:

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).

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…:
p. 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)…."
p. 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."
p. 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)."

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*).

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.

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".

B) Language
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 FJZ-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.

4) Product identification and validation of the mechanism

Once the hurdle of the text passed, a few interesting results seem to be reported (but, again, need to be much better presented).

- 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 C5H9NO5, 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 C5H7NO5 and C5H9NO6 were also observed and tentatively attributed to epoxide compounds but not more conclusively and at low signal intensities. If I understand the text correctly, C5H8O3, an isomer of HPALD, and C5H8O4 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.

- "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).

- Although not related to the present study, the intense detection of hydroperoxides (NISOPOOH) 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).