



EGUsphere, author comment AC2
<https://doi.org/10.5194/egusphere-2022-587-AC2>, 2022
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Reply on CC1

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., EGUsphere, <https://doi.org/10.5194/egusphere-2022-587-AC2>, 2022

We thank Mike Jenkins for the comments. Find below our responses to the comments.

Comment: My main reason for contributing this comment relates to the comparison of measured OH reactivity (k_{OH}) in the chamber with that calculated using the modelled concentrations for the set of species (Fig. 9 for the FZJ-NO₃ chemical mechanism, and Fig. A11 for MCM). I understand that the calculated OH reactivity is determined from the summation of $k_{OH}i [X]_i$, where $[X]_i$ is the modelled concentration of species "i" and $k_{OH}i$ is its rate coefficient for reaction with OH, as used in the given mechanism. The presented results show that FZJ-NO₃ does a much better job than MCM, with the result used as one piece of support for the validity of the FZJ-NO₃ isoprene mechanism (in the Abstract). A main reason for the poorer performance of MCM in recreating the OH reactivity is given as the high modelled concentration and rate coefficient for the species NISOPOOH (lines 765-767), and its large contribution to modelled OH reactivity is clearly shown in Fig. A11.

As represented in MCM, however, the reaction of NISOPOOH with OH results in prompt quantitative OH regeneration and does not therefore remove OH at all. It therefore should contribute zero to the modelled OH reactivity and this is misrepresented in the presented results. This is actually mentioned by the authors on lines 671-672. Whilst the mechanism and products applied in the MCM are a historical simplification, more explicit and up-to-date representations also result in some prompt OH regeneration, including that applied in FZJ-NO₃ (based on Caltech). More widely, this is generally the case for species containing hydroperoxide groups. Another well-known example is the set of ISOPOOH species, which are converted to epoxydiols and OH almost quantitatively in both FZJNO₃ and MCM. Has this been taken into account in the ISOPOOH contributions shown in Figs. 9 and A11? The calculated OH reactivity should therefore be determined from the summation of $k_{OH}i [X]_i f_i$, where f_i is the fraction of the reaction leading to immediate OH loss. I believe that this would bring the MCM results into better agreement with the observations, and possibly suppress the FZJ-NO₃ results a little. Might it also be possible to simulate the measurement method at selected times by adding a pulse of OH in the model and analysing the decay to get a total modelled OH reactivity as confirmation?

Response: Indeed, the method for measuring OH reactivity does not allow for detecting OH reactants, which produce OH radicals in their reaction with OH on a very short time scale. OH production from this type of reaction is expected to be much faster than the timescale of the total OH loss rate, so that it does not impact the shape of the OH decay measured in the instrument. No simulation is required to confirm this in our opinion. The

question is what is most useful to be compared in the discussion of the manuscript. We use the comparison between measured and modelled OH reactivity to discuss the production of NISOPOOH species in the three mechanisms. The reaction rate constant of NISOPOOH with OH in the MCM is more than a factor of 2 faster than in the other 2 mechanisms (Table 2), so that NISOPOOH concentrations in the MCM would be even higher if reaction rate constants of the Caltech / FZJ-NO₃ were applied. In order to compare the production of NISOPOOH in all models by using OH reactivity, it makes sense to us to assume the same efficiency with which OH reactants in the OH reactivity measurements are. As epoxide formation from NISOPOOH in the reaction with OH is likely happening as shown for ISOPPOOH, a 100% OH yield as assumed in the MCM is rather an upper limit, though the exact yield is not known. In the Caltech and FZJ-NO₃ mechanisms, the OH yield is around 10%, so that the majority of NISOPOOH would be detectable by the OH reactivity instrument. This should also apply for ISOPPOOH, for which the reaction channel producing OH in its reaction with OH has a branching ratio of less than 10% in all mechanisms including the MCM.

We changed in the abstract: "The validity of the FZJ-NO₃ isoprene mechanism is further supported by a good agreement between measured and simulated hydroxyl radical (OH) reactivity."

We added in the caption of Fig. 9: "The reactivity from hydroperoxide compounds (NISOPOOH, ISOPPOOH) is partly invisible for the LP-LIF instrument, because these species produce OH radical after reacting with it. The OH yield is rather uncertain, but it is expected to be less than 10% for example in the Caltech mechanism." In addition, we added in the caption of Fig. A11: "100 % yield is assumed in the MCM."

We added on p31 L763: "However, part of the reactivity from hydroperoxides is invisible for the OH reactivity instrument, because OH is partly produced in their reactions with OH. Approximately 90% of the reactivity is detected assuming an OH yield of 10% as implemented in the Caltech and FZJ-NO₃ mechanisms. In contrast, an OH yield of 100% is assumed for NISOPOOH in the MCM, which is likely too high as formation of epoxide products is expected to be a major reaction pathway."

Comment: Lines 135-137: Although understanding has clearly moved forward in the recent work, the point about not all nitro-oxy RO₂ radicals not being converted (or only being partly converted) to HO₂ and OH in the presence of NO was also recognised and discussed many years ago in relation to their measurement using the chemical amplification technique (e.g., Jenkin et al., 1997; Ashbourn et al., 1998, section 4.5).

Response: We added the reference Ashbourn accordingly in Line 137, which has a DOI.

Comment: Line 652: The authors make the statement "Rate constants for the reaction of the first generation organic nitrates with ozone are in the range of 10⁻¹⁹ to 10⁻¹⁸ s⁻¹ cm³ in Lee et al. (2014b)". While this is correct for the b-4(OH),3(NO₃) hydroxynitrate species (which is not formed significantly from NO₃ + isoprene), Lee et al. reported rate coefficients of about 3 x 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹ for both E- and Z- isomers of the d-1(OH),4(NO₃) hydroxynitrate species, 2-methyl-4-nitrooxybut-2-ene-1-ol, which is formed from NO₃ + isoprene (see Table 3 of their paper). Therefore, the statement on line 652 is only correct for one of the three species Lee et al. (2014b) studied – the only one that is not formed from NO₃ + isoprene.

Response: We included in the discussion the possibility of faster rates (L652): "Rate

constants for the reaction of the first-generation organic nitrates with ozone (Reaction R28, R31, R34, R37) are in the range of 10^{-17} to 10^{-19} cm³ s⁻¹ in Lee et al. (2014b), with rates being relevant for only the ozonolysis of δ nitrate alcohols and hydroperoxides for typical oxidant concentrations during the night. As only δ species are implemented in the MCM, the overall relevance of these loss reactions are overestimated under atmospheric conditions in the MCM (Table 2)."

Comment: Regarding b-hydroxynitrate species, I also note that the deactivating NO₃ group is more remote from the double bond in the b-hydroxynitrates formed from the NO₃-initiated chemistry compared with those formed from the OH-initiated chemistry, with the activating OH group being adjacent to the double bond. The b-hydroxynitrates from the NO₃-initiated chemistry might therefore be expected to be more reactive to ozone than those formed from the OH-initiated chemistry (e.g., the b-4(OH),3(NO₃) species studied by Lee et al., 2014b).

Response: We followed the values given in Wennberg et al., 2018, where either of the b-3,4 nitrate alcohols are proposed to react faster with ozone than their b-1,2 counterpart.

Comment: Discussion of MCM chemistry: The paper correctly points out some simplifications in the MCM NO₃- isoprene chemistry to highlight where the understanding of the chemistry has moved forward. One of the main reasons for differences is that the MCM represents the chemistry as proceeding entirely via the d-1(NO₃),4(OO) route. Early experimental work suggested this was the dominant route, and even in the more recent work of Schwantes et al. (2015) and Wennberg et al. (2018), this was still considered slightly more important than the b-1(NO₃),2(OO) route, which is now regarded as the most important isomer in Vereecken et al. (2021) and the present study. Once this important point is established, some of the comparisons/discussions seem a little artificial and misleading because they are comparing information for the β -1,2-RO₂ radical (and products) in the FZJ/Caltech mechanisms with information for the d-1,4-RO₂ (and products) in MCM – those differences being logical and expected. These are a few examples:

Table 2: In the caption its states "For simplicity rate constants are given for a temperature of T = 298K and only for the organic nitrate that is produced from the most abundant β -1,2-RO₂ radical".

Clearly, this cannot be the case for any of the MCM entries because the b-1(NO₃),2(OO) radical is not represented, so presumably the parameters for the d-1(NO₃),4(OO) radicals are used instead. This point should be made.

Note also that "ISOPCNO₃" is the MCM name specifically for the species HOCH₂CH=C(CH₃)CH₂ONO₂, formed from the d-4,1-RO₂ radical (during OH-initiated oxidation) or d-1,4-RO₂ (during NO₃-initiated oxidation). I assume that the results presented generally as ISOPCNO₃ are covering all hydroxynitrate (or nitro-oxy alcohol) isomers. Would a more generic term (ISOPNO₃) therefore be more appropriate?

Response: We added in the caption of Table 2 that values for the MCM refer to the d-isomers. With regards to the nomenclature, we would like to keep the name of the nitrate alcohol to remain consistent also with the carbonyl and hydroperoxide names, where we use the name of the one species present in the MCM to now denote the whole class.

Comment: I also note that the HPALD species in Table 2 are formed from the d-1,4-RO2 and d-4,1-RO2, and are not organic nitrates. Therefore, the table caption would seem to need some adjustments.

Response: We replaced "organic nitrates" with "major organic products from the reaction of isoprene with NO3."

Comment: Figure 6: This figure explicitly presents "Loss reactions of the most abundant β -1,2-RO2 species". This species is not represented in MCM, so there should be no MCM chemistry presented. As indicated above, the species at the top of the figure is not ISOPCNO3.

Response: In order to simplify the comparison of the different mechanisms, we chose to still include the MCM in this figure. The difference in considered RO2 is highlighted by the use of dashed arrows. We moved the according statement in the caption: "Dashed red arrows indicate corresponding reactions of the d- RO2 species which is the only RO2 represented in the MCM."

Comment: Lines 324-326: When discussing rate coefficients for RO2 + RO2 reactions in the Caltech/Schwantes et al. (2015) work, the following statement is made: "From their findings, a low reaction rate constant of $3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for the recombination reaction of the most abundant nitrate β -1,2-RO2 radical was found, orders of magnitude lower than the generic rate constant used in the MCM of $1.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ".

There seem to be several issues here. (i) because the MCM only represents the primary d-1,4-RO2 radical, $\text{CH}_2(\text{ONO}_2)\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OO}$, the generic rate coefficient applied to its reaction is that for a primary peroxy radical. It is therefore very logically orders of magnitude higher than that would otherwise have been assigned to a tertiary RO2 radical at the time in the MCM ($6.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This point could be made.

(ii) The rate coefficient in the MCM is strictly for the parameterised reaction of the given peroxy radical with the atmospheric pool of peroxy radicals. It is not a self-reaction rate coefficient and should not really be compared directly with it. For systems with restricted numbers of peroxy radicals, the MCM team generally recommends considering an explicit representation of RO2 self- and cross-reactions.

(iii) I cannot find the value of $3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in Schwantes et al. (2015) or Caltech (Wennberg et al., 2018). Schwantes et al. (2015) appear to estimate a value of $1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for β -1,2-RO2 (with much higher values for other isomers) but end up using a value of $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for all isomers in their simulations. The Wennberg et al. (2018) full mechanism uses $6.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for β -1,2-RO2. Some additional information on the origin of the $3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ value would be helpful.

Response: Thank you for spotting this mix-up. All the used values in the FZJ-NO3 mechanism are calculated according to SAR (Jenkin et al., 2019), from where the 3×10^{-16} value originates.

We clarified the tertiary and primary nature for the comparison with the MCM in the paragraph starting L324: "Rate constants of RO2 + RO2 reactions for nitrate RO2 in the

Caltech mechanism were derived from the measurement of isomer specific product distributions in the experiments of Schwantes et al. (2015). From their findings, a reaction rate constant of $7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ for the self-reaction of the most abundant nitrate b-1,2-RO₂ radical was applied. As this rate refers to a tertiary radical instead of a primary, it is slower than the rate constant used in the MCM of $1.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Rate constants for other nitrate RO₂ were estimated in the Caltech mechanism to be in the range of 10^{-12} and $10^{-13} \text{ cm}^3 \text{ s}^{-1}$. In the FZJ-NO₃ mechanism all the rates for the nitrate RO₂ self- and cross-reactions were calculated from structure activity relationship (Jenkin et al., 2019) resulting in an even lower rate constant for the self-reaction of the tertiary b-1,2-RO₂ of only $3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ and for the cross-reactions of this radical with other primary nitrate RO₂ of 2 to $10 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. The rates of the reactions within the pool of the other nitrate RO₂ are on the same order of magnitude as the values in the Caltech mechanism.”