Comment on egusphere-2022-587: "Comparison of isoprene chemical mechanisms at atmospheric night-time conditions in chamber experiments: Evidence of hydroperoxy aldehydes and epoxy products from NO$_3$ oxidation" by Carlsson et al..

This paper, in conjunction with the recent study of Vereecken et al. (2021), provides some important new experimental and theoretical information to help improve the detailed understanding of the NO$_3$-initiated oxidation of isoprene and its representation in chemical mechanisms. It uses experimental data to test the performance of the new FJZ-NO3 mechanism (Vereecken et al., 2021) in comparison with those of the Caltech and MCM isoprene mechanisms. The paper correctly highlights some limitations and simplifications in the MCM NO$_3$-isoprene chemistry, which has not had a targeted update in 20 years, the only changes being to some generic rate coefficient values and specific areas of overlap with the OH-initiated chemistry.

Main comment on modelled OH reactivity

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_{OHi} [X]$_I$, where [X]$_i$ is the modelled concentration of species "i" and k_{OHi} 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 FZJ-NO3 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_{OHi} [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?

Other comments and observations:

While reading through the paper, I also noticed a few other things that authors may wish to consider.

Lines 135-137: Although understanding has clearly moved forward in the recent work, the point about not all nitro-oxy RO_2 radicals not being converted (or only being partly converted) to HO_2 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).

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} cm^3 in Lee et al. (2014b)".

While this is correct for the β-4(OH),3(NO_3) hydroxynitrate species (which is not formed significantly from NO_3 + isoprene), Lee et al. reported rate coefficients of about 3 x 10^{-17} cm^3 molecule^{-1} s^{-1} for both E- and Z- isomers of the δ-1(OH),4(NO_3) hydroxynitrate species, 2-methyl-4-nitrooxybut-2-ene-1-ol, which is formed from NO_3 + 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 NO_3 + isoprene.

Regarding β-hydroxynitrate species, I also note that the deactivating NO_3 group is more remote from the double bond in the β-hydroxynitrates formed from the NO_3-initiated chemistry compared with those formed from the OH-initiated chemistry, with the activating OH group being adjacent to the double bond. The β-hydroxynitrates from the NO_3-initiated chemistry might therefore be expected to be more reactive to ozone than those formed from the OH-initiated chemistry (e.g., the β-4(OH),3(NO_3) species studied by Lee et al., 2014b).

Discussion of MCM chemistry: The paper correctly points out some simplifications in the MCM NO_3-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 δ-1(NO_3),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 β-1(NO_3),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-RO_2 radical (and products) in the FZJ/Caltech mechanisms with information for the δ-1,4-RO_2 (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-RO_2 radical".

Clearly, this cannot be the case for any of the MCM entries because the β-1(NO_3),2(OO) radical is not represented, so presumably the parameters for the δ-1(NO_3),4(OO) radical are used instead. This point should be made.

Note also that "ISOPCNO3" is the MCM name specifically for the species $HOCH_2CH=C(CH_3)CH_2ONO_2$, formed from the δ-4,1-RO_2 radical (during OH-initiated oxidation) or δ-1,4-RO_2 (during NO_3-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?

I also note that the HPALD species in Table 2 are formed from the δ-1,4-RO$_2$ and δ-4,1-RO$_2$, and are not organic nitrates. Therefore, the table caption would seem to need some adjustments.

Figure 6: This figure explicitly presents "Loss reactions of the most abundant β-1,2-RO$_2$ 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.

Lines 324-326: When discussing rate coefficients for RO$_2$ + RO$_2$ reactions in the Caltech/Schwantes et al. (2015) work, the following statement is made: "From their findings, a low reaction rate constant of 3×10^{-16} cm^3 s^{-1} for the recombination reaction of the most abundant nitrate β-1,2-RO$_2$ radical was found, orders of magnitude lower than the generic rate constant used in the MCM of 1.3×10^{-12} cm^3 s^{-1}".

There seem to be several issues here. (i) because the MCM only represents the primary δ-1,4-RO$_2$ radical, CH$_2$(ONO$_2$)C(CH$_3$)=CHCH$_2$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 RO$_2$ radical at the time in the MCM (6.7×10^{-15} cm^3 molecule^{-1} 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 RO$_2$ self- and cross-reactions.

(iii) I cannot find the value of 3×10^{-16} cm^3 molecule^{-1} s^{-1} in Schwantes et al. (2015) or Caltech (Wennberg et al., 2018). Schwantes et al. (2015) appear to estimate a value of 1.8×10^{-14} cm^3 molecule^{-1} s^{-1} for β-1,2-RO$_2$ (with much higher values for other isomers) but end up using a value of 5×10^{-12} cm^3 molecule^{-1} s^{-1} for all isomers in their simulations. The Wennberg et al. (2018) full mechanism uses 6.9×10^{-14} cm^3 molecule^{-1} s^{-1} for β-1,2-RO$_2$. Some additional information on the origin of the 3×10^{-16} cm^3 molecule^{-1} s^{-1} value would be helpful.

References (not already cited)

Ashbourn, S. F. M., Jenkin, M. E. and Clemitshaw, K. C.: Laboratory studies of the response of a peroxy radical chemical amplifier to HO$_2$ and a series of organic peroxy radicals. J. Atmos. Chem., 29, 233–266, 1998. https://doi.org/10.1023/A:1005992316512

Jenkin, M. E., Derwent, R. G. and Saunders S.M.: The calculated fractional response of the chemical amplification technique to peroxy radical populations on a boundary layer trajectory over Europe, in B. Larsen, B. Versino, and G. Angeletti (eds), Proceedings of the 7th European Symposium on Physicochemical Behaviour of Atmospheric Pollutants, the Oxidising Capacity of the Troposphere, European Commission, Luxembourg, pp. 144–148.