Atmospheric Chemistry and Physics Discussions

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Comment on acp-2022-333

Anonymous Referee #2

Referee comment on "Evaluation of isoprene nitrate chemistry in detailed chemical mechanisms" by Alfred W. Mayhew et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-333-RC2, 2022

General Comments:

This paper nicely compares three different complex chemical mechanisms to explore how each represents organic nitrates from both OH and NO3 oxidation of isoprene. This study is quite useful and interesting to show the differences between these mechanisms. However, as explained below there needs to be more clarity in how dilution was constrained in the model and better calibration of the main isoprene organic nitrates including isoprene carbonyl nitrate (ICN), isoprene hydroxy nitrate (IHN), and isoprene hydroperoxy nitrate. Assuming that the sensitivity of all isomers and all organic nitrate types regardless of functional groups is similar to IEPOX very likely leads to inaccurate conclusions in the overall magnitude and even the diurnal pattern of these organic nitrates, which makes it difficult to use the measurements to assess, which mechanism is correct, which seems to be the purpose of this study. Major revisions to include a more complex calibration for these isoprene organic nitrates especially IHN and ICN, which have been previously calibrated by other I- CIMS, are needed as explained further in the specific comments below prior to publication.

Specific Comments:

Page 3 line 91 – There are a couple versions available from the code repository referred to in Wennberg 2018. Can you be clearer which version you used here? Both number and if it was full/reduced?

Page 4 line 110 – Please further explain the sensitivity/calibration assumptions used here. What is the rationale to use IEPOX calibration for all types of organic nitrates (IHN, ICN, IPN) and all isomers? I recognize calibrations of IPN are uncertain as no standards are available, but IHN has been calibrated for several other I- CIMS instruments (Xiong et al., 2015 and Lee et al., 2014 (https://doi.org/10.1021/es500362a) and less, but still some

information is available for ICN too also using an I- CIMS (Xiong et al., 2016, https://doi.org/10.5194/acp-16-5595-2016). These three papers demonstrate that different isomers and functional groups can cause very different sensitivities in the I- CIMS for these organic nitrates. Can you use the isomer distribution from the models and the isomer dependent sensitivities from these past works to more accurately calculate the measurements of these organic nitrates from the I- CIMS? Please provide either significant justification for not doing this with an estimate for uncertainty added or use a more complex assumption for the sensitivities of all the isoprene derived nitrates, but especially IHN, which has already been well studied by I- CIMS.

Page 4 line 125 – Can you explain how you calculated these RO2 reaction rates further? Perhaps an example would help. When you say you use an average of all RO2 reactions do you also add in the reactions with acyl peroxy radicals that have faster reaction rates? Another more consistent approach is to do something similar to what MCM assumes, which is the geometric mean of the rate of the self-reaction of RO2 + RO2 and rate of CH3O2 + CH3O2? http://chmlin9.leeds.ac.uk/MCM/categories/saunders-2003-4_6_5-gen-master.htt?rxnId=4270.

Page 4 line 125 - Can you provide the reaction mechanism files (or a Table in the supplement with the changes) for at least the Caltech mechanism used here since you made updates beyond what is available publicly? This is important for data/code transparency. Providing the reaction mechanism files for all three mechanisms would be best.

Page 5 line 153 – Can you further explain this sentence: "For multifunctional compounds, the largest deposition velocity was selected." Selected from where: Table S3 or from Nguyen et al., 2015?

Page 5 line 154 – do you mean divided by here: "The rate of deposition was determined by multiplying the assigned deposition velocity by the measured boundary layer height." as listed in the user guide: https://github.com/AtChem/AtChem2/blob/master/doc/AtChem2-Manual.pdf page 16.

Page 5 line 157 – Why did you choose this constant dilution rate? Do you have a reference for this? How does the dilution rate used in this paper compare with other box-modeling studies in the same region or similar regions? The papers you reference above (Reeves et al., 2021; Whalley et al., 2021) that also did box-modeling for APHH used a diurnally varying dilution rate dependent on glyoxal and the ventilation lifetime was a lot shorter than that used in this work. Considering that even MVK + MACR, which should be reasonably well represented chemically, are overpredicted maybe dilution should be stronger? How did you evaluate/constrain this?

Section 3.3: See above comment, especially for IHN when several studies have demonstrated that the different isomers have different sensitivities in the I- CIMS and we

know from the modeling that the distribution of isomers will change diurnally (Figure 10 and last paragraph of Section 3.3), assuming the sensitivity of all isomers is similar to IEPOX likely leads to inaccurate conclusions in the overall magnitude and even the diurnal pattern, which makes it difficult to use the measurements to assess, which mechanism is correct. As suggested above, please update the measurements to consider these isomer dependent sensitivities. Also 1,2-IHN has been shown in Vasquez et al., 2020 to have rapid hydrolysis on aerosols. Have you considered this in your modeling? If not, how would not considering this impact your results?

Page 10 Line 321 – If you know that IEPOX is not likely a good calibrant to represent ICN because the I- CIMS is more sensitive to alcohols than aldehydes/ketones, can you choose a different calibrant based on these past literature studies (those referenced in this paragraph or Xiong et al., 2016) to better represent the ICN sensitivity? Without a better calibration for ICN or estimate of uncertainty, it is hard to determine which mechanism is best representing this chemistry.

Page 11 line 353 – As mentioned above, it is not enough to state that you "potentially have significant issues with calibration factors". That's maybe okay for a compound like IPN, which have few standards and no past studies addressing the sensitivity on the I-CIMS, but you "certainly" not "potentially" have significant issues with calibration factors for IHN and ICN, for which other studies have reported absolute and relative sensitivities for the I- CIMS that could be used in this work.

Figure 5, For the NO3-initiated oxidation of hydroxycarbonyls in Figure 5, please add oxidants/reactants above the arrows for clarity and consistency with other plots.