

Interactive comment on “The Production and Hydrolysis of Organic Nitrates from OH Radical Oxidation of β -Ocimene” by Ana Cristina Morales et al.

Anonymous Referee #2

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Morales & Jayarathne et al. present laboratory study where B-Ocimene was oxidized by OH radicals in the presence of NO to form organic nitrates. The series of chamber experiments were used to investigate the hydroxynitrate yield and the impact of RH on the yield, SOA yield, and hydrolysis rates of the hydroxynitrates in the aerosol phase and the role of pH on hydrolysis. As there is minimal information about many of these processes for many compounds in the atmosphere, this study provides valuable constraints that will be beneficial for the atmospheric chemistry community. However, many technical aspects need to be described in better detail prior to publication. Upon addressing the comments here (and Reviewer #1, which has similar comments), the paper will be a valuable addition to ACP.

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Major: Pg 4 Line 99 - 100: Why was the maximum RH only 70%, as this is below the deliquescent point of ammonium sulfate, the main seed used? How would you expect that to change the results discussed here, as this would inhibit aqueous chemistry? Further, why was ammonium sulfate the main seed used? Various studies have shown that forested environments have sulfate aerosol this is more like ammonium bisulfate (e.g., Weber et al., 2016, Nat. Geoscience), which may lead to different chemistry and uptake of the hydroxynitrates? Would this impact the aerosol yields and other aspects investigated during the chamber experiments? Finally, drawing more attention to the experiments that were allowed to self-nucleate (thus organic seed) maybe useful to discuss the role (or lack there of) or organic vs inorganic seed.

Pg 5, In 133 - 135: It is stated that synthesized α -pinene hydroxynitrate standard was used to calibrate the CIMS for the ocimene hydroxynitrate. What is the uncertainty associated with this? Were any experiments conducted, comparing for example a voltage scan (e.g., Lopez-Hilfiker et al., 2016, AMT) or the standard and the species measured from the chamber, to compare the binding energies of the α -pinene and ocimene hydroxynitrate to determine if the sensitivity may be similar?

Pg 6, In 144 - 147: Figures and an explanation of the amount of correction these experiments produced is needed. Is it in line with the general correction that has been observed in prior studies (e.g., Krechmer et al., EST, 2016; Krechmer et al., 2017, EST; Liu et al., 2019, AMT; Liu et al., 2019, Comms. Chem.; Matsunaga & Ziemann, 2010, AST)? Also, were the lines and instrument investigated for potential loss and corrected for (e.g., Deming et al., 2019, AMT; Pagonis et al., 2017, AMT)?

Pg 6, In 150 - 152: During the quality control experiments to evaluate collection efficiency of the gas- and particle-phase species, were any experiments conducted or any observations made to determine if there were any losses or side reactions that occurred that would influence the results? How were the filters treated after collected the samples (immediately analyzed, stored for XX time in fridge, etc.) and would this impact the results?

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Pg 7, ln 176 - 177: What acid/buffer solutions were used to make the bulk pH reactions? Also, were any experiments conducted with other type of acids, as the SN reaction may change? If not, can any comments be made about that?

In general, a subsection discussing all the uncertainty and how they are propagated into the error bars for the figures are extremely necessary. Right now, it is hard to discern how the error bars were calculated and what errors contributed/what the main error(s) were.

Pg 8, ln 212: Some of sources of uncertainty are mentioned here that were not brought up in the methods sections. A focused section that lays all the sources of uncertainty would help with these type of sentences.

Pg 12, ln 311 - 348: -Recent work has shown that the use of bulk solutions vs aerosol has large impacts on the chemistry, as aerosol is a much higher concentration solution, leading to higher ionic strengths and faster or slower reactions (Liu et al., 2020, PNAS). Wondering if this was considered for the results discussed here? If not, at least mention this limitation to raise awareness that the rates maybe different. -It was briefly mentioned, but further discussion about primary vs tertiary hydrolysis is warranted here. For example, since different type of nitrates are formed, do the results discussed here and shown in Fig. 8 indicate a predominance of tertiary nitrates and the generally rapid hydrolysis? Would a "second" line from primary expected at all, or are the yields for primary expected to be low enough to not have a noticeable 2nd, slower hydrolysis rate? -Finally, it is not clear which experiments in Table 1 were used for this section. Please specify.

Pg 13, ln 333 - 335: This sentence seems very misleading, as there have been numerous studies that has measured appreciable concentrations of organic nitrates, with different techniques, in various locations (Ayres et la., 2015; Fry et al., 2013; Fry et al., 2018; Lee et al., 2016; Kiendler-Scharr et al., 2016; Ng et al., 2017). I strongly recommend rephrasing.

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Figure 7: It is not clear how the structures were determined.

Minor

Throughout the text, please check references. There are many locations where the Name et al., year or year do not have the proper parenthesis. Also, some of the references at do not have proper abbreviations for journals.

Pg 7, ln 172: was the solution linearly increased during the 2 to 10 min?

Pg 9, ln 226 - 231 & Fig 4: Were the results compared against the parameterization for yields from Carter and Atkinson (J. Atmos. Chem., 1989)? If not, it maybe valuable to do that comparison for reference for organic nitrates that have not been measured.

Pg 10, ln 257 (and others): It would be useful to also state what the C^* is along with the vapor pressure, as many aerosol chemists think in C^* and it provides an easy comparison about partitioning (e.g., C^* 0 or 1 means a lot of the products will be in the aerosol-phase and are more semi-volatile but C^* 4 - 6 mean that it's more intermediate-volatile and less likely to be in the aerosol-phase).

Fig 4: It's unclear what the different lines represent.

Fig 6: I agree with Reviewer #1 that this figure currently doesn't seem warranted, and it is currently mentioned in the text (once I think).

Other fig: Finally, I agree with Reviewer #1 that a figure showing the time series of the gas-phase species measured by the CIMS would also be useful (along with other parameters such as aerosol mass concentration, b-Ocimene, etc.).

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