



EGUsphere, referee comment RC4  
<https://doi.org/10.5194/egusphere-2022-1131-RC4>, 2022  
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## Comment on egusphere-2022-1131

Anonymous Referee #4

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Referee comment on "Selective deuteration as a tool for resolving autoxidation mechanisms in  $\alpha$ -pinene ozonolysis" by Melissa Meder et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-1131-RC4>, 2022

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Meder et al. discuss the use of deuterated  $\alpha$ -pinene standards to investigate its oxidation by ozonolysis. The authors selectively replaced hydrogen atoms with deuterium atoms to investigate at what carbon centers hydrogen/deuterium abstraction occurred. The authors used a high resolution chemical ionization orbitrap mass spectrometer to differentiate peaks associated with the deuterated samples and based on obtained mass spectra, discussed likely oxidation mechanisms. The work presented in this manuscript is novel and attempts to address a challenging gap in knowledge regarding oxidation mechanisms for  $\alpha$ -pinene ozonolysis. Overall, the manuscript presents important data that should be accepted for publication in ACP once some major comments have been addressed.

### Major comments

- Although this manuscript presents some convincing arguments, I feel it would benefit from some structural changes that would significantly streamline and clarify the work presented. Primarily the manuscript should be reorganized to follow a more logical flow. For example, the "selective deuteration and autoxidation sections" contains a mixture of literature motivation and methods used, and as such could be instead integrated into the "introduction" as well as the "methods" sections as is appropriate. Additionally, the authors should consider reorganizing the structure of their results and discussion section (e.g., switching the order of sections 4.1 and 4.2). Data should be presented first followed by its interpretation and discussion, i.e., there should not be a section on "interpreting the mass spectra" before "experiment overview" where mass spectra should be introduced.
  
- This manuscript would also benefit from some additional details regarding experimental

conditions, instrument details and uncertainties, etc. Although the authors state that they were focused on the interpretation of general trends in the mass spectral data between different deuterated species, including these quantitative details would help readers to interpret the data presented and importantly the limitations of the work that are described by the authors. Furthermore, a lot of useful information is present in the manuscript, but it can be challenging to find in its current organizational state. For example, some of these important details (e.g.,  $\alpha$ -pinene mixing ratios) were not stated in the text, but instead had to be determined via figures. Additionally, even though the authors reference existing literature for the instrumental methods, enough details should be given so that readers know the essentials without having to refer to other publications.

- The number of experiments conducted is unclear. Were replicates of these experiments conducted or just the 4 listed? Given the large experimental uncertainty, replicate measurements would be of significant benefit to help constrain these results and allow for a more rigorous interpretation of the experimental data. Furthermore, a summary of experiments and conditions would be beneficial.

#### Minor comments

- The color scheme of the figures could be improved. It would be very beneficial for the authors to stick with a common color scheme and employ this throughout the manuscript. Also, shaded regions and lines do not have to have a pattern if an appropriate color scheme is chosen.
- The authors are attempting to determine the mechanism through which  $\alpha$ -pinene undergoes ozonolysis. However, OH is also generated since an OH scavenger was not used during the experiments. The authors do not comment on this in the manuscript discussion. Further mention of this should be discussed. In particular, do the authors expect that the kinetics of OD vs OH generated to impact potential OH oxidation chemistry?

- There is a lot of discussion in the introduction regarding decrease in reaction rates due to the kinetic isotope effect (KIE), yet the authors claim that a KIE is not observed with their data. Why do the authors propose this is?
  
- The authors state that the data were divided into two periods "C<sub>high</sub>" and "C<sub>low</sub>" when the reaction rates for  $k[\alpha\text{-pinene}][\text{O}_3]$  were  $0.5 \text{ ppt s}^{-1}$  and  $0.015 \text{ ppt s}^{-1}$ . Can the authors please elaborate on how these periods were chosen?
  
- If the chamber is being operated in a steady state continuous flow mode, why is the signal for the precursor dropping over time but ozone is relatively stable?
  
- The authors cite Rissanen et al. stating that "D-atoms can be exchanged to H-atoms in contact with water vapour in cases where a C-D bond was broken". The experiments were conducted at  $\text{RH} < 1\%$  so it is unlikely that these processes should be significant under the experimental conditions. However, under ambient conditions RH is much higher. How do the authors expect RH might affect the experimentally observed results?

#### Specific comments

Line 66- The authors state "The purity of each compound was >95% as determined by <sup>1</sup>H NMR spectroscopy and we were unable to observe residual proton resonances associated with the deuterated carbon positions for any sample..." This is misleading as only NMR spectra are given for the <sup>3</sup>D<sub>1</sub> α-pinene sample. Was a purity of >95% also obtained and characterized by NMR for the other two deuterated α-pinene samples synthesized?

Line 137- "RH" should be in brackets.

Line 150- How much did these concentrations vary? Please state a range in the text. These can be determined from Figure 5 but should be stated in the text.

Line 157-158- The authors state "the instrument has been shown to be effective in detecting HOMs". It would be beneficial for the authors to more information here regarding instrument sensitivity, etc. Perhaps adding parts of the "data analysis" section here would be helpful.

Line 162- The authors state "the results were comparable" in reference to the using both a VOCUS-PTR-ToF and PTR-ToF to conduct experiments. Without showing the data or giving any sort of quantitative comparison, it is hard to make these statements. Consider rephrasing or adding details to convince the readers that this is in fact the case.

Line 173- Please state the sensitivity here.

Line 177- The authors state "We excluded all isotopes that contained deuterium, because using selectively deuterated precursors distorts these signals". It is unclear what the authors mean here. If you are trying to measure deuterated samples, then understanding the instruments response to these species is key to obtaining quantitative data.

Line 214- Please state the limit of detection of the instrument.

Line 240- This section is labeled "experiment overview". Data are being discussed here and not the experimental procedure. Consider renaming this section.

Line 241- The authors state "we conducted four experiments with..." Were these 4 different types of experiments or only 4 experiments total? It is unclear if or how many replicates of these experiments were conducted.

Line 308-311- It would be helpful to include the fraction of times that e.g., Ds were lost. Statements such as "often" or "rarely" are somewhat ambiguous.

Line 337- The authors state "...the differences in steady-state precursor concentrations between the experiments". There are not explicitly given in the manuscript (other than

what can be deduced from Figure 5) and should be added as part of the methods section. Also, the term steady state should not be used here as it implies that the concentrations are not changing. However, according to Figure 5, and the authors themselves on Line 242, this is not true for several of the experiments.

Figure 8- Please state slopes and offsets for the linear fits listed in graphs 8b-d.

Line 403- "there was a bug in the pump" is unclear. Was this a mechanical issue? Can the authors please clarify this in the text.

Figure A2- Were the  $\alpha$ -pinene oxidation products not measured by orbitrap? As such their mass spectra should not be in "unit mass resolution". Also, it would be of benefit to either label the peaks or list the m/z associated with each HOM for ease of reading.

## References

Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kangasluoma, J., Sarnela, N., Junninen, H., Jørgensen, S., Schallhart, S., Kajos, M. K., Taipale, R., Springer, M., Mentel, T. F., Ruuskanen, T., Petäjä, T., Worsnop, D. R., Kjaergaard, H. G., and Ehn, M.: The Formation of Highly Oxidized Multifunctional Products in the Ozonolysis of Cyclohexene, *Journal of the American Chemical Society*, 136, 15 596–15 606, <https://doi.org/10.1021/ja507146s>, PMID: 25283472, 2014.