

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-703

Anonymous Referee #1

Referee comment on "Secondary organic aerosol and organic nitrogen yields from the nitrate radical (NO₃) oxidation of alpha-pinene from various RO₂ fates" by Kelvin H. Bates et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-703-RC1>, 2021

This manuscript investigates the SOA yield from a-pinene + NO₃ under different RO₂ fates. It is shown that significant amount of SOA is produced from RO₂+RO₂ reactions, while SOA yield from other RO₂ reactions, including RO₂+NO, RO₂+NO₃, and RO₂+HO₂, is minimal. The presented results based on chamber experiments with extensive chemical characterization are convincing. However, the significance of this finding, including the manuscript title, is exaggerated and not well-supported. It is mainly because the RO₂ fate at night in the atmosphere is highly uncertain. Previous studies on a-pinene + NO₃ focused on RO₂+HO₂ pathway, because that was believed to be the dominant fate of RO₂ at night. What is missing from this manuscript is the evidence that RO₂+RO₂ is dominant at night. The authors cite Aryes et al. (2015) and Romer et al. (2018) to argue that 30-50% RO₂+HO₂ and 30-50% RO₂+RO₂ (Line 225) in the summertime in the SE US. However, the reader glimpsed those references and did not find explicit and careful analysis on the RO₂ fate. Another important caveat is that in chamber experiment, a-pinene RO₂ reacts with RO₂ with 8-10 carbon atoms. In the ambient, however, a-pinene RO₂ is more likely to react with RO₂ with fewer carbon atoms (i.e., from isoprene), leading to lower SOA yield than chamber experiments. Overall, the reader appreciates the authors' careful work to explore the effects of RO₂ fate on SOA formation and recommend publication after the following comments are addressed.

Major Comments

- Concerns regarding the RO₂ fate as elaborated above.
- The SOA formation from a-pinene + NO₃ is estimated by subtracting the SOA from a-pinene + O₃ and a-pinene + OH. Such estimate has severe uncertainty, because of the synergistic reaction pathways, which the authors acknowledges, but did not carefully take into account. The estimated SOA yield from a-pinene + NO₃ likely represents an upper limit.
- The estimate of RO₂ fate heavily relies on kinetic model, which bears uncertainties in

the kinetics of RO₂ reactions. The RO₂+RO₂ rate applied in this study (1e-13) is slower than those in recent findings which report the a-pinene+O₃ RO₂+RO₂ rate is on the order of 1e-12(1) or even 1e-11(2). Although the reasoning for using 1e-13 is briefly mentioned in the manuscript, sensitivity tests regarding the effects of RO₂+RO₂ rate on the yields of SOA and other products should be conducted.

- Because of the unclear RO₂ fate at night, the manuscript title is not appropriate. The reader suggests something like "SOA yield from a-pinene + NO₃ under different RO₂ fate"
- When simulating the RO₂ fate under summertime conditions observed in the SE US, the kinetic model only contains a-pinene chemistry. As a-pinene only accounts for a very small fraction of VOC in the ambient, the ambient RO₂ fate is largely driven by the chemistry of other VOCs. In other words, the simulated RO₂ fate does not represent the RO₂ fate in the SE US. This challenges the representativeness of the "simulated nighttime experiment" and should be carefully acknowledged in the manuscript.

Minor Comments

- Line 240. Why is the SOA yield higher in RO₂+NO than RO₂+NO₃?
- In figure 4, all experiments seem to fall into two groups, six experiments above the dashed line and the majority of experiments below the line. Does any factor drive the segregation? Labeling the data points by experiment would be useful and a good start point. What's the regression slope (i.e., ozonolysis-corrected SOA yield) if only experiments below the dashed line are fitted?

Reference

- Y. Zhao, J. A. Thornton, H. O. T. Pye, Quantitative constraints on autoxidation and dimer formation from direct probing of monoterpene-derived peroxy radical chemistry. *Proceedings of the National Academy of Sciences*, (2018).
- T. Berndt *et al.*, Accretion Product Formation from Ozonolysis and OH Radical Reaction of α -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene. *Environ Sci Technol* **52**, 11069-11077 (2018).