

Interactive comment on “A comparative and experimental study of the reactivity with nitrate radical of two terpenes: α -terpinene and γ -terpinene” by Axel Fouqueau et al.

Anonymous Referee #2

Received and published: 7 August 2020

GENERAL COMMENTS

In this manuscript the authors present results of an experimental study of the kinetics, products, and mechanisms of the reactions of NO₃ radicals with two monoterpenes: α - and γ -terpinene. Both compounds have two C=C double bonds, although in one case they are conjugated and in the other not. The study seeks to determine how these structural differences affect reaction rates, gas-phase products and mechanisms, and secondary organic aerosol (SOA) formation. Experiments were conducted in either a glass or stainless-steel chamber and gas phase products were monitored with a PTR-MS and in situ FTIR. SOA formation was monitored with an SMPS and composition

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was probed by FTIR analysis of filter samples.

The relative and absolute rate constants measured for each monoterpene compare well with each other, with previously measured rate constants, and with predictions of structure-activity relationships. The authors present plausible gas-phase mechanisms to explain the formation of the proposed products identified by the PTR-MS, which include multifunctional compounds containing various combinations of nitrate, carbonyl, and hydroxyl groups. When combined with vapor pressure estimates the proposed products also explain the very large differences in the SOA yields measured for the two monoterpenes. Overall, this is a very comprehensive study and presents new results on the nighttime chemistry of monoterpenes that will be useful to the atmospheric chemistry community. I think the paper should be published in ACP after the following minor comments and have been addressed.

SPECIFIC COMMENTS

1. Line 86: The purity of the α -terpinene is not very high. Do the authors have any idea what else it contains? Are there any observed products that might not be explained by reaction of α -terpinene?
2. Line 335 and beyond: SOA yields are explained strictly in terms of physical partitioning of monomers from the gas phase to the particles. Clafin and Ziemann, J. Phys. Chem. A, 2018, showed that the SOA formed from the β -pinene + NO₃ reaction consists almost entirely of acetal dimers formed in the particle phase. Could similar reactions occur in these systems, and how would the presence of oligomers alter the interpretation of SOA yields?
3. Line 335 and beyond: No mention is made as to the effects of loss of gas-phase products to the chamber walls. I would think this is quite high for stainless steel and possibly glass, and these sorts of products. This should be discussed.
4. Line 389: Could add SOA results from Clafin and Ziemann, J. Phys. Chem. A,

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2018.

5. Line 468: Peroxynitrates can decompose to a carbonyl + HNO₃ in the condensed phase. How might this affect the results?

TECHNICAL COMMENTS

1. Line 208: I think “et” should be “and”.
2. Line 476: “bound” should be “bond”.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-504>, 2020.

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