

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-1020

Anonymous Referee #2

Referee comment on "Observations of gas-phase products from the nitrate-radical-initiated oxidation of four monoterpenes" by Michelia Dam et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1020-RC2>, 2022

General Comments

This manuscript describes an experimental study of the reactions of four monoterpenes with NO₃ radicals. Experiments were conducted in a flow-through stainless steel chamber and gas-phase products were analyzed online using a chemical ionization mass spectrometer with a NO₃⁻ ion source (NO₃-CIMS) and a thermal desorption cavity ringdown spectrometer for nitrates (TDCRDS). Particle size and volume concentrations were monitored with a scanning mobility particle sizer (SMPS). Kinetic modeling was employed to estimate concentrations of O₃ and NO₃ radicals to verify that the monoterpenes primarily reacted with NO₃ radicals. Attempts were also made to estimate loss of products to the chamber walls by measuring decay rates in the absence of reaction. The results were used to identify and quantify reaction products and place them in various classes (monomers, dimers, etc.), measure elemental ratios, and develop reaction mechanisms to explain the formation of the detected products for all the monoterpenes.

I think the measurements were well done, and could provide useful insights into the products and mechanisms of these reactions. The nighttime reactions of monoterpenes with NO₃ radicals are of significant current interest because of the impacts of organic nitrate formation on NO_x sequestration and secondary organic aerosol formation, as well as a desire to understand how monoterpene structure influences reaction products and mechanisms.

Unfortunately, I found much of the manuscript very difficult to understand. The authors base their interpretation of the results on proposed reaction mechanisms, and that discussion encompasses most of the paper. But in their presentation, they rely too much on the text to do this without providing figures of detailed reaction mechanisms that a reader needs in order to be able to follow along. The mechanisms shown in the main body

of the paper are condensed to the point that they are of little value, and those in the SI are only slightly better. The text is extremely dense and detailed, and in my opinion spends too much time attempting to explain every observation. As a result, I came away not knowing what the main points were. I strongly suggest that the authors make a major effort to narrow the discussion to the main points, and create figures that allow a reader to explicitly follow all the reaction steps discussed in the text. Since I am normally quite comfortable with VOC oxidation mechanisms, I think that unless this is done the paper will be unreadable to most people who might be interested in the topic. In light of these problems, I think the manuscript might be publishable in ACP, since the experiments are interesting and of high caliber, but not without major revisions. I provide some specific comments below, but given the overall difficulties I had understanding much of the discussion, there are large sections for which I did not provide comments.

Specific Comments

- Page 2, line 15: Do you mean peroxy radical isomerization reactions?
- Page 2, line 17: Why do you quote O₂ concentrations > 10E15/cm³ when they are ~10E18/cm³ in the troposphere?
- Page 6, line 7–11: The rate constant for α -pinene + O₃ is 8.4E-17. It is also most reasonable to use values for alkenes with similar structures, especially where the C=C bond is in the ring and a methyl group is attached, since that has a large impact on the rate constants. The α -pinene + NO₃ rate constant is 6.2E12. See Atkinson and Arey, Chem Rev. 103, 4605 (2003).
- Page 6, line 14–16: Is 6E10/cm³ to estimated total detected product concentration? It doesn't have the right units for a calibration factor. If so, what does this correspond to as a yield, and which experiment does it apply to? And why do all the figures except 8 report ion counts instead of concentrations?
- Page 6, line 19: What do you mean by reaction intermediates? Radicals? Which ones?
- Page 7, line 27: Are you suggesting that RO + RO reactions occur? This is not possible, since RO isomerization, decomposition, or O₂ reactions occur on microsecond timescales, while bimolecular RO + RO reactions would occur on second timescales or longer.
- Page 7, line 32: What do you mean by number of generations? In standard usage the number of generations is the number of reactions of C=C bonds in the molecule with NO₃ radicals, so here 1 or 2 generations might be formed. Also, because the presence of NO₃ in the molecule is a clear indication of NO₃ addition, the N/C ratio would be a better indicator of the number of generations.
- Table 1: What is meant by RO + H? The only RO reactions that form ROH are H-shift isomerization.
- Page 9, line 10: Do mean a bimolecular reaction to form a RO radical? That would not be considered decomposition, which generally refers to a unimolecular bond cleavage and dissociation.
- Page 11, line 1: See Comment 13.
- Page 11, line 8: Don't you mean loss of acetone?
- Page 12, lines 14–16: I think the aldehyde in Figure 5A is more likely to be formed by an RO₂ + RO₂ reaction via the Russell mechanism than by an RO + O₂ → R=O + HO₂ reaction, since this RO radical could isomerize much faster than the O₂ reaction.
- Page 14, line 25: I think this should be "...total detected organic...".
- Page 16, line 19: I think this should be "...major detected species...".

Technical Comments

- Page 3, line 2: thujene should be capitalized.
- Page 4, line 18: (Sect. SI??)
- Page 5, line 12: Table ??
- Page 6, line 4: (??)
- Page 4, line 7: (Table??).
- Page 6, line 18: Sect. ??
- Page 7, line 2: (see SI Sect. ??).
- Page 7, line 11: Should be "experiments".
- Page 7, line 16: (Figure??)
- Page 8, line 2: SI(??)
- Page 8, line 4: (SI Figure ??).
- Page 8, line 6: (Figure ??).
- Page 9, line 4: SI Sect. ??
- Page 9, line 7: Delete "are".
- Page 13, line 16: (Sect. ??).