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Comment on acp-2021-1020

Anonymous Referee #1

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-RC1>, 2022

General

The manuscript investigates the oxidation of several monoterpenes by NO₃. The authors selected four bicyclic monoterpenes with different ring sizes and structures, in order to reveal mechanistic information from observed product distributions. New particle formation was observed in two out of four cases, and its occurrence was related to the product distribution. The core of the analysis focused on product distribution and suggested pathways to rationalize the observations. Overall, the manuscript is quite interesting and quite well written. The in the description of the mechanistic parts, especially in the beginning the authors could try to give more aids to the reader, e.g. by referring more often to the mechanistic schemes. The manuscript could be suited for publication in ACP. There are some minor issues which could lead to better readability and some major comments the authors should address before the manuscript could be published in ACP.

Major comments:

Mixing in the chamber, wall losses

p.4, l.6 and p.5, l12: From Figure 2, the chamber seems to be rectangular not cylindric. If so, I am wondering how perfect the mixing will be. How do you ensure (fast) mixing?

p.4, l.23: Do you know the typical mixing time? I am also asking, because the lifetime of N₂O₅ of about 11 min. (p.6, l.2) in such a metal chamber of this size appears to be quite long. Or do you establish large gradients towards the walls? Actually, the value given in the main manuscript of 1.5E-3 s⁻¹ differs from the value in the SI (1.25E-3 s⁻¹, p.S6, l.5)

p.7, l.2: SI Section 0.5 does not really show the wall loss as a function of O:C. It discusses only the range of wall loss coefficients. The example shown in Figures S7 indicates more a wall equilibrium, because the wall loss trace becomes a constant and not zero. A bit difficult to understand for the example of the heavily functionalized C₂₀ compound. The raw signal looks as expected, though. What will happen if you fit

$$c(t) = \exp(-(\tau(\text{wall}) + \tau(\text{dil}) \times t)$$

and set $\tau(\text{dil})$ to the nominal residence time?

I am also wondering, why the dilution trace (=NO₂) appears to be linear. Maybe it is better to use a log scale for demonstrating the losses. (By the way, I guess the units on the y-axis of Figure S7 should be "cm⁻³")

p.7, l.10: Regarding the TD-CRDS measurement. What is the molar yield of the condensable organic nitrates. I guess it is of the order of percent? The yields detected by CIMS seem to be much lower. I expect the product spectrum not to be too different compared to the previous studies mentioned. Insofar the losses in a 2 m Teflon line seem not to be too critical for non-HOM, which should be the majority. Did you calibrate such line losses?

The shortest lifetime of HOM is about the same as for N₂O₅. Can this be an indication of the typical mixing time in your chamber? Once entering the thin diffusion layer on the walls the molecules get lost? Could it be that you lose significant amounts of organic nitrates on the metal walls, with a rate close to your mixing time? How stable are functionalized organic nitrates on dry walls made of stainless steel?

C7 compounds

p.9, l.15ff: The residence time for the inlet utilized by Draper et al. (2019) was with 150 ms only about a factor of two longer than yours of 80 ms. Do you think the sensitivity to C7 compounds from Δ^3 -carene is limited by the reaction time of cluster formation? Then it should scale with the reaction time (at same reagent ion concentration)? However, isn't it more a fast dynamic forming and breaking of the reagent ion molecule clusters?

Or do you think C7 compounds are observed by Draper et al. because they are formed in their inlet due to the longer reaction time? But then, how can you be sure that you don't have chemistry going on in your inlet, too. As said, the residence times in both inlets are not too different. (I assume, both work at ambient pressures.)

The issue of different detection of C7 compounds is actually critical. If chemistry in the ion source can shift the product distribution significantly, how can you then be sure that your product (fragment) ranking and distribution represents the situation in the chamber? Or the other way round: if the C7 compounds were not detected or lost in your inlet, then they must have been still there in the chamber, as shown by Draper et al.. However, you explain mechanistically why they must be missing. As a consequence, many of your mechanistic explanations for fragmentation processes would be standing on weak feet.

Can you think of other reasons for low C7 concentrations in D-Carene in your case compared to Draper et al., 2019.

Minor

p.5, l.8 and p.6, l.14-19: I suggest moving the calibration issues up to the Experiment section.

p.6, l.20: These yields are extremely small or did you mean molar yields and not "percent" yields, Please, check. The same in Figure 6.

p.7, l.27: Is recombination by RO+RO really a source of dimers?

p.8, l.11 - p.9, l.1: "these experimental conditions" To which conditions are you referring to?

p.9, Table1: I would separate the "-" sign by spaces, now it can be misinterpreted as chemical bonds.

p.9, section Carbon Numbers: I suggest more often to refer to the mechanistic schemes when you explain a pathway.

Why do you use the word "alpha" instead of the Greek letter?

In parts the section contains a bit lab slang: e.g. "creates a new alkyl radical alpha to" should be "in a position to". This regards the description of the molecule by top, left and right bonds, too. Wouldn't it be better to number the bonds and atoms, where needed?

p.10, l.8: What do mean by "not currently supported by modelling". Do you mean by theoretical kinetics?

p.13, l.5: a-pinene: N0 is higher, but N1 is lower than in the other MT. The sum of N0 and N1 in Figure 6 is a bit lower compared to b-pinene and Δ^3 -carene. This not the same as described in the text.

p.13, l.12f: This sentence is hard to understand.

p.13, l.31. C7 + C10 should make a C17 dimer, I guess.

p.14, l.26: What is about hydroperoxy groups?

p.14, l.33f: Monomers show a smaller spread in O:C than the dimers, which is claimed to be similar. I am not sure if the notation "anti-correlated" to observed new particle formation is the right formulation here.

p.16, l.1: It is not clear what you mean by "difference", between formation rate and sink. Do you want to say that different products have different time series because of different formation rates and sinks.

p.16, l.5: The time series of curves for Δ^3 -carene and b pinene in Figure 8A do not look sigmaoidal. Please explain in more detail what you did for fitting the rise times.

And related: what is the time resolution of your measurement (how many data points enter a fit? The rise times could be faster than your mixing times. What would that mean for your analysis?

Actually, isn't that type of time series analysis in contradiction to your concept to operate the chamber as a flow through reactor? Again, it depends on the mixing time, better on a small ratio of mixing time over rise time.

p.17, l.27ff: I think these conclusions are not really justified by the data, The variation of O:C in the monomers is not very strong. There are not sufficient observations to claim correlations. You have 4 cases, α -pinene being an exception and α -thujene not doing what is expected from the dimer fraction. One has to perform more experiments probably with either more MT or at different O:C, monomer:dimer for the same MT. You must weaken that conclusion.

Typo's and small errors

p.2, l.17: I suggest to using "nitroso-alkyl radical"; it is more precise than "nitroso-alkene radical"

p.4, l.9: Something is missing. I guess VOC were not generated by a zero-air generator but transported into the chamber by using it. I suggest to skipping it here, because you describe it later anyhow.

p.4, l.11: O₃ is not a nitrogen compound?!

p.7., l14: Information is doubled in this sentence.

p.8, caption Figure 4: I guess reagent ion was excluded from formulas assigned. Please check.

p.8, l.9: "rearranges" instead of "shift"? A bond may shift but a molecule rearranges.

p13, l.31: R3 in Figure 5 c?

p14, l.28: ... except "for" α -pinene ...

References:

l.21, p.35: DOI is double.

Supplement:

p.1, l.4: the compound(s) is(are) missing: ...for ???...

p.S8, header section 06: "b-pinene"