

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-1011

Anonymous Referee #1

Referee comment on "An experimental study of the reactivity of terpinolene and β -caryophyllene with the nitrate radical" by Axel Fouqueau et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1011-RC1>, 2022

Fouqueau and co-workers present an experimental kinetic, mechanistic, and multiphasic study on the nitrate radical-initiated oxidation of two atmospherically relevant terpenoid hydrocarbons, terpinolene and beta-caryophyllene. Experimental studies of this type are very valuable for furthering our understanding of atmospheric oxidation processes, which the authors tackle using a two chamber systems and a variety of analytical approaches. In general, the work is well-presented and once the authors have addressed the following points, I would be happy to recommend publication of this work in Atmospheric Chemistry and Physics.

General comments:

Yields of SOA in chamber experiments such as these are generally challenging, with various complications such as: a dependence on the starting concentration of the alkene reactant; a dependence on the amount of alkene reactant that has been consumed; and a dependence on the aerosol mass loading. Given that chamber experiments tend to be run under higher than ambient concentrations of the alkenes and their oxidation products, it is generally unclear whether the yields that are presented here would actually apply to ambient conditions.

Let us assume that if one were to oxidize enough of almost anything in a chamber environment, it would eventually form aerosol as the chamber contents reach supersaturation with respect to a condensable component. For example, some of the estimated vapour pressures that are present in the beta-caryophyllene mechanism are very low ($\sim 5 \times 10^{-11}$ atmospheres). I think that this would mean that a concentration of such a compound would reach supersaturation in the air at a concentration of approximately 50 ppt. If we took a typical concentration of consumed [BVOC] to be 400 ppb, then we could estimate that if the branching ratio towards this low vapour pressure product was any larger than 1/8000, then such a molecule would overcome its vapour pressure within your chamber conditions, and would therefore begin to condense.

So the question remains, what could we actually expect to be the true SOA yield to be under ambient conditions, considering that BVOCs would be diluting and mixing during oxidation, in contrast to the chamber experiments presented here? Perhaps it is mostly the different concentration regimes that are used in the various literature experiments that lead to the spread of SOA yields?

Added to this, the authors are quite inconsistent in the SOA yields that they mention in the abstract and throughout the text. In the abstract, they list maximum SOA yields of 60% for both compounds. In section 4.1, they suggest that beta-caryophyllene could be as high as 90%. In the conclusions section, the authors seem to favour the 5% and 40% values at 10 micrograms per cubic metre. I am therefore not exactly sure which of these numbers (if any) I should be considering from this work.

Minor comments:

Line 13: ... to form (a) number of...

Line 17: it isn't clear what you are "following up" on, you should either delete this, or provide further details.

Line 18: monoterpene (singular).

Line 20: since there is some previous data, you cannot state that there is a lack of experimental data, since lack denotes an absence.

Line 25: are also, not also are. Precursors, not precursor.

Line 35: Globally, there have been some changes since 1995. Is there a more up-to-date account of VOC emissions from the various sources?

Line 53: For me, "proved" is a rather strong word to use, especially without a citation to back up your assertion. Scientifically, it is generally easier to disprove something, rather than prove it. Please consider a rephrase.

Line 81: requested is not the right word. Required?

Line 96: detail, not details.

Line 120 (whole paragraph): Where are the data for these integrated band intensities?

Line 127: Reaction, not Reactor.

Line 130: It is potentially confusing to talk about the reactor in the instrument in this sense, since you are dealing with other types of chamber reactors in this study. Would it be better to give it a more specific name such as a drift tube or an ion-molecule region?

Line 136 (whole paragraph): Again, it is nice to be able to point to the actual data for these band intensities that you are referring to.

Line 144: It is not entirely clear, but it seems like what you are describing is not a rate exactly, but the extent to which the chamber contents have been diluted. Rephrase.

Line 146: Please describe how the dilution rate was measured.

Line 172: were particle filters also employed? If not, what is the rationale for avoiding them?

Line 181: how small?

Lines 199 – 202: There are other recommendations besides IUPAC. There are other recommendations for this reaction: the recent recommendation of McGillen et al. (2020) $5.7\text{E-}11$, who chose to accept the earlier recommendation of Calvert et al. 2015. This same reference was employed recently by Newland et al. 2021, which showed good consistency with other reference compounds used in this work suggesting that the uncertainty is really not so high.

Line 207: (A) mechanistic study, or Mechanistic stud(ies) were conducted...

Line 208: Past tense of leave: left

Line 209: dark (for) (approximately)

Line 209: it isn't purely wall-losses that you should be concerned about. What about other dark losses?

Line 220: Product formation

Line 234: Do you have any idea how accurate SIMPOL is for the classes of compound that you are applying it to?

Line 235: March (not Mars).

Table 1: I don't like the formatting of BVOC name. Perhaps you can rotate the names by 90 degrees, which will allow you to avoid these inconsistent abbreviations.

Line 259: Since you're just doing two different techniques, you might as well specify them in full.

Figure 2 caption: there are no round marks, only square marks and triangles.

Figure 3: It is apparent that the absolute measurements have a large amount of experimental variability. It would be instructive for the authors to suggest reasons why this may be the case. Is it possible that reaction times are sufficiently rapid that they are affected by mixing times and instrument response time?

Line 298 (whole paragraph): I find this comparative discussion of reactivity to be more confusing than it is educational. You mention the enhanced stability of the exocyclic double bond as evidence for the increased reactivity of terpinolene (which seems to be strange and unexpected). You also mention that the conjugated system of alpha-terpinene leads to a stabler alkyl radical. If I am understanding this correctly (and there is a good chance that I am not), you are arguing that if the reactant or product is stabler, then k is bigger. So, I must insist that you state this argument more thoroughly. Are you trying to justify this on thermodynamic grounds? Something else? Let the readers know.

Table 3: You acknowledge that there are potentially large uncertainties in these estimates. Do you expect that there errors that you are providing here would be symmetrical in each case. I think this would be surprising. Please can you explain how these errors were calculated?

Table 3: Similar to Table 1: I don't like the formatting of BVOC name. Perhaps you can rotate the names by 90 degrees, which will allow you to avoid these inconsistent abbreviations.

Lines 406 – 409: I agree with the authors about the sensitivity of SOA yields to various experimental parameters. Is it possible that [NO₂] and radical concentration in general could also play an important role in SOA formation? It is important to note for example that although you have made specific efforts to reduce N₂O₅, you will inevitably have higher [NO₂] than in a normal environment. Can the authors suggest a route towards understanding this SOA yield of these terpenoid compounds in a more fundamental way?

Line 413 - 414: Although I just-about understand what you mean to say by this statement, I don't think this is a good way of saying it. Whether the slope was zero for a secondary product would very much depend on $\Delta[\text{alkene}]$ over which the slope was calculated. Please consider a more robust rephrase of this statement (or delete it).

Figure 6 caption: beta-caryophyllene is written incorrectly.

Lines 434 - 437: Since the yields of ONs are dependent upon the starting concentration of VOC, and since the concentration of VOC is higher than typical ambient concentrations, is it possible to obtain a good quantification of ON under ambient conditions?

Line 451: field studies

Line 452: component(s)

Line 454: In a region that was impacted by NO₃ radical at night, one would expect elevated NO_x concentrations. This would enhance nitrate yields in chemistries that were initiated by other oxidants such as OH, so I am not sure that this comparison with the field is very insightful.

Line 456: I don't think it really confirms anything. At best, I would suppose that it suggests that NO₃ chemistry may contribute towards SOA production.

Line 460 - 461: Is this really true? Do you know that all classes of compounds are detected in an accurate and sufficiently sensitive way using this approach? Please justify this statement.

Table 4 caption: please provide a definition of the various intensities that you are listing in this table.

Sections 4.3.1. and 4.3.2.: this section is quite difficult to keep track of. I don't have any very constructive things to say here, only that it is difficult to maintain focus on this part of your paper.

Line 586: gas not gaz

References:

Calvert et al. (2015). ISBN: 9780190233020

McGillen et al. (2020). DOI: 10.5194/essd-12-1203-2020

Newland et al. (2021). DOI: 10.5194/acp-2021-745