

Interactive comment on “Different Pathways of the Formation of Highly Oxidized Multifunctional Organic Compounds (HOMs) from the Gas-Phase Ozonolysis of β -Caryophyllene” by S. Richters et al.

Anonymous Referee #2

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This is an interesting manuscript describing a continuation of the work from this laboratory on studying autoxidation reactions of biogenic terpenoids. The experiments seem carefully conducted with a previously described instrumentation that is especially suited for studying end product distributions of complex VOC oxidation reactions. However, number of conclusions derived in this paper, especially concerning “the extended autoxidation mechanism”, seem somewhat hastily derived - or already reported. Thereby I’m not sure if the manuscript, as it currently stands, brings enough new insight to merit its publication in ACP.

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Most importantly, I do not see a need for “an extended autoxidation mechanism” for various reasons. Firstly, it is of obvious relevance what is understood as “the old mechanism”. If the “old mechanism” is only thought of including peroxy radical isomerization + O₂ addition steps, then I guess we could talk about a “new mechanism” at some level. However, the whole process is dependent on easily abstractable H-atoms and suitable molecular geometries enabling the abstractions – this is about what is clear at the moment. At the current stage it’s not unambiguously clear what kind of steps are needed to progress the autoxidation chain to reach into the most highly-oxidized products in monoterpene oxidation (recently Kurten et al. 2015 suggested that bimolecular steps might be needed to advance the α -pinene oxidation). What seems intuitively clear, however, is that we’re only beginning to understand the importance and the details of the autoxidation progression. So at this level it seems very preliminary to talk about “extended autoxidation” as we do not have a clear concise picture what constitutes the “normal autoxidation” in this context. In any case, probably you cannot really isolate the different pathways, but can account for branching between pathways under different conditions. So in my humble opinion, there is no need to bring up a “new extended autoxidation mechanism” – it is all the same autoxidation, just with a few additional steps.

Secondly, the pathways suggested to represent this “extended mechanism” constitute unambiguous reaction steps – the CO₂ elimination and endoperoxide formation. Importantly, it does not seem to be possible to separate this CO₂ elimination pathway from a CO-loss pathway brought up previously in autoxidation studies (e.g., Rissanen 2014, 2015, Mentel 2015). Both of these processes occur from acyl type radicals – the CO loss before O₂ addition and the CO₂ loss after the O₂ addition. So while it is definitely worth to (and you should) discuss the potential of this type of reaction pathway, with current results it is impossible to be sure which type of dissociation process actually occurred. This should be made absolutely clear, and reference to papers where CO-loss was discussed should be given. Thirdly, the endoperoxide formation that is given as the explanation to account for the formation of “too less acidic hydrogens” (see D2O

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experiments) has already been suggested in exactly in the same context in previous literature concerning HOM formation (Rissanen et al. 2015, Kurten et al. 2015). So to sum up, it is hard to see the novelty of this paper especially as the main results of β -caryophyllene ozonolysis were already published previously (see Richters, et al. 2016). Hence, even though the manuscript appears to be generally well made, I cannot support its publication without severe changes in the interpretation of the mechanistic pathways and corresponding modifications for the manuscript text.

Minor points: Some of the terminology seem a bit awkward. In certain places it seems useful to label where the oxygens come from (i.e., O,O-formalism), but in most cases I think it only hinders the reading. So I would propose to stick with common C_xH_yO_z formalism most of the time and then use the more difficult format where you are talking about the mechanism.

Can there be a different detection sensitivity for the peroxy radicals in comparison with the closed-shell products? It seems somewhat counterintuitive that the RO₂ radicals could have such a long lifetimes under the present experimental conditions.

How was O₃ handled? I assume that the “18O₃” flow still contains about 95 to 99% of 18O₂ (due to O₃ generator generating efficiency) and thereby this could lead to significant difficulties in tracking the amount of O-atoms that are left from ozonolysis and do not result from secondary reactions after the initiation. This would be especially severe in trying to understand the contribution of different pathways (see Section 3.2.).

Page 3, Line 27: The use of CH₃COOH is not mentioned. Also in Page 4 and line 13.

Page 4, Line 3: How was caryophyllene sampling done? Did the GC and PTR methods indicate any differences in determined concentrations?

Page 4, line 20: What is meant by mass spectrometer setting?

Page 5, Line 8. The number quoted is only the estimated concentration of highly oxidized RO₂. How large do you assume is the pool of other radical species (e.g., how

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much are there less oxidized RO₂s and HO₂)?

Page 5, Lines 20-32: Similar H/D exchange behavior was observed and discussed in Rissanen, et al. 2015.

Page 6, Line 25-25: How can the yield change when changing ionization method? What you want to say is that the detection sensitivity varies between products and ionization methods. But what this means to the determined yields then? Does these yields then mean anything?

Page 7 (and others): Be careful with Figure and Table numbering. Currently there are “Figs.” and “Figures” which are not in numerical order.

Page 7, Line 19: Couldn't this be as well accounted for by a reaction in which 18OH (derived from VHP decomposition) starts the autoxidation sequence?

Page 9, Line 10-15: How certain are you that the H/D exchange was 100% complete? For example, in Rissanen et al. 2015 and incomplete H/D shift as seen in reagent ions was shown to result in partial H/D shifts in products too. So how accurate is the determination of the importance of different pathways, based on H/D shift?

Page 10: Would make sense to change section 3.4. to 3.1. to improve the readability.

Page 11, Line 11: Similar epoxide formation is well-known from atmospheric isoprene oxidation (e.g. Paulot et al. 2009)

Page 11, Line 16: RO₂ + RO₂ is usually considered as progression, not termination.

Page 11, Line 27: Is this the first time nitrate ionization has been reported to see simple carboxylic acids?

Conclusions first sentence: Rather “end-product analysis was used to infer oxidation pathways”.

Page 12, Line 26: I think the discussion on VOC sources etc. should be moved to

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discussion, after all it's not what was studied in this work.

Page 13, Line 1: "These, up to now undiscovered reaction pathways..." This sentence is an overstatement and simply not true. (In Line 10 a more appropriate wording is used).

Figure 7: I find it a bit odd that at the same time it's stated that the abstraction is "an example only" and then resulting species are said to be detected in the spectra. And the assumed epoxide structure seems questionable.

References: T. Kurtén, et al., J. Phys. Chem. A, 2015, 119,11366. T. Mentel, et al. Atmos. Chem. Phys. 2015, 15, 2791. F. Paulot, et al. 2009, Science, 325, 730. S. Richters, et al. Environ. Sci. Technol. 2016, 50, 2354. M. Rissanen, et al. , J. Am. Chem. Soc. 2014, 136, 15596. M. Rissanen, et al., J. Phys. Chem. A, 2015, 119, 4633.

[Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-207, 2016.](#)

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