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Atmospheric Chemistry and Physics
Discussions

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 #3

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The manuscript, "Different Pathways..." by Richters et al. is well written, presents thorough experimental work and detailed spectral analyses that allowed the authors to identify three different pathways by which the Criegee intermediates formed by the ozonolysis of beta-caryophyllene undergo isomerization to become HOMs. The authors utilized a CI-API-ToF-MS with acetate as well as nitrate ionization coupled to a flow-tube. The use of isotopically labeled ozone and water vapor allowed robust identification of the ways in which the various RO2 peroxy radicals are formed, mainly, that a diene (presumably larger than a certain size) can undergo auto-oxidation in a few different ways to form unique molecular products. The branching ratios of these three

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pathways are also quantified. The work presented will be a significant contribution to the growing body of research on these HOM species, thus, should be published in ACP with some clarifications.

The D2O experiment (highlighted by figure 3 and SI figure 1) is key to differentiating "norm. AutOx." and "ext. AutoOx." since the byproducts of each channel normally (in the absence of D2O) have the same molecular composition. The shift in mass by 1 amu between the y=1 and x=2 products (similarly, y = 2 and x=3) in the D2O experiment allows their distinction. How efficient or fast is the H/D exchange for these acidic H/D atoms? Is it possible that the y=1 peak is really "norm AutOx." product but with just one of the -OOH groups that has undergone H/D exchange?

It appears that (in figures S1 and figure 3) that the red and blue peaks (y=1 and x=2) add up more-or-less to the corresponding black peak (no D2O). Would you expect this to be the case given that a compound with an endoperoxide group should have a different sensitivity (i.e. possess different ion cluster stability) compared to a compound with just hydroperoxide groups? The fact that red and blue add to up black would then suggest y=1 is really x=2 with one less H/D exchange.

Given a reaction time of 7.9 seconds would you expect H/D exchange to be complete? Was there a time dependence experiment conducted (as in section 3.6) with D2O that demonstrates that the peak height for y=1 relative to x=2 does not change with residence or reaction time? If not, perhaps state in the manuscript that a peak where y=1 would reside was not observed for alpha-cedrene (monoalkene) in Richters et al [2016 ES&T figure 3]. Was [D2O] » [H2O] such that at equilibrium essentially all -OOH groups would be present as -OOD?

As reported in lines 15-20 on page 6, the sensitivity (or ion cluster stability) difference between acetate and nitrate ionization to these HOMs (particularly those with one -OOH moiety) is quite large. It is reported (lines 21-30 page 6) that the "norm. AutOx" accounts for "between 29 and 35%" of HOM RO2 formation. This assertion is less than convincing. The two values do not really represent a range. It is two numbers from two different ionization schemes, each of which detects these compounds with varying efficiencies. There is a factor of 2-3 difference in these branching ratios for the "ext. AutoOx" and "ext. AutoOx -CO2" pathways for the two ionization schemes. Given such large discrepancy, how is reliable or informative are the 29 and 35% numbers or any of these numbers? A discussion is needed on how the varying sensitivities of the ionization schemes are reconciled for this to be quantitative in any way. Moreover, though quantifying an absolute HOM yield is not the objective of this work, I find it uncomfortable that a single sensitivity value obtained from an inorganic acid (H2SO4) is applied to all of these multifunctional organic hydroperoxides and endoperoxides. Though this approach now has become routine, I strongly urge the authors to consider a more robust technique in the future to account for the varying sensitivities (depending on size, ring number, functional group, etc.) to these organics.

Are the authors able to rule out pathways other than the three reported here? Are all peaks in the spectra accounted for by the three pathways? If not, what fraction of the observed peaks (at least the ones that can be reasonably identified as 1st generation products) are attributed to the three pathways? Is the alkoxy radical (RO dot) formation and subsequent degradation/isomerization relevant at all here?

Please include a brief discussion on variables that may affect the branching ratios of the three pathways. Ambient pressure/temperature? Carbon number? The number of rings? Would MT or isoprene undergo "ext. AutoOx" and "ext. AutoOx. -CO2?

In the future, the authors may want to consider not using the blue/red color combination since many have trouble distinguishing the two.

The term "acidic H atoms" is a bit vague. Please re-word in way that doesn’t imply that these are H atoms from acid functional groups only. Perhaps "non-alkyl H atoms"?

Line 5 of page 9: "...three or two..." to "...three and two..."

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SI figure is really informative and deserves to be in manuscript not SI. Possible to combine with figure 3 or replace figure 3?

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