



EGUsphere, referee comment RC1  
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## Comment on egusphere-2022-1131

Anonymous Referee #1

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Referee comment on "Selective deuteration as a tool for resolving autoxidation mechanisms in  $\alpha$ -pinene ozonolysis" by Melissa Meder et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-1131-RC1>, 2022

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In their article "Selective deuteration as a tool for resolving autoxidation mechanisms in  $\alpha$ -pinene ozonolysis," the authors present an interesting effort to use deuterated isotopologues to understand the potential mechanisms for the formation of highly oxygenated molecules from oxidation of a common atmospherically important compound. Overall, it is a neat study that appears to be conducted carefully and knowledgeably. I recommend its publication after addressing mostly minor comments below.

Major comment:

(1) I am left a little bit wanting for a more in depth discussion of mechanisms in the results section. There is a lot of great discussion of the data, but not effort to interpret the data in the context of existing (or new) proposed mechanisms other than that of Iyer et al.

For example, on line 299, the pathway that removes D from the D3 is different from the proposed one, so it should account for some of the 50% not accounted for by Iyer, correct? Do you have any proposed mechanism for what that pathway is, and if so, does it account for any of the loss observed for the D2? If not, do you have any ideas about the loss of the cyclobutyl carbon? If those are all different pathways, it would almost fully explain the product. The tool the authors are using here seems quite powerful and it would be nice to see some new ideas for the mechanisms proposed or at least specifically discussed in the context of Figure 2. Can some of these formulas be given more clear example structures that would be consistent with existing (or new) mechanisms and account for the H/D data presented here?

(2) In Figure 8 and its discussion, why use number of oxygens as a proxy for lost? It seems to me that somehow breaking out the quantification by amount of D lost would be relevant. Part of the reason differences in yield are lower than in Rissanen is because not all of the ions have actually been impacted by a kinetic isotope effect. A figure like Figure

8, but only for ions in which some portion are deuterated, or perhaps colored by mass fraction of deuterium. For example, if 50% of C<sub>10</sub>H<sub>14</sub>O<sub>7</sub> is actually C<sub>10</sub>H<sub>13</sub>D<sub>1</sub>O<sub>7</sub>, color it as maybe the weighted number of deuterium (0.5) or as fraction of hydrogens that are heavy (0.5\*0+0.5\*(1/14)). This might make an actually kinetic effect stand out. Otherwise, that implies there is no KIE - why might this be, given the results of Rissanen? What other reaction would outcompete? Given that there is usually going to be a non-deuterated abstraction available elsewhere in the molecule, shouldn't that usually outcompete? Could some of the differences in the relative yields and overall mass spectra be explained by KIE? For example, are the ions around 310 that are suppressed in the D1 relative to the D0 (see Fig A2) heavily deuterated, thus possibly explained by KIE? Overall, it would be great to see a little more deep thought into what the mass spectra as a whole tell us about the KIE and also the potential mechanisms (comment 1)

Technical comments:

Line 22 and throughout: Defining "HOM" as the plural "highly oxygenated organic molecules" leads to prevalent odd grammar. In some places, it is fine, such as line 24 ("HOM ... have been shown"). However, it means it is basically grammatically impossible to refer to a single highly oxygenated organic molecule. For example, line 87, "a closed shell HOM" means "a closed shell highly oxygenated organic molecules", which is not grammatically correct, and there isn't really a good way to make this sentence grammatically correct if HOM is defined as plural. I recommend defining HOM singularly and using HOMs as the plural.

Line 34: Run-on sentence. Instead of "[and] it can be a", use "as in the case of"

Line 39-40: I'm not sure I understand what this sentence means, try to clarify a bit what was shown in that paper.

Lines 48 and 111: Delete "molecules"

Line 183-185: Run-on sentence

Line 233 and 236: Should be "by a large margin", not "with a large margin"

Line 238: Do I understand correctly that it is not completely inactive, just mostly so? Or can even an inactive carbon lose some of its H/D?

Line 266-267: I'm not sure I understand what the authors mean by there being "numerous isoprenes for every molecule". Do they mean for each molecule they will investigate multiple D/H isotopes? Or do they mean something about the natural distribution of isotopes? Re-word.

Line 326: What was the value reported by Bianchi et al.?

Methods section is written very informally. I'm not actually sure this is an issue, but it does feel a little odd. For example "the PTR instruments were calibrated for sensitivity, and we used that information to get the precursor concentrations from the ion signal" - the use of the word "get" here is a very informal use. A more typical writing style for a manuscript might be "the PTR instruments were calibrated to estimate a response factor, which was used to convert ion signals into precursor concentrations." The informal language is seen throughout the manuscript, but particularly in the methods. I think whether this is an issue or not is an editorial decision.

Figure 1 is very helpful and clear

Figure 4 - I am generally strongly opposed to bar charts in log space, because the idea of a bar chart is that height or area of each bar should represent relative magnitude, which is not true in log space because there is no true zero and the relative heights of bars provide little information about their relative magnitude. However, given that this particular is illustrative and not particularly focused on quantitation, I'm not necessarily opposed to it here.

Figure A2 - label left and right as monomer and dimer. It is also very interesting that the overall distributions of ions is not the same for each precursor (for instance ratio of cluster around 310 and 315 is different for the D1 and D3 precursor), do the authors have any thoughts on this?