

Review of "Selective deuteration as a tool for resolving autoxidation mechanisms in α -pinene ozonolysis" by Meder et al., (egusphere-2022-1131)

In this manuscript, Meder et al. investigated ozonolysis of normal and partially deuterated α -pinene, focusing on the distribution of highly oxygenated molecules (HOMs) with different numbers of D atoms and HOM yields when different partially deuterated were used. This technique of utilizing partially deuterated precursors indeed will help to better understand reaction pathways, but the authors should have gone much further beyond their current discussion. Especially, they are advised to connect their observation to potential mechanisms, and at least try to suggest the formation routes of some of the most abundant products. I would recommend major revision of this manuscript.

Main concerns,

1. The authors seem to overlook OH radical formation in the ozonolysis of α -pinene. In fact, the OH yield is pretty high, which leads to a dispensable fraction of OH+ α -pinene in this system. I mean, then the observed distribution of (partially deuterated) HOMs does not necessarily reflect the ozone chemistry. Also, OH might react with the HOM products, further altering their distribution. How to evaluate the impact of secondary reactions on HOM distribution? By the way, why wouldn't the authors give the extent of consumption of precursors in each case?
2. It was stated that "autoxidation was perturbed in predictable ways by the deuteration" (Line 40, Page 2). On the other hand, there is only one paragraph that discussed confirmation of a detailed reaction pathway by Iyer et al. 2021. The rest just ends up with "C-3 and C-10 are active and C-7 is mostly inactive". If they can exclude potential interferences from OH+ α -pinene and OH+HOMs as I raised above, the authors might be able to figure out routes beyond the Iyer et al. 2021 study.
3. Figure 6 is confusing to me. Please at least give one example of the definition in the caption. For example, in the case of C₁₀H₁₄O₇, when ³D₁ was the precursor, -0D corresponds to C₁₀H₁₃DO₇ and -1D corresponds to C₁₀H₁₄O₇? When ⁷D₂ was the precursor, -0D corresponds to C₁₀H₁₂D₂O₇, -1D corresponds to C₁₀H₁₃DO₇, and -2D corresponds to C₁₀H₁₄O₇?

Why aren't there a -3D in the upper panel of Figure 6? Do the authors suggest loss of 3D in ³D₁ was not observed?

The color scale in Figure 6 might be modified for a better differentiation.

Minor comments

4. (Paragraph 2, Page 2), selective deuteration has been used to study autoxidation mechanisms in the 1,3,5-trimethylbenzene + OH system (Wang et al., ACP 2020, 20, 9563-9579), which is highly relevant to this study.
5. The author states that "the purity of each compound was >95%" in line 66, and that "PTR measurements suggests that over 88% of the measured pinene in our chamber contained exactly the number of D-atoms specified" in Line 218. The two numbers are close, but could still lead to a problem for the purpose of a mechanism study. Please revise or justify.

6. "Inactive" is not a perfect word to describe whether or not a D atom goes through autooxidation. Since this manuscript judge by the distribution of products, but even for the "inactive" precursor with selective deuteration at the C-7, products with loss of D atoms were observed, which suggests that something happened to the C-D bond.
7. (Line 302), one can also argue that C₁₉H₂₈O₁₁ can be formed from a ³D₁ precursor, since the signal of C₁₉H₂₈O₁₁ in the case of a ³D₁ precursor could be attributed to mostly loss of a D atom. Does this mean that C₁₉H₂₈O₁₁ is formed via one monomer that reacts at C-3 and the other at C-10?