

Selective deuteration as a tool for resolving autoxidation mechanisms in α -pinene ozonolysis

Major Comment

The first thing I would highlight is the effort gone into presenting this work in a digestible way. The colour coding of the deuteration, and then presenting the reaction routes with this colour coding makes working out how the products are potentially formed straightforward.

The big picture results of this study is that vinylic C-3 and allylic methyl C-10 carbons are active but the cyclobutyl ring carbon, C-7 is not. Via the C-3 isomer, $\sim 50\%$ of its loss is consistent with the literature Iyer *et al.* mechanism. In general, only one D loss occurs in the oxidation process, but there is a mechanism where the CH₃ is lost, and strong evidence for this is seen via the $^{10}\text{D}_3$ isomer data. Regarding the total HOM yield, there is little difference between the deuterated isomer (and normal α -pinene) and is around the 5% yield; but the $^7\text{D}_2$, which is inactive, does have the highest yield. However, the lack of significant kinetic isotope for the active $^3\text{D}_1$ and $^{10}\text{D}_3$ is surprising. There probably should be a little bit more about potential mechanisms that produce little or no kinetic isotope effect. Is there a predicted isotope effect via the Iyer *et al.* mechanism?

However, things are probably simplified too much, and while I like this approach there should be acknowledgement of the extra stuff going on. The most obvious is that at the early stage of ozonolysis a significant amount of OH is made, and this is going to react with the pinene to make different peroxy radicals that are going to undergo auto-oxidation leading to HOM formation. You note that for $^3\text{D}_1$ via the Iyer mechanism accounts for about 50% of the signal. Could it be that OH chemistry is accounting for this missing signal?

While I might be showing my ignorance of the experimental details, as I understand it a slow flow of O₃/ α -pinene is introduced into the chamber and it typically takes about 40 minutes to flow out. So the experiment is essentially a snap shot in time at 40 minutes. However, the system never seems to reach this 40 minute snap shot in time, and the products are evolving over a much longer timescale. Does this indicate that the surface of the chamber is playing a role in these experiments? If this is the case, can you be sure that the products are the result of only gas-phase chemistry. I think some acknowledgement of the role of the chamber surface is required. Or can it be dismissed?

Overall, this work has demonstrated that via deuteration of the target alkene some of the HOMs that form via ozonolysis can be assigned to specific isomerization steps. This is useful information. There are a number of things that can be done to put this work into better perspective, but overall I have no problem recommending this paper for publication.

Specific comments

Line 80

The O8-RO2 product remains the only experimentally and computationally supported HOM-forming pathway in this system

This mechanism involves the 3D_1 bond breaking. Then this route should show a kinetic isotope effect? Is there a number from theory?

Line 130

if the H-shift is 1000 times faster than any competing reaction, substituting for a D-shift will barely impact the branching of the reaction,

While true about the branching ratio, but it will take longer to form if deuterated, hence yields should be lower, certainly at early times.

Line 145

We injected α -pinene into the chamber using one of two methods: an overflow set-up for small amounts of precursor, and a syringe pump set-up when there was enough precursor for using a 5 μ l syringe to take a sample. In both cases, the evaporated α -pinene was injected into the chamber with a small N2 flow.

So what was the typical [pinene] in the chamber at the start? I can see the answer to this in Figure 5. Perhaps it should be stated in the experimental section.

Line 177

We excluded all isotopes that contained deuterium, because using selectively deuterated precursors distorts these signals.

Is this exclusion only for determining the instruments sensitivity?

Line 199

We calculated the HOM yield from the production and loss terms of HOM when the concentration of HOM [HOM] did not change significantly over time (Ehn et al., 2014):

But your experiments have a constant residence time in the chamber, so what you means by "time"

Line 223

Similarly HOM dimers can contain between twice the number of deuterium atoms in the precursor and zero deuterium atoms.

There needs to be more on HOM dimers. Perhaps introduce them in section 2.2. What is a typical HOM dimer yield in this study? Are they at steady-state?

Line 242

As can be seen from Fig. 5, optimal steady-state conditions were not achieved in all cases, in particular when the injection was performed using the overflow setup (Fig. A1a), as was the case for 7D2 and 10D3.

Again, as the time in the chamber of constant, i.e. time before measurement, where is this change with time coming from? I presume it is linked to things going to the walls before the walls are at steady-state, which is not the same as the steady-state of equation (2). If you run a model of the system, what time does this predict for steady-state, where I presume the model will have loss to the wall as a constant.

Line 263

as in normal experiments the radicals and closed-shell species would be at different integer masses and thus easily distinguishable.

But you have done “normal experiments” when doing D₀. So can you show some radical data? Are the radicals at steady-state?

Line 299

“For the 10D3 C₁₀H₁₄O₇, about 20 % has lost a D-atom, while the other 80 % behaved according to expectations from Iyer et al. (2021).”

80% if no other mechanisms is considered!

Line 338

However, this change can be compared to the change of two orders of magnitude observed by Rissanen et al. (2014) for fully deuterated vs non-deuterated cyclohexene, suggesting that deuteration had a minimal role, if any, for the HOM yields of our precursors.

It is clear that C—D bonds have been broken in this study, but to observe slight change in the yield is surprising. I think a little more speculation on this observation is required.

Line 350

This may be an indication that the D-shifts were still fast enough to outcompete other reaction pathways despite the deuteration. On the other hand, it is possible that the autoxidation could proceed through the next most competitive pathway not shut down by the deuteration and end up losing deuterium atoms later in the process, especially in the case of the more oxidised products.

While deuteration might not change reaction paths, it should slow the rate to products? So the second sentence explanation is more likely. Would you like to speculate how the D is happening later in the process and not show a significant kinetic isotope effect?