Review of ***Elucidation of the myrcene ozonolysis mechanism from a Criegee Chemistry perspective*** by Chen et al.

## Significance

Formation of condensable chemicals initiated by gas-phase ozonolysis of volatile organic compounds (VOCs) contributes significantly to atmospheric secondary organic aerosol (SOA) budgets. The molecular level mechanism is generally understood to evolve through the well-known Criegee mechanism which produces two distinct zwitterion / diradical species called Criegee intermediates (CIs). These CIs are known to have a rich uni- and bimolecular chemistry, commonly dominated by unimolecular decomposition and reaction with water dimer under atmospheric conditions. The current study focuses on myrcene, an often-overlooked acyclic monoterpene with three double-bonds, and reports the apparent importance of its two CIs, which dominate the initial oxidation product distribution, on atmospheric SOA formation. The work utilizes complementary investigation methods from matrix isolation and chamber investigations to quantum chemical computations and attempts to understand myrcene oxidation chemistry by synthesizing the output from these distinct methodologies.

While the topic of the work is certainly of interest to the readers of ACP, in the current form it is difficult to assess what has actually been accomplished here. Specifically, the current level of documentation does not allow to fully assess the reliability of the results as the methods and results appear only partly described. Also, to me it seems that the type of oligomerization reaction described here would be seriously kinetically limited in the atmosphere, and thus I do suspect there could be some easier explanation for the observed product signals. I'll detail my concerns below.

## Major comments

First the kinetic limitation: I suspect that most of the gas- and particle-phase results could be explained by the more common peroxy radical (RO2) chemistry without the need to invoke exotic Criegee intermediate (CI) oligomerization reaction which is generally limited by the availability of the very reactive CIs in almost any conceivable atmospheric environments. That is, the CIs simply cannot find an "already dimerized" reaction product to form a "further trimerized" product, because they react away in multitude of reactions with several of the co-produced oxidation products (e.g., any products with carbonyl groups). It is simply difficult to see how the CI concentration could ever be so high to permit sequential reactions with the same products under such reaction time and oxidizing conditions. To me it seems far more likely that recently uncovered pathways in RO2 + R'O2 reactions, where RO (and R'O) radical rearrangement occurs after the initial peroxy radical cross-combination reaction and leads to products with various amounts of carbon and oxygen in the "dimeric" structures, is the explanation here. Please have a look at Peräkylä et. al. (https://pubs.acs.org/doi/full/10.1021/jacs.2c10398) and Frandsen et al. (https://pubs.acs.org/doi/full/10.1021/acsearthspacechem.4c00355) for the mechanism and topical examples. Could they explain what is seen here? Again, it is hard to see how the numbers would match and allow the oligomerization to happen, and that's why I urge the Authors to back up the current sequential oligomerization conclusions by a gas-phase kinetic modelling of the relevant reaction system using some prototypical reaction rate coefficients.

Second is the lack in documentation: Many important details are missing, and the current story appears to choose the results across the very specific investigation methodologies without clearly referencing on what part of the study the results have been obtained. Please remember that the minimum amount of documentation is always such that the work can be repeated and hence the results verified in a replicate study. Now, I am not sure how I could repeat the matrix isolation work, which is likely the best described of the experimental procedures, though still appears to miss the temperature of the mixing jet and the details of mixing the reactants, the volume of the chamber, the timescale of deposition and reaction, the purity of the O3 mixture, for example. The aerosol formation study seems to be missing more details including the timescale, the used reactant and sampling flows, the details of aerosol particle and gas compound detection, the details of the LC-MS technique and so on. The computations seem to be missing almost all details, and it is not clear what has been computed. You should give the computational details and the resulting molecular geometries in the SI. The current level of documentation in the SI is inadequate, and you must add all the relevant details to be able to replicate the study.

**More specific comments**

Note that in this reaction system ozonolysis initiates all the observed oxidation chemistry and based on your results in Table 2 the co-produced OH also makes a big, apparently dominating impact on SOA mass. Now, when you add water, you decrease the whole oxidation sequence – also the important OH that would be generated from the CI isomerization through the VHP decompositions. Thus, it is very unclear if the reduction in SOA occurs specifically through scavenging of the Criegee intermediate and preventing its oligomerization or because the added water reduces also the further sequence of reactions contributing to SOA in the system.

Moreover, when zooming on the SOA yields in Table 2, they indicate that OH chemistry played a major role in forming the observed SOA (i.e., 91 vs 346 ug/cm^3). How was the OH scavenging determined to be 99% completed? Were there any repeated experiments using the hexane scavenger?

So, you say that increasing RH decreased the SOA yield. But there's no apparent change between 0.5% and 20% humidity, and the humidity only plays an apparent role at 50% RH. This leads to a question that how was the particle size measured, and subsequently the SOA mass determined?

I suspect the particles were dried before sizing, correct? (=not documented here). I would expect the particles to collect considerably more water at 50% than at 20% RH, so maybe the “missing SOA” mass at higher humidity is simply evaporating water. Could this be the case? Again, hard to say with the missing documentation. As a related result the data in Figure 6 are hardly conclusive as the results at 0.5% and 20% RH look very similar and the HA addition seems to modulate mainly the C13 product, which makes sense if it was affected by a RO2 + RO2 → RO + RO +O2 step. Also, contrary to the text, the C7H10Ox products appear to be decreasing with OH scavenging as well. Is this the case when looking at the details?

From the figures it is unclear what species were detected and what are just assumed based on mechanistic principles. This is especially true for figure 5: Is the Figure 5a a measured spectrum or just a visualization of the identified peaks? Note that you will obtain the C10H15Ox radical by hydrogen abstraction reaction too, and under such a high loading conditions RO2 + RO2 also surely occurs generating the odd oxygen product species through alkoxy radical isomerization reaction.

**Comments about the methodology**

These are specialized techniques that must be explained carefully. The reader probably does not know that the signals are not exactly comparable across Ar matrix at 35K and particle-phase at room temperature. These are very different physical worlds, but now it sounds like it is just okay to equate chemical observations from the matrix to gas- and particle-phases. Why would you expect so? The minimum is that you explain to the reader why you think you can equate these worlds.

I am also a bit worried about the experimental conditions, but due to lack of documentation it is hard to be sure. So, CIs react with many of the present oxidation products with rapid rates, and if you really are observing CI related oligomerization, then it implies that you are using very high concentrations. Otherwise, it is very hard to see how you could see such reactive species oligomerizing in the gas-phase. However, from the Table 2 it seems that the highest primary oxidation rate is around 0.002 $s^{-1}$ (corresponding to *k* x [O3]) which is rather low in comparison to atmospheric oxidation rates but still appears to rapidly result in the very high particle loads obtained without seed particles. Please explain what does not add up in these results.

Generally, it is very unrewarding to read “experiments were conducted under different conditions”. From the quite vague results given on the particles it seems that the experiment had very high oxidizing conditions, which seems surprising indeed in absence of seed particles. For example, it is said “. The dominant size range of SOA expanded from 50-250 nm during myrcene ozonolysis (Figure 3).” How can you reach so high particle loads without seed particles? What was the history of the used chamber setup? Could that have affected the results?

More about the chamber experiments:

- What is the timescale of the chamber experiments: It seems your growth rates are very high to obtain so many particles at so little time.
- A representative figure of the experiment as a function of time showing the O3, myrcene and some product time profiles would help to put the results in context.
- How was the chamber experiments performed? Based on adding O2/O3 mixture with a syringe it sounds like you were doing batch-mode experiments, right? With the current documentation it is unclear.
- Spark generators do generally produce a lot of NOx. Did you measure how much NOx is in your reaction gas?
- The spectra given in Figure 4 are hard to compare. Especially the spectrum with hexane scavenger is very noisy and it is pretty much impossible to compare it to the peaks in the others. Also, it seems to contain more peaks than the other experiments, but the measured SOA yield is less. Does this mean that these specta are not relevant to the SOA observations?
- What is the cut-off size and the maximum size detected by the aerosol instrumentation?
- How stabile was the O3 syringe injection?
- What are the details of the LC-MS measurements? Please explain why you would get Na+ and NH4+ clusters from a normal H3O+ source? Or what was the utilized ion source? What settings were used in the MS/MS analysis?

Why did you study the system by computations? Were they performed only to get the corresponding IR absorptions? If yes, then this should be explained clearly. Also, the accuracy of the predictions should be discussed. Currently the details of the computations are apparently missing.

What was the temperature in the twin-jet mixing stage. I'm trying to understand at what conditions the MT+O3 reaction occurred as it is difficult to see how you could form the Criegee in the cold matrix through POZ isomerization.

Some of the new peaks resemble mor like noise, for example the 880 and 1074 cm^-1. How do you define a new peak exactly?

You said that "(The peaks with relative abundance of less than 1% were ignored)." But the Spectra shown in Figure 4 contain 100s (or 1000s?) of peaks and you have only labelled 5 and given a handful of others in the text. Thus, how many of the peaks were neglected? You should ideally provide the peaklist for signals (above some threshold) observed during the experiment.

Clearly more details are needed to understand the experiments done, and thereby also the proposed chemistry, which is discussed next.

**Comments about the proposed mechanisms**

The manuscript makes several claims about the potential mechanism of oligomer formation by Criegee intermediate reactions and their relevance for SOA formation from myrcene.

First of all, I would like to take the time to explain that in chemistry the word "mechanism" has a very strong meaning and is reserved to explain how the molecules transform. What is meant here by the same word in several instances is hardly a mechanism. Thus, mentions like "The mechanisms may also exist in other monoterpenes ozonolysis, which offering new insights into the contribution of CIs to SOA formation." do not make much sense without detailing the molecular steps.

Related: "The coexistence of these CIs of different molecular sizes led to a distinctly different ozonolysis mechanism for myrcene compared to that of cyclic monoterpenes (e.g., α-pinene, limonene)". No. It is the same mechanism for both but with acyclic species the bond breaking leads to two species, whereas with cyclic species only one product is generated.

And further: I can't seem to make sense of the following statement: "Our findings further demonstrated that when evaluating SCIs contribution pathways to SOA, the molecular size of SCIs must be prioritized especially during monoterpenes ozonolysis."

And further: You say that "To our knowledge, this was the first time this synergistic mechanism has been proposed." – this seems like an awkward statement as there is no actual mechanism presented.

And further: "MI-FTIR experiments unequivocally verified that myrcene ozonolysis proceeded via the Criegee mechanism." – this is confusing as it is completely unclear what would be the "other mechanism" the Authors are referring to? Ozonolysis is commonly expected to proceed through the Criegee mechanism.

The detected compounds are C7, C10, C13 and C16 species, which all appear to have also alternative production paths, especially through RO2 chemistry. What is noteworthy is that in the current chamber experiments very high growth rates are obtained even in apparent absence of seed particles which testifies the very high oxidation conditions used in the experiments. Under such conditions many sorts of radical recombination can occur – potentially even the sCI + RO2, which I still find much more unlikely than the RO2 + R'O2 processes.

"Current studies have not confirmed that the C10-CIs generated from monoterpene ozonolysis can contribute to SOA formation through oligomerization." This makes sense in considering the reactivities of the CIs and sCIs discussed in the above comments and again appears to point out that it is more likely you are observing $RO_2$ chemistry. Perhaps this is possible in high concentrations in a laboratory setting, but even then, it is not so easy to make sCIs oligomerize due to abundance of other potential sCI reaction partners generated during oxidation (e.g., any species containing carbonyl functionality).

**Comments**

I would strongly recommend language editing by a native speaker as the text contains several apparent ambiguities that hinder understanding the work. Some examples below:

When you talk about unimolecular degradation of sCI contributing to SOA it seems odd. Note that "degradation" seems to imply the molecule breaking into small pieces whereas you probably just mean the OH loss through a VHP that kickstarts the autoxidation process. I can only assume you mean this as nothing like that has been explained in the article (e.g., this is omitted from Figure 1, for example).

Figure captions should be expanded to explain clearly what is shown in the figures. Some examples: It took me a while to realize that the myrcene + $O_3$ spectrum is included in Figure 2 as it is currently poorly labelled and not mentioned in the caption. Figure 1 is messy and hard to follow and will require a long explanation of the steps shown (e.g., the all-important VHP decomposition is not marked).

I can't understand the following: "The OH radical yield from myrcene ozonolysis was generally high, which also confirmed that the larger CIs generated during this process tend to react via unimolecular decay pathways (Cox et al., 2020)". Why "generally"? Why "confirm" here?

The following seems to contradict itself: "The initial ozonolysis mechanism of myrcene had been established as shown in Figure 1 based on the current studies."

"As shown in Figure 4(b), the peaks corresponding to $C_{10}H_{18}O_4$ and $C_{10}H_{18}O_5$ disappeared after the addition of the OH radical scavenger, as expected. The $C_7H_{10}O_2$ peak remained, which further demonstrated that $C_7H_{10}O_2$ originated from SCIs-derived products. Compared with the mass spectrum without the scavenger, the contribution of the oligomers in Sequence 2 markedly increased." With this low-resolution figure, it is hard to say what peaks decreased and what increased. To me it looks like the sequence 2 peaks actually decreased. Also, the next claim "Correspondingly, the contribution of Sequence 2 to SOA formation decreased progressively with increasing RH as shown in Figure 4(c) and (d)." I really can't read from the current figure.

As this is ACP the page content is not limited. Thus, you should put the SI material directly into the main text to improve readability.

**More minor comments:**

- Please refrain from using “extreme” when it is not needed. There is definitely no “extremely high abundance of water vapor” and Criegee does not react at extremely fast rates.
- What is a “a heated three-way U-shaped tube.”?
- There is no Table 1.
- “Zhang et al. found that limonene yield gradually increased with increasing RH” – I don’t think you mean limonene concentration was increasing.
- Please explain in the text why you added formic acid to the mixture?
- Mark the peaks with the corresponding assignments in Figure S1.
- What is the difference in sequence 2 and sequence 2N?
- Note that it is generally not possible to label the products to -OOH and -OH species simply by their measured composition. It is plausible these could be the products but with the current techniques and experimental conditions it appears that you have no way to be sure about them. Reword accordingly.
- The following is misleading “Quantum chemical calculations have revealed that multiple SCIs may **undergo oligomerization reactions with water vapor to form oligomers** with lower volatility (Chen et al., 2019).” – this is not what the cited article says or what you mean here.
- This is ambiguous “Both in the α-pinene and limonene ozonolysis, SCIs-derived products contribute to both monomers and dimers formation of SOA” – of course the reaction initiating the whole oxidation systems contributes. Please be clearer what you mean.
- Open all abbreviations. For example, POZ does not appear to be explained.