

Atmos. Chem. Phys. Discuss., referee comment RC3
<https://doi.org/10.5194/acp-2022-636-RC3>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2022-636

Anonymous Referee #3

Referee comment on "Large differences of highly oxygenated organic molecules (HOMs) and low-volatile species in secondary organic aerosols (SOAs) formed from ozonolysis of β -pinene and limonene" by Dandan Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-636-RC3>, 2022

The authors describe a set of experiments in which volatile organic compounds (VOCs), either limonene or beta-pinene, were oxidized by ozone in a flow tube. The subsequently formed aerosol particles were then analysed using different techniques. The main analytical tools used in the work are the scanning differential mobility particle sizer (SMPS) for measuring the size distribution of the formed aerosol particles, and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to characterize their chemical composition from filter samples.

In its current form, I find that the manuscript lacks sufficient detail of the experimental procedure to support its conclusions. I feel that more data would be required to validate the results. Also, I would strongly suggest making the data used for the manuscript freely available. In addition, some of the introduction and conclusions sections are rather generic. For these, I would suggest for the authors to have a thorough look at the reference material, and form a coherent story based on that. Below, I have listed a set of concerns that I think need to be addressed before publication can be considered.

- The reaction conditions. The authors list in Section 2.1 that they used a 7 l flow tube. This was operated with flows of 1 lpm N₂ to evaporate VOC (MFC 2 in Fig. 1) and around 2 lpm synthetic air through the ozone generator (MFC 3). Was MFC 1 used at all? The listed flows add up to 3 lpm: at this flow rate, the residence time in the tube would be 2 min 20 s, but the authors state a residence time of 5 min. Where does this discrepancy come from?

- In addition, a large fraction of the total flow consisted of nitrogen. However, HOM are formed in autoxidation, i.e., in the reaction with atmospheric O₂. Did you consider this effect?

- I suppose the listed ozone concentrations are without VOC in the flow tube. You have

relatively imprecise estimates for the VOC concentrations. You could get better values by monitoring the ozone concentration change upon adding the VOC and calculating back from there. Did you do this?

- The reaction rate of limonene with ozone ($2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$) is over ten times that of b-pinene with ozone ($1.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$). So, for similar starting concentrations, you would, as a first approximation, expect over ten times more limonene to react. And so, assuming similar SOA yields, you would expect ten times more SOA from the limonene reaction. Limonene would be expected to form even more aerosol than this, as it typically has a higher SOA yield, and SOA yields typically increase with increasing reaction rate. Yet, you observe similar aerosol production, both in size distribution (Fig. 2) and in mass (Table S1). In mass, you even get clearly less mass for limonene for most conditions. How do you explain this?

- I'm very crudely estimating that in Fig. 2, you have around 15 000 particles per cubic centimetre for both limonene and b-pinene in the high ozone case. Assuming a mass mean diameter of 90 nm and a density of 1.5 g/cm^3 , this would correspond to a mass concentration of some 70 ug/m^3 . In Table S1, you collect around 200 ug of SOA in an hour. This would mean collecting around 3 m^3 per hour, or 50 litres per minute. However, your total flow is much smaller. Am I missing something? Or how do you get those numbers? Could you please provide the data for Fig. 2, or the whole SMPS data?

Additional point by point comments on the text:

Intro, lines 38-65: the text flows poorly here, and is rather generic. I would reformulate your message and write it down again.

Line 60: the term ULVOC was not used by Bianchi et al., and has only been introduced later

Line 77: "opposite trends in SOA formation potential": what does this mean?

Line 80: "Nucleation rate of monoterpene SOA" does not really make sense here: nucleation rate and SOA yield are two separate (though connected) concepts. Here you seem to refer to SOA yield

Lines 82-83: I don't understand this sentence

Line 84-85: The same applies to low-volatility vapours. And the high ozone here means a high oxidation rate, and a high initial particle production rate. This makes condensation to particles a competitive sink for vapours, as opposed to wall loss.

Line 90: what does "gradient" mean here?

Line 102: what about the total flow, and MFC1? Already with the numbers here, 1/3 of the flow is N₂, which will already drop the O₂ concentration in the flow tube considerably. This may influence HOM formation, as they are formed in autoxidation, i.e., with atmospheric O₂

Line 103: What was the flow through MFC1? This is not listed, but with 1 lpm through the VOC and 2 lpm through the O₃ generator, the total flow is already 3 lpm. In a 7 l flow tube, this should give a residence time of 2 min 20 s.

Line 105: how did you vary the ozone concentration?

Lines 107-108: at 1 ppm, the ozone lifetime towards limonene oxidation is around 200 s, and 2500 s for β -pinene. This means that in the 5 min almost all of the ozone should react in the limonene case, while in the β -pinene case, only around 10 % reacts. Combined with the higher SOA yield of limonene, we should see much more SOA in the limonene case. This is, at least to some extent, seen in the SMPS data, but the opposite is seen in the collected mass. As the majority of the article is based on the filter analysis, this should be addressed

Line 115: what flow rate is this? To the SMPS?

Lines 116-117: what experimental tests? And what are these results on aqueous phase radicals that are mentioned a few times, but not really presented?

Line 117: what wall loss was negligible? For sure there are different types of wall losses, both of vapours and of particles

Line 149: About the isotopic peaks: will this not lead to overestimation of some compounds, as isotopic signals from neighbouring masses overlap with them?

Line 161: I don't really understand where this comes from. For example, C₁₀H₁₄O₁₁ would fall under highly oxidized organic compounds, and I can't really think of any realistic examples of more oxidized HOM. Also, the method does not distinguish between -OOH group and two -OH groups, while the latter is twice as oxidized. Do you still think this classification makes sense?

Lines 189-190: The reference talks about ambient measurements, where volatilities were estimated with the SIMPOL parametrization. So, I would not use it for such a general statement.

Line 191: Do you mean that these compounds were assigned as HOM monomers and dimers?

Lines 200-201: As the ozone increases, the whole reaction rate increases. And if SOA yield stays the same, or at least doesn't go dramatically down, the size and concentration of the particles should increase. So, this does not point to any specific compounds or mechanism yet

Lines 201-202: Do you mean that organics promote the formation and growth, and thus increase the survival probability of the particles? Now it sounds like you mean that the specific organics themselves survive, which, as far as I know, is unknown

Lines 207-208: "increase oxygen reaction": what does this mean?

Lines 209-210: Is this your result, or someone else's?

Line 214: I only see a slight decrease. Also, please avoid using "significantly" unless talking about statistical significance

Line 227: Abundance or relative abundance? I would expect the abundance of pretty much anything to go up with ozone in these conditions

Line 237: "condensation reaction channel": what does this mean?

Line 251: You are using quite a narrow definition of HOM, if I understand correctly (the predefined formulae on line 191). Looking at Fig. 5, I think many more would also qualify

as HOM.

Line 251: We can't see from the plot that they are dimers. Also, it might be useful to label some of the largest peaks in the plot

Line 252: What is RA? Relative abundance? I don't think it's defined

Lines 323-324: add references

Lines 329-330: The reference talks about slightly different element number ranges. Please be careful with references: now it sounds like Pospisilova et al would be talking about these exact numbers

Lines 330-332: Hard to follow sentence

Line 336: High probability based on what?

Line 337: where do these compounds come from here?

Figure 10: is this all based on work of others? Or do you have some more support for these channels in particular? If not, I would leave this figure out

Line 342: You are measuring monoterpene oxidation here, so presumably all of these are monoterpene oxidation products

Line 343: Do you mean that C₁₀H₁₆O₉ was only detected in b-pinene SOA?

Lines 347-348: this is very speculative

Lines 349-351: Hard to follow sentence. Also, C₁₀H₁₆O₈ does not necessarily come from C₁₀H₁₅O₈, it may also have other sources. And it only forms from C₁₀H₁₅O₈ upon reaction with HO₂. Finally, I don't think detecting these products "verifies" this pathway.

At maximum, it does not contradict the pathway, but does not rule others out either. For instance, $C_{20}H_{30}O_{12}$ could also form from $C_{10}H_{15}O_{10} + C_{10}H_{15}O_4$.

Lines 355-358: First you talk about formation of oligomers from closed shell monomers. But the Berndt et al reference is for gas-phase formation of accretion products from RO₂-RO₂ reactions

Lines 358-359: What observation? The reference is not about particle phase chemistry, but gas-phase

Line 363: I would also expect highly oxidized dimers in this range

SI:

Table S1: These numbers don't make sense to me. At low O₃, why do you get 70 ug of SOA in 0.4 h for beta-pinene, but only 30 ug in a full hour for limonene? And in nearly two hours, still only 30 ug? Limonene should have a higher SOA yield. Also, the SMPS shows more mass for limonene.

Table S1: median-->medium

Fig. S1: for each ozone concentration, are the results the average of the two filters?