

Atmos. Chem. Phys. Discuss., referee comment RC1
<https://doi.org/10.5194/acp-2022-85-RC1>, 2022
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Comment on acp-2022-85

Anonymous Referee #1

Referee comment on "Identification of highly oxygenated organic molecules and their role in aerosol formation in the reaction of limonene with nitrate radical" by Yindong Guo et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-85-RC1>, 2022

General comments

The manuscript by Guo et al present interesting results of highly oxygenated organic molecules (HOM) from the limonene+NO₃ system. This system is of large atmospheric relevance, yet such measurements have hardly been performed before. The experiments are of high quality, and I think the manuscript nicely fits within the scope of ACP. I have several questions and comments to the authors, as outlined below, with my major concern being the interpretation of some of the results.

Specific comments

- Lines 110-127: Different instruments have been shown to have different sensitivities to molecule groups, and even CIMS instruments with different reagent ions observing the same elemental composition can often show totally different temporal behavior. Considering this, the different reported HOMs in these papers might not be the same thing. It might be useful to group the papers in such a way that a reader knows which instrument measured the reported HOMs. In addition, I think Yan et al. (2016) (<https://doi.org/10.5194/acp-16-12715-2016>) could also be mentioned when discussing reported NO₃-induced HOM.
- Fig. 1: Please multiply the NO₃ time trace by (at least) 10 to make the values legible.
- Line 162: Do you expect that isoprene would be left on the walls? Is it possible that SVOC isoprene oxidation products are coming off the walls instead?
- When discussing the atmospheric relevance of this work, I think the authors should reference their conditions to the findings by Bates et al. (2021) (<https://doi.org/10.5194/acp-22-1467-2022>).

- I find that including some high resolution fits is very helpful for a reader to assess the certainty of peak assignments, and therefore suggest that some examples be included. Ranging from ions that are unambiguous to ions that are on the limit of what you included in the paper. For example, the conclusions mention trimers with six N-atoms, and the quality of these fits would be interesting to see.
- It is many times stated that "carbonyl products outnumbered hydroxyl products, indicating the importance of the unimolecular RO₂ termination pathway". This may be true, but I would like to see some estimate of the importance of RO₂+RO₂->RO+RO followed by RO+O₂->R=O+HO₂. I also don't know why the RO-forming reactions are not included in the list of reactions starting on line 96. It is after all typically the dominant pathway.
- Lines 189-190: " a large fraction of limonene was already reacting away during the VOC injection before it was homogeneously mixed in the chamber." It took me a while to understand what this meant. But it then also raises the question that if all the HOM yields are determined from the first 3 minutes after injection, what is the influence of incomplete mixing? This will impact both the limonene + NO₃ reactions, the RO₂ fates, and the amount of HOM measured, if there are "hotspots" in the chamber with clearly higher concentrations. Was there a fan used for mixing?
- Related to the above, I find the reported wall loss rate of HOM (6e-4 s⁻¹) to be extremely low when comparing to any other chambers where HOM loss rates were reported, even when considering the large volume of SAPHIR. A lifetime of almost 30 min for low-volatile species seems very surprising, especially if the chamber was actively mixed (and if it was not, then I would expect very large inhomogeneities). The long lifetime seems to be based solely on tracking one molecule, C₁₀H₁₅NO₈, by Zhao et al (2018). At the same time, the paper by Peräkylä et al. (2020) suggests that this specific molecule (at mass 339 Th) hardly condensed in their seed addition experiments, suggesting that it may be a bad surrogate for LVOC.
- This also brings me to my main concern with this manuscript, namely the interpretation of the observed HOM, and in particular the time series. There are several aspects of the data that I find hard to understand. Some of them you have addressed, but I am not convinced of the speculations, and some it seems are not discussed much at all. Below a list of open questions:
 - The interpretation of first and second generation compounds: Normally it is of course true that compounds requiring one oxidant attack appear before compounds requiring two. In a situation where you would have a constant oxidant concentration and a constant HOM sink, the interpretation would be as straightforward as presented in this manuscript. However, now neither of these is true. If we focus only on P1, the NO₃ concentration drops dramatically when the limonene is added, as does the N₂O₅, but after that both increase during P1. The oxidation rate of limonene is the source of primary RO₂, but this parameter (i.e., limonene*NO₃) is not presented anywhere in the manuscript as far as I can tell. Therefore, I cannot tell what behavior I should expect for the first generation products based on the source strength. The NO₃ trace is also plotted on such a scale that it is impossible to read out anything from it. This should be amended, as it is one of the most important parameters in the experiments.
 - Similarly, the sinks are always important, and as I stated above, the low wall loss rate seems questionable to me. If indeed the loss rate was so low, I would expect a continuous increase of most products throughout P1, since oxidation is still taking place. I see indication in many figures (e.g. Figs 1, S4, S9) where the drops of the initial peak for some HOM are faster than the wall loss would predict, and this despite additional production still going on, which should cause the drop to be slower than the wall loss rate.
 - As an even clearer point relating to the production and loss dynamics, when limonene is added for the second time, many HOM (Figs 1, 4, 5, S3, and in particular S10 and S11) drop very fast, with lifetimes of minutes as far as I can tell. I believe the only time this is addressed is in conjunction with Fig 5 where it is said that this

drop coincides with “the onset of particle growth” and thus indicates a role for dimers in NPF. I think the authors need to come up with a convincing line of argumentation why all these HOM seem to drop exactly at that time when limonene is added. The condensation sink does not make a dramatic jump exactly there, and many highly oxygenated monomers and dimers increase again towards the end of P2, when the CS should be still greater, suggesting that CS is not the cause of these changes. In Fig. S9 some dimers even increase dramatically at that time, to later decrease while other types of dimers increase, suggesting that changes in the source strengths are of importance. The dynamics of oxidants and RO2 fates is complex, and I can only guess what is going on, but the data would to me be explainable if the loss rates were much higher than assumed in the manuscript, and the changes mainly governed by changes in source strengths, e.g. total oxidation rate, relative oxidation by O3 vs NO3, and termination by NO3 or RO2.

- Concerning RO2 fates, Fig S2 shows loss rates of RO2 radicals at different times. At the same time, 6 ppb limonene was injected but only around 1 ppb is left after 5-10 min, suggesting that 5 ppb limonene ($>1e11 \text{ cm}^{-3}$) has reacted in this 10 min. The loss rates in Fig. S2 suggest lifetimes of around 5 min for RO2 during this period, which means that there should be $>1e10 \text{ cm}^{-3}$ RO2 in the chamber, as each reacted limonene forms an RO2. This concentration seems very high. Or alternatively, the loss rate of RO2 from reactions with other RO2 seems very low. Have the authors considered that the RO2+RO2 reactions may be faster than predicted by the MCM as they are likely to be much more functionalized than the RO2 used to derive the MCM rates? Even for the primary C10H16NO5 RO2, I could expect that the RO2+RO2 reaction were closer to $1e-11 \text{ cm}^3/\text{s}$ as was found for the primary C10H15O4 RO2 from a-pinene + O3 (DOI: 10.1021/acs.est.8b02210). Much higher than the $\sim 1e-13 \text{ cm}^3/\text{s}$ given by the MCM for these radicals. How would this impact the interpretations of the manuscript?
- Related to many of the points above, like expected behavior for primary and secondary products, the oxidation rates, and the RO2 fates, I suggest that you include some model results in a revised manuscript. For example, it would be very interesting to see how well the MCM run is able to match the measured NO3 and N2O5 behavior, as well as limonene. Likewise, the RO2 concentrations should be included. If the main parameters are captured correctly, I would expect that model could nicely output the time series of NO3*limonene as well as NO3*Limonene_oxidation_products, as metrics to show the expected behavior of first and second generation products. If this type of model results match well with the observations (and interpretations), I would be much more convinced.
- The conclusion of the dimers and trimers being important for NPF because they only appear during P1 in Figs 5 and 6 is brought into question when considering that only the N2 dimers (shown in Fig 5) show this feature, while N1, N3 and N4 dimers (Figs S9-S11) all show relatively high concentrations also much later in the experiment, when the CS is far higher than during the transition from P1 to P2. In addition, I am skeptical to the particle concentration trace in Fig. 1b. It keeps increasing up until 2h, but the size distribution gives no indication of new particles being formed after the first hour. Instead, the size distribution seems to barely detect any particles below 20 nm, and the mode just appears at that size. I see no discussion on this point, but the obvious conclusion for me is that the detection limit of the SMPS is about 20 nm, and the particle concentration trace derived from that data is the concentration of particles larger than 20 nm. As such, the particle concentration has likely in reality been decreasing after the initial particle burst during the first minutes or tens of minutes of the experiment. This needs to be discussed.
- Lines 317-319: “it is likely that C10H16NOx radicals converted immediately after their formation”. This is a very broad statement, as it includes all radicals, including the primary O5 radical. If this was the case, Fig. S2 would no longer make any sense, since there would be no RO2 around. I would expect very low sensitivity for RO2 radicals with less than 7 O-atoms in the CIMS, and therefore a more likely scenario is perhaps that

the primary RO₂ either do not efficiently undergo autoxidation, or alternatively, that the RO₂ lifetimes were so short that autoxidation was outcompeted.

- Lines 452-453: "the most abundant C₂₀H₃₂N₂O_x was expected to have an oxygen number of 18 according to the accretion reaction mechanism". At least I would not "expect" this, as seemingly all earlier studies discussing this topic have suggested that the dimers have lower O/C because the less oxidized RO₂ radicals are involved. As you also cite 4 papers for this, the "expected" should be removed.
- Lines 570-571: "in the early stage of the experiment when new particle formation (NPF) had not occurred yet". As I said earlier, the time when NPF occurred is not visible from your data, and likely happened much earlier than the SMPS concentrations indicates. In addition, you have said that trimers are the most likely candidates to initiate nucleation, and the trimers formed almost instantly, suggesting that NPF would also start immediately.
- Line 605: How do you come to these numbers? At 1 ppb limonene, the lifetime should be <5s.

Technical corrections

- The term "SOA growth" is used several times in the abstract, and it is confusing to me, as would be terms like "sulfate growth" or "black carbon growth".
- Lines 179-180: I suggest not to mention this 14% uncertainty here, since it gives the picture that this is the total uncertainty, although that is given later.
- Use of %: In the abstract the Hom yield is given as "5 % (+1.7 %/-0.7 %)". It is not trivial to understand this. I assume that it means 0.8-3.2 % as the uncertainty range, but more commonly +/- X% would mean percentage and not percentage points. On line 183, are these percentages or percentage points?
- Figure 3: An O-atom based Kendrick plot is unlikely to be obvious to the majority of readers. Please add somewhere a sentence about what the y-axis means.
- Lines 358-360: What about the carbonyl formation from alkoxy radicals?
- Figure 5: Why is the peak intensity on the right axis in the top panel? It seems strange to me, and it took me a long while to realize what the arrows in the plot meant.
- Lines 447-448: While correct, this sentence seems to suggest a causality opposite to what one would expect.
- Line 582: I think "N" is missing.
- Line 609: "Volatile commercial products"?