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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Formation of highly oxygenated organic molecules from chlorine atom initiated oxidation of alpha-pinene” *by* Yonghong Wang et al.

Anonymous Referee #2

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General comments: This work by Wang et al. describes gas-phase measurements of highly oxygenated organic molecules (HOM) from alpha-pinene + Cl oxidation. The study was motivated by recent findings that ClNO2 could be an important source of Cl in certain regions. Chamber experiments were performed to study alpha-pinene + Cl reactions with and without NOx. HOM were measured using NO3–CI-APi-TOF. The experiments, measurements and analysis are all using the well-established HOM study approach while looking at a new reaction system. The result of a HOM yield of 1.8 (0.8 – 4)% adds this new system to the HOM-forming family. Overall, the manuscript is well written and demonstrates new findings regarding HOM formation chemistry, and thus should be eventually published at ACP. But a few major concerns need to be addressed

first.

Specific comments: 1. Line 139-142. Elaborate on this statement. What does this “C” value mean? How do you estimate HOM concentration (ppt) from measured in NO3-CIMS (cps) using this coefficient? This has been described in prior work as referred, but as a standalone article, it should be clarified, at least briefly. Also, how big of uncertainty might be caused by using this value directly? Presumably, the rough calibration was based on H_2SO_4. I’m curious whether different instrument configurations (i.e., normal TOF vs. LTOF) could lead to different calibration/quantification results. I’m sure that authors or other users have used the LTOF to calibrate HOMs using H_2SO_4. I suggest that the authors at least do such rough calibration and constrain the calibration coefficient. A substantial portion of the conclusion is based on this assumption and simply saying the instrument was not calibrated due to the lack of calibration methods is not satisfactory.

2. Through personal communication with other LTOF users, it was suggested that the APi-LTOF could leak to more molecular fragmentation in comparison to APi-TOF. Is this consistent with what the authors observed in this study? If so, would that lead to ambiguity interpreting monomer vs. dimer HOMs?

3. There are a few errors in Line 173-177. In the mass balance equation (which also needs an equation index), the unit of each term should be concentration/time (e.g., ppb/min). Thus, Q_in and Q_out do not represent concentrations, but the flow rate/volume. Make corrections accordingly.

4. In Figure 4, it seems the largest monomer is a C9 product ($C_9H_{12}O_8$). Do the authors have an idea of the structures or formation mechanisms of the $C_9H_{12}O_x$ products? Also, the monomer HOM measured here are unlike the other alpha-pinene oxidation studies (e.g., alpha-pinene + O_3, HOM dominated by $C_{10}H_{16}O_x$; alpha-pinene + OH, HOM dominated by $C_{10}H_{18}O_x$). Here the HOM are dominated by $C_{10}H_{14}O_x$. This is very interesting. I suggest the authors discuss the mechanism in this route.

5. Line 247-250. To make this argument sufficiently, it probably needs the timeseries of more than just one RO2. Also, quadratic relationship should be more clearly shown by plotting RO2s against reacted alpha-pinene (like Figure 1 in Zhao et al., 2018 PNAS).

6. Line 264-265. This interpretation is not accurate. The AMS measures only the elemental composition. Let's do the math here for example, if a particle-phase molecule of a Mw of 300 has one Cl atom (Mw 35.5), then the Cl/Org $\sim$ 13%. A measured Cl/Org $\sim$ 3% suggests about 23% of the molecules contain Cl on average. This is not a trivial fraction. Of course, this number could vary if the average Mw of particle-phase molecules change, which the authors could provide better estimates. The point is that 3% Cl/Org does not mean Cl contribute little to SOA. If considering that Cl addition could also lead to products without Cl through fragmentation, it seems the abstraction: addition occurs at 3:1 or lower fractions. Abstraction is still larger, but one cannot rule out Cl addition. It might not produce HOM, but definitely contribute to SOA formation.

7. HOM formation under high NOx. More information should be provided in this section. For example, how much O3 are formed? Given the reaction rates with ïĄą-pinene, the authors could also constrain the fractions of alpha-pinene reacting with O3 vs. Cl. If alpha-pinene + O3 is the dominant process, then the HOM could be mostly from alpha-pinene + O3 and the statement in Line 287-289 might be wrong. Alternatively, if alpha-pinene + O3 is not the dominant process for alpha-pinene, then the author should consider adding alpha-pinene + O3 in equation (1) and (2) and split HOM contribution from both oxidants. In this way, if the HOM yield from alpha-pinene + O3 is known based on the authors' prior work, then the HOM yield from alpha-pinene + Cl in the presence of NOx could be estimated as well. I'm also curious whether the monomeric range mass spectrum as shown in Figure 4 changes when NOx in present (e.g., different dominating patterns).

8. The most interesting finding to me in this manuscript is that Cl oxidation of alpha-pinene occurs mostly via abstraction, rather than Cl addition. As a general comment, I feel the authors should add some discussion of this preference. Has this been reported

in prior studies? If not, then the authors should point out that this mechanistic behavior needs to be studied in detail in future work.

Technical comments: 1. Line 39 in Abstract. Change "NO3-based" to "NO3–based" and define "CI-APi-TOF".

2. Line 165. NOx = NO + NO2 should be defined earlier in the manuscript.

3. Line 229-230. References are needed.

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