

Comment on acp-2021-353

Anonymous Referee #3

Referee comment on "Secondary organic aerosol formation from the oxidation of decamethylcyclotrisiloxane at atmospherically relevant OH concentrations" by Sophia M. Charan et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-353-RC3>, 2021

This is an important contribution to the literature on the oxidation of volatile methyl siloxanes, to the literature on aerosol formation from volatile chemical products, and on the interpretation of experiments on SOA formation done at high concentration. It should be published in ACP after addressing the following points.

Major points.

1. The abstract should be revisited, particularly by the senior authors with comprehensive experience across all the aspects of the study (modeling implications, flow tube experiments, chamber experiments). I think the major contributions of the work is that (a) both chamber and flow tube experiments were conducted, (b) a wide range of OH concentrations were looked at experimentally, and (c) these were analyzed in a comprehensive manner with two other datasets from literature. None of these aspects really come out in the abstract clearly.
2. The abstract is confusing chemical transport models and emission inventories: "SOA yields used in emission and particulate matter inventories."
3. The results start very abruptly and the text at line 156 is not doing anything other than referring the reader to the table. The reader has to do all the work themselves. Could the authors help out and provide the important context?
4. Line 166 is important. I quote the manuscript here: "If a chemical process occurs in which the reaction of D5 and OH forms an intermediate or a second-generation product that then either reacts with OH or fragments, then the competition between the two outcomes is moderated by the relative time required for self-reaction or reaction with OH."
(a) I think this could be written more clearly.
(b) Line 166 says fragments but 167 self-reaction. Are these same process?
(c) the OFR literature shows that the community is aware of this issue. The concern,

however, is usually on the other side – that high OH will lead to fragmentation reactions at the gas-particle interface, or that high OH will lead to fragmentation reactions in the gas phase on similar timescales as condensation of low volatility gas phase products ... not that high OH will lead to particle formation while NOT reacting with OH will lead to fragmentation and/or high volatility compounds. This is an interesting route and a valuable contribution to bring it up.

(to clarify, a and b are reviewer comments where I am looking for a response and/or change to the MS. c is just a reviewer comment)

5. Comment: I think the paper has a critical point on the possible role of fragmentation reactions (or reactions that simply lead to high volatility products) that are zero order in OH and in reaction partners that are correlated with OH. Thus, if first generation oxidation products have such pathways (e.g. rearrangement or autooxidation, for example, leading to high volatility products or to conformations that prevent subsequent formation of low volatility products), and these do not involve OH (but the formation of low volatility products does involve multigenerational oxidation with OH), then there will be a strong OH concentration dependence on yield. For example, if the first generation product of OH attack rearranges to a volatile species with a characteristic time of n seconds, and to form low volatility multi-generational products, OH needs to make a 2nd attack prior to those n seconds, then yields will be dependent on OH and independent of OH exposure. However, there are other mechanisms that could lead to similar dependences, such as concentration effects in the gas-phase, the particle phase, and the gas-particle interface leading to higher order effects not seen at low concentrations.

Reviewer request: acknowledge that there are more mechanism options that could lead to the same functional dependence on concentration of OH.

6. Regarding fates of the first generation oxidation products that are zero order in OH and in reaction partners that are correlated with OH, but that lead to high volatility products or to conformations that prevent subsequent formation of low volatility products (I believe this is what is required for the strong OH dependence) ... is there evidence, perhaps from the gas-phase mass spec, of such reactions? If so, please report hypothetical reactions and compounds.

7. Comment: The paper implies that reactions (or SOA formation scenarios) can be divided into a class where OH exposure matters, and another where OH concentration is dominant. Not sure this is a useful designation. It is more complicated than that, and it is the fate of the species in the reactor (fixed or flow) that matters, not strictly the OH concentration. I believe the atmospheric chemistry communities that use both types of tools are increasingly aware of the strength, weaknesses, and factors to look out for in data interpretation and extension to models (Lambe et al. 2012, Lambe et al. 2015, Palm et al. 2016, Peng et al. 2016).

Reviewer request: reconsider the classification, or provide support for the binary classification.

8. Abstract line 10, "necessity of OH concentrations similar to the ambient" is probably overstated. There is a literature on the necessary conditions for atmospheric relevance of OFR / PAMS / flow tube type experiments, and this is taking an end run around that literature and oversimplifying the requirements for atmospheric relevance.

9. The introductory material on flow reactors versus chambers is underdeveloped and would benefit from a rewrite and citation to the literature on the topic (e.g., line 40, "researchers use both flow reactors and chambers").

Minor points

1. The paraphrase of Coggon et al. (2018) at line 19 is not quite accurate and should be revisited.
2. Not sure "Cl is negligible" in the correct interpretation of Alton et al. (2020). The global value was 4.6% for D5, but up to 25-30% for Toronto and Boulder under certain conditions.
3. As an update to Hobson et al. (1997) on deposition sensitivity, one could refer to the work of Janecek et al. (2017), where dry deposition was quantified and dry deposition modeling parameters were discussed in detail.
4. The megacity vs. non-megacity distinction at line 38 is not clear.
5. The foundational work in the UNC chamber on organosilicon oxidation should probably be mentioned in the introduction (Latimer et al. 1998, Chandramouli et al. 2001).
6. Explain "batch mode" line 45
7. Introduction should make it clear that the paper presents new results from both a flow reactor and chamber were used, and give a roadmap to the different sections of the paper.
8. Line 104 – perhaps state (list a paper or report) where a figure can be found with that static mixer shown.
9. Line 113 – could a time series of a typical chamber experiment be included in SI, showing the steady state stability of the precursor implied at line 113 (negligible wall loss).
10. I respect and value the important work on uncertainty quantification, but placing it in the caption of the Table is not ideal. Relocate to methods and/or results and/or SI as appropriate.
11. Having explicit labeling of chamber vs. CPOT would be helpful, so that one does not have to know which device is associated with which experiment number.

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