Comment on acp-2021-965
Anonymous Referee #3

Referee comment on "Secondary Organic Aerosols from OH Oxidation of Cyclic Volatile Methyl Siloxanes as an Important Si Source in the Atmosphere" by Chong Han et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-965-RC3, 2022

The manuscript by Han et al describes several cVMS aerosol yield experiments in an oxidation flow reactor (OFR). They use their derived yields to make estimates of cVMS-derived SOA at various locations. cVMS chemistry and aerosol yield is an open question in the field and the results are of interest to the community. However, I have several major comments that I would like to see addressed before I could recommend publication.

Major Comments

- The results of this study need to be discussed in the context of Charan et al., (2021). Charan et al. (2021) found that the aerosol yield for D5 oxidation varied with the OH exposure in an unusual way. I note that when considering the Charan et al., (2021) work, it would be prudent to wait for the ACP version of the manuscript as several points of discussion regarding possible explanations of the differing yields were modified following public discussion. A particular result from Charan et al. (2021) that should be discussed in the context of the current study is that OFR experiments led to higher SOA yields than environmental chamber experiments.
- Further details about the radical chemistry need to be included in the manuscript. While information is given on the ratio or RO2 + NO to RO2 + HO2 reactions in the high NOx experiments, there is no discussion on how prevalent RO2 + RO2 reactions were or even the (not atmospherically relevant) RO2 + OH. Differences in the fate of the peroxy radical in the OFR experiments compared to chamber experiments is one possibility that could explain the Charan et al (2021) results, however, the investigation of RO2 fate was beyond the scope of that paper. I encourage the authors to describe the radical chemistry of these experiments in more detail as it could aid in understanding the apparent discrepancy between OFR experiments and chambers for this chemical system.
- Given the prevalence of cVMS, it is easy for contamination to occur. I would like to see more information on control experiments that were performed to check for
contamination and possible impacts on cVMS yields. Additionally, I think the manuscript would benefit from including more examples (SI is ok) of the measurements. In particular, I would like to see some examples of the SMPS data and AMS time series absolute values (not in terms of fraction). The SMPS data in particular should be included as it is central in the yield calculation.

- The back of the envelope calculations for the cVMS SOA loadings need to be better justified. For instance, why is 8.5 days selected for the urban sites? That seems long considering typical transport times. There should also be discussion of the results of Milani et al., (2021) and Pennington et al., (2021) and the consistency or not of these back of the envelope estimates with those studies.

Minor comments

- Figure 2 (and analogous SI figure for high NOx). Given that the cVMS precursors only differ in the number of (C2H6OSi) units, I would have expected to see somewhat more similar mass spectra from their oxidation products. I find it intriguing how different the MS are between the experiments and find some of the ions unexpected. For instance, C12H11O2Si5+ from D5 oxidation is intriguing given the addition of C and loss of O from the parent species. I recognize the electron ionization spectra of complex mixtures can be challenging and non-intuitive to interpret, but I wonder if the authors have considered possible explanations for some of these ions and what they might imply for the identify of oxidation products. Additionally, I wonder if the PTR provides any information on gas-phase oxidation products that is useful.

- Lines 268-270: I would think that continued breaking of Si-O bonds would lead to more volatile products since after the first bond breaking, it would lead to fragmentation and thus smaller molecules.

Technical comments

- Line 70: The conclusion of Alton and Browne, (2020) is more subtle than suggested here. They suggest that while Cl is minor globally, loss locally (for instance in Los Angeles) could be more important given the spatial and temporal overlap of cVMS emissions and sources of Cl (i.e. from ClNO2). This is an important distinction if cVMS yields are high as suggested by this work.

- Lines 84-85: “...indicating necessary conditions when extrapolating SOA yields to the ambient atmosphere.” This sentence does not make sense. Please reword.

- Table S2: Please keep D5 in the same units for all the studies.

- Line 229: Alton and Browne (2020) did not state anything about the relative volatility of different cVMS oxidation products. The only discussion on volatility concerned wall loss and that one of the first-generation oxidation products had a lower vapor pressure than the parent cVMS. Moreover, that vapor pressure is still high enough that it is unlikely to contribute to SOA except at high loadings. Additionally, they did not report D6 results.

- The use of n/z and n/z rather than Si/C and Si/O adds complexity to the paper that I think is unnecessary. I think it would be easier for the reader to understand the results if Si/C and Si/O are used.
- Lines 265-266: This discussion of oxidation as occurring by substitution of one functional group for another is confusing and misleading. I suggest editing to be more clear about the chemistry occurring (OH abstracting a H, etc.).

References


