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Comment on acp-2021-353

Anonymous Referee #1

Referee comment on "Secondary organic aerosol formation from the oxidation of decamethylcyclopentasiloxane at atmospherically relevant OH concentrations" by Sophia M. Charan et al., Atmos. Chem. Phys. Discuss.,
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This manuscript describes new secondary organic aerosol (SOA) yields from decamethylcyclopentasiloxane (D5) oxidation by OH at a range of OH exposures/concentrations and compares the new results to previous publications. The authors find that the SOA yield varies significantly based on the experimental conditions and argue that differences in OH concentration is the cause of this variation. They stress the importance of understanding the effects of OH concentration versus OH exposure in conducting SOA yield experiments. D5 is a volatile chemical product (VCP), a class of compounds that is of emerging interest and importance for air quality. The yields reported here at lower OH concentrations are much smaller than previously published yields and thus previous estimates of SOA from D5 in urban areas may be overestimated. I believe these results merit publication in this journal; however, I think revisions and consideration of additional points are necessary before I can recommend publication.

Main comments

- For me, the main take-home of this work is that the SOA yield for D5 + OH may be substantially lower than previous reports. I think this is an important point and it signifies D5 is a chemical system requiring further investigation. Indeed, there is emerging evidence suggesting that the chemistry of siloxanes differs from more traditional VOCs (e.g., Ren and da Silva, 2020; Fu et al., 2020). As to the cause of the SOA yield varying based on OH exposure/concentration, I think better support as to why/how it varies with OH concentration is necessary if the authors wish to make this a main point of the paper. Personally, I think the extended discussion on the role of OH concentration versus exposure detracts from the take-home point of the paper. I think the new yield measurements merit publication even without a detailed investigation of why the yield differs between experiments. In my opinion, either the focus on the role of OH concentration versus exposure should be deemphasized or a more complete consideration of the chemistry should be included.

- I agree with the point that it is important to understand how the experimental conditions impact SOA yields so that yields can be appropriately extrapolated to the ambient atmosphere. However, I think that the conclusions regarding the experimental issues of high OH versus concentration (lines 266-269) are oversimplified. The current presentation points to high OH concentration as a fatal flaw for this chemical system. However, the OH exposure versus concentration issue is a concern about the relative role of processes that scale with OH and are atmospherically relevant versus those that do not scale with OH (e.g., peroxy radical (RO₂) isomerization) and/or that might scale with OH but are not typically important for most systems (e.g. RO₂ + OH). Consideration and analysis of the chemistry within the experiment are important for determining if high OH experiments will always be difficult for this chemical system (for instance if photolysis or isomerization are important) or if high OH experiments are possible with careful planning (e.g. by running under conditions to limit RO₂ + OH; for instance see Peng and Jimenez (2020) and references therein). This distinction between high OH experiments being possible but requiring careful experimental consideration versus difficult and unlikely to provide useful information is an important consideration for how the community plans, performs, interprets, and extrapolates chamber and flow reactor experiments. I ask the authors to consider these points when making a recommendation about future experimental conditions.
- In my opinion, the thinking of how OH exposure versus concentration affects this chemical system is poorly articulated. The reasoning outlined in lines 165-167 is confusing to me, at least in part because it seems like first-, rather than second-, generation product is a more appropriate term to use. Please clarify the mechanisms that may be impacting this system. To do this, I believe that further information on the radical chemistry in the chamber and CPOT experiments. For instance, one possibility at high OH is that RO₂ + OH becomes important. Does the estimated HO₂/OH ratio for the experiments support this idea? Would it be possible to adjust the HO₂/OH ratio in the experiments to avoid this condition while still maintaining high OH concentrations? Overall, information on how the RO₂ lifetime and fate (isomerization or reaction with NO, HO₂, RO₂, OH) varies across the experimental conditions is necessary for the reader to judge if high OH is the fatal flaw it is made out to be. I recognize that investigating this chemistry for D5 is difficult since little is known about the gas-phase chemistry of D5, however, educated guesses are possible and necessary for an exposure versus concentration argument.
- The idea that concentration and exposure are not necessarily interchangeable is well-known from the heterogeneous chemistry literature (e.g., Liu et al., 2011; Renbaum and Smith, 2011; McNeill et al., 2008). For SOA, Lambe et al., (2015) found only small differences between chambers and flow reactors for many systems. Additionally, Peng and Jimenez (2020 and references therein) have investigated this using models and provided recommendations for operation. At least the work comparing SOA between chambers and flow reactors should be discussed.
- I am not convinced that later generation products can be disregarded (lines 235-236). The contribution of later-generation products to the SOA yield is discarded based on a lack of correlation between the yield and the OH exposure normalized to D5 reacted and the finding that for experiments 16-17 where all the D5 does not react has a higher yield than experiments 18-19 where all the D5 does react. However, experiments 16 & 17 have a higher absolute concentration of D5 compared to experiments 18 & 19. Could the results be influenced by RO₂ + RO₂ reactions leading to lower volatility products and hence more aerosol in 16 & 17 compared to 18 & 19? Although RO₂ + RO₂ is typically slow, it can be fast for some RO₂. Additionally it has been shown that dimers and products containing more than 5 Si are important in D5 generated aerosol (Wu and Johnston, 2016, 2017). While it is unclear if the dimers are formed via gas- or condensed-phase chemistry, those results do suggest that there may be a D5 concentration dependence. Overall, I think a more detailed characterization of the RO₂ chemistry and D5 concentration dependence is necessary before higher generation oxidation products are deemed to not matter (lines 235-236). While D5 RO₂ + RO₂

chemistry generating dimers may be unlikely to occur in the ambient atmosphere (thus reinforcing the point that there needs to be careful consideration of how experimental conditions relate to the atmosphere), this is different from the OH exposures versus concentration argument.

Minor Points

- Lines 114-120: I think the discussion on 5% of the oxidation products being lost to the walls is somewhat misleading. While I agree that first-generation oxidation products such as the ester will have minimal wall-loss, they will also contribute minimally to aerosol if absorptive partitioning dominates. Later generation products may have higher wall-loss.

Technical

- Figures 1-3: Colors and shapes are hard to distinguish, particularly in the legend and for the red squares and blue circles in Fig. 1a. Perhaps removing the black outline (or making it thinner) and/or making the points bigger would help.
- Please include the RH for the experiments in Table 1.

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