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Comment on acp-2021-353

Anonymous Referee #2

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 paper describes chamber and flow-reactor measurements of secondary organic aerosol (SOA) yields from the OH oxidation of decamethylcyclopentasiloxane (D5), an important organic compound in indoor environments. There are two major results from this work: (1) chamber yields are much lower than previous measurements, whereas flow-reactor yields are quite high, and (2) this difference is attributed to the use of atmospherically unrepresentative OH levels in the flow-reactor experiments. Both of these are important topics, and certainly will be of interest to the readership of ACP. However the manuscript focuses mostly on the 2nd result; I think the paper would be stronger if it spent more time discussing the 1st one (the yields themselves) as well. This could include providing SOA yield parameterizations for use in modeling, and/or describing implications for indoor/urban air quality. In addition, I had a number of questions and comments about the 2nd conclusion (OH concentration and exposure); these are described below.

1) Much of the manuscript is focused on examining the role of OH concentrations vs. OH exposure; however this discussion (or the possible underlying mechanism) was not always clear:

- 166-169: I had a hard time following this explanation. This is in part because the language is very general, mentioning "intermediates" and "fragments" but not providing concrete examples. Are these intermediates/products radicals or molecules? And why is the focus here on only second-generation (but not first-generation) products? Some more discussion of specific pathways (e.g., oxidation of products, RO₂ self-reactions, oligomerization reactions, etc.) would be helpful.

- Similarly, a major conclusion of the work (line 265) is that “It is the OH concentration, and not the OH exposure, that affects the SOA yield”; but little explanation for why this might be the case. Can the authors suggest some potential mechanisms? (The CIMS data might be of use here.)

- My initial interpretation of the data (especially Fig 2) was that the later-generation condensable products are what lead to SOA formation; since these may not be formed until most D5 reacted, yields will be higher when $\Delta D5 / \text{initial} D5$ approaches 1. The implication of this would be that yields are highly dependent on extent of reaction. Lines 226-236 argues against this interpretation, but I don't follow the argument. Differences in fractions of D5 reacted between experiments 16-17 and 18-19 are described, but these differences are quite small (97-98% vs 100%). A much bigger difference is the absolute amount of D5 reacted (~ 240 ppb vs ~ 80 ppb) – this could lead to large differences in aerosol loadings, which in turn could affect yields due to differences in semivolatile partitioning. The oxidation chemistry might be different as well. Given such large differences, it doesn't seem straightforward to make any conclusions about SOA-formation mechanisms just from comparisons of yields or fraction of D5 reacted.

(Also, the statement “the fraction of D5 reacted correlates with the [OH]” (line 235) seems self-evident, given the role of OH concentration in reacting away D5, as shown in Equation 1.)

- There's a good deal of literature on the possible nonlinearities associated with OH exposure (that [OH] cannot always be ramped up to accurately simulate long atmospheric timescales), (examples include Renbaum and Smith, *Atmos. Chem. Phys.* 2011, 11, 6881–6893, Liu et al. 2011, *PCCP*, 13, 8993-9007, and Palm et al. 2016, *Atmos. Chem. Phys.* 16, 2943–2970), but these aren't discussed in this paper. It's probably worth discussing these treatment in the context of the present results.

- The authors argue for a “the necessity of OH concentrations similar to the ambient environment when extrapolating SOA yield data to the outdoor atmosphere.” What are the implications of this work for other laboratory studies? The last several years has seen a huge increase in the use of oxidation flow reactors for studying SOA chemistry (e.g., *Chem. Soc. Rev.*, 2020, 49, 2570-2616). Is the argument then that these results are flawed, and should not be used in models?

2) A central point of the paper is the relative importance of OH exposure and OH concentration; I have a number of comments related to the calculation of these quantities:

- 144-146: I'm unclear on how OH exposure was estimated using SO₂. At first I assumed SO₂ was added to the reactor (as is sometimes done in OFR experiments), but instead from the text it appears that these SO₂ levels were taken from a different set of experiments from a different laboratory (Janecek et al. 2019); this should be described in greater detail. If that is indeed the case, I think it's unlikely that the experiments were "identical" – they presumably used a different reactor (with different flows, concentrations, SA/V ratios for wall loss, etc.). And if SO₂ is high enough (relative to the D5) it can affect (decrease) the OH exposure. Therefore such an estimate may well lead to large errors in estimated OH exposure, and probably shouldn't be used in a quantitative way (at least without large error bars).

- 149-150: I don't think these are possible explanations, since Equations 1 and 2 should hold regardless of the sources and sinks of OH.

- For calculating OH exposure from Equations 1 and 2, were these single point calculations (estimating exposure from one time point, t), or were they fit to a curve? This latter approach (which is possible at least for the chamber experiments) would give a more precise value.

- 142: the value of k_{OH+D5} used was from one study, but as noted in line 126 other studies have found values that span a factor of ~2 (Atkinson et al: 1.55e-12 cm³ molec⁻¹ s⁻¹, Safron et al 2.6e-12 cm³ molec⁻¹ s⁻¹, etc). This in itself adds a factor of ~2 uncertainty to the OH exposure estimate.

- Based on the above comments, I believe there's substantial uncertainty in the estimated OH exposures in this study. These should be included as error bars in Fig 1 and 2, and incorporated throughout the text in the discussion of results.

Minor comments:

29: calculate -> determine?

76: why were the concentrations used to calibrate the FID so much higher than those used in the experiment? What sort of error in SOA yields might this lead to?

Table 1: it would be helpful to also give the RH and fraction of D5 reacted for each

experiment.

121-122: While I agree that wall-loss corrections would not change the conclusions of the paper substantially, a steady-state reactor can still have vapor-phase losses. This can result from extremely low-volatility species, which can sorb to walls essentially irreversibly; also see Krechmer et al. *Environ. Sci. Technol.* 2020, 54, 12890–12897. (In addition, the text on line 202 implies that vapor wall loss in the flow reactor could indeed lead to a suppression of SOA yields.)

204-205: The comparison should probably be in terms of the dependent variable (SOA yield) not the independent one ($[OH]$).

219-221: I'm unclear on how to interpret the "OH exposure divided by reacted D5" metric; this is a nonstandard metric so some more explanation would be useful. The explanation on the following sentence ("the number of OH radicals available per reacted D5 molecule") isn't quite right since that should be unitless, whereas exposure/deltaD5 has units of time

251-260: The case is made that the yield differences are not from differences in $[NO]$ or RH. Might the oxidation conditions (O_3 vs H_2O_2) play a role?

294: I had to look up the "ICARUS" database (no URL was given); it appears not to have been updated since 2019 (with most data being from 2016-2017) and so apparently is no longer active.