EGUsphere, referee comment RC2
https://doi.org/10.5194/egusphere-2022-681-RC2, 2022

Comment on egusphere-2022-681

Anonymous Referee #2

Referee comment on "Modeling the influence of chain length on secondary organic aerosol (SOA) formation via multiphase reactions of alkanes" by Azad Madhu et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-681-RC2, 2022

Madhu et al. present their work on modeling SOA yields from the oxidation of linear C10 through C20 alkanes. The model is described well and a lot of effort was invested in the research. However, the use of an outdoor chamber to conduct systematic tests of NOx and particle seed type on SOA yields was a flaw in the experiment design. The day-to-day variability in conditions, namely temperature and light, clouded the very impact of these variables the authors sought to test on SOA yields. Perhaps as a result, the demonstration of model peformance on SOA loadings (shown in Figures 2 through 5) is unconvincing. For instance, the explanation of the observed morning SOA burst in some of the experiments that the model fails to capture was seriously lacking.

Likewise, the discussion on the effect of NOx on autoxidation, the main driver of SOA formation they report, is thin. What is the implemented rate of autoxidation for each alkane precursor? A sensitivity test of the rate of autoxidation on SOA yield is reported on line 370 to be shown in Figure 5, which does not show that at all (only the sensitivity results of wall loss rates). What are the levels of Hox and Nox in the chamber for the duration of each experiment? Both would undoubtedly affect RO2 fates and lifetimes, neither of which is discussed in the section of Nox impact on autoxidation. Figure 6 shows that SOA yields increase with decreasing Nox. However, Figure 2 shows that the model underestimates SOA loading at high Nox and overestimates at low Nox. This, as a result, possibly undercuts the key model results of SOA yield vs Nox shown in Figure 6. Proper explanation of glaring caveats is not discussed. Authors go on to attribute the decrease in SOA yield with Nox to the partitioning of non-autox products, but that explanation is unclear and buried in a Table in the SI. A clearer demonstration with a graphic is needed.

I would have like to have seen optimization of model parameters (volatility, reactivity, and/or aging) using the suite of observations made. Or at the very least, show Figures 6 and 7 (which are the key figures) but with observations shown as well. This would ground the model and allow the authors to make conclusions that currently seem like extreme extrapolations. For instance, the levels of SOA in the chamber are beyond atmospherically relevant. The high loadings most likely affected the relative contribution of gas partitioning versus heterogeneous chemistry to SOA loading. Additionally, the authors conclude from this modeling exercise that straight chain alkanes are important for urban SOA - without showing much evidence. This is not backed up by the results shown.

It is my opinion that major revisions are required for this work to be published in ACP.

Minor

Line 153: Why 51 species? Where is this from?

Line 24: symbol in front of C15 did not render

Line 125: multiplication symbol did not render properly

Line 128: the "i" in alpha_i needs subscript

Figure S1. Is that starting from an alkoxy radical? Initial compound is blurry. How does the hydroperoxy group convert to a carbonyl? Please explain in the caption.

Instead of “or” for organic phase, “in” for inorganic, consider using “org” and “inorg” for clarity

Figure 2. Consider not using black and grey for MCM and MCM+autox. Something more different.

Line 321. Should cite Fig 5 not Fig 6?