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Referee Comment on "Secondary Organic Aerosol Formation from Camphene Oxidation: Measurements and Modeling"

Anonymous Referee #1

Referee comment on "Secondary organic aerosol formation from camphene oxidation: measurements and modeling" by Qi Li et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-587-RC1, 2021

This manuscript describes a series of experiments and simulations designed to investigate the variables upon which SOA formation from the OH-initiated oxidation of camphene depend in the ambient atmosphere. In particular, the authors investigate the NOx-dependence of SOA yields, and find that increasing NOx counterintuitively increases SOA yields. Mechanistic modeling enables the authors to pinpoint the source of this effect via elevated yields of highly oxidized molecules produced from a series of b-scissions and oxygen additions following the reaction of the initial camphene + OH + O2 peroxy radical with NO. Furthermore, under "extreme" high-NOx conditions, SOA yields decrease, which the authors again hypothesize is due to the nuances of the camphene oxidation mechanism, whereby the exclusive reaction of peroxy radicals with NO can eventually form more-volatile products. These effects are at times complicated by the other changing variables between experiments, including the initial hydrocarbon loading and the SOA mass formed, both of which can change vapor-wall effects, but the authors are able to make a compelling case for the mechanistic reasoning behind NOx-dependent SOA yields.

Now that I read the rest of my comments below, it sounds like a lot of complaints, but I really think this an an excellent synthesis of experiments and modeling and an important step in our understanding of how RO2 fates influence important outcomes like SOA formation from VOCs in the atmosphere. It's great to see such a comprehensive study and with such complementary modeling and experimental parts that both bring a lot to the table -- in particular, the way the mechanistic modeling is able to explain the complex NOx dependence of the SOA yield. More comprehensive consideration of both sources of uncertainty and vapor wall effects could make this a still stronger paper, but it's great already!

General comments:

1) The lack of consideration of vapor wall effects is puzzling. The authors cite two studies that saw little difference between seeded and unseeded experiments, but any effects would still be highly dependent on the initial hydrocarbon loading (how does that compare to the other studies?) and the precise details of the oxidation mechanisms leading to SOA formation. Because the conclusion of this paper is precisely that camphene's SOA-formation mechanism is *different* from many other VOCs, with a predominantly positive NOx dependence, it's not clear that we should be able to extrapolate from other VOCs' vapor-wall effects (especially if other VOC's make a lot of SOA from low-volatility products like dimers, while camphene's are intermediate-volatility compounds). One could just as well cite plenty of studies that do see a strong effect of initial seed surface area on measured SOA yields, which are demonstrably due to the competition between vapor-wall and vapor-particle partitioning (e.g. Zhang et al., 2014 & 2015; Schwantes et al, 2019). It is not clear from the sources cited here that the same effects aren't at play in the UC Riverside chamber.

The positive dependence of SOA yield on dHC (L 252) and M(0) (L 225), especially at low values of dHC and M(0), could easily be explained by wall effects, whereby lower initial SOA formation leads to higher losses of compounds that would otherwise form SOA to the walls instead of to (newly formed) particles in experiments with lower [HC]0 and M(0). This could also compound the effects of the low SOA yields at low NOx -- if the yields are slightly lower at low NOx, the reduced initial particle formation leads to greater losses of SOA precursors to the walls rather than to particles, which thus leads to an even lower measured SOA yield. Vapor-wall effects will therefore have a tendency to exaggerate any observed differences in SOA yields. The authors seem to admit this might be a problem on L 380-381, describing model-measurement discrepancies.

I don't mean to suggest that the authors need to start from scratch or perform a whole new set oof experiments to see how [HC]0 or the introduction of seed particles might change observed yields, although either would be extremely interesting. But some discussion of the effects that vapor wall losses could play here is certainly merited, along with how it would change the conclusions drawn from the observations.

2) The concept of the "extreme NOx regime" is introduced slowly and in such a way that some of the earlier claims in the paper don't seem supported by the data, or at least aren't clear until much later on. The "extreme NOx regime" is mentioned briefly at L 257 but not explained until later, so many of the earlier statements -- that SOA yield is high when there's added NOx, or that it depends on M(0), for example -- at first seem misleading when the accompanying figures show that above a certain point, added NOx seems to decrease yields. The payoff only comes around page 17 when the chemical reasoning behind the decreased SOA yields in W1 and W2 is explained. I'm not suggesting a complete restructuring of the paper, but I think it could be improved if this chemical explanation were more concretely hinted at earlier, and if the reduced SOA formation at "extreme" NOx were mentioned in the abstract as well.

As an example, at L 221-227, it sounds like the lower SOA yield in W7 relative to W6 and WO6 relative to WO5 will be a dependence on M(0). I understand that it's tough to put everything in an order that explains it all clearly at once, but Fig 2 is particularly misleading because it and the associated discussion makes it sound like this is going to be a dependence on SOA mass, but only much later do you explain it's actually a dependence on RO2 fate, where the high RO2+RO2 chemistry in WO6 and "extreme" NOx chemistry in W7 decrease yields. (As a side note, given the few points on this graph and the fact that WO5 and WO6 have very similar M(0), it almost doesn't seem like you can say there's a "trend" toward lower SOA yields at highest M(0) levels). It would be helpful to briefly mention here what the actual dependences are, even if you'll wait until later sections to explain them more fully.

3) Uncertainties and replicability -- on the topic of Figure 2, it would be much easier to assess whether W7 and WO6 represent a decreasing trend at high M(0) if we had some estimate of uncertainty on either axis, ideally in the form of error bars. Overall, this paper could benefit from more discussion of the potential places where experimental or modeling uncertainties may confound the interpretation of results. On the experimental side of things, how replicable are wall-loss experiments, and therefore how much error is introduced by the wall-loss corrections, which would presumably carry through to SOA yield? On the model side, how well-constrained are the rates of the RO2 reactions that allow you to estimate the branching fractions in Figure 5, and how well constrained are the product yields in Figure 7? If possible, this could be described along with the instrument and model descriptions in the methods section, and uncertainty ranges could be added onto numbers reported in tables (e.g. Table 2) and/or error bars added to figures.

A corollary to this is that sometimes the places with the most uncertainty and model-measurement disagreement are the most interesting to dig into, because they have the potential to show what is lacking in our current understanding of the chemistry in question. To that end, I think the statements about model-measurement disagreement on L 377 & 387 deserve more explanation. First, what could be causing the big differences at low NOx between GECKO simulations and observations? OH recycling, or higher background NOx? And second, why might the modeled absolute SOA yields with added NOx be overestimated by up to a factor of 2? How much could this be due to wall losses, uncertain VBS parameters, or the mechanism itself? I know these model-measurement differences may seem too big to tackle here and like they're beyond the scope of the paper, but even just some speculation thrown in here could be useful to guide the reader's thinking!

Specific / editorial comments:

L 96: What is "2mil"?

L 183: What does "final peak particle diameter" mean? Is it the highest-diameter particle measured or the median/mean particle diameter at some "final" time?

L 184: Here and throughout, it would be helpful to be more specific with the definition of "SOA yield". Is it the mass yield or a molar yield assuming a chemical identity for the SOA-phase compound(s)? Is it the yield measured at its maximum, the end of the experiment, or a specified photochemical aging time? Even if you define it once somewhere in the paper, to avoid confusion it's nice to consistently refer to it as specifically as possible (e.g. as "peak SOA mass yield") wherever it's subsequently brought up.

Fig. 1: Agreement between measured and modeled values would be much easier to see if c and e were plotted together; same with d and f.

L 243-244: The claim that the SOA yield curves "already plateau or nearly plateau by the end of experiments" doesn't seem to be supported by Figure 3, where all the high-NOx experiment yield curves are flat or even decreasing (how can that be explained, by the way?!) by the end of the experiment, whereas every single low-NOx experiment yield curve still has a positive slope. Based on the change in slopes, how long might it take for the low-NOx experiments to plateau, and how much higher could their yields rise? Without knowing that, it seems an apples-to-apples comparison might cut off all the experiments at the same approximate photochemical aging time and see how they differ -- but cutting off some of the high-NOx experiments at ~15 h photochemical age to better compare to the low-NOx experiments' maxima could cause a considerable change in reported yields, even bringing W1 to a "final" SOA yield lower than that of some of the low-NOx experiments. How much would extrapolating the low-NOx yield curves to high aging times where they plateau, or conversely cutting off the high-NOx yield curves at much lower aging times, change the analysis in this paper?

L 270-271: It's unlcear to me what the "accumulated total [RO2]" is measuring or is useful for. Does this count each b-scission-plus-O2 step as an independent production of RO2 toward the cumulative total? In this case, it's kind of conflating the fraction of hydrocarbon reacted with the number of b-scission reactions per camphene+OH reaction, right? Since it's not further discussed (unless I'm missing something) I'm not sure why it's brought up here.

L 290: Needs a comma, not a semicolor

L 300: Since there's no aromaticity, this compound can't be described as phenolic. It's an alcohol, though.

L 304: "Peroxy", not "proxy"

Fig. 7: The compound produced in the +NO (0.806)/+NO3/+RO2 (0.5)/+RCO3 pathway from RO2-e should be an alkoxy radical; the way it's drawn, it looks like a stable compound. Also, there is some indication that RO2 + HO2 reactions of large and/or functionalized peroxy radicals can produce reasonably high yields of alkoxy + O2 + OH rather than the radical-terminating hydrooperoxide ROOH, although it seems this mechanism assumes 100% ROOH formation (see, e.g., Praske et al. 2015, Kurten et al. 2017). How would this pathway change the model interpretation?

L 435: This sentence is confusing and appears to have a grammar issue. Maybe replace the "but" with ", it"?

L 438: "experiment" should either be plural or replaced with "the experiment"

L 438: How did the RO2 + NO pathway lead to the highest RO2 production? Is this because it had higher OH and therefore more camphene reacted, or is this referring to the "accumulated total [RO2]/[HC]0" discussed above (see comment on L 270-271)

L 443: Why is the ratio in parentheses presented in the opposite order to the way it's described here?

L 462-463: Is "IS" supposed to be "IA"?

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