

Interactive comment on “Multi-generation OH oxidation as a source for highly oxygenated organic molecules from aromatics” by Olga Garmash et al.

Anonymous Referee #2

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General Comments:

The authors have reported on a series of experiments aimed at quantifying the total and speciated HOM formed from the oxidation of important aromatic VOCs using two different facilities: a flowtube and an environmental chamber. The data analysis is enlightening and a number of useful interpretations are made that will help the field continue to advance understanding of this potentially impactful atmospheric phenomenon. In general though, I found the lack of quantitative conclusions disappointing. The yield estimates provided are somewhat provocative because they are so high compared to previous reported values, but it is unclear how the atmospheric model

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community should use these estimates, or if they should use them at all. I recommend this manuscript be published, but I have some reservations with the overall messaging.

The bottom lines appear to be, 1) HOMs from aromatics are confirmed and 2) when constructing an laboratory-based model, everything matters. If the authors could extend their message to how their findings relate to HOM formation from biogenics (both in terms of magnitude and sensitivity to chamber conditions), which is comparatively well-studied and which has been implemented in some large scale models, it might enhance the narrative. A key point I was missing was the authors' interpretation of how important these processes are in and downwind of the urban atmosphere. Do they have some idea if aromatic oxidation can be a substantial source of ultrafine particle formation events, or is it still too early to tell?

Specific Comments

1. Definition of molar yield: I appreciate the authors decision to use an operational definition of HOM yield, which is more in line with traditional methodologies for estimating SOA formation in large-scale models. In the short term, this option is easier to transcribe into models. However, the cost is that it is harder to account for sensitivity to environmental conditions like OH and NO_x and translate chamber residence time to variable model time steps. Clearly, this approach of lumping the multigenerational formation together with the prompt formation is more suitable for aromatic VOCs (a point the authors make), but the timescale for this formation given on Page 19, line 9-10 is 10 h – 15 days. Some global models run with chemistry time steps on the order of tens of minutes to multiple hours. But regional models can be in the range of 5 minutes down to 45 seconds for high resolution cases. And LES models are even faster. Can the authors please consider discussing this aspect of how their data will be used? Are yields defined in this way really useful to large-scale models or are they more useful to other experimental efforts trying to constrain the total HOM formed.

2. The authors' point that OH and NO_x should be considered when predicting HOMs

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from aromatics is well-taken; they have demonstrated it well. However, can they provide a parameterization for these effects that can be explored by other groups. The only option they have left the reader with is to interpolate the data in Table 1. If the authors do not think such a parametrization would be helpful, please discuss why.

3. Section 3.5: I recommend adding a table of all of the HOM molecules considered for the kinetic model of the seed experiment, to the appendix or supplemental. Are ions reported because multiple formulae apply to one ion in some cases? Equations 6, 7, and 8 indicate the kinetic model needs molecular weight and diffusion coefficient in air of every species of interest. If so, these parameters could be reported as well. I also recommend adding the formula to each of the sub-panels in Figures A1 and A2.

4. Page 15, line 9: HOM molar yield is set to 5%? Apparently I am confused about this model. I was under the impression that each HOM molecule would have a specific yield based on its relative abundance in the spectra from the base experiment. Is this not the case? Please consider explaining this portion of the approach clearer in the text.

5. The authors connect their experiments to previous SOA studies to try to explain the variability seen in the literature with what they have learned about HOMs. But the only parameter discussed is seed aerosol concentration. Are there any other features of HOM formation the authors think are connected to the apparent variability in historical SOA yields?

Typos/Suggestions

1. Table 1 caption: quadrupole?
2. Page 13, Line 6-7: Are you reporting SOA yields in this work?
3. Page 14, Line 5-6: Please provide an equation relating k_{loss} to k_{wall} and CS.
4. Page 14, Line 27-29: What is the magnitude of uncertainty introduced from unidentified or omitted peaks?

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5. Page 22, Line 9-11: Please rewrite this sentence to make it clearer that “total mass loading” is total PM mass (organic + inorganic) and that the percentage numbers are relevant to the organic only mass. There’s nothing incorrect about this as-is sentence, but it could be reordered to make it easier for the reader to digest quickly.

6. Page 23, line 2-3: This statement “This clearly suggests... compete with CS.” has been shown in other studies documenting the effect of seed aerosol and they should be referenced.

7. Figures A1 and A2: Do the authors have an explanation for the range of variability observed for different m/z. Some of them are relatively smooth, and others change wildly. Are the latter intermediates?

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