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Discussions

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

Anonymous Referee #1

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General comments

Overall, this paper has shown that OH + aromatics (mainly benzene) produce a significant amount of highly oxidized molecules (HOM) that act as a reservoir for particles.

OH + VOC (aromatics) $\Rightarrow$ HOM $\Rightarrow$ particles

HOM are an array of compounds (with 6 or more O) that are the result of initial OH addition to the aromatics. Good evidence is provided that given enough time multiple OH reactions can take place and produce a larger array and amount of HOM.

The challenge for this type of work is how to parameterize the data. In the abstract,

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Discussion paper

they ask the modellers to consider these reactions, but this will only happen if such results are parameterized. At the moment this type of study is only semi-quantitative, i.e. there is an explanation for the HOMs but no rate coefficients. THIS IS THE BIG CHALLENGE.

Until a quantitative model is developed there is a problem of knowing which study is closest to atmospheric conditions. The study by Molteni(2018) indicated that HOM yields for benzene are 0.1-1% but in the present study, the yields are much higher 4 – 14%. Which is the correct result for atmospheric modelling? Are both studies in agreement, but it is the conditions that produce different yields?

Specific comments

page 7, 8 "Hydroxyl radicals were produced via photolysis of water at 184.9nm." I would make it clear that for each OH produce there is an HO2 (H + O2). This means in this reactor RO2 + HO2 is going to be significant and potentially suppress HOM formation. In the JPAC, OH is from O3/H2O (254nm) so only makes only OH

page 7, 10 "uncertainties in the VOC and OH concentrations were large enough that no quantitative analysis was attempted" Below an estimate [VOC] is made, so can an estimate of OH be made? What is [H2O] approximately?

page 8, 12 "The UV lamp (Philips, TUV 40W, λmax = 254nm) was located inside the chamber and was shielded from both ends with UV-absorbing glass tubes." How even is this light distributed in the chamber?

From Figure 2, it takes 5 hours before reaching steady-state. Is this time to SS representative of all the experiments? If I understand correctly, you are waiting for

OH + VOC (aromatics) $\Rightarrow$ HOM $\Rightarrow$ particles

to reach steady-state and the MS data is only analyzed once SS is reached? Is there valuable data in the first 5 hours? If the HOM ratios are changing during this build-up time there should be further clues to the HOM formation mechanism? In the Helsinki

experiments you have not reached SS, so where along this HOM concentration curve is applicable? DOES ANYONE HAVE A KINETIC MODEL TO EXPLAIN FIGURE 2?

In Equation 5, γ is in the denominator.

page 15, 4 "for each HOM molecule i" Can you indicate the value of i, i.e. how many HOMs are considered?

page 16, 8 "HO2 can also be produced in our reactor making a reaction with HO2 an important bimolecular termination pathway in our system." Please make in clear in the experimental that HO2 is made from H2O photolysis.

Is there any specific reason that 185 nm was used to generate OH. If 254 nm and O3/H2O was used then there would be a more direct comparison to the JPAC experiment. Can the lamp be translated along the reactor to change the contact time? I note that Molteni(2018) used an excimer lamp at 172 nm. Both 185nm and 172nm will photolyze aromatics, but this is not the case for 254 nm.

The results in Figure 3 show that a range of HOMs are formed and the text provides some explanation of the type of reactions required to make each HOM. I was wondering if this could be quantified further. For instance, the dimers require an RO2 + RO2 bimolecular reaction. What sort of rate coefficient is required? While you state you do not know OH concentrations in the Helsinki experiments this makes it a difficult question, but in the JPAC experiments maybe this is possible.

page 18, 13 "The OH production from H2O photolysis stayed constant in our experiments, but the VOC acts as a sink for the OH radicals, which means that higher VOC concentrations will result in lower OH concentrations." Is there a reason why benzene or toluene was not lowered to maybe promote 2 OH reactions? If you had the bubbler before the MFC would you have greater control of the [VOC]?

In the Helsinki experiments, if the residence time could be changed then the mechanism of how these HOMs are formed might be clearer and even provide some kinetic

assignments. If the lamp was located further along the reactor would this significantly change the residence time?

Page 18, 31 "At small oxidation rates, the total HOM concentration increased linearly, but reached a plateau around 3-4 $\times$ 108 cm-3 at higher oxidation rate." This plateau is true for the light green square but not for the dark blue!

From Figure 4 b, HOM yield appears to be linear in OH. Surely there must be a limit where the HOM yield plateaus? If the HOM yield is increasing with more multiple OH reactions, does this mean that HOMmulti $\Rightarrow$ particles is slower?

Page 19, 11 "Our estimated HOM yields from benzene oxidation were 4.1-14.0%, which can be compared to a value of 0.2% provided by Molteni et al. (2018). Their value likely corresponds to the HOM yield of the first OH oxidation step, potentially also impacted by a second step, suggesting that more than 90% of the "HOM- forming potential" of benzene comes from multi-generation OH oxidation." I'm confused here as to which study is relevant to the atmosphere. Molteni(2018) had a factor of ten less HOM than the present study, is this consistent with the OH concentration they used in their experiment? Which HOM yield would go into a model? Can you provide more discussion in the paper about this difference? Have you artificially raised the [OH] in order to bring about large [HOM]?

If you looked at the HOMi signal at early times, the 5 hours before steady-state, can you see the various HOMi evolving in time?

Now if you are saying that the HOM yield is 10 times smaller for 1 OH reaction, then should the HOM spectra dramatically change, i.e. big difference between Figure 3 and 5?

Page 21, 1 "However, after this, OH oxidation can only proceed via H-abstraction, and if the subsequent termination reactions occur by loss of OH or HO2, a 5 decrease in H-atoms will take place. In other words, it is to be expected, that multi-generation OH

oxidation will produce also molecules with fewer H-atoms than the parent VOC." Are these high [OH] HOM relevant to the atmosphere?

Page 21, 3 "Another possibility is that the dimer formation upon RO2+R'O2 reaction would be less likely for the RO2 formed at high OH." I would have thought RO2 + RO2 is more likely the higher the OH concentration.

Page 23, 22 "but also for some precursors for multi-generation HOM formation that are undetected by our instrument (or detected at lower sensitivity)." But I thought you are saying that the multi-generation HOM are from the primary generation HOM.

OH + HOMprimary $\Rightarrow$ HOMmulti

What sort of intermediate before HOMmulti do you think might be present that is not detected? I understand why BPR is not detected but not what you are presently suggesting.

Page 24, 30 "In addition, we conclude that atmospheric models should take into account HOM yield dependence on the chemical regime when implementing quantitative laboratory results." Can you make it clear which study is relevant to the atmosphere, the present work (high HOM yield) or Molteni(2018) (low HOM yield).

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