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Comments on acp-2021-201

Anonymous Referee #2

Referee comment on "Highly oxygenated organic molecules produced by the oxidation of benzene and toluene in a wide range of OH exposure and NO_x conditions" by Xi Cheng et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-201-RC2>, 2021

Comments on "Highly Oxygenated Organic Molecules Produced by the Oxidation of Benzene and Toluene in a Wide Range of OH Exposure and NO_x Conditions" by Cheng et al.,

In this manuscript, Cheng et al., investigated the oxidation products of benzene and toluene using a PAM flow tube reactor under low- and high-NO_x conditions. The authors used a nitrate-based tof-CIMS to measure the oxidation products (HOMs), and some unmeasured species, such as HO_x and RO_x, were quantified with a chemical model designed for the PAM. By investigating the behavior of different HOM classes under different OH dose and NO_x level, the authors suggested that 1) their system is more favorable for highly oxygenated products, 2) multi-generation OH oxidation is likely via the H-abstract route, and 3) Many even the majority of N-containing HOMs are likely peroxyacyl nitrates. Based on these results, some reasonable atmospheric implications were given.

In general, I found this manuscript interesting and provided enough insights into the oxidation scheme for benzene and toluene. However, I do have some concerns, which should be addressed before it can be accepted for publication in ACP.

General comments:

- How much the oxidation system of PAM with high OH concentration can be extrapolated to presented the real atmospheric conditions is always a major concern of the community. The lifetime of many effectively non-volatile HOMs is in the order of minutes, but the minimum equivalent OH exposure time in this study is 0.8 days. Also, at low OH concentrations, it is to be demonstrated if the ppm-level O₃ dominates the oxidation of the first-generation HOM products, which likely have an endocyclic double bond. Likewise, the NO₃-initiated oxidation at high-NO_x levels may also play an

important role. These should be at least mentioned in the manuscript.

- The authors investigated the oxidation of benzene and toluene, and clear differences in the products and their response to different oxidation conditions were observed. However, readers might hope to see some more detailed explanation of these differences, rather than only some descriptions. However, it is ok if the authors show more dedicated studies in their follow-up manuscript.

Detailed comments:

L103-109. SP-AMS IS mentioned. However, no real data from this instrument was discussed in this manuscript.

L125-127. Based on the observation, the authors suspected that another one or two steps of auto-oxidation may occur after BPRs form. This is an important observation, as it is different from what has been proposed by Wang et al., 2017, and thus may provide new insights. Can the authors propose a reaction scheme similar to Scheme S2?

L165. It should be clarified that "Garmash et al. (2020) shows relatively high signals of C₆H₈O₉ and C₁₂H₁₄O₈ **in the flow tube experiments**, whereas..."

L171-172. The authors attribute the more steps of auto-oxidation in their experiments to the longer residence time. This is one possible reason. Can the authors exclude the possibility that the concentrations HO₂, RO₂, NO_x in Garmash et al., (2020) were higher than those in this study, so that the auto-oxidation was suppressed to a greater extent?

L187-188. It is interesting to see that the dimeric HOMs decrease when OH exposure increases for toluene HOMs. It deserves a bit more explanation/speculation than just say "Whether this phenomenon is related to the substituted methyl group or not needs further investigations".

L255-260. The yield is probably one key message that readers would like to fetch from these studies. Thus, the big differences in the yields reported by different studies should be better explained. As the authors concluded that multi-generation oxidation is important in benzene and toluene oxidation, the highest yield by Garmash et al., (2020) and the lowest yield by Monteni et al., (2018) cannot be explained by the residence time, because the OH exposure in Monteni et al., (2018) is the highest among these studies. It may point to either the auto-oxidation is more important, which are different among these

studies controlled by the termination reactions, or the peaks counted for "HOMs" are different. I can read from Table S4 that in Monteni et al., (2018), the OH dose and benzene concentration were highest, and thus the highest RO2 concentration can be expected for that experiment, possibly leading to a termination of RO2 auto-oxidation prematurely.

L275. Why do the authors assume that $[\text{NO}_x]:[\text{HO}_2]$ should control the overall trend of HOMs? It think $k_1[\text{NO}] + k_2[\text{NO}_2] + k_3[\text{HO}_2]$ is better than $[\text{NO}_x]:[\text{HO}_2]$, because all of them lead to termination reactions that control HOM formation. Here, k_1, k_2, k_3 is the average first-order rate constant of the bi-molecular reactions with RO2.

L294-295. Could NO3 radical also be important in the formation of other HOMs, particularly for high-generation products?