

Response to reviews

We thank the reviewers for their constructive comments that help improve the manuscript. We provide below the point-by-point responses to those comments. Reviewer comments are in **bold**. Author responses are in plain text labeled with [R]. Line numbers in the responses correspond to those in the revised manuscript with all track changes accepted. Modifications to the manuscript are in *italics*.

Reviewer #2

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.

[R0] We thank the reviewer for the valuable feedback. Detailed responses to the comments are given below.

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.

[R1] The purpose of OFR experiments is to explore the influence of various conditions on the product distributions and to some extent the formation mechanism of multi-generation oxidation of VOCs. While chamber experiments mimic better ambient environments, OFR experiments are easier to be set up for a wide range of conditions. Indeed, many of the HOMs observed in the OFR have been seen in ambient environment, although the OH exposure in the OFR is equivalent to several days of atmospheric photochemical age. For example, many of the detected isoprene nitrates during the SOAS 2013 campaign have been reported as the second- and third-generation OH oxidation products of isoprene under high-NO_x conditions in the OFR experiments (Massoli et al., 2018). Also, the HOMs observed in the OFR from aromatic oxidation (including those

plausibly formed by multi-step OH oxidation) explain a significant portion of the HOMs observed in Beijing (unpublished results from the PKU and BUCT measurements).

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.

[R2] The OH exposure in our experiments is about 1.1×10^{11} to 2.5×10^{12} molecules cm⁻³. The OFR-based photochemical box simulations show that the aromatic oxidation reactions in our experimental conditions were dominated by OH rather than O₃ (Lambe et al., 2011; Peng et al., 2016). Similar to other OFR studies, we think the reaction rates of O₃ with oxidation products that contain double bonds are likely slower compared with that of OH (Molteni et al., 2018; Wang et al., 2020). The NO₃ concentrations in the OFR range from 0.01-0.09 ppb, for which the NO₃ oxidation of phenols may contribute efficiently to the formation of nitrated phenols in the OFR experiments because of the high branching ratio. Table R1 lists the general reaction rates of RO₂ with OH and NO₃ estimated for Exp. #28 (Jenkin et al., 2019). For such rates, the NO₃ reactions with HOM products might be minor under our experimental conditions compared with the OH reactions. To clarify the potential influence of O₃ and NO₃, we have added the above discussion in Line 89-96.

Table R1. The reaction of RO₂ with OH and NO₃ for Experiment #28

Oxidants	Concentration (molecules cm ⁻³)	Rate coefficient (cm ³ molecules ⁻¹ s ⁻¹)	Rate (s ⁻¹)
OH	3.04×10^9	1.20×10^{-10}	0.4
NO ₃	2.21×10^9	2.40×10^{-12}	0.01

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.

[R3] We thank the reviewer for the suggestion. The focus of this paper is the effects of oxidation conditions for a wide range of HO_x and NO_x levels on the product distributions. The formulae of the detected HOMs do not necessarily link to specific functionalities. It is therefore difficult to discuss much about the reasons of the difference between toluene and benzene results. We do have a follow-up manuscript in which we investigate the effects of alkyl substitution based on oxidation experiments of six different alkyl aromatics.

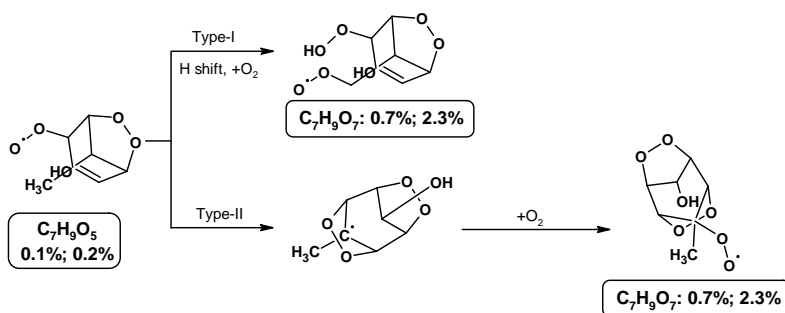
Detailed comments:

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

[R4] We used the Aerodyne LTOF-SP-AMS to measure the SOA mass concentrations for the calculation of the condensation sink. We have clarified this in Line 115 as follows: “...(*LTOF-SP-AMS*) for the calculation of condensation sink in wall-loss corrections of HOMs”.

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?

[R5] We have added Scheme S3 as an example for the proposed mechanism in the Supplement. Two potential routes for the further oxygen additions to the BPR follow the scheme proposed by Molteni et al. (2018) for mesitylene oxidation. One route represents the traditional autoxidation mechanism with internal H abstraction and oxygen addition as described by Wang et al. (2017). The other route involves cyclization forming a second oxygen bridge, which produces a carbon-centered radical followed with the addition of another oxygen molecule (Molteni et al., 2018). Toluene could undergo these two routes for the second step of auto-oxidation occurred after BPRs form because of the methyl group, which is different from benzene.



Scheme S3. The proposed mechanism of further autooxidation from the BPR $C_7H_9O_5$. Type I and Type II pathways are proposed by Wang et al. (2017) and Molteni et al. (2018).

L165. It should be clarified that “Garmash et al. (2020) shows relatively high signals of $C_6H_8O_9$ and $C_{12}H_{14}O_8$ in the flow tube experiments, whereas...”

[R6] Corrected.

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 HO_2 , RO_2 , 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?

[R7] We agree with the reviewer about this possibility because the concentrations of HO_2 and RO_2 were not provided in the paper from Garmash et al. (2020). We have added a sentence in Line 202-204 as follows: “*Alternatively, the differences in HO_2 and RO_2 concentrations among different studies that remain unclear might affect the extent of auto-oxidation*”.

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”.

[R8] As replied to the other reviewer’s comment #12, we have added more discussion in Line 218-224 as follows: *“One potential contributor to the difference of the dependence of dimer formation on OH exposure is the more significant elevated RO₂ concentrations (0.2 to 0.9 pptv) as the OH exposure increases for benzene oxidation than those (0.3 to 0.5 pptv) for toluene oxidation while the HO₂ concentrations in the two sets of experiments are similar (1.5-2.4 ppbv). The enhancement of RO₂ concentrations may promote the dimer formation through the self or cross reactions of RO₂ (Mohr et al., 2017). On the other hand, a previous study indicates that the accretion of RO₂ depends on the functional groups of the RO₂ (Berndt et al., 2018). On the other hand, a previous study indicates that the accretion of RO₂ depends on the functional groups of the RO₂ (Berndt et al., 2018). Whether the decreasing concentrations of dimeric products with OH exposure is related to the steric effects of the substituted methyl group of toluene requires 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.

[R9] The OH concentration listed in Table S4 for the study of Molteni et al. (2018) is the initial OH concentration, which should decrease significantly as the reaction proceeded. We have updated Table S4 for this information. Therefore, we cannot evaluate the actual OH exposure in the study of Molteni et al. (2018) and discuss further about the possible reasons. To clarify, we have added the following information in Line 304-308: *“The study of Molteni et al. (2018) only provided the initial OH concentration as listed in Table S4 that should decrease significantly as the reaction proceeds, for which we cannot rule out the possibility of low OH exposure that leads to fewer oxidation steps (i.e., lower yields of HOMs).”*

L275. Why do the authors assume that [NO_x]:[HO₂] 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 RO_2 .

[R10] Here we focus on nitrogen-containing HOMs. $[\text{NO}_x]:[\text{HO}_2]$ as well as $[\text{NO}]:[\text{HO}_2]$ and $[\text{NO}_2]:[\text{HO}_2]$ is chosen to differentiate the potential transition from $\text{RO}_2 + \text{HO}_2$ to $\text{RO}_2 + \text{NO}/\text{RO}_2 + \text{NO}_2$ dominated regimes. The use of $k_1[\text{NO}] + k_2[\text{NO}_2] + k_3[\text{HO}_2]$ is perhaps better for understanding the terminations but not our intention here.

L294-295. Could NO_3 radical also be important in the formation of other HOMs, particularly for high-generation products?

[R11] As replied in [R2], the NO_3 reactions with HOM products might be minor under our experimental conditions compared with the OH reactions. Autooxidation may occur at a rate of 10^{-3} to 1 s^{-1} (Bianchi et al., 2019). Therefore, for RO_2 radicals that have high autooxidation rates, they may also preferably proceed with further autooxidation to form HOMs.

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