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# *Interactive comment on* “Mechanistic Study of Formation of Ring-retaining and Ring-opening Products from Oxidation of Aromatic Compounds under Urban Atmospheric Conditions” *by* Alexander Zaytsev et al.

**Anonymous Referee #2**

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In this work, the authors presented results from oxidation experiments of aromatic compounds, toluene and 1,2,4-TMB. These aromatic compounds are important VOCs in urban areas, and their oxidation leads to significant ozone and secondary organic aerosol (SOA) formation. In this study the authors employed a number of new analytical techniques to measure the gas and particle phase composition, and compared to the latest version of Master Chemical Mechanism (MCM), which summarizes the current understanding about the mechanisms. Furthermore, the time trend analysis using gamma kinetic parameterization is a novel method to look at the multigenerational chemistry.

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Discussion paper

This manuscript is well written, and I only have some minor suggestions. I recommend publication of this manuscript in ACP.

Minor scientific comments:

1. It would be good to know on a bulk or general level, how these results improve the understanding of the chemistry. For example, I wonder what the carbon closure now is, with these new measurements. Figure 3 is probably a good place to show that.

2. Somewhat related: One key piece of information shown in Section 3.3 and Fig. 6 is that the total SOA mass measured by AMS and NH4 CIMS compare very well, and so do the O/C ratios. This is an important discovery and should be highlighted in the abstract.

3. The multigenerational chemistry of many of the products is a key contribution. I expect that the accompanying paper describing the methods will be well received. There are some ambiguous ones that have non-integer m (e.g. 1.7-1.8). What is the general uncertainty in this analysis?

4. Related to comment/question 3: I expect that some experiments with oxidation of later generation products would be very helpful. For example, oxidation of cresol (which is commercially available) should yield lower m for some of the products. Perhaps even examining the decrease in m would help apportion the relative amount for each generation. I think these are important experiments anyway given that the authors are claiming the importance of phenolic and benzaldehyde pathways in HOM production.

5. The experiments were all conducted under RH of 2%. While I completely understand the rationale to create a well-controlled environment, it may be worthwhile to mention this is a potential limitation of this study and discuss implications. I do not see water playing an important role in the gas-phase chemistry, but could potentially shorten the lifetime of particle-phase hydroperoxides, epoxides and organic nitrates.

Minor technical comments:

Methods: I do not understand why the authors would use hexafluorobenzene as a tracer for both chamber wall loss and dilution of VOCs. I can see hexafluorobenzene is a good tracer for dilution, but I do not expect it to be lost to the chamber walls. Based on the chamber volume and air refilling rate, the dilution rate can be estimated. Is the hexafluorobenzene decaying faster than this dilution rate? If so, why is it being lost to the walls?

CO and formaldehyde were mentioned in methods, but no results were presented.

Methods: Particle-phase compounds were quantified using I- CIMS, but for the gas phase compounds the authors claim I- CIMS is quite uncertain. Are the uncertainties in quantification the same for both phases?

Section 2.4: how large are the time steps?

Section 3.1: Is it possible that the epoxide was not detected because of thermal decomposition for the particle phase measurements, or fragmentation during ionization?

Section 3.2.1, Line 13: BPR has been defined earlier.

Section 3.2.1 Line 29-30: Presumably the lifetimes are calculated using generic $RO_2$+NO and $RO_2$+$HO_2$ rate constants? What rate constants were used?

Tables 1-3: what are the uncertainties in m from the fits?

Figure 6: why is there a discontinuity at 14 hours of exposure for toluene? Was more OH precursor added? Similarly there seems to be one as well for TMB at 4 h.

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