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Comment on acp-2021-201

Anonymous Referee #1

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-RC1>, 2021

The manuscript by Cheng et al. investigates the formation of highly oxygenated organic molecules (HOMs) from the oxidation of benzene and toluene in a range of OH exposure and NO_x conditions generated from flow-tube based experiments. Despite a recent discovery, HOMs have received increasing attention due to their high oxygenation and low volatility thereby constituting a widespread source of SOA in the atmosphere. A number of studies have suggested HOMs can be steadily produced through the autooxidation pathway from a number of hydrocarbon precursors of both biogenic and anthropogenic origins. This is a well-motivated and timely work that examines how environmental factors impact the HOMs product distributions from the photooxidation of benzene and toluene, two hydrocarbons that have received numerous investigations in the past, yet the crucial pathways leading to SOA formation remain uncertain despite decades of investigations. Some interesting observations are presented, such as the contrasting dimer formation kinetics between the benzene and toluene systems, and the optimal [NO_x]:[HO₂] ratio that favors certain HOMs production, although the mechanism underlying these observations is elusive and warrants further evidence. Overall, it is a very detailed and interesting work. I recommend the manuscript for publication in Atmospheric Chemistry and Physics after the following comments being addressed in the revised version.

General comments:

My major comments are related to the interpretation of the trends and dynamics of the HOMs products in response to various flow tube conditions. Hundreds of HOMs products were identified in this work with the use of the 'inlet-less' nitrate CIMS that is highly sensitive to these 'sticky' molecules. It is however a great challenge to keep track of the trends and patterns of all these compounds without a good understanding of their chemical properties and formation mechanisms. I find the categorization of these compounds should be better clarified. The closed-shell products in general should include all stable products including both monomers and dimers. But it seems like here the authors use this term to specifically describe monomer products with a molecular formula of C_xH_yO_z. Perhaps 'closed-shell monomer products' would better represent this category. The open-shell products define all radical intermediates including both RO₂ and RO radicals. Whether these two types of radicals can be differentiated with the identified molecular formula needs to be clarified. Do these radicals ever possess higher carbon

numbers (dimer-like type) than their hydrocarbon precursor? In general, the text should be clear in the formulations and definitions. While the readers appreciate categorization that certainly helps to reduce the complexity in interpreting the behaviors of hundreds of compounds, some unique information of individual species might get buried in the grouping process. I recommend the authors provide a list of the most abundant HOMs products that account for perhaps over half of the oxidized carbon in both benzene and toluene systems, along with the conditions that favor the production of each HOM compound. This would help at least elucidate dominant reaction mechanisms that govern the reaction fluxes. On a related note, have the authors thought about the potential of using PMF analysis to help to extract typical trends and patterns of different groups of HOMs compounds?

Another concern I would like to share with the authors is whether the CIMS measurements constitute sufficient information for the assignment of different functionalities to a given molecular formula based on even/odd numbers of oxygen and hydrogen atoms. HOMs produced from the autooxidation pathway are generally recognized as multi-functionalized poly peroxides. The ring-retaining oxidation chemistry of aromatics further complicates the pathways that lead to the formation of oxygenated compounds. That being said, multiple combinations of different functional groups exist for any given molecular formula with high oxygen numbers. Have the authors conducted any collision induced dissociation experiments for the HOMs molecules and identified any characteristic fragments? Without further structural information of individual HOMs molecules, the categorization of certain molecular formulas as peroxides/alcohols here seems a little handwavy. I have a similar impression about whether the CIMS measurements alone are sufficient to drive the mechanisms discussed in the text, or rather using established mechanisms to rationalize the observations. For example, the authors highlight that 'multi-generation OH oxidation plays an important role in the product distribution, which likely proceeds more preferably via H subtraction than OH addition for early-generation products from light aromatics'. Indeed, recent studies have proposed a unique pathway in the aromatic oxidation process, i.e., the ring-retaining chemistry that constantly takes up oxygen in the aromatic ring. The relevance and importance of this branch in the experimental conditions (e.g., high HOx intensities) of the present work needs to be explicitly discussed. In addition, the extent of OH exposure directly determines the number of RO₂ formed and consequently the likelihood of autooxidation that leads to HOMs production, but whether OH oxidation proceeds via abstraction or addition seems not directly supported by the observations presented in the text.

Specific comments:

- Line 15: This is a vague statement. Is there any unique feature of the OFR system used here that likely promotes the HOMs formation compared with previous studies? or just simply based on the longer residence time / slower flow rate?

- Line 185: It is interesting to see that 'the concentrations of fragmented, closed-shell and open-shell products first increase and then slightly decrease with the increasing OH exposure' for the toluene case. Have the authors thought about any potential fragmentation process that breaks these HOMs molecules apart?

- Line 190: Responses of the dimer products to increasing OH oxidation of toluene was found different compared with the benzene system. While the presence of the methyl branch on the aromatic ring might play a role in fragmentation, it is ultimately the RO₂ self/cross combination process that results in the dimer formation. Have the authors compared the relative increases in both RO₂ and HO₂ levels in response to the increasing OH exposure in the benzene and toluene oxidation experiments?

- Line 195-200: Functionalities cannot be simply inferred here solely based on the molecular formula without any additional structural information. Another layer of uncertainty that adds to the level of complexity is the rates and number of generations of autooxidation pathways.

- Line 245: Another factor playing in here might be the much slower reaction rate of benzene toward OH radicals.

- Line 255: The authors need to provide more details about how the wall losses in flow tube and sampling lines are corrected in the molar yield calculations.

- Line 282: How does the OH level change along with varying [NO_x]:[HO₂] ratios?

- Line 335: There have been a few numbers of recent studies demonstrating the formation of HOMs from the oxidation of alkyl-aromatics. This is a good place to summarize how the present study contribute to new insights into this system and what makes this study unique compared with previous studies.