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Atmospheric Chemistry and Physics Discussions
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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 #1

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Zaystev et al. report interesting experimental and mechanistic studies of products originated from the oxidation of toluene and 1,2,4-trimethylbenzene with OH radicals. The authors make use of several instruments based on chemical ionization coupled to high resolution mass spectrometry (CIMS and PTR). The experimental work is based on conducting photooxidation experiments, followed by the analysis of gas and particle phase products. The analysis is based on chemical ionization techniques in the gas phase using several reagent agents to target specific class of compounds. A complementary mechanistic work (kinetic model and Gamma kinetics parametrization) was used to model the experimental data. Although these experimental techniques provide powerful information about the formulas, they lack definitive structural information. I do have several concerns associated with the present manuscript:

1. Clarity of the manuscript, the novelty, and the technical interpretation of the data. The authors need to do more through job to clearly describe the objective of the study. Why gas phase and particle phase were measured? In several occasion, I got lost and it was difficult to follow which instrument/reagent agent was used for what and why (a table in the SI will be beneficial for example)? The gas phase was conducted to help with mechanism, however the particle phase was also analyzed but was not discussed (why and how these particle species were formed: partitioning, heterogeneous chemistry. . .). Organonitrates were mentioned but not discussed! The uncertainties were not discussed here (see my minor comments). Toluene and 124-TMS were studied in the literature and several important studies were not reported/discussed (e.g. Kamens/Jang group on toluene, Kleindienst work, Laskin work etc..). Several papers report chemical species observed in toluene SOA and in ambient PM2.5 in several places around the world. Do these species were observed here? 2. Another important point that need to be discussed by the authors: artefacts associated with these techniques mainly thermal degradations of polar compounds/side chemical reactions (see recent papers by Jimenez and P. Ziemann groups for example). I have provided two references below (some co-authors in this study were also associated with these artefacts studies: a. Xiaoxi Liu, Benjamin Deming, Demetrios Pagonis, Douglas A. Day, Brett B. Palm, Ranajit Talukdar, James M. Roberts, Patrick R. Veres, Jordan E. Krechmer, Joel A. Thornton, Joost A. de Gouw, Paul J. Ziemann, and Jose L. Jimenez b. Effects of gas–wall partitioning in Teflon tubing and instrumentation on time-resolved measurements of gas-phase organic compounds. Demetrios Pagonis, Jordan E. Krechmer, Joost de Gouw, Jose L. Jimenez, and Paul J. Ziemann

3. Given the analysis of gas and particle phase species in this work, it would be useful to include table(s) that outline partitioning coefficients of these species. A discussion

will be beneficial here since gas and particle are linked together! How this study could be beneficial to urban atmosphere and the contribution of aromatic to ambient organic aerosol? Are these HOMs species important? While this study might provide valuable information for a better understanding of the chemical pathways from the photooxidation of toluene and 124-TMB, the results presented here are not sufficiently discussed and/or do not present a real novelty (most products observed here were reported in the literature!).

other comments. 1. Abstract 1. Page 1, line 14. Change “A series of” with “eight” report how many experiment were conducted. 2. Page 1, line 17. Need to add the reagent chemicals used for the two PTRs to be consistent with the CIMS (e.g. H_3O^+ PTR, . . .). 3. The end of the following sentence is hard to understand “An extensive suite of instrumentation including two Proton-Transfer Reaction Mass-Spectrometers (PTR-MS) and two Chemical Ionization Mass-Spectrometers (NH_4^+ CIMS and I^- CIMS) allowed for quantification of reactive carbon in multiple generations of oxidation”

2. Introduction 4. Page 2, line 5. Needs reference(s) 5. Page 2, line 9-10. The authors state that 124-TMB is a good candidate (serve a model molecule) for substituted aromatic compounds? Please add reference(s) here and clarify this statement? This class of compounds behave widely differently vis-à-vis “chemistry, SOA production, OH rate constants. . .” 6. Page 2, line 11. Delete “often” 7. Figure 1. Suggest adding a second panel on the right side associated with 124-TMB (similar to the toluene). 8. Figure 2. Is the chemistry under low NOx relevant here (either under the chamber conditions or under urban high NOx conditions)? Hydroperoxide channels are minor! The paper focusses on high NOx! It is unlikely that these chemicals are formed under the conditions presented in this study. I suggest this figure should describes the chemistry relevant to the conditions reported in this study. There is a large number of such mechanisms reported in the literature? 9. Page 2, lines 20-21. Delete the sentence associated with low NOx. 10. Please add “BPRs” to figures. 11. Please correct the title of Figure 2. Also in figures 1 and 2, references should be provided in the titles

since the mechanism presented is not new to this study. Are the structures provided in Figure 2 experimentally determined in the literature? This should be stated clearly if these structures (mainly HOMs) were only proposed based on chemical formulas obtained from HR-CIMS/PTR and mechanism/computational chemistry. 12. Page 3, line 1. Delete “the “ in “. . .the detailed mechanism. . .” Please provide experimental evidence that NOx level was 10 ppb. 13. Page 3, line 2. The chamber conditions were stated in several part of the text as high-NOx conditions. Here they introduce “moderate”. The description of the conditions should be consistent through out the text. It is confusing and arbitrary throughout the literature how high-NOx and low-NOx conditions are defined? 14. Page 3, lines 1-7. This section does not provide clearly the work conducted in this study. Either the experimental or the mechanistic work? Define that gas phase and particle phase were the focus. In some area of the paper it seems that only the gas phase products were measured and in some other parts the particle phase (SOA) were analyzed. Please clearly define that both gas phase and particle were analyzed using these two instruments running under different reagent chemicals to analyze a wide range of compounds. The CIMS was used to analyze particle phase.

3. Methods 15. Page 3, line 11, please provide the flow rate used to keep the chamber volume constant (this important for dilution)? 16. Are the temperature and RH being constant throughout the experiment? When turning the light ON in general T and RH change due to reactions and heat from the UV lamps? Comment here. Time series of T and RH should be provided in Figure S1 top. 17. Page 3, line 13-14. “We performed a series of photochemical experiments, in which toluene and 1,2,4-TMB were oxidized by OH under high-NO conditions (Table S1).” Please provide NOx (NO and NO2) concentrations in Table S1. What the authors refers to high NOx conditions? Provide references here! 18. Please provide range of RH and T in Table S1 since term “approximative” was used. 19. Page 3, line 14. “First, dry ammonium sulfate particles, used as condensation nuclei, were injected in the chamber reach a number concentration of (2.5 - 5.7)·104 cm-3.” Table S1, shows particle loading after seed injection in the order of (2.6 - 5.7).104 cm3 (no changes of the particle number after

the light was ON and within the experimental error). Is this number stays the same throughout the experiment? Please clarify this in the footnote. This is important since HOMs were observed and will indicate if nucleation occurred or just growth of seed particles!!

I'm curious how much aerosol mass was formed? - Table S1 should provide the amount of aerosol formed minus the seed aerosol injected. Specify the time of the reaction for these values? It is not stated in the manuscript that these values are associated with peak aerosol and compounds? - How much toluene was reacted? Since these experiments were conducted at low HC and NOx concentrations, uncertainties should be discussed, and error bars should be provided for toluene and 124TMB. Providing time series in figure S1 top for example or in a separate figure will make the manuscript stronger? 20. Page 1, line 16-17. "Nitrous acid (HONO) was later injected as an OH precursor." It is not clear here! Table S1 shows that HONO was injected initially and during the experiment. Please clarify this statement? Please provide the source of NO in this section? 21. Page 3, line 18-19. Data in Table S1 not consistent with the statement here? HONO in Table S1 was between 28 and 60 ppbv. Either Table S1 or the text needs to be corrected? 22. HONO was injected before the light was on. There is no background OH before the light was ON? Was the chamber in the dark before t=0? Figure S1 bottom shows background for NO2, O3, and HONO+NOX? It is beneficial if C6F6 was presented also in Figure S1 top (dilution). - O3 was high (~15 ppb) before light was ON! From where O3 was generated before light ON? 23. "The concentration of NO in the chamber was estimated to be ~0.3 ppbv while NO2 concentration was approximately 10 ppbv" I believe this is the initial concentration? In the manuscript the authors describe the experiments were conducted under high-NO? This is confusing? From this statement and Figure S1, the experiments were conducted under high NO2? Please clarify this? How NO was estimated? 24. I suggest adding experiment ID in Table S1. Then, associate the experiment ID in each figure/table and where the data is discussed in the text? It is hard to link the origin of the data when discussed in the text figures and tables? 25. I'm confused with the term initial in Table S1. Are the authors referring before the light was ON? The system seems to be dynamic (clean-air was continuously injected: dilution always occurring)" The initial concentrations of toluene and 124TMB is very difficult to measure since the system was dynamic? I believe any quantitative data will be associated with high uncertainty? Provide error discussion in the manuscript! When conducting chamber experiments at low HC and NOx concentrations, initial HCs and NOx should be presented prior to light is ON and during the experiment. The instruments used should provide these data? Dilution data (C6F6) also should be provided in Figure S1? 26. Page 3, line 22-23. "The reagents were allowed to mix for several min, . . ." It is not clear if the chamber was mixed well (since no fans were used) before the start of the reaction (light ON?) It is not easy to conduct these kings of experiments: the chamber is always under dilution "continuously with clean air" at the same time injecting a known amount of reagents before the light is ON. It is necessary to provide the time series of all parameters measured and used to conduct the experiment? T, RH, HONO, HCs, SOA formed, C6F6. . . [Note, the amount of HC injected and the volume of the chamber does not provide accurate concentrations!] In general, HCs and HONO as well other reagents should be injected continuously in the chamber until a stable concentration is attained for all reagents, then stop the HC injection and turn ON the light (start of the reaction). Comments from the authors is need here! I do see the use of C6F6 to measure the dilution rate and it was discussed rarely in this paper. 27. Table S1. Particle loading should be (2.6 - 5.7) 104 instead of (2.6 - 3.5)104 as stated in line 15, page 1. 28. Suggest using "Experimental section" instead of "Experimental design" 29. Pages 3-4: chamber instrumentation. The description of the instruments is difficult to follow and switching between CIMS and PTR notations is hard to follow. All instruments use chemical ionization. At the beginning the authors state that four instruments were used (two CIMS and two PTR) and in this section it seems that three instruments were used: (1) page 4, line 1 ("including the I- CIMS instrument; and two PTR (CIMS H3O+ and NH4+. This section needs to be clarified and consistent with the manuscript. Recently artefacts and sampling issues were reported, and this should be discussed in the paper (see my general comments). 30. What reagent gas was used for the Vocus-2R-PTR? 31. The authors should provide the 10 compounds used in the calibration of I-CIMS and PTR3 in SI. Using these instruments for aerosol characterization may be associated with sampling artefacts as discussed recently (see my general comments) 32. Page 5, lines 4-24. Please provide time series for [ArVOC]0 for toluene and 124-TMB as I suggested before? Data obtained from PTR! 33. Page 5. The yields were described but were not provided in the paper! 34. What “b” represents in eq. 3? 35. Page 4, line 31. Is the light intensity was measured? 36. Page 4, 5: Gamma Kinetic parameterization. Can the structure affect the results (the parameters obtained)? This model is applied to formulas here? 37. Page 6, line 18. Figure 1 should incorporate both HCs as I stated before. 38. Page 10, line 18. Define TD-NH4+ CIMS. 39. Figure 6. Figure 6 title. I think there is an error! (a) should be toluene and (b) should be 124-TMB. Please clarify? Also is total organics or total organics carbon? 40. Page 10. “The O:C ratios calculated from individual species measured from thermally desorbed SOA using NH4+ CIMS were ∼0.95 for toluene SOA and ∼0.7 for 1,2,4-TMB SOA. These ratios are in good agreement with the atomic O:C ratios measured by AMS (0.85 and 0.65 for toluene and 1,2,4-TMB SOA, respectively) (Canagaratna et al., 2015).” Does this comparison was applied to the same SOA size for the AMS and CIMS? 41. Page 10. “Products observed in the gas phase are compared to those detected in the particle phase to further understand the mechanism of SOA formation from aromatics precursors.” Can partitioning coefficients be obtained for these products? Please provide organic species present in both gas phase and particle phase and their estimated partitioning coefficient? Table for example. 42. The section describing on page 10, lines 25 - 32. “non-fragmentary” “ring-retaining” “ring scission” “fragmentary” is not clear to me. Could the authors describe how the thermal fragmentation either in the gas phase or the particle phase reported on page 10 can affect the data (formula and structures) provided in this manuscript? Are the HOMs detected not originated from artefacts in the inlets? These compounds with high O:C ratio are expected to be in the particle phase but numerous studies including this one report them in the gas phase? 43. In

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Discussion paper

general, chamber backgrounds NOx always is present (although clean air was used) due to wall chemistry and the history of the chamber (heterogeneous wall chemistry). Comments!

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