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Atmospheric Chemistry and Physics
Discussions
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Interactive comment on “Impact of molecular structure on secondary organic aerosol formation from aromatic hydrocarbon photooxidation under low NO_x conditions” *by* L. Li et al.

Anonymous Referee #1

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SUMMARY

This paper investigated the impact of molecular structure on the photooxidation of aromatic SOAs. The effect of the alkyl substitutes on the yield of chamber generated SOA, the chemical composition and the physical properties of SOA were studied. The authors concluded that oxidation of products promote the elevation of SOA yields. They found that the aromatic oxidation increased with increasing alkyl substitute chain length and it also varies with the branching position of an alkyl group on aromatic ring. Using their chamber data, the authors classified aromatics into five groups and ranked them as ortho (o-xylene and o ethyltoluene) > one substitute (ethylbenzene, propylbenzene and isopropylbenzene) > meta (m-xylene and m-ethyltoluene) > three sub-

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stitute (trimethylbenzenes) > para (p-xylene and p-ethyltoluene). Overall, all data of this paper need statistical evaluation providing uncertainties in processed data or the errors associated with data points in Figures and Tables. The comparison of data from different aromatic systems and the data interpretation should be based on statistical significance. The explanation of SOA yields and the processed data from analytical instrument are very empirical and needs better interpretation with rationales based on kinetic mechanisms in both the gas phase and aerosol phase. The authors should provide better atmospheric imprecation of the observation and the outcomes of this study based on SOA formation in ambient environments and the classification of aromatic hydrocarbons in current air quality models .

Comments:

1. Page 6, line 5-10. The SOA formation has been performed at very dry conditions (RH<0.1%), which is very different from ambient environment. The SOA formation can be affected by humidity. Particularly, heterogeneous reactions is sensitive to aerosol water content because some of carbonyls and epoxides can be hydrated with available water in aerosol and oligomerized. Such reactions are also influenced by aerosol compositions and the hygroscopic properties of aerosol. In addition to the reactivity of oxidized carbons in aerosol, the aerosol phase water can modulates the reduction of viscosity of aerosol media, which also affect aerosol growth. Thus, the order in aerosol growth determined at very dry conditions may be/may not be different from aerosol growth in higher humidities. The authors should discuss about the potential influence humidity on aerosol growth and the rank observed in this study.

2. 2nd paragraph, Section 2.2. The aerosol samples were evaporated at 600oC followed by impaction. Such high temperature promotes charring of organic compounds and is able to modify chemical compositions of organic compounds. This should be clarified.

3. For Table 1, the author need to provide the uncertainty associated with SOA yields.

Please provide the unit with variables instead of footnote. All Figures and Tables need the uncertainties or the errors associated with data.

4. Section 3.1 SOA yield. (a) For SOA yields, the authors employed the two product model that was derived by Odum et al. The experimentally observed SOA yield varies with VOC/NOx ratios and NO/NO2 ratios. The authors describe that HC/NO ratios range 11.1 to 171. Does the aerosol at HC/NOx = 11 have the same chemical composition of the SOA at HC/NOx=171 ? Although all experimental conditions fall into the high NOx regions but they are various. Please discuss about the potential effect of NOx on SOA formation within the experimental conditions of this study. (b) The HC/NOx ratios between aromatic systems in Table are not same. Without the rationale for the effect of HC/NOx on SOA yields, the rank of SOA production from different SOA loses its meaning. (b) SOA yields are influenced by the amount of initial hydrocarbon and its reaction rate. When the aerosol is quickly formed, the loss of gaseous oxidized carbons to the reactor wall becomes smaller (Ng et al, 2007). The authors should clarify weather aerosol yields between different systems are not biased due to the potential loss of gaseous compounds to the wall by different reaction rates and initial experimental conditions. (c) In addition to the kinetic reactivity of hydrocarbons, the determination of SOA yields are subjective to the duration of chamber operation. The authors need to explain how the yield of SOA was determined based on reaction time and aerosol growth.

5. Page 8, lines 10-15 and Figure 1. It seems that the substitute length also affects the yield of SOA (C8 vs C9). The data should be treated by the statistical evaluation.

6. Figure 2. Where are the actual data point from each aromatic hydrocarbon in Figure 2 ? Please include the maker for each data point and the uncertainty of data points.

7. 1st paragraph, Section 3.2.1. It is difficult to follow the description of mass fragmentation in the text. It would be better to organize mass fragmentation information using Table. How does the aerosol have carboxylic functional groups (CO2). Does carboxylic

acid form via gas phase oxidation of hydrocarbons or autooxidaiton in particle phase ? What are the precursor structures to produce carboxylic groups.

8. Line 20-21, page 10. “While m/z 43 (C3H+7) and 57 (C4H+9 20) are often considered as markers for hydrogen-like organic aerosol . . .”. What does “hydrogen-like organic aerosol” mean ? The explanation about mass fragmentation is unclear.

9. Last paragraph in section 3.2.1. The authors proposed that longer alkyl substitutes may not lower the oxidation per mass as further oxidation but observed the similar f44 and f43+57+71 of toluene suggesting unidentified oxidation. The interpretation of the analytical data is based on partitioning theory because authors’ interpretation focused on gas phase oxidation. The oxidized carbons such as carbonyl are reactive in aerosol phase and can be transformed into oligomeric matter. In the past, the characterization of SOA have shown that oligomeric matter was significantly contributed to aromatic SOA mass. The interpretation of the data here was very empirical. The authors needs to rationale for observed data with better interpretation based on kinetic mechanisms.

10. Page 8, line 30 - Page 9, line 2, for Figure 1. It is uncertain whether the one alkyl substituent on the aromatic ring is clearly separated from meta-positioned aromatics without statistical significance. 11. Section 3.2.2 (H/C vs O/C). The data points in Figure S6 are scattered. The reviewer is sure how the authors chose the representative point from each diagram. The difference between the representative point from each diagram should be statistically determined. Without statistical assessment, it is hard to conclude the fact but it looks that difference in representative (averaged) points between systems would be insignificant within standard deviation of scattered data except few systems.

12. 2nd paragraph, in page 13. The explanation about H/C and O/C ratio is empirical and need better interpretation in the point of kinetical mechanisms.

13. Atmospheric Implication section. The authors need to provide the implication of the observation of this study to ambient environments. It has been known that toluene

is the most abundant in urban areas where NOx and humidity are high. Can the observation of this work be applicable to ambient environments? In the current CMAQ, there are two class of aromatics: high and low yield aromatics. Toluene is currently in the group of high yield aromatics. How can the observation of this paper be applied to the current air quality model ? Is the classification of five groups of aromatics in this study meaning ? All chamber studies have been limited to high concentration of initial conditions (VOC and NOx) due to detection limit of analytical instrument. What is the implication of this work to the SOA in the low concentration environments (ambient air) ?

14. For Figure 5, the author could explain why the predicted density of 1,3,5-TMB is much lower than the measured density.

15. For Figure 6, the author should provide the uncertainty of VFR(end) values.

16. In the Table 1, the author should check the M0 value for 1215A, which is very high (M0=1501).

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