Reviewer #1

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 substitute (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.

The statistical evaluation is addressed in the revised manuscript and a detailed analysis of the statistical evaluation are included in the replies to Comment 5, 10 and 11. Additional mechanism discussion is included in the revised manuscript to provide interpretation for the results. See replies to Comment 9 and 12 for details. The implications of this work to ambient environments and air quality models is further enhanced as described in Comment 13.

A point by point reply to the reviewer is listed below.

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.

We agree SOA formation is potentially affected by humidity due to heterogeneous reaction. The current study provides a fundamental relationship among SOA formed from different aromatic isomers under dry conditions.

We add the following sentences in Page 19, Line 7 (end):
Previous studies found that the humidity insignificantly impacts SOA yield from aromatic hydrocarbons (Cocker, et al., 2001) or maintains the SOA yield relationship between isomers (Zhou, et al., 2001). Therefore, it is predicted that the observation found under dry conditions in this study, especially the molecular structure impact on SOA formation from different aromatic isomers could be extended to atmospherically relevant humidity conditions. However, recent studies observe that the hydration of carbonyls and epoxides could lead to further heterogeneous reaction and oligomerization (Jang, et al., 2002; Liggo, et al., 2005; Minerath and Elrod, et al., 2009; Lal, et al., 2012). It is possible that aerosol compositions and the hygroscopic properties could be altered after the heterogeneous reactions, especially under humid conditions. The impact of molecular structure impact on SOA formation under humidity condition needs to be further studied to extend the findings in the current work.

2. 2nd paragraph, Section 2.2. The aerosol samples were evaporated at 600°C 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.

The AMS used in our study followed standard measurement techniques for SOA studies. Heating in the HR-TOF-AMS is conducted under vacuum, which minimizes “charring” of the organic species. We add a “under vacuum” at page 7 line 12 (2nd paragraph, Section 2.2) for clarification. The sentence now reads

“The sample was vaporized by a 600 °C oven under vacuum followed by a 70 eV electron impact ionization.”

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.

We insert following sentence addressing SOA uncertainty in the methods section at Page 8 Line 9: “The uncertainty associated with 10 replicate m-xylene and NO experiments SOA yield is <6.65%.”

The standard deviations of O/C, H/C, \( f_{44} \), \( f'_{43} \), \( \delta_{O} \), and \( \text{VFR}_{\text{end}} \) are now included in the revised manuscript along with the standard deviations shown in the original manuscript for density.

We modified the manuscript to provide the unit with variables instead of footnotes as requested.
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.

Only ~10% of experiments have HC/NO larger than 60 ppbC:ppb. The majority of experiments have similar NO conditions. NO could impact SOA formation by either forming organic nitrate or reducing peroxide radical concentrations. First, aerosol at HC/NO = 11 ppbC:ppb may have slightly different SOA chemical composition at HC/NOx=171 ppbC:ppb due to a higher organic nitrate fraction. However, less than 5% of organic matter is organic nitrate in this study and therefore exerts little impact on overall yield and chemical composition. Second, lower HC/NO might lead to lower peroxide radical concentrations and therefore lower SOA yield. However, no significant correlations between SOA yield and radical concentrations are observed as discussed at Page 9 Line 11-15 and presented in Table S5. This shows the lack of correlation between radical concentration and yield. Therefore, NO is not a major factor to SOA yield within the experimental HC: NO range used in this study.

Seeded experiments to minimize gaseous compounds wall loss were conducted in our chamber experiment with no significant difference observed between the seeded and non-seeded experiment. This indicates that the gas-phase wall might not be expected to be significant for experiments in our chamber for this aromatic SOA study.

We add the following sentence at line 8 Page 6 in the revised manuscript.

Seeded experiments to minimize wall effects have also been conducted in our chamber experiment with no measurable difference observed between the seeded and non-seeded experiment.

We agree that SOA yields are subjective to the duration of chamber operation. In this work, SOA yield is calculated after 6-8 hours of photooxidation for each experiment. All the precursors studied have similar kOH (Table S1) or similar kOH[Precursor] (Li, et al., 2016). We selected comparable photooxidation time (6-8 hours) for all precursors and therefore the SOA yields are comparable.
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.

We agree with the reviewer that substitute length also affects the yield of SOA (C8 vs C9) as stated on Page 10, line 1-7. However, the difference caused by substitute length is less significant than substitute location as shown in Fig. 1. Differences in SOA yield due to length is within the SOA yield standard deviation (now shown). There may be differences among all one substitute aromatics, which is answered in detail in the reply to Comment 10. We add the following sentence at line 6 Page 10 in the revised manuscript. “However, the differences between xylenes and their corresponding ethyltoluenes are not statistically significant.”

Section 4 further discusses the differences associated with substitute length (original manuscript on Page 10, line 7): “These differences are explained by the proposed alkyl group dilution effect (Sect. 4).”

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.

The actual data points from each aromatic hydrocarbon in Figure 2 become obvious after adding standard deviation on both the x-axis and the y-axis as suggested in Comment 3.

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 autooxidation in particle phase? What are the precursor structures to produce carboxylic groups.

We add Table S6 to provide the requested peak information.

CO2+ is a common peak from AMS when measuring aerosol. It is less likely that CO2+ is associated with carboxylic functional group in this study. There are other possible CO2+ fragment sources. For example CO2+ may come from the oligomerization of small cyclic furanones described in earlier work (Li, et al, 2016).

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.

This is a typo. It should read “hydrocarbon-like organic aerosol” instead of “hydrogen-like organic aerosol”. An m/z 57 and m/z 71 in field studies or ambient atmosphere usually associate with hydrocarbon-like organic fragments, C6H9+ and C5H11+, respectively (Zhang, et al., 2005; Ng, et al., 2010). However, m/z 57 and m/z 71 in chamber studies, especially for ethyl and propyl substituted aromatics photooxidation, are majorly C3H5O+ and C4H7O+, which are oxygenated organic aerosol (OOA). Ng. et al (2010) developed f43 (majorly C2H3O+) and f44 (CO2+) for ambient OOA categorization without m/z 57 and m/z 71 since m/z 57 and m/z 71
are majorly HOA in ambient atmosphere. However, C$_3$H$_5$O$^+$ (m/z 57) and C$_4$H$_7$O$^+$ (m/z 71) should also be included beside C$_2$H$_3$O$^+$ in SOA chamber studies as OOA to compare the oxidation of different aromatic hydrocarbons. We replace Line 20-24, page 10 with sentences below:

While m/z 57 (C$_4$H$_9^+$) and m/z 71 (C$_5$H$_{11}^+$) are often considered as markers for hydrocarbon-like organic aerosol in ambient studies (Zhang et al., 2015; Ng et al., 2010), oxygenated organic aerosol C$_3$H$_5$O$^+$ and C$_4$H$_7$O$^+$ are the major fragments at m/z 57 and m/z 71, respectively, (Fig. S4, Table S6) in current chamber SOA studies, especially during the photooxidation of ethyl and propyl substituted aromatics. Therefore, m/z 57 and m/z 71 are also considered beside C$_2$H$_3$O$^+$ at m/z 43 in SOA chamber studies as OOA to compare the oxidation of different aromatic hydrocarbons.

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 f$_{44}$ and f$_{43+57+71}$ 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.

We suggest that longer alkyl substitutes may not lower the oxidation per mass by relying on both the observation in section 3.2.1 and the elemental ratio prediction method (alkyl dilution theory) in Discussion part (section 4). Higher OSc (lower H/C and higher O/C) is observed in longer chain single alkyl substitute aromatics than the alkyl dilution theory predicts from toluene data. Oligomerization, as suggested by the reviewer, consists of highly oxidized monomers (e.g. glyoxal) and could therefore also increase the overall OSc. Therefore, we add following sentence at Page 12 Line 17:

It is also possible that oligomerization from highly oxidized carbonyls contribute more to the SOA formation from aromatics with long chain alkyl substitute.

Previous theoretical studies predict that alkyl substitute plays a role in oligomerization, e.g. glyoxal favors acetal oligomerization and methylglyoxal prefers aldol condensation to form oligomers (Barsanti and Pankow, 2005; Krizner, et al., 2009). However, these two oligomerization kinetic mechanisms produces products with similar formulas. No matter which mechanism is favored, SOA elemental ratio should not be affected. Therefore, the percentage of oligomerization to other reaction mechanisms rather than the difference in oligomerization mechanism seems a better explanation for the observation in SOA formed from long chain single alkyl substitute aromatics.

Therefore, we also add the following sentences in the Discussion section at Page 18 Line 6:

It is also possible that oligomerization from highly oxidized carbonyl component might be more favored for long chain single alkyl substituted aromatics.
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. We agree that one alkyl substituent on the aromatic ring SOA yield is not clearly separated from meta-positioned aromatics in Figure 1. However, it can be concluded from chemical composition and volatilities (VFR) that one alkyl substitute aromatic hydrocarbon is more oxidized than meta-positioned aromatics. The statistical parameter for the curve fitting is provided in the revised Table 2 as mentioned in the reply to Comment #5. It can be clearly seen that MSRE is much larger in one substitute aromatic fitting than meta-aromatic fitting. This indicates potential SOA yield differences within the one substitute aromatic hydrocarbons along with observed SOA chemical composition differences among one substitute aromatic hydrocarbons (Sections 3.3.2 and 3.2.3). Further studies are warranted to provide more information on SOA yield. At this time, we fit one alkyl substitute aromatics and meta-position aromatics separately.

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.

The scattering in Fig S6 is majorly due to a few early period data at the low mass loading when aerosol just starts to form, which have higher H/C and lower O/C than the latter time. However, o-xylene data contains data that does not follow the aerosol aging trend observed for the other isomers. Therefore, we delete the obvious outliners in Fig S6-f-o-xylene and Fig S6-6 o-Ethyltoluene and adjust Fig. 3, Fig. 4 and Fig 7 accordingly. We provide standard deviation for H/C, O/C and OSc in Fig 4, Fig 7b and supplemental materials as answered in question 3.

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. The kinetic parameters (kOH) for initial oxidation of ortho, meta and para containing aromatic hydrocarbons are all similar (Table S1). This suggests there may not be a significant difference among all these isomers from kinetic perspective. We draw the conclusion in the paper empirically based on what we observed in our measurement.

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)?

We address the relevance of NO\textsubscript{x} conditions in current study to the ambient atmosphere at the beginning of Atmospheric Implication section. Toluene remains the second highest SOA yield (lower than benzene, especially at higher mass loading, see Li, et al., 2016) precursor according to our earlier work (Li, et al., 2016); however, it is not a target aromatic in current studies. This paper focuses on isomer or molecular structure impact on SOA formation. Current work provides sufficient data to distinguish among para, meta and ortho position containing aromatics and therefore is able to subcategorize the previous “low” and “high” yield aromatics (e.g. only one p-xylene data point in Odum, et al., 1997). The five groups of aromatics and their two product modeling curve fitting provide the practical parameter for more detailed SOA modeling. All SOA yield data provided is under more atmospherically relevant NO\textsubscript{x} conditions than the earlier “high” and “low” yield work improving reliability of fit parameters as inputs to atmospheric models. Study at the lower atmospheric NO\textsubscript{x} concentrations provides yields twice as high as those from earlier work at very high NO\textsubscript{x} concentrations greatly impacting the model predictions from model prediction (e.g., CMAQ).

We add following sentences to emphasize the importance of this study to model and ambient environment at Page 19, Line 7:

Moreover, the five subcategories of aromatics and their two product modeling curve fitting parameters in this work at more realistic NO\textsubscript{x} loadings provide a more precise prediction of SOA formation form aromatic hydrocarbons under atmospheric conditions.

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

Thank you for this observation. In fact we observe density underestimation in all meta position containing aromatic hydrocarbons including \textit{m}-xylene, \textit{m}-ethyltoluene and \textit{1,3,5}-TMB. The underestimation is associated with a bias in elemental ratio analysis from AMS as discussed in Li, et al., 2016; Nakao, et al., 2013.

We add following sentences in Page 16 Line 13:

A comparatively large negative error is found in meta containing aromatic hydrocarbons including \textit{m}-xylene, \textit{m}-ethyltoluene and \textit{1,3,5}-trimethylbenzene. It is noted that there should be more alkyl substitutes in SOA formed from meta position aromatics than other aromatics since meta position alkyl substitutes are more likely to participate into SOA products than other aromatics (Section 3.2.1 and Section 3.2.2). Previous work suggests that the increase of methyl groups could lead to a change in several key organic fragments (e.g., CO\textsuperscript{+}, CO\textsubscript{2}\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+}) thereby altering the default fragment table for elemental ratio analysis. This agrees with the density underestimation in SOA formed from meta position aromatics and supports the preference of meta position alkyl substitute to SOA products.

15. For Figure 6, the author should provide the uncertainty of VFR\textsubscript{end} values.

We add uncertainty of VFR\textsubscript{end} values in revised manuscript
16. In the Table 1, the author should check the M0 value for 1215A, which is very high (M0=1501).
It should be 151. Fixed.

Reference


