Referee's Comment in Italic Font; Author's response in Red and Manuscript revision in Blue without Italic Font.

In this manuscript, the authors Li et al. studied formation of secondary organic aerosol from aromatic hydrocarbons, quantified the formation yields and investigated the chemical and physical properties in order to infer the differences in underlying mechanisms between different molecular structures. The hydrocarbons studied spanned from C7 to C9 and from 1 to 3 alkyl substitutes on the aromatic ring. These hydrocarbons are important for urban areas, and have not been well studied compared to benzene and toluene. The authors presented a variety of measurements (yields, aerosol mass spectrometer, density, volatility) conducted with state of the art instrumentation. The experiments are well designed and the manuscript is generally well written with relatively minor typos. However, I believe that the data interpretation is weak and it is very difficult to draw conclusions based on the data presented, especially with regards to SOA yields. I recommend major revisions before the manuscript can be considered for publication in ACP.

Major comments:

1. The biggest weakness of this manuscript is that the SOA yields are quite varied and many of the conclusions drawn by the authors are not very convincing. In Fig. 1, there are no error bars shown for the individual yields and Mo, and for the empirical fits. For example, the authors conclude from this figure that ortho compounds yields are similar and regression was performed on the combined data set. However, one could easily argue that o-xylene yields and m-ethyltoluene yields are similar and should be fitted to the same curve. Also, one of the major conclusions about ortho-compounds having higher yields is very weak. At atmospherically relevant Mo (Mo < 40 ug/m3), the yields are all very similar. Any differences in mechanisms do not translate to significant differences in formation yields (smaller than experimental uncertainties in yields).Therefore, one can argue that molecular structure plays a relatively minor role.

We insert following sentence in method at Page 8 Line 9 to provide error bar for yields, as what replied to reviewer 1 in Comment 3: The uncertainty associated with 10 replicate m-xylene and NO experiments SOA yield is <6.65%.

We agree that yields are hard to distinguish by only looking limited datasets at a low mass loading (eg. M_o < 40 ug/m^3). Our current fitting parameters already provide a good estimation for SOA formation under low mass loadings.

The argument about the minor role of molecular structure is not true as significant differences are suggested by the physical properties and chemical composition trend. The categorization of aromatic hydrocarbons for yield fitting are based on the measured data and the molecular structures such as the relative position of substitutes and the number of substitutes. Our yield categorization agrees with the observation found in later physical properties and chemical

composition trend part. For example, *o*-xylene is found to be more oxidized than m-ethyltoluene according to chemical composition (Fig. 2-4) and therefore it is reasonable to be categorized into different group.

2. Another critique I have about this manuscript is the lack of mechanistic insights revealed by the experiments. I read the earlier paper on carbon dilution theory by the same authors, and found that the AMS data were very useful in identifying the general effect: methyl substituents divert OH oxidation from the ring, leading to less oxidized SOA components. A similar approach is used here but much less effectively. It is unclear from the proposed theory why the position of the alkyl substituents matters. Again, the authors claim that SOA from ortho-compounds is more oxidized than that from para- and meta-compounds. Why is that the case? The authors can make this manuscript much stronger if they can propose mechanisms along with careful experimental work to support them. Since the theme of the paper is molecular structure, I think these explanations are very important and deserve more attention. Can the authors propose any mechanisms (does not have to 100% proven, only needs to be plausible) that may be consistent with the results? AMS data are not suitable for resolving isomer-specific differences. More speciated measurements (such as LC or GC/MS) will provide more insights.

We provide the mechanism leading to the difference in SOA formation from meta, para and ortho position in Section 3.2.2 Page 11, Line 20-Page 12 Line 10. Some mechanisms are also added as mentioned in the reply to Referee #1's Comment 12.

"A robust prediction of SOA H/C and O/C trends for longer (C2+) alkyl substituted aromatics based on the methyl substituted aromatics will suggest a similarity in the role of methyl and longer alkyl to SOA formation; an underestimation or overestimation will indicate different oxidation pathways for aromatics with differing alkyl substitute length." as described in the reply to Regeree #2's Comment 1-(4). The proposed theory is to demonstrate the impact of alkyl substitute length. The impact of position is filtered out since aromatics with similar alkyl location are used for the prediction as stated in Page 17 Line 21-24.

Following sentences is added on Page 19 Line 1:

"It is possible due to the alkyl substitute location impact on the further oxidation of five-membered bicyclic radicals. Different carbonyl compounds can form as the ring opening products from the dissociation of five-membered bicyclic radical. It is assumed that oligomerization of these carbonyl compounds can contribute to SOA (Li, et al., 2016). Aromatic hydrocarbons with para position alkyl substitute tend to form more ketone like dicarbonyl compounds than other aromatics. Ketone might contribute less to oligomerization formation compared with aldehyde as suggested in Li, et al (2016)".

The following sentence is added on Page 19 Line 2:

It might be due to a higher percentage of carbonyl with alkyl substitute formed during the oxidation of meta containing aromatics (e.g. methylgloxal, 2-methyl-4-oxopent-2-enal), which

contributes to oligomerization and thereby SOA formation.

More speciated measurements are warranted in future studies

3. Similar to my previous comment (and other reviewers' comments), the AMS does not really provide information about specific chemical composition. For example, the statement in Section 3.2.2 "SOA components from all isomers are located in between slope= −1 and slope= −2 lines suggesting that SOA from these aromatic hydrocarbons is composed primarily of acid (carbonyl acid and hydroxycarbonyl) and carbonyl (ketone or aldehyde) like functional groups". The elemental ratios does not suggest that the SOA *contain* these functional groups, but rather they suggest that the SOA composition *evolve* as if they were adding these function groups. This is a very important difference that should be noted throughout the manuscript. The AMS elemental ratios help elucidate the bulk composition and evolution, not the specific chemical composition and mechanism, as suggested by the manuscript. I believe that AMS was useful in showing O/C changes from benzene to toluene to xylenes, but the specific isomeric differences in this paper are not convincingly argued in this manuscript.

We agree that elemental ratios suggest that the SOA composition *evolve* as if they were adding these function groups. We will delete the following sentences:

"SOA components from all isomers are located in between slope=-1 and slope=-2 lines (Fig. S6) suggesting that SOA from these aromatic hydrocarbons is composed primarily of acid (carbonyl acid and hydroxycarbonyl) and carbonyl (ketone or aldehyde) like functional groups. The elemental ratio of SOA from p-xylene photooxidation was nearly located on the acid line (slope=-1)"

All the isomers start from the same precursor location in the Van Krevelen graph and therefore the difference in aerosol phase composition indicates the difference in oxidation. We agree that AMS is not specially for the detection of detailed species. However, the overall chemical composition provides the oxidation state of SOA and can be used to interpret the different extend of oxidation and related mechanisms.

4. It is not clear to me why the authors chose to conduct the experiments under low NOx conditions. These highly substituted aromatic hydrocarbons are emitted in urban areas, and have lifetimes around 1 day or so. Even in rural areas, the NO levels are quite high, resulting in at least 50% oxidation by RO2+NO pathway (see Ortega et al., ACP, 2014). One could argue that the experiments conducted are still experiments with NOx (unlike HO2 dominated experiments). However, the HC/NOx ratios are not fixed (ranges over 1 order of magnitude), bringing into question the relative role of NOx. Why aren't the experiments conducted with a fixed HC/NOx ratio, or with NOx so high that it is not limiting?

The low NO_x we mentioned here is compared with earlier work as described on Page 4 Line 9. The NO_x range we use is comparable to urban atmosphere. Range is clarified in revised manuscript (See reply to Referee #2 Comment 1-(1)) and is not the major driver of the

differences in SOA formation between the isomers. There might be a difference in the so called NO range when RO_2+HO_2 is dominated (See reply to Referee#2 Comment 1-(1)).

NO is depleted very fast at the beginning of the photooxidation and HO_2 and RO_2 reaction is dominating the major period of the photooxidation(see Reply to Referee #2 Comment 1-(1)).

Other comments:

5. Pg 5 line 2: what is the significance of the furanone relative abundances? Does it point to a particular propensity of fragmentation and/or SOA formation from one particular molecular structure?

The abundances of these products are

1.4 (± 0.39)% of 3-methyl-2,5-furanone is observed in toluene oxidation (Forstner et al., 1997);

7.4 (±3.8) % 3-ethyl-2,5-furanone in ethylbenzene oxidation (Forstner et al., 1997).

The reference here is to give an example of molecular structure impact on aromatic oxidation products. The observed results in earlier work are not directly comparable to our work and therefore the exact abundance is not included in the manuscript.

6. Pg 9 line 20: The parameters are for fitting purposes only, and are semi-empirical at best. Because the Odum 2-product equations are non-linear, alpha and K are coupled parameters (i.e. one can use a higher alpha and lower K and still get a decent fit to the experimental data). Therefore I suggest the authors not derive insights into relative volatilities from the fitted parameters.

The semi-empirical two product model is based on the fundamental theory gas-particle partitioning. α_1 and K have different impact on the curve and the pair we reported here is based on a best fit. It is partially empirical because two lumped groups are assumed. This model fitting parameters can't tell us which detailed species are favored in SOA from different aromatic. However, the difference among α and K provide the general information about the high volatility and low volatility products. Therefore, we would like to keep these implications from the yield parameters.

7. Pg 14 line 2-11: Is it possible that photolysis of aromatic carbonyls is playing a role in affecting the H/C of SOA?

It is possible. However, aldehydes higher than formaldehyde appear to react dominantly with OH radicals (Atkinson and Arey, 2003).

8. Table 3: It seems to me that the correlations are quite weak (around 0.5 at best) and the p-

value is always greater than 0.05, sometimes much greater. From a statistics point of view, the correlations are inconclusive. I suggest rewording in main text to call these "weakly correlated". (". . . best correlated. . ." is misleading).

Done.

Use "correlated" instead of "best correlated". on Page16 Line 7

Delete "strong" before "correlation" on Page16 Line 25

Delete "well" before "correlated" on Page16 Line 2

9. Sect 3.3.2: Can the authors isolate the effect of kinetics and molecular structure by comparing VFR at the same extent of reaction?

All experiments are conducted under comparable kinetics and similar extent of reaction. (See k_{OH} discussion in the reply to referee #1 Comment 4 last part).

10. The authors alluded to the carbon dilution theory they proposed in an earlier publication (Li et al., 2015a) many times throughout the manuscript without explaining the theory. This theory is relatively novel and is not well known. Therefore I suggest adding a short section to explain the theory early on in the manuscript and show how this will be applied to the molecular structures studied in this work.

Following sentence is added in revised manuscript on Page 17 Line 17 to add a short section to explain carbon dilution theory:

Carbon dilution theory proposed by Li et al (2016) successfully explain that methyl group impacts remain similar in SOA elemental ratios as in the aromatic precursor. The chemical composition of SOA formation from alkyl substituted aromatics is predicted by simply adding the alkyl substitute into the chemical composition of SOA formed from pure aromatic ring precursor (benzene).

We also add explanation in the revised manuscript to show how the theory is applied to this work. Please see reply to referee #2 1-(4)

Technical comments:

11. Pg 2 Line 5: eight to nine carbon should be "C8- to C9-" or "eight- to nine-carbon"

Done. Changed "eight to nine carbon" to "eight- to nine-carbon"

12. Pg 2 Line 23 IPPC should be IPCC

Fixed.

13. Pg 2 Line 26 What does growth potential mean?

Changed "have larger growth potential than biogenic aerosol sources" into "are more likely to increase"

14. Pg 3 Line 14 Toluene and C8 aromatics do not dominate aromatic SOA, because they are not SOA themselves, but are precursors to SOA. I suggest rewording this sentence.

Changed "Toluene and C8 aromatics dominate anthropogenic SOA" into "Toluene and C_8 aromatics dominate the anthropogenic SOA precursors".

15. Pg 5 line 12: references to mass loading (Shilling et al. 2009 and Pfaffenberger et al 2013) and NO effect (Eddingsaas et al. 2012) on SOA formation are for a-pinene, not for aromatics. The authors should clarify that point.

Add "(a-pinene)" after literature in revised manuscript to clarify the SOA precursor.

16. Pg 6 line 13-20: are the chemicals used without further purification?

Yes.

17. Pg 7 line 8-9: "Volume fraction remaining" should be all capitalized

Done.

18. Pg 7 line 13-14: clarify that fx is the *mass* fraction of organic signal at m/z = x

Done.

19. Pg 7 line 19: "squirrel" should be capitalized

Done. Change to "Squirrel 1.56D / Pika 1.15D"

20.Pg 8 line 10: organic mass concentration should be Mo (o for organics), not M0. M0 would suggest that it is an initial mass concentration

Fixed.

21. Pg 10 line 17: what does the n stand for? It might be more useful to use n to denote the carbon number of the alkyl substitute. So for m/z 57 is derived from an ethyl-substituted aromatic, so n would be 2, and the formula would be C_(n+1)H_(2n+1)O+.

Add "n =carbon number of the alkyl substitute" after $C_nH_{2n-1}O^+$

The formula should be $C_nH_{2n-1}O^+$ while using n to denote the carbon number of the alkyl substitute.

21. Pg 10 line 21: "hydrogen-like organic aerosol" should be "hydrocarbon-like organic aerosol"; it seems quite obvious to me that it is not possible to have a C3H7 or C4H9 fragment from aromatic compounds here. Even isopropyl benzene does not yield C3H7 upon EI fragmentation (see NIST spectra). I suggest removing that explanation to make it more concise.

Fixed. "hydrogen-like organic aerosol" should be "hydrocarbon-like organic aerosol"

We want to keep the explanation to clarify the different between chamber conditions and ambient.

22. Pg 11 line 25: This section is very hard to follow. Is there a proposed mechanism of how an oxidation product of aromatic compounds can produce m/z 43 that is also consistent with proposed carbon dilution theory? It would be very beneficial here to use a figure to illustrate the key points.

We add Figure in supplemental materials to demonstrate the proposed mechanism. (New Fig. S7)

23. Pg 12 line 1: do the authors mean ROOH here? The bicyclic peroxides formed in aromatic oxidation are internally bridged, and are therefore ROOR, not ROOH (or hydroperoxides). I presume that in the presence of NOx, RO2+HO2 is negligible and ROOH is not formed. Also, is there a reference for peroxides not yielding CO2+ from the AMS literature?

Change "bicyclic hydroperoxides" to "bicyclic peroxides"RO_2+HO_2 dominated since ozone is formed (see Reply to Comments 4).

CO_2^+ can come from carbonates, cyclic anhydrides and lactones (McLafferty and Turecek, 1993). This indicates that the CO_2^+ should come from a fragments with -O-C-O- structure. Neutral CO_2 should be formed before EI to generate CO_2^+. Thermal decarboxylation is a possible pathway to form CO_2 from compounds such as aliphatic acid (McLafferty and Turecek, 1993).We hypothesize that it is impossible to form a neutral CO_2 if CO_2^+ comes from -C-O-O-. We do not find a reference to support that peroxides not yielding CO_2^+ from the AMS.

We deleted "More importantly, the difference in f44 implies that substitute location influences the further reaction pathway to form CO_2^+ since CO_2^+ is not readily available from bicyclic hydroperoxides." Add following sentences to demonstrate the source of CO_2^+ on page 11 Line 26.

CO_2^+ are generally formed during MS electrical ionization from carbonates, cyclic anhydrides

and lactones (McLafferty and Turecek, 1993) indicating that the CO_2^+ is associated with -O-C-O- structure. Within the AMS, the CO_2^+ is also associated with decarboxylation of organic acids during heating followed by electrical ionization of the CO_2. We hypothesize that CO_2^+ formation from bicyclic peroxides is insignificant since CO_2 loss is not expected to come from -C-O-O- structure during thermal decomposition. Therefore, it is the reaction products of bicyclic peroxides that lead to the formation of CO_2^+ and the difference in f_{44}.

24. Pg 13 line 8: "The current study concentrated on" should be "The current study concentrates on"

Fixed.

25. Pg 17 line 20: the chemical formula C2H2n+1 seems wrong

Fixed. It should be C_nH_{2n+1}

26. Figure 2: there should not be a continuous scale for molecular structure; Also for all the figures, the experiment numbers should be noted as such. Otherwise the numbers do not mean anything to readers

Used color legend instead of color scale in revised manuscript.

27. Figure 4: can the bars be color coded to correspond to those in other figures (e.g. Figs.5 and 6)?

Done