

## ***Interactive comment on “Impact of molecular structure on secondary organic aerosol formation from aromatic hydrocarbon photooxidation under low NO<sub>x</sub> conditions” by L. Li et al.***

### **Anonymous Referee #3**

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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

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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 ( $\text{Mo} < 40 \text{ ug/m}^3$ ), 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.

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 be 100% proven, only needs to be plausible) that may be consistent with the results? AMS data are not suitable for resolv-

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ing isomer-specific differences. More speciated measurements (such as LC or GC/MS) will provide more insights.

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.

4. It is not clear to me why the authors chose to conduct the experiments under low-NO<sub>x</sub> 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 RO<sub>2</sub>+NO pathway (see Ortega et al., ACP, 2014). One could argue that the experiments conducted are still experiments with NO<sub>x</sub> (unlike HO<sub>2</sub> dominated experiments). However, the HC/NO<sub>x</sub> ratios are not fixed (ranges over 1 order of magnitude), bringing into question the relative role of NO<sub>x</sub>. Why aren't the experiments conducted with a fixed HC/NO<sub>x</sub> ratio, or with NO<sub>x</sub> so high that it is not limiting?

Other comments:

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

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molecular structure?

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.

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

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).

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

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.

Technical comments:

Pg 2 Line 5: eight to nine carbon should be “C8- to C9-“ or “eight- to nine-carbon”

Pg 2 Line 23 IPPC should be IPCC

Pg 2 Line 26 What does growth potential mean?

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.

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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.

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

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

Pg 7 line 13-14: clarify that  $f_x$  is the \*mass\* fraction of organic signal at  $m/z = x$

Pg 7 line 19: "squirrel" should be capitalized

Pg 8 line 10: organic mass concentration should be  $M_o$  (o for organics), not  $M_0$ .  $M_0$  would suggest that it is an initial mass concentration

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  $C_{(n+1)}H_{(2n+1)}O^+$ .

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  $C_3H_7$  or  $C_4H_9$  fragment from aromatic compounds here. Even isopropyl benzene does not yield  $C_3H_7$  upon EI fragmentation (see NIST spectra). I suggest removing that explanation to make it more concise.

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.

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  $NO_x$ ,  $RO_2+HO_2$  is negligible and ROOH is not formed. Also, is there a reference for peroxides not yielding  $CO_2^+$  from

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the AMS literature?

Pg 13 line 8: “The current study concentrated on” should be “The current study concentrates on”

Pg 17 line 20: the chemical formula  $C_2H_{2n+1}$  seems wrong

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

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

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