

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 #2

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The manuscript presents information on yields for the photooxidation of single ringed-aromatic structures. The senior author has been measuring yields from aromatic hydrocarbons (AHCs) for more than 15 years and is well versed. In this particular manuscript, the structure of the aromatic hydrocarbon (AHC) has been varied to examine differences in the organic aerosol (OA) yield. Thus, a series of 12 alkyl-substituted C8 and C9 AHCs have been examined. For these experiment, the aerosol yield has been determined using the Odum two-product model. Other OA parameters examined include the ratio of aerosol mass spectrometry (AMS) peaks attributed to OA, the OA oxygen-to-carbon (O: C) ratio, the oxidation state (OS), density, and volatility. The authors conclude that changes in the OA chemical composition and volatility influences

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the yield typically by increasing the mass for increased oxidation. The authors also consider the atmospheric implications of this study.

The study addresses an issue of perhaps abstruse importance. The oxidation of alkyl-substituted AHCs and the formation of secondary organic aerosol (SOA) has been examined extensively over the last 20 years and this work appears to cover some old territory. Many of these topics were addressed in Odum et al. 1997a, b (authors' references) and the present manuscript provides a bit more insight. Admittedly, the AMS was not around and the aerosol density from the volume distribution was considered to be unity in the 1990s. However, this work also represents a step backwards. Whereas Odum et al. 1996, 1997a sought to simplify aerosol yields, this work goes in the other direction and makes an argument (at least implicitly) that the yields should be addressed more precisely, a contention that I don't feel has been justified (see Table 2). That said, the experiments appear to have been carefully performed and there certainly are enough of them. Unfortunately, the initial conditions are all over the map and makes it very difficult to get a sense of the reproducibility of a given experiment. Virtually, nothing is said about uncertainty.

My major substantive comments regarding the manuscript are as follows: (1) these experiments hardly qualify as being under low NO_x conditions. The removal of RO₂ radicals competitively by NO or RO₂ determines the regime that the reaction is in. I would consider the low NO_x regime as conditions where the RO₂ radical-radical reactions become more important than the NO reaction. As a rule of thumb, I would say that this is certainly at no more than 5 ppb of NO for the conditions of these experiments depending, of course, on the specific RO₂ radicals from the precursor AHC. (2) The version of SAPRC referenced to Carter and Heo (2013) is specifically geared to ozone prediction, that is, conditions where NO_x dominates early product generations (two, at most three). As stated in Carter and Heo, (2013; Atmospheric Environment) SAPRC-11 is not geared for PM predictions. For this to be the case, the importance of RO₂ + RO₂ reactions should be adequately predicted as should the SOA mass. That

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is the point of the model and to predict radical concentrations as they were an end in themselves. The experimental SOA values could then constrain the model. That said, I question how well SAPRC-11 predicts radical concentrations under low NO_x conditions. (3) Several sections need a complete writing overhaul. Section 3.2.1 is barely comprehensible. Many sections in the Results and Discussion presents data (e.g., S6) as if they were self-interpretive. The manuscript is written for the audience being other scientists in their research group. There is considerable jargon and the writing is highly imprecise hardly worthy of a scholarly journal. (4) To the extent possible, the authors should give a greater physical interpretation of the metrics they present in Section 3. Some are obvious (e.g., Sec. 3.2.2) others far less so (Sec. 3.2.1; 3.4).

Some comments and suggestions:

P5, L27. The goal of the research states the obvious. Perhaps more insight will motivate the reader to actually read the paper.

P6, L7. UV-350 bulbs have considerable radiation in the UVB which accentuates the photolysis of carbonyl compounds to a considerable extent which accelerates PM formation by increasing the radical concentrations. Thus, the two-product parameters developed (Table 2) may not be applicable for predictions of ambient AHC PM (Tables 2 and S3)

P6, L18. Provide a chemical name for the standard OEKANAL.

P6, L23. How is mixing achieved in this large chamber; fan, diffusion, other?

P7, L10. Calling a bunch of peaks attributed to innumerable organic compounds completely fragmented by 70 eV electrons as a chemical composition stretches the concept of molecules beyond recognition. I would hardly call this metric a chemical composition in any traditional sense. Perhaps the word "effective" could be incorporated to indicate that this is simply a parameterized metric.

P7, L23. The authors should reference the 2013 Atmospheric Environment article by

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Carter and Heo rather than the CARB report. The article went through peer-review and should be more reliable.

P8, L11. The sentence is unneeded; include the information in the caption.

P9, L3. To use the word "claimed" in a pejorative fashion is particularly bad form. If you believe the statement in Odum et al. is wrong, simply state it.

P9, L14. Delete the sentence. The supplement does nothing to support the sentence other than to simply repeat itself and refer to a paper in preparation. Nothing is gained by including the sentence in the paper or in the supplement.

P9, L23. Why is the assumption needed? The two-product model is just a fitting exercise anyway.

P9. It might be worthwhile to examine partitioning using a volatility basis set (VBS) to see if any insight could be gained beyond the standard two-product fit which at this point is rather dated. This might provide a more useful metric for describing the partitioning of the AHC products.

Sec 3.2.1. This section suffers from a lack of an understandable interpretation of the various fragments from the AMS output and their combinations into the combined metrics (e.g. Eq 1). An annoying aspect of this section is the comparison with other work before any interpretation is provided (e.g., P11, L5, 16; P12 L6, 25,....). How do we even know that the conditions are applicable between these experiments and the ones being compared to?

P13, L7. LV-OOA and SV-OOA are presented both undefined and without context.

P13, L8. The sentence as written belongs in the introduction. The intent of the sentence needs a rationale from the data. It is not self-evident.

P14, L21. "a more accurate metric. . ." More accurate than what?

P16, L1. Eliminate first name for Borrás.

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P17, L15. Use of the term “theory” (in any scientific sense) strikes me as somewhat pretentious. I would consider it as more of a conjecture.

P18, L8-16. What does the term “extremely low” mean? Provide a value for comparison. I would characterize most of this part as speculation. Also, experimental limitations in Forstner et al., 1997 (their specific quartz filter configuration) suggested that the furan-type compounds were in the particle phase but were almost certainly in the gas phase. The metrics in the present paper refer only to particle phase OA. The reference should be avoided here.

Section 5. I seriously doubt that any of these parameterizations would appear in any wide-used air quality model. I would consider the work mainly for academic purposes.

P19, L2. Replace “entend” with “extent”.

P19, L3. Nothing is “proved” here. The work simply provides “evidence for”.

P25, L8. Replace the ACPD manuscript with newly published ACP paper.

Table 1, S2 and text. How many AHCs were studied: the text say twelve AHCs (P5, L7), Table 1 gives ten AHCs, and Tables 1 and S2 together give fourteen. Which is the right number? (For good measure, Figure 6 shows eleven precursors.)

Table 3. What’s the point of the table if the p value are greater than 0.05. Certainly, the p-value for VFR and k (OH) is not zero.

Figure 1. The final points control the shape of the curve. The data below 20 ug m⁻³ would be of most interest for atmospheric applications.

Figures 2, 3, 7. Am I missing something? Why are there no symbols for the values; is there that much uncertainty? The use of colors for the precursors in Table 2 is particularly annoying. Are not words sufficient without colors?

In Figure 4, what are the estimated uncertainties in the model-generate radical concentrations. Carter and Heo, 2013 suggests that these could be substantial.

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Table S3. How about the C9-trimethyl compounds studied? Why not put the parameters obtained from the TMB compounds in the table? It would also be informative to include the data for toluene (which must have been studied at some point) for comparison with the other single position substituents, ethylbenzene and n-,i-propylbenzene.

Table S4. The value of this table for predicting radical concentrations is very limited as noted above. It may be useful for urban NO_x conditions but not where RO₂ + RO₂ is the dominant source of the aerosol. It doesn’t surprise me that the p-values for virtually all comparisons in S5 are no different than the null hypothesis.

SI Table 3 should be Table S6. Use lower case k in the table.

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