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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation of Highly Oxygenated Low-Volatility Products from Cresol Oxidation" *by* Rebecca H. Schwantes et al.

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Response to Review 1

Comment: "The authors present a mechanistic study of toluene photooxidation. They focus on the chemistry of first and higher generation products form toluene photoxidation. As analytical tool they apply CF3O- CIMS. The results are compared to MCM3.31; and missing parts according to the new results were added /modified in two steps. These model improvements led to better consistency between the model results and measurements. Quantification was in parts inherently limited by absence of suited calibration compounds. Very positively, the authors put some efforts in characterizing the sensitivity of their CIMS for the expected compounds and compound classes. The authors also show the importance of higher generation product to SOA formation. The

results are new and interesting, and as toluene is an abundant aromatic VOC, they are an important contribution for understanding VOC degradation and SOA formation in the atmosphere. The very interesting paper is well structured, and overall well written. However, I had some difficulties to follow some of the parts in the experimental section. I have the impression that this did not depend so much on the level of details that are given, but on notations and "unlucky" formulations. I think with a little effort that could be improved easily. I will list some examples below."

Response: Thank you for the helpful comments and suggestions. As suggested, we have edited the experimental section to make it clearer. We have attached as a supplement a pdf file including a comparison between the ACPD version and the edited version for ease of viewing changes.

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Comment: "The scope of abstract and conclusion are not quite balanced. While the abstract focus more on o-cresol and benzaldehyde, the conclusion focus solely on 3-methyl catechol."

Response: We have revised the conclusion to better balance the focus.

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Comment: "p.1, line 10: this sentence is somehow askew. It requires either reformulation or a reference to the yield 0.7, like "reported yield" or so."

Response: We have added "reported yield" and included a reference.

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Comment: "Section 2.1 Experimental Design: here some info about the light source(s) is (are) missing: You refer to H2O2 photolysis as OH source on one hand, but later to jNO2 as a measure of photooxidation and a light source to prevent NO3 formation. I suggest, shortly to describe the main features / spectral dependence of your light

source."

Response: Thanks for this observation. We have added more description about the light source used in the Caltech chamber. Also we listed more photolysis rate constants and provided more description about how NO3 photolysis impacts the results in this study.

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Comment: "p.5, line 1f: this is difficult to follow. Why do you speak about complex interaction when you obviously address the analyte*CF3O complex. Similar the analyte*F- adduct is formed by F transfer, but formation process and result are not identical. Also p.5, line 25 ff: "Traditionally, an analyte (A) is detected either at the F^- transfer reaction (A+19) or complex formation (A+85)." Probably, better "detected" as "F- adduct" or "CF3O- complex"?!"

Response: Thanks for this observation. We have restructured this section and also revised the terminology we are using to make this clearer. As recommended, we revised the labeling to separate the terminology used for the formation process and the resulting ion. We also added in more reference to the reactions (R1-R6) to further define and remind the reader of the terminology used.

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Comment: "p.5, line 8: is the 500 ml glass bulb the FTIR cell ?"

Response: We apologize for the confusion. It is a separate glass bulb. We have revised this section to make this clearer.

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Comment: "p.5, line 14ff: I don't understand what are result and consequence from these comparisons. Please, clarify."

Response: Thanks for noticing this. We have revised this paragraph and the following

paragraph to make the results and consequences for these comparisons clearer. In summary: There is only one study (Etzkorn et al. 1999) quantifying o-cresol with FT-IR. o-cresol is difficult to quantify because it is easily lost to surfaces, so we wanted to independently verify the Etzkorn et al. 1999 results. Since there are no similar studies for o-cresol, we compared the m-cresol results from Etzkorn et al., 1999 to those from PNNL.

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Comment: "p.5, line 20: I guess the bulb was meanwhile empty of o-cresol?"

Response: We have revised the text to be clearer. In summary: The FT-IR cell was filled with o-cresol. Then over more than an hour sequential FT-IR measurements were performed to monitor the loss of o-cresol to the glass cell walls. —

Comment: "p.5, line 28: it would be helpful to mention that "your" purified air is somewhat humid (RH?). Or is it O2 in air vs N2 that makes the difference?"

Response: We have removed this sentence and instead only referenced Table 2. We have also revised Table 2 and added in a note describing the approximate RH levels in the dry N2 versus purified air.

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Comment: "p.5, line28: "Likely the presence of water destabilizes the molecular ion formed from $CF3O^-$ ionization leading to more fragmentation." I guess, you mean that the presence of water affects F- transfer adduct most?! Please clarify."

Response: We have revised this idea throughout the methods section to make this clearer. We have also decided to explain the F- transfer adduct as a fragment itself.

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Comment: "p.6, line4ff: I find the use of the word "consistent" difficult to misleading (here and at some instances). Please, check and maybe reformulate to be clearer."

Response: We have changed this instance of “consistant” to “stable” to avoid confusion. We also updated the use of “not consistant” when describing the 3-methyl catechol water calibration to “decreased”.

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Comment: “p.6, line8: I guess you mean that a calibration with purified air at RH??, lead to the same results as dosing water to the system? Please, clarify.”

Response: We apologize for the confusion. Your assumption is right; we have revised this sentence to make this clearer.

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Comment: “p.6, line20: “Unlike complex interactions, $F-$ transfer reactions are increasingly likely to decompose into smaller fragments”. Compare my comments above; I suggest to clearly separate the notation for the “formation process” and the “resulting ion””

Response: We have fixed this terminology throughout this section to be clear when we are describing the process of ionization versus when we are referring to an actual ion. Throughout the text to improve clarity, we now state “ion” whenever we are referring to the ion itself.

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Comment: “p.6, line22: “Unlike o-cresol, the sum of all unique signals and small fragmentation products for3-methyl catechol is not consistent for the relative humidities used in these experiments.”, Again what does “consistent” mean here?”

Response: Here we changed “consistent” to “decreased as the relative humidity increased”. Also we revised the next sentence to further explain why this decrease occurred.

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Comment: “p.6, line26: I guess that is because the RH increases in the course of the experiments. Please, clarify.”

Response: We have changed “change” to “increase”, to be more explicit. The RH increases slightly over the course of the experiments because of minor leaks in the Teflon chamber walls.

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Comment: “p.7, line14: What is an array of signals?”

Response: We have revised this sentence for clarity. We meant that there was a wide variety of other signals as well as those mentioned in the previous paragraph.

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Comment: “p.10, line18: in Figure 3, you use notation “dihydroxy toluene”. Please make clearer that this is the same as 3-methyl catechol or replace it.”

Response: We apologize for the confusion. 3-methyl catechol is the dominant isomer of dihydroxy toluene. Our CIMS cannot differentiate between the isomers of dihydroxy toluene, so throughout most of the text we refer to “dihydroxy toluene” as dihydroxy toluene since the isomers are not known. We refer to 3-methyl catechol when we inject it into the chamber because then the exact isomer is known. We have revised the description in figure 3 to clarify this and also added in more description in the second paragraph of section 3.1.

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Comment: “p.10, line 21: the info that this referring to the high NOX experiment and Figure 4 is missing.”

Response: We added in “under high-NO conditions” and referenced Figures 4 and 10b&d as suggested.

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Comment: “p.13, line 28: Shouldn’t the yield be dependent on the organic mass produced? Please, discuss more. “

Response: We have added in several sentences to better explain the method we choose to estimate the contribution of cresol to toluene SOA. Mainly, the experiments in this study were specifically designed to investigate chemistry rather than SOA yields. SOA yield studies are performed differently than the studies used in this work. For example, most experiments in this study were performed without seed aerosol. Instead we use the SOA yields measured by Zhang et al., 2014; These experiments were specifically designed to measure SOA yields and take into account particle and vapor wall losses.

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Comment: “p.14, line11: typo “theoretical””

Response: Thanks, this has been corrected.

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Comment: “p.14, line22: maybe better “increasing OH substitution”?”

Response: Thanks, this has been revised as suggested.

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Comment: “p.14, line 26: this sentence is difficult to follow, please reformulate.”

Response: This sentence has been reformulated.

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Comment: “p.14, line 29: “favors” the O2 reactions channel, maybe better.”

Response: We have restructured this sentence.

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Comment: “p.17, line 20: typo, These isomers. . .”

Response: We left this as isomer(s) to represent that this could be one isomer or several isomers. We cannot be certain with the present technique how many different isomers are present.

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Comment: “p.18, line 24: I understood you destroyed NO3 by visible light (p3, line 25)?”

Response: We apologize for the confusion. We have revised this paragraph to better explain our reasoning. Also we have added in the methods section the rate constant for NO3 photolysis and explained the type of lights used.

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Comment: “p.19, line 17: do you mean “expected”?”

Response: We changed “suspected” to “assumed”. Our point in using “assumed” is that we only know that various decomposition products form, and we “assume” or “suspect” they are from the bicyclic intermediate pathway, but this is based on other studies. Unfortunately, our CIMS is not sensitive to the bicyclic intermediate product.

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Comment: “p.19, line 19: I cannot relate these statements to what is shown in Figure 5 and 6. There are more than two, i.e. many products generated via bicyclic pathway.”

Response: We apologize for the confusion. We have revised this terminology to state that two product types form: a functionalized ketone/aldehyde and an unfunctionalized ketone/aldehyde.

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Comment: “p.19, line 27: I don’t understand Figure S4 and its caption. What is matching and not matching in this Figure?”

Response: We have added another couple sentences in the supplement to describe this figure. See last paragraph of Section S1.

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Comment: “Suppl. p.7, line1: if it is just the branching, the modelled sum should be ok. It looks like it, does it?!”

Response: For clarity, we added a reminder here that phenyl hydroperoxide was not detected by the CIMS either because it does not form or is not stable in the ion chemistry of the CF3O- CIMS as stated in the main text. If the phenyl hydroperoxide forms and is not detected by the CIMS then yes you are right the sum of peroxybenzoic acid and benzoic acid for both the experimental data and kinetic model results are fairly similar. However, if phenyl hydroperoxide does not form, then the kinetic model predicts more products than are detected by the CIMS.

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Comment: “Suppl. p.7, line 9: typo “Nitrosophenol””

Response: Thanks, this has been corrected.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-887/acp-2016-887-AC1-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-887, 2016.