

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

Anonymous Referee #1

Received and published: 7 November 2016

General comment:

The authors present a mechanistic study of toluene photo-oxidation. They focus on the chemistry of first and higher generation products from toluene photooxidation. 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

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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.

The manuscript should be published in ACP after the authors considered the minor points below.

Minor comments:

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.

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.

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.

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”?!

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

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

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

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?

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.

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.

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.

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”

p.6, line22: “Unlike o-cresol, the sum of all unique signals and small fragmentation products for 3-methyl catechol is not consistent for the relative humidities used in these experiments.”, Again what does “consistent” mean here?

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

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

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.

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

p.13, line 28: Shouldn't the yield be dependent on the organic mass produced? Please,

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discuss more. p.14, line11: typo “theoretical”

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

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

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

p.17, line 20: typo, These isomers. . .

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

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

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.

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

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

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

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

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