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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 Review 2

Comment: "General This is a very interesting and impressive paper on the oxidation of cresol studied at the Caltech chamber. Generally, it contains a wealth of new findings extending the knowledge on aromatics oxidation considerably. Apparently, despite the study of aromatics oxidation over some decades now, this appears another field where the now available mass spectometric techniques allow for the identification of reaction products which have not been identified before, especially for low NO conditions - but see and consider the note below. On the other hand, the paper confirms a lot of findings as they are implemented tinto the MCM 3.3.1, many of them for high NO conditions which are expected to be met in regions where aromatic VOC emissions coincide with

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Discussion paper

elevated NO and NOx levels. It seems that especially for low NO conditions many new observations are made but the authors should include into their paper a discussion where conditions with low NO enabling prefence of ROO + HO2 over ROO + NO can really be met. The paper has the potential to deliver valuable changes and additions to chemical schemes such as the MCM 3.3.1. as it conains infomation of the formation of products in oxidation generations beyond one and two."

Response: Thanks for your helpful comments and suggestions. To address your main question (where/when is the chemistry described in this work most relevant?) and to put the work in broader context we have added an atmospheric relevance section (new Section 5) after the discussion section. Also we have added text to Section 3.1 and updated Figures 3 and 4 to better articulate that the main products from 3-methyl catechol oxidation are produced under both low- and high-NO conditions. We have attached as a supplement to the reviewer 1 response a pdf file including a comparison between the ACPD version and our edited version for ease of viewing changes.

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Comment: "p3, line 27: While it is understandable to avoid further complications during the present study, it would be extremely interesting to do a similar study at higher RH and then see the coupling to aqueous chemistry"

Response: We agree and hope that future studies will expand this work to better understand the coupling to aqueous chemistry.

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Comment: "p18, section 4.2.4: Maybe a reference can be given for the classic formation of the endo-peroxide ? I wonder if a intramolecular H-shift could occur in systems like the peroxyl / endoperoxides at the different stages of the mechanisms discussed so that a hydroperoxide might form from this and not only by + HO2 / - O2 ? Maybe it would be timeöy to discuss such possibility."

Response: Yes, a reference has been added for the classic formation of the endoperoxide. Thank you for this suggestion. We have added reference to a possible H-shift that might occur prior to formation of the bicyclic intermediate peroxy radical in section 4.2.4 and section 4.1. Because this H-shift is suggested to be negligible for the phenol system from theoretical work by Xie et al., 2013, we also assume that products from this pathway will be negligible in this work. Given the large number of compounds detected in this work separating out possible products from the H-shift pathway from other pathways already discussed is speculative. Unfortunately, we cannot experimentally verify that this H-shift is minimal.

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Comment: “Figure 3: The main additions here are on the catechol oxidation.”

Response: Yes, this is true. The detected first-generation products from cresol oxidation are consistent with other studies. Identification of the second- and later- generation products from cresol oxidation is the focus of this work.

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Comment: “Figure 4: I do not understand "See Figure 2 " written at the catechol up right in the scheme. Probabyl this should be ’Figure 3 ’ ? Please explain / correct.”

Response: We apologize for the confusion. This is a typo and has been fixed. Thank you for bringing this to our attention.

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Comment: “References: I wonder if the paper PAN, Shan-Shan, and Li-Ming WANG. "The Atmospheric Oxidation Mechanism of o-Xylene Initiated by Hydroxyl Radicals." Acta Physico-Chimica Sinica 31.12 (2015): 2259-2268. should be mentioned because it contains remarkable recent considerations on xylene oxidation”

Response: We have referenced this paper in section 4.2.4 while responding to com-

ment 3.

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