

Interactive comment on “Formation of highly oxygenated organic molecules from aromatic compounds” by Ugo Molteni et al.

Anonymous Referee #2

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Review of: Formation of highly oxygenated organic molecules from aromatic compounds. By Molteni, U. et al.

Significance This is an interesting work describing the important observation of highly-oxidized molecules (HOM) from aromatic oxidation reactions. Although certainly important observation in a current “hot-topic” field, and as such should merit its publication, I have a problem how the results are presented. It almost seems as this has been written with a format more suitable for general wider audience in a magazine format, and not really addressed to the atmospheric chemist and physics community. I feel that a certain amount of details of the experiments and the setup have been omitted, which could greatly help researchers in the field performing these type of experiments. Due to this formatting issue in many cases it seems that the text just assumes too much from the reader. This will become clearer from the large amount of specific comments

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given below and starting with: “What do you mean by..”.

So while I find the topic extremely interesting and the finding important, I cannot recommend publication in the current form. I further stress that most of this is due to the current presentation form and all of the problems can be fixed relatively easily. Thus I strongly suggest that the authors take time to modify/rewrite the text according to the comments given below, after which I can recommend publishing.

Major Comments:

Abstract should contain the major details of the work described in the manuscript, i.e., what was studied with what methods and what were the main results, and Conclusions should contain summary of the results and their significance. At the moment they do not do this. More precisely, currently Abstract is missing many of these details and Conclusions feels more like an extension of Discussion. I suggest significantly improving the current presentation. In the Abstract you talk about identified compounds, although there were no single compound really identified in the whole study. This should be changed. In the Abstract you talk about mechanistic pathways – was there more than the one shown for mesitylene in Figure 6? Also in line 53 you say that you talk about “potential pathways and possible mechanism”, but I feel that currently the mechanistic aspects are only briefly discussed. More details of the OH radical production, especially the geometry and the distance OH needs to travel, could be helpful. It was stated that this setup has been used to generate HO₂, which is co-produced by H₂O photolysis in presence of O₂, but HO₂ is much less reactive and thus can travel much further, whereas OH is easily lost to impurities and walls (and as far as I understood OH needs to travel through two 90 degree bends, from which at least the other is a turbulent zone?). Was there only one experiment with one hydrocarbon? Was the OH production always exactly the same? These should be stated clearly. It would be very helpful to give the precursor structures to help the reader understand the significance of these oxidation processes. Line 84: Could you include a figure showing the process of OH concentration determination as it is very central to the whole topic. Line 86: You

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talk about reactive non-aromatic double bonds together with 140 ppbv ozone – how is it “expected” that O₃ reactions do not play a role here? Line 112: Would you expect the dimer/monomer ratio to be constant? If, then why so? This should be stated. Furthermore, what do you mean by this being a good proxy? How and why? Line 117: How much of the given abundancies could be actually due to shifting transmission of the mass spec? Is this a potential problem? Line 118: I guess this also assumes that the $k(\text{RO}_2 + \text{HO}_2)$ is similar for all systems? Should be stated. Moreover, according to Table 1 different VOC concentrations were used (which have different rate coefficients with OH), which leads to different [RO₂] and to different strength of RO₂ + RO₂, right? Line 127: You should clearly separate speculation, i.e., do you know if the stated radicals are forming observed dimers? Lines 145 to 174: In talking about products which main difference is the amount of O-atoms, it seems a bit confusing that all of them have the same label “z”. Could you think of any other way of representing them so that it would not seem they all have the same “z-amount” of O-atoms. Line 174: Does this formula mean that you found products with 4 and 6 H-atoms more than in the parent VOC?. How could you get to a product with 6 H-atoms more than in the parent structure? Can you give an example how this could happen? Line 181: What do you mean by “lower than expected H-atom number”? Line 192: What do you mean by “much less H-atoms than terpenes”? Line 192: Methyl group is not generally considered a good leaving group. Could you add a brief explanation or a reference? Line 194: The occurrence of multiple OH attacks seems somewhat obvious from the observed product compositions. However, the given OH concentration together with such a short residence time in the flow tube does not seem to allow much 2nd generation oxidation (and of course even less 3rd generation). I think this fact should be addressed in the text. Perhaps a chemical reaction simulation could help to get an idea of the needed RO₂ lifetimes and the OH + product reaction rates to justify the high amounts of products evident from figures. Actually, the figures seem to indicate way higher product concentrations than what was the used reagent concentration ($=[\text{OH}]$). For example, Figure 3 gives a concentration of $>3 \times 10^9 \text{ cm}^{-3}$ for a single product, even though the stated

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[OH] was only $2 \times 10^8 \text{ cm}^{-3}$ which should equal to the maximum product concentration, right? Line 201: What do you mean by “conjugated radical in an allylic position”? This should be rewritten. Line 205: What do you mean by “This mechanism varies among the ArHC tested.”? How is the mechanism changing? Line 211: A reference should be added for: “termination reactions of alkoxy radicals make double bonds”. Is that a possible reaction for alkoxy radicals? Line 229: Oxygen bridged bicyclic radicals were not discussed in the text. Line 230: The oxygen addition to allylic positions was not really discussed in the text. Line 236: There was no discussion about phenolic structures in the main text. As already stated above, the current conclusions would rather fit as a continuation of discussion and not as a “conclusions” chapter. Line 245: Please rewrite sentence starting with “Furthermore..”. Figure 1: Excimer. Figure 2: I wonder what was your calibration procedure for the mass spectrometer? Figure 4 caption: What do you mean by “ethylbenzene does not follow this empirical observation”? What is the empirical observation, and how ethylbenzene does not follow it? Figure 5: This figure needs some improvement: How do you go from C₉H₁₃O₃ through alkoxy radical to C₉H₁₃O₆? Also, you say that yellow box contains even oxygen species, even though it has also odd oxygen species. Table A-1: You talk about species losing methyl groups in the text, but what explains the benzene products with less C-atoms than the parent?

Minor Comments:

Line 35: I don't think CCN (anymore) exert an influence on pre-industrial times (i.e., be careful with the wording). Line 44: I guess it's really hard to prove that something does not happen, right? So I'm a bit wondering why so many references have been grouped to indicate that no HOMs were seen by studies that did not use the current methods able to detect the HOMs in the first place. Line 49: Multiple non-aromatic double bonds exists also in many terpenoid species, so it's wrong to argue that this is a property of aromatics alone. Line 67: I think it could help the reader if you could provide a bit more details about OH generation. At least I cannot fully understand the method how it's described now. Do you have an injector or why is the coaxial geometry mentioned? Line

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79: "acid-base reaction" – do you mean salt formation? Line 96: The stated "monomer" and "dimer" ranges overlap. Line 99: Which one is 14 Th – methyl or ethyl group...? Line 107: What "a mechanism for Van der Waals interactions.." means? Is there a "mechanism"? Line 108: I don't understand why would you talk about 800 Th cluster as a particle while talking about mass spectrometric results? Could you explain the significance of adding this here? Line 121: I wonder if a "monocyclic dimer" is a correct term here, if you do not know if the ring is retained in the reaction or not. Maybe better to reword to state that it is a "dimer" that was generated by monocyclic ArHC. Line 125: What is an "auto-termination reaction"? Line 125: Where is the comparison between unimolecular and bimolecular channels based on? Line 128: What is a "higher-order cluster"? Line 134: add -s to "pathway". Line 150: Both products have same number of O-atoms (=z). Line 153: Rather odd number of H-atoms? Line 157: Is Hyttinen 2015 the right reference for this? Line 162: I don't think Kirkby 2016 is generally a good reference for peroxy radical mechanisms as it seems to contain all the mechanistic aspects in its supplementary material. Line 166: Also reaction 4b forms RO radicals. Line 167: Oxygen molecule. Line 169: What do you mean by "discrepancy between the intensity of the peaks"? Line 196: For which compounds the third OH attack is seen? Line 211: Should be Kurten 2015? Line 218: Too less C atoms in biphenyl dimer. Line 219: Aromatic rings are generally considered rather unreactive than reactive. Line 234: Should be "and" not "or". Line 467: Should be "due" not "doe". Table 1 caption: Why do you state "mixing ratio" here? Table 2: Would it make more sense to express the fraction in percentage so that the O:C and the fractional part would not be mixed so easily? Figure 3 caption: There are no compositions in the given inserts, although they're mentioned. Can the mass spec really retrieve accurate compositions for the pentamers? Line 242: I'm not sure if you should talk about identification here, rather "have curiously the same compositions as..". In addition I think also this part should be in Discussion section. Appendix B: Figures of the parent compounds also here would make the figures more interesting.

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