

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

Anonymous Referee #1

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The authors describe experimental findings from a flow-tube study on HOM formation from the reaction of OH radicals with a series of aromatic compounds. OH radicals were generated by water VUV photolysis at 172 nm. The OH+aromatic reaction carried out in a flow system was separated from the OH radical production. Nitrate CIMS was chosen for HOM detection. OH radical concentrations in the system were obtained using an indirect way via a scavenger method. HOM formation from aromatic compounds represents an interesting topic within the framework of SOA precursor formation. It could be a very important process for SOA formation in urban areas. This manuscript needs a couple of clarifications and further explanations before publication can be recommended. Here my comments:

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- Line 17: From my perspective, the authors do not present “identified products”, they simply show product signals and they discuss possible moieties or structural elements of these products.

- Line 48: It is better to say: “. . . aromaticity is lost (or is abrogated)”

- Line 65: OH radicals were generated by water photolysis using a Xe excimer lamp. The atmospheric chemistry community does not commonly use this approach of OH formation. It should be explained here more in detail what are the main reaction steps in a water/air mixture after irradiation at 172 nm. I guess it is also important to comment on the formation of other products like HO₂, H₂O₂ and ozone and their concentration levels in the reaction gas. How important is especially the reaction of OH radicals with HO₂ before entering the mixing zone with the flow containing the aromatic compound? It is not enough to state some references only.

- Line 81: Obviously, the reagent ion spectrum showed a strong signal of trifluoroacetate arising from fluorinated contaminants of the Nafion membrane. Was there also a strong signal of the “dimer”, i.e. the trifluoroacetate adduct with trifluoroacetic acid? It would be fine to see a reagent ion spectrum as recorded for commonly used reaction conditions (maybe in Appendix). Was the trifluoroacetate concentration low enough that a possible contribution in the ionization process can be excluded?

- Line 84: What was the procedure applied for the determination of the “average” OH radical concentration? Was the disappearance of deuterated butanol monitored by PTR-MS when OH formation was switched on? What was the initial butanol concentration? I guess it has been done in absence of the aromatics, or not? The authors used a kind of a discharge technique. Consequently, the initial OH concentration was much higher than the “average” concentration of 1.9×10^8 molec./cc.? Please provide more information. In addition, the authors could show a figure with OH, aromatic and total HOM concentrations as a function of time or reactor length.

- Line 92: At this point it is not clear where the (molar?) HOM formation yields are

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coming from? Did the authors measure the disappearance of the aromatics by PTR-MS, if measurable? Or did the authors calculate the amount of converted aromatics based on their measured OH radical concentration? The concentrations of converted aromatics along with the total HOM concentrations should be stated in Table 1 or in a separate table. What was the calibration factor used for the HOM concentrations measured by nitrate CIMS, where does it come from and what is the detection limit for these HOMs? Please clarify the way of concentration determination for reacted aromatics as well as for the HOMs.

- Line 95 and Fig.2: Main peaks in Fig.2 should be numbered and this numbering should be also given in the corresponding signal table in Appendix. It makes it easier to understand the signal assignment.

- Line 110 and Table 2: The detected product distribution is strongly dependent on the reaction conditions and, therefore, only valid for the conditions of this experiment. That should be clearly mentioned at this point.

- Line 124: What does it mean "more oxygenated radicals have a higher probability to undergo an auto-termination radical reaction"? Please state this pathway and give more information for that.

- Line 161: Do the authors believe that they are able to detect RO radicals by nitrate CIMS? What is the expected RO lifetime with respect to isomerization and for a possible reaction with O₂ (depending on the structure)?

- Line 167: "uptake an oxygen atom" ?

- Line 223: At the end of this paragraph a discussion on possible ozone reactions of products is welcome. The ozone concentration in this experiment is quite high and the products have to contain double bonds after losing the aromaticity. Moreover, a statement is needed how the results of this study can be used to explain the formation of SOA precursors for urban conditions where the reaction of RO₂+NO dominates the

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RO₂ fate in most cases.

- Fig.5: What does "Product with DB" mean?

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