

Referee report on Molteni et al. " Formation of highly oxygenated organic molecules from aromatic compounds."

Major comments:

The language and the tone of voice have improved significantly from the previous version, which to my mind is in order considering the remaining open questions in the mechanistic details of the aromatic oxidation reactions. Now the results are presented more as an important new observation with less mechanistic details, which I think is adequate for the present. Thus, I can recommend this article for publication after few remaining issues, outlined below, have been duly addressed.

One particular, very recent publication would be good to inspect in this context: S. Wang et al. "Formation of Highly Oxidized Radicals and Multifunctional Products from the Atmospheric Oxidation of Alkylbenzenes" *Environ Sci. Technol.*, 2017, 51, 8442. It is a joint theoretical-experimental description of "HOM" formation from alkylbenzenes. It seems there are some slight discrepancies between these studies, which could be worth mentioning in the discussion.

I am still having a bit hard time in understanding the used OH concentrations, and their influence on the oxidation system. The average OH concentration mentioned is $2 \times 10^8 \text{ cm}^{-3}$, and this concentration should be enough for at least 3 OH attacks(!), which seems like a hard thing to accomplish in 20 second reaction time – to still yield a measurable product signal. Then in simulation of Appendix C a value approaching 10^{12} cm^{-3} was used for initial OH concentration, although the main text gives the impression that all of the experiments were with the same photolysis source and power. In addition, it is said in the introduction that the OH reaction with aromatic system leads to "highly reactive products to more oxidants", and that the high reactivity is due to the non-aromatic double bonds. So it leads me wondering could the 140 ppb of ozone in the tube affect the secondary chemistry, if 3 OH attacks is possible too? Moreover, if 140 ppb O_3 was obtained at the setting with a concurrent $2 \times 10^8 \text{ cm}^{-3}$ OH production, what was the corresponding value in the experiment with $8 \times 10^{11} \text{ cm}^{-3}$ initial OH? Could this discussion be made more consistent, and also, somehow clarified?

Minor comments:

1. Line 13: Wang et al. (ref given above) have published "HOMs" from alkylbenzenes.
2. Line 43: benzene is not the only aromatic ring, so the sentence needs some rewording.
3. Line 45. Same Wang et al. has shown experimentally and theoretically that HOM form from alkylbenzene oxidation reactions.
4. Line 46. Is Calvert 2002 the best reference for presenting carbon balance from oxidation of aromatic compounds? 50% seems like a very low number.
5. Line 58 onward: Could you state the purities of the compounds, and which were liquid and which solid.
6. Line 67: Could you shortly explain how a "HO2 generator" is suitable for OH generation. This does not come clear from the text. Also, as OH is much more reactive than HO2 I wonder if you needed to modify the generator?
7. Line 82: I do not understand why fluorinated compounds are mentioned if they do not play any role in the text.
8. Line 87: Multiplication sign missing.
9. Line 97: One dot too much.
10. Line 99: First n in m/z, or the biggest peaks summing up to 80%?
11. Line 220-222: I cannot follow how you get to 4 hydrogen more than the parent compound here.
12. Line 228: Usually aromatic rings are exceptionally stable...

13. Line 229: I don't think "easier" is the right word here. I think "probable" would be closer to adequate wording.
14. Line 243-246: Why is "Type I" and "Type II" brought up in conclusions, but not in anywhere else?
15. Line 246: "Type II" autoxidation was already brought up (at least) in: Rissanen et al. J. Phys. Chem. A, 2015, 119, 4633, and Richters et al. Atmos. Chem. Phys., 16, 9831, 2016.
16. Line 250: Initial step of what?
17. Line 255 and 256: I think especially this finding could be discussed in light of results presented in Wang, S. et al 2017 (ref given above).
18. Line 270: Well, it is not a terribly big contribution. You suggested maximum HOM yield of 1.4%.
19. Table 1: Can you give a lumped value for the HOM yield from xylenes?
20. Table 2: It would be could to indicate which part of the products is assumed to be clusters, and which covalently bound molecules, as the naming "monomer, dimer, ..." can be confusing here.
21. Appendix A: There are some HOMs that have even H but have a charge. How do you suppose these species were charged in the CIMS? Just curious here.
22. Appendix C: Perhaps add an opening paragraph explaining what is being presented?
23. Line 590: Would be nice to know more details of the mixing zone, and the time reaction mixture spends there in an ordinary experiment.
24. Line 590: Not "time in the lamp".
25. In Appendix C. The simulation uses a rather high value of OH. Why so?