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Atmospheric Chemistry and Physics Discussions
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Interactive comment on “Formation of highly oxygenated organic molecules from aromatic compounds” *by* Ugo Molteni et al.

Anonymous Referee #3

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General

The authors describe a flow tube study of formation of highly oxidized molecules from aromatic precursors. The material presented is new and interesting. The paper is interesting to read and the data a presented in a suited manor. The paper contains some degree of speculations about the proposed mechanism but still tolerable as it may induce more research and discussions. After considering the minor comments below the paper should be published in ACP.

Minor comments

p.4, l.92: If you present molar yields, you must have information about the sensitivity of your mass spectrometer. In addition the y-axis in Figures 2 and 3 seem to be given in molecule concentration. (If not, that should be clarified in the captions.) At

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other parts of the manuscript you mention that you cannot quantify dimers because the transmission of your TOF-MS is unknown. In this manuscript, any information about the sensitivity of your instrument is missing. How did you estimate the molar yields then? Please, state precisely in the experimental section, what you did to determine the sensitivity or what the basis of your assumptions is.

p4, l.119: Does the split off of O2 explain the lower oxidation degrees of dimers assuming RO2+RO2 = ROOR +O2 or not?

p.4, l.119f and p.6, l.162: I would propose to give here Mentel et al. 2015 somewhat more recognition as they described, based on experimental observations in context of autoxidation, this type of dimer formation including mixed dimers a year before Kirkby et al. 2016. The same is true for the alkoxy path.

p.4, l.192ff: "Additionally, more oxygenated radicals have a higher probability to undergo an auto-termination radical reaction compared to a radical-radical recombination (RO2· + RO2· or RO2· + HO2·)." I don't exactly what you want to say with this statement in context of degree of methylation and dimer fraction. Less methylated aromatic compounds tend to more auto-termination? What means auto-termination - termination by internal reaction?

p.8, l231ff: I think, that one should differentiate clearer between autoxidation by H-shift to peroxy radicals on one hand and by attack of the peroxy moiety to internal double bonds on the other hand. Although both reactions are internal rearrangements they are still of different character, as the first needs "mobile" H-atoms and the latter double bonds with potential to allyl radical formation. As a consequence the HOM formation in aromatic systems would be based - at least in parts- on a different mechanism?!

p.10, l.284: I urgently request to give a full, correct bibliographic reference to the book by Calvert. You can find it, if you google it is a little bit ridiculous.

Typos

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p.4, l.96 Thomson

p.7, l.218; “strongest dimer is $C_{12}H_{14}O_8$ for benzene and $C_{12}H_{22}O_8$ for biphenyl, respectively”. I guess a typo, as $C_{12}H_{22}O_8$ cannot be a dimer resulting from biphenyl.

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