

Referee Comments on:

Molecular transformations of phenolic SOA during photochemical aging in the aqueous phase: competition among oligomerization, functionalization, and fragmentation

L. Yu et al. ACPD, 15, 29673-29704, 2015

Summary:

The authors present a detailed chemical characterization of aqueous SOA formation from phenol, syringol, and guaiacol oxidation with OH radical (from HOOH) and $3C^*$ (from 3,4-dimethoxybenzaldehyde, or 3,4-DMB). They utilize AMS and nano-DESI MS to provide elemental ratios information and average molecular weights of the compounds formed during the reaction progression, finding that functionalized and high MW products (including oligomers) dominate the aqSOA at the beginning of reaction followed by increasing importance of fragmentation. The manuscript is overall well-written, though there are some major questions about the methodology used that need additional clarification, in particular the potential role of 3,4-DMB as both an oxidant source and precursor in aqSOA formation. The selection of experimental variables as compared to the real atmosphere should also be expanded, as it is harder to gauge if current interpretations of the data may be as atmospherically relevant. Further, the manuscript often refers to molecular level characterization with proposed molecular structures and the goal of mechanism development, but there are no attempts to propose mechanisms to support the structures or functionalization assumed. Still, this is a fundamental laboratory study with results that would be of interest to the community and appropriate for ACP, provided major changes are made as suggested below.

Major Comments:

1. Pg. 29675: It would be more beneficial if the authors could do a calculation to report the fraction of the initial carbon that is estimated to end up down the pathways of fragmentation, functionalization, and oligomerization pathways.
2. Pg. 29676 lines 12-19: The sequence of these two sentences seem contradictory. In the first, the statement that oxidative fragmentation becomes more important on the timescale of atmospheric aging seems to be in conflict with the second stating that SV-OOA eventually turns into LV-OOA with atmospheric processing and transport. Do these processes really happen on different timescales? Definition of "atmospheric aging" timescale versus "atmospheric processing and transport" timescales seem warranted.
3. Pg. 29678-29679 2.1: There is no explicit description of how the phenols are actually measured and calibrated for. Please clarify the instrumentation and methodology.
4. pg.29678, line 21: Can the authors describe in more detail the selection of 3,4-DMB as a source of $3C^*$ as oxidant source and provide a mechanistic schematic of this oxidation scheme? Considering the dimethoxy features that are similar to that of the methoxyphenol precursors used, what bearing does this have on the data interpretation? How do the authors separate oligomerization, for example between cross reactions of 3,4-DMB and the oxygenated products formed during reaction? This also seems to lead to interferences as stated in p. 29682, lines 27-29.

5. Pg. 29680, line 18: Can the authors describe more why it is reasonable to assume peroxide groups are negligible in the given systems?
6. Pg. 29682 line 27-pg. 29683, line 2: The extent by which 3,4-DMB is a participant in the formation of aqSOA production is very confusing. The authors describe here that ~ 70% of the original 3,4-DMB is reacted after 6 hrs and likely forms low volatility species. This means there is another reactant in this system and therefore it should be included as part of [ArOH] that is tracked over time and included in yield calculations as a precursor to aqSOA. This would likely lower the yields.
7. Pg. 29683, line 11: Considering there is no proposed “reaction mechanisms” to form phenolic aqSOA presented in the current manuscript, the authors should remove this phrasing or provide a proposed mechanism based on the reported molecular composition. In general, the manuscript would be improved greatly if there were more mechanistic schemes presented to go along with the proposed routes of fragmentation, functionalization, and oligomerization.
8. Pg. 29686, lines 6-8: Did authors do experiments with these systems stopping illumination mid-run to check if the “higher MW oligomeric compounds” fate is only photodegradation or photolysis? That is, these product signals should stabilize. Is additional oxidation with OH or 3C* not a potential route?
9. Pg. 29687, lines 1-2: Authors should give more detail on the calculation of their illumination being equivalent to several days of tropospheric aging. How do authors derive an equivalent aqueous OH exposure or 3C* exposure that is on the same basis as atmospheric aging/processing. This would best be explained in Section 2.1 as part of the methodology for choices in precursor and oxidant concentrations.
10. Pg. 29688, lines 12-15: The authors should address the extent by which their findings that ELVOCs/oligomers formed in these experiments may be affected by methodology described in Section 2.1. For example, how do the solution concentrations of precursors chosen (are these actually reasonable for cloud droplets of biomass burning plumes?), the solution pH being adjusted to 5 (is that typical of cloud droplets), and full drying of the aerosol before sampling affect the product distributions observed?

Technical Details:

1. Pg. 29681, line 14: Recommend changing “decomposition” to “reaction” or “decay”, so as not to imply the
2. Figure A1. Include a legend of the different experimental conditions represented by the data plotted as in Figure 6.
3. Pg. 29682, line 17-18: Reword so that it does not sound like -H, -OH, -OCH₃ add to a double bond (in the way that for example, OH radical, would add to a double bond). Authors probably mean that the double bonds become saturated with incorporation of these functional groups?
4. Pg. 29682, line 22: Add in reference to Fig. 1d-f as well since refer to O/C figures here too.
5. Table 3: “Top 10” should be changed to “Top 18”.
6. P. 29685, lines 15-17: Reword this sentence as it is confusing at the phrase, “...increase with aging time.”