

Interactive comment on “Chemical characterization of SOA formed from aqueous-phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical” by L. Yu et al.

Anonymous Referee #1

Received and published: 15 September 2014

General comments:

Yu et al studied the formation of non-volatile organic compounds through two aqueous mechanisms: oxidation via OH radical initiated by HOOH photolysis, and oxidation through $3C^*$ initiated by photolysis of an aromatic aldehyde (which also includes OH oxidation due to the formation of HOOH via this route). The authors used a variety of analytical methods to describe the composition of the SOA at the half-way reaction mark. This study builds upon Sun et al (2010), adding a molecular-composition

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analysis based on both positive and negative ion mode high-resolution nano-DESI-MS. The authors conclude that hydroxylation and various oligomerization reactions (e.g., coupling of phenoxy and aromatic alkyl radicals) are responsible for the aqueous SOA formation. This is an interesting analytical study that offers insight into a class of poorly-understood reaction mechanism in the aqueous phase, and should be published as such. There are areas that would benefit from clarification and further discussion, which I outline in the specific comments. In particular, it would be valuable to discuss mechanistic differences in guaiacol, syringol, and phenol in terms of the additional methoxy groups as activating substituents in the OH/ $3C^*$ or abstraction vs. addition pathways of these radicals.

Specific comments:

1. Including structures of guaiacol, syringol, and phenol would be helpful for understanding the discussion in the introduction and much of the text.
2. The authors state in several areas a consistency with Smith et al that the aromatic species react “faster” with $3C^*$ than OH. What does this mean exactly? Are the reaction rate coefficients $k_{3C^*} > k_{OH}$ or the effective rates $k_{3C^*}[3C^*] > k_{OH}[OH]$? If the former, what is the ratio? If the latter, can the authors make such a meaningful comparison without knowing $[3C^*]$ that is derived from $5\mu\text{M } 3,4\text{DMB} + hv$ and $[OH]$ from $100\mu\text{M } \text{HOOH} + hv$? Further, as the $3C^*$ study includes OH oxidation (Fig 7), how can the entirety of the reaction be attributed to $3C^*$?
3. Additional to the above comment, can the authors provide estimates of steady-state $[\text{Oxidant}]$ from HPLC-UV decay trace of the aromatic precursors?
4. [Experimental methods] The authors explain later in the text that the reason they blow dry one sample (then later reconstitute in water) and freeze dry the other is to remove the semivolatiles from the blow dry case. Why not explicitly state this in the experimental methods?

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5. [Experimental methods] If Milli-Q water served as the analytical blank, did the mass of 3,4DMB count towards the mass yield of the 3C* oxidation system? Were controls performed in the photolysis of 3,4DMB alone and evaporated in the same way?
6. [21158, line 1] What is the significance of “near 100%” mass yield, when this value can be exceeded from oxygen incorporation into the phenolic structure?
7. [21158, lines 26-29] I find this speculation strange. Why would ESI efficiency (in both pos/neg mode) be reduced for “highly oxidized species” when the positive mode ionization is partially cluster formation and the negative mode ionization is deprotonation? Also, more support is needed if one is to claim that ESI alone causes decarboxylation of organic acids – as this ionization mechanism should be excellent for the detection of organic acids in the negative mode without extensive fragmentation. Do authors have evidence that certain carboxylic acids standards undergo this instrument-assisted decomposition in standard ESI? Levsen et al 2007 that is cited is not appropriate here, as Levsen and coauthors studied losses of neutrals from precursor ions through collision-induced dissociation in an ion trap (e.g., energy was supplied to purposefully fragment ions) as opposed to this study.
8. [21159, lines 1-5] After considering the 1 – 4% of organic acids that were not analyzed in nano-DESI, what would the corrected O/C be? My assumption is that it does not make much of a difference in the O/C.
9. [21160, lines 6-7] Specifically which kind of functional groups in phenol aqSOA would not be well-ionized by both the positive and negative mode nano-DESI that was used here? If there is an aromatic group intact, (+) nano-DESI should ionize these compounds well.
10. [21164, line 3] The AMS results are only quantitative if the specific ion (e.g., C₁₆H₁₈O₆⁺) does not show up as smaller fragments, thus dispersing the signal of the molecule. Do authors have evidence that this is the case from calibrations with standards? Further, this is nitrate-equivalent mass which has its own assumptions

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about ionization and line-transfer efficiency.

11. [21165, lines 1-4] Can the authors expand on why the structures of guaiacol and syringol would lead to these observed mechanistic differences?
12. [21166, lines 5-6] The authors mention that they examined the optical properties of “phenolic aqSOA” but only discuss syringol? Do phenol and guaiacol follow the same general behavior? Why not show their spectra?
13. [21166, line 18] Again, this is an interesting point, i.e., that the $t_{1/2}$ reactivities is higher for compounds with fewer methoxy groups within one oxidation system, that should be expanded to discuss structure-activity relationships.
14. [21167, lines 15-end] While the particular AMS ions listed appear to be useful in this single-precursor system study, I disagree that these nominal mass assignments can be “signatures” in the ambient environment. Concerns about EI fragmentation aside, nominal mass resolution at a high m/z as 306 produces a large array of possible molecular formula candidates when sources are unknown. In the atmosphere, there is little evidence that these molecular formulas are unique to a particular chemical system. The authors should also consider the possibility that nominal even-mass ions like 306 can be assigned to either a C_xH_yO_z aromatic ion radical or C_xH_yO_zN cation in the atmosphere. For identifying the impact of phenolic aqSOA, it seems more promising to apply nano-DESI, as the authors have done, to field samples than AMS.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 21149, 2014.

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