

Atmos. Chem. Phys. Discuss., referee comment RC3  
<https://doi.org/10.5194/acp-2022-595-RC3>, 2022  
© Author(s) 2022. This work is distributed under  
the Creative Commons Attribution 4.0 License.

## Reviewer Comment on acp-2022-595

Anonymous Referee #3

---

Referee comment on "Comparison of aqueous secondary organic aerosol (aqSOA) product distributions from guaiacol oxidation by non-phenolic and phenolic methoxybenzaldehydes as photosensitizers in the absence and presence of ammonium nitrate" by Beatrix Rosette Go Mabato et al., Atmos. Chem. Phys. Discuss.,  
<https://doi.org/10.5194/acp-2022-595-RC3>, 2022

---

This manuscript describes a comparative study of the photosensitization by phenolic and non-phenolic methoxybenzaldehydes in reactions of guaiacol (another phenolic compound, but without an aldehyde functional group), with and without the presence of ammonium nitrate salts. The experiments were conducted in bulk aqueous phase samples in a solar simulator.

The combination of photosensitizing reactions of methoxybenzaldehyde species with ammonium nitrate photochemistry in a series of experiments is especially interesting. The primary conclusion is that the non-phenolic species DNB is approximately 4 times more effective as a photosensitizer than the phenolic species vanillin, and produces slightly more brown carbon. The manuscript includes a great number of qualitative comparisons, but the authors highlight the most important ones in the abstract and conclusion. It will be of interest to atmospheric scientists studying mechanisms of formation of brown carbon and aqueous secondary organic aerosol.

My first concern is that the authors may have oversimplified the complex task of comparing the photosensitizing abilities of VL and DNB, when VL is reacting away at  $\sim 20\times$  the rate of DNB (a factor of  $8 \times 2.4$ ). The reactivity of VL is so great that it successfully competes with GUA in the reaction with the VL triplet ( $3VL^*$ ), reacting with it 24% of the time over the course of the reaction even though the VL concentration is  $10\times$  less than GUA. (I estimated this reaction fraction from the stated  $2.4\times$  faster decay rate of VL times the VL / GUA concentration ratio of  $0.01\text{mM}/0.1\text{mM}$ , resulting in a relative loss rate for VL of 0.24 if GUA loss rate = 1.) If one takes into account  $3VL^*$  reactions with both VL and GUA, DNB would be at most only 3 times faster than VL at promoting photosensitization reactions in general. A more nuanced kinetics analysis would thus be helpful for GUA + VL and GUA + VL + AN reactions. Furthermore, it could allow some qualitative statements in the paper, such as those in line 204 and 207, to become quantitative: when integrated over the full course of the reaction, what is the impact of the loss of the reactant VL on the total amount of products generated?

Other comments:

Line 95: How are products counted if they appear in both positive and negative modes of ionization?

Line 335: What could highly oxidized species decompose into, that would not be detected and therefore not contribute to the measured O/C ratio? Is this statement alluding to CO<sub>2</sub> production?

Figure 3: at the top right, C12 and C11 products are referred to as functionalized monomers. How is this different from a ring-opened dimer? How exactly do the authors distinguish functionalization from dimerization?

Figure 4: In this graph, does 1 or zero = no change in integrated absorbance? In other words, is it normalized somehow?

Technical corrections

Line 94: "represent" should be "characterize"

Line 328: should this say "likely has a furanone group"? Otherwise, how do the authors know this is the correct structure from the many possibilities?