



## Referee comment on acp-2021-396

Anonymous Referee #2

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Referee comment on "Aqueous SOA formation from the direct photosensitized oxidation of vanillin 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-2021-396-RC2>, 2021

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The manuscript describes very well-designed studies of vanillin photooxidation in bulk liquid solutions where pH, concentrations, reactant ratios, dissolved gases (N<sub>2</sub> or O<sub>2</sub>), ions (nitrate, bicarbonate) and other species (isopropanol) were varied in many combinations. The work is technically sound, with the loss of reactants, the identification and quantification of products, and the absorbance changes in solution all monitored hourly. The authors exhaustively discuss the differences between each experimental variation, pulling out as much detail as possible. This paper will be of interest to those interested in biomass burning aerosol and brown carbon formation, and is publishable after major revision to address the following points.

In places the discussion veers off into speculation, or suggests theories that aren't adequately explained enough to be convincing to the reader, as noted below. Generally the discussion is convincing and well-connected to the literature, but the discussion section reads like it has a thousand detailed conclusions, leaving the reader often feeling "lost in the weeds" and blunting the impact of the work. In general, the focus of the paper could be improved by moving Table 1 to the SI, removing a lot of speculative discussion, and bringing Tables S2 and maybe S3 from the SI to the main paper. These tables are more vital to the discussion at many points, in my opinion.

I do not trust using results for IPA to make generalizations about the effect of all VOCs on vanillin photooxidation. The authors repeat this questionable generalization several times throughout the manuscript, including twice in the abstract. Especially because the authors' explanation for the effect of IPA on their results relies on alcohol / water microstructure arguments, generalization to all VOCs seems unwarranted. Plus, IPA would be present only at very low concentrations in aqueous aerosol or cloud droplets due to its high volatility. It would be more appropriate if the authors remove (or heavily qualify) all statements about VOCs.

At several points, the authors discuss rather small differences between experiments (factors of 1.2 to 1.5) as significant, but the uncertainties in the parameter values being compared are never quantified. This raises doubts in readers' minds about which differences are actually statistically significant. Some discussion of uncertainties and random error is needed.

The argument that 3VL\* is more reactive in its protonated form as an explanation for the observed pH effects does not make sense to me. The pKa of VL is 7.4, which means that more than 99.9% of it is protonated in all experiments, negating the possibility of any detectable acceleration at low pH by this mechanism. Furthermore, the authors describe reasonable alternative explanations for their observed pH effects, such as the more efficient photolysis of HONO vs NO<sub>2</sub>- producing more OH radicals at low pH. However, the questionable claim that 3VL\* is more reactive in its protonated form is repeated several times throughout the manuscript (for example, lines 267, 270, 280, 449 and 500). This claim needs to be convincingly justified or removed from the manuscript.

Specific comments:

Line 25: The authors conclude that photosensitized reactions of VL were "more efficient" relative to nitrate-mediated photo-oxidation. However, as pointed out by the authors, VL is much more light-absorbing than nitrate. Can the authors make a comparative statement after taking this difference into account? Which is more efficient on a per-photon-absorbed basis? This would be a more appropriate comparison of reaction efficiency.

Line 226: The authors at several points claim that VL triplet states and nitrate photolysis products have a "synergistic effect," but evidence in support of this claim is lacking, or at best the evidence supporting it is not adequately explained. The inadequately supported claim is repeated in line 497.

Line 258: This explanation of opposite pH trends at 0.1 and 0.005 mM VL is extremely speculative.

Line 272: For greater clarity, it would be helpful if the manuscript would always match product formulas mentioned in the text to the structures shown in Table S3. Is this product structure #21 in Table S3?

Line 297: is this dimer product structure #5 in Table S3?

Line 334: The solvent cage effect explanation seems questionable. Why would two negatively charged ions share a solvent cage, given their electrostatic repulsion? Furthermore, in line 339 the authors state that "NaBC did not cause any substantial change in the decay of VL," thus making this whole solvent cage discussion irrelevant to the data at hand.

Line 341 – 346: the authors state that "no tetramers were observed in VL\*+NaBC" and "VL+AN+IPA had more oligomers," and then go on to suggest that the formation of oligomers can be promoted by inorganic ions, likely via the generation of radicals such as .CO<sub>3</sub>. No evidence has been provided, as far as I can tell, that NaBC promotes oligomer formation, so I was confused by the authors' claim here that bicarbonate does in fact promote oligomer formation via .CO<sub>3</sub> radicals.

Line 363: ESI-MS is routinely used to detect macromolecules in biochemistry. This suggestion that the method cannot detect molecules with more than 25 carbons is an erroneous conclusion to draw from Lin et al. (2018).

Line 379: The logic needs to be better spelled out here. Why is the formation of more oxidized products suggested by a larger fraction of small-mass products observed for 1:1 VL/nitrate mixtures compared to 1:100? Do small product masses imply fragmentation, or is there a competition with oligomerization?

Line 389:  $C_8H_9NO_3$  should be identified as product structure #2 (an amine) on Table S3.

Line 408: The nitrate photolysis explanations may not be needed, given that the observed enhancement of nitrate on guaiacol decay rates was only a factor of 1.2. Is this a statistically significant change?

Line 418: The word "Similarly" is being used to relate two seemingly dissimilar observations, causing needless confusion. In the previous sentence, VL shows much higher absorbance enhancement than nitrate, but in this sentence nitrate is being compared to an experiment without nitrate.

Line 471: This sentence is confusing. Doesn't this work address (among other things) the effects of nitration on triplet-generating aromatics?

Line 481: Why would VL photodegrade 10 times slower in ALW relative to dilute cloudwater? This effect is important for applying this work to the atmosphere. Could the authors provide some theory or explanation here?

On Table S2, experiments without nitrate are listed as "—" in the column of normalized abundances of N-containing compounds. Is this because no N-containing compounds were detected in the top 50, or because these samples were not analyzed for N-containing compounds?

It would be helpful to map the reactant molecule onto the Figure S12 graph.

Technical Corrections:

Line 349: "increased" should be "increase"

Line 377: "an important" should be "a more important"

Line 459: "decompose" should be "decomposes"

Sodium nitrate in my opinion would be better abbreviated "NaN" to be more consistent with other abbreviations such as "NaBC."

Table S3: Compound number 4, the most abundant product in some studies, is missing an oxygen atom. It should be clarified that structure #1 is the reactant molecule vanillin rather than a product.