Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC3
https://doi.org/10.5194/acp-2021-396-RC3, 2021

Comment on acp-2021-396

Anonymous Referee #3

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-RC3, 2021

This study investigated the aqueous photo-oxidation of vanillin (VL) via both direct photosensitized reaction and nitrate-mediated photo-oxidation and discussed the influence of secondary oxidants from triplet excited states (^{3}VL*), solution pH, VOCs, and inorganic anions, etc. in detail. The experiments and data analysis are well done, and the mechanisms that are proposed are plausible. This study provides valuable information about the chemical composition, optical properties, and possible reaction mechanisms for SOA formed from the VL photo-oxidation under different conditions. However, there are a few major and minor comments I would like the authors to address before it is considered for publication in ACP.

Major comments

(1) With the experiment design, it is difficult to directly compare ^{3}VL* pathway and nitrated-mediated pathway, as also mentioned by the authors that the VL concentration was very high, and ^{3}VL* chemistry dominated in all the VL + ammonium nitrate (AN) experiments. Maybe more precisely, what was compared was photo-oxidation of VL via ^{3}VL* chemistry with and without nitrate. However, both the title and some places in the manuscript are misleading.

(2) I suggest the authors restructure the manuscript: on the one hand, to move part of the figures and tables from the SI to the manuscript, e.g. Table S2 and Figure S12, to make it easier to follow. On the other hand, to simplify the article by cutting some "maybe interesting" but not that important/related findings/discussions to make the main storyline clearer.

(3) It is very interesting to see the changes in optical properties, and their relation to the changes in chemical composition. However, I only see very general discussions about it (e.g. line 234-238 and line 282-289). It will be nice to discuss the specific compounds, possible chromophores, and to explain the changes in the optical properties. To explain the pH-dependency, the authors cited Pang et al. 2019a, which reported the pH-dependent light absorbance of nitrophenols. However, the dominating products in this study were those without N, different from those in Pang et al. 2019a. In addition, the chemical composition of SOA with pH 4 and pH < 4 are quite different, which could also lead to different functional group/chromophores, and changes in optical properties

(4) Adding the experiments of guaiacol (GUA) is a little bit confusing, as the title is the photo-oxidation of VL. I understand it is a good addition to the manuscript, and these experiments nicely compared the photo-oxidation of GUV via the two pathways. However, the conclusion (line 25-26) "guaiacol oxidation by photosensitized reactions of VL was observed to be more efficient relative to nitrate-mediated photo-oxidation" is still problematic, as the concentration of VL in GUA + VL experiment was still 10 times higher than the observed value in the cloud and fog but the concentration of AN in GUA + AN experiments was similar to the observed concentration.

Minor comments

Line 27-28 In the abstract, the sentence "which nitrate photolysis products can further enhance" sounds not clear to me.

Line 121 Did you average these replicates for mass spectra and/or decay rates? Please clarify it.

Line 168-169 It would be nice to explain it together with the chemical composition shown in Figure 1.

Line 181 "VL*" should be "^{3}VL*"?

Line 187 In both VL* and VL + AN under N2-saturated conditions (Fig. 1(a) and (b)), trimer signals are very high. Any explanations?

Line 212 Could you give some numbers to show "majority"?

Line 255 Should it be pH 4?