



Comment on acp-2021-396

Anonymous Referee #1

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-RC1>, 2021

Overview

The authors examined the aqueous photodegradation of vanillin (VL), a carbonyl-containing phenol emitted from biomass burning, and accompanying formation of aqueous SOA (aqSOA). They then measured the composition of the aqSOA using high-resolution mass spectrometry and UV/Vis absorption. They also determined the impact of purging solutions with N₂ (to remove dissolved oxygen) as well as the addition of ammonium nitrate (a photochemical source of hydroxyl radical, OH) and/or one of two hydroxyl radical scavengers (isopropyl alcohol or bicarbonate). They attempt to explain their results qualitatively based on a few dozen reactions, but there is little experimental attempt to text the mechanisms.

Vanillin has been studied in several past works, but this paper adds new information on the composition of the resulting aqSOA. The purging with N₂ is novel, but the interpretation of the results is not clear, and I disagree that these experiments show that secondary oxidants dominate VL loss. Unfortunately, the nitrate concentration added was too low to impact kinetics (because VL direct photodegradation is so fast), but it's interesting that it impacted the products formed. Finally, the authors seem compelled to try to mechanistically explain most of their results, but their explanations are very speculative and should be significantly cut. There are a several other major and minor issues, as described below.

Major Comments

1. The normalized abundance of products (line 131) is used throughout the paper as a key metric, but it's unclear if this is a robust endpoint, in part because its uncertainty is never discussed. Based on the major products that have been identified (both via MS and IC), what is the likely range of ionization efficiencies (IEs) of the products and how much uncertainty does this introduce in the product abundance measure? There is additional uncertainty in the quantification of VL, which is described on line 134 as semi-quantitative. Altogether, what is the relative uncertainty in P from day to day and experiment to experiment?

This is an issue because there are several times when the normalized product abundance results are inconsistent with other, seemingly more quantitative metrics. For example, in

section 3.1.3., the presence of OH scavengers had no significant effect upon VL decay or aqSOA light absorbance, but there were differences in the normalized abundance of products. Given the uncertainty in IE and other aspects of the product measure, I would be wary of attributing much significance to the normalized abundance of products as an endpoint when it's inconsistent with the more quantitative measures.

2. Throughout the manuscript, the low decay rate of VL* under N₂ is taken to mean that the triplet state of VL isn't involved in VL decay and that secondary, O₂-dependent, oxidants are responsible for VL decay. However, the N₂-purging control experiment result is ambiguous, since secondary steps in VL decay via triplets might require oxygen to proceed. For example, a major fate of the ketyl radical formed by the 3VL* + VL reaction is to add oxygen. In the absence of oxygen, the ketyl radical will still form, but it's forward path (O₂ addition) is blocked, possibly leading to eventual return to the reactants (and little apparent VL decay). So N₂ purging is likely to not only remove secondary oxidants, but also to interfere with subsequent steps in the 3VL* - VL reactions. Thus the oft-stated conclusion that secondary oxidants from 3VL* are responsible for VL decay is not correct (e.g., on line 184). Without knowing the impact of O₂ on the reaction intermediates in the triplet reaction, it is impossible to know what the N₂-purging result means.

Another strike against the "secondary oxidants" theory is that the proposed secondary oxidants are unlikely to be important for VL decay. For example, the 1O₂* + VL reaction is slow under the pH conditions here (where there is negligible phenolate). In air-saturated solutions, the 1O₂* and 3VL* concentrations should be roughly equal (see the McNeil and Canonica review in ESPI), but at pH 4 (and below) the rate constants for phenols with 3C* are much faster than the 1O₂* values. The bottom line is the 1O₂* is unlikely to be important. Similarly, HO₂/O₂- was proposed as an oxidant for phenols, but these are very weak oxidants that react slowly with phenols. Finally, OH is apparently unimportant as well, based the OH scavengers having no significant impact on VL decay; however, it is possible that most of the IPA or bicarbonate was purged from the sample prior to illumination (as discussed below). Regardless, photolysis of H₂O₂ (formed from the 3VL* + VL reaction) will be slow, giving little OH.

3. Mechanism discussion. The authors seem compelled to try to explain all of their observations using one or more reactions, but since there is no quantitative examination of these mechanisms, they are all very speculative and mostly not useful. Worse, in some (many?) cases, the proposed mechanisms are inconsistent with some of the data. Fundamentally, without building a kinetic model of the mechanism and testing it against the observations, it is difficult to know whether the proposed reactions are important. The authors put too much emphasis on trying to mechanistically explain their observations and these explanations end up being mostly conjectures that are not grounded in data. These mechanistic speculations should be greatly reduced, especially if they are inconsistent with the kinetic or light absorption data and/or if they rely primarily upon the "normalized abundance of products" metric, which seems highly uncertain.

For example, on line 226, what trends were reinforced in the presence of nitrate? Looking at Table S2, ammonium nitrate has no effect on the kinetics, does not change the normalized product abundance at pH 2.5 or 3 (but does increase it at pH 4), and has no impact on OS(C). Later, in Fig. 2, we see that the presence of nitrate only negligibly increased the long-wavelength absorbance of the products. Overall, the bulk of the observations suggest that nitrate has a minor impact on VL decay, consistent with the fast direct photodegradation of VL.

4. I am concerned that the authors purged IPA and bicarbonate from solution during each experiment since solutions were bubbled continuously. Do they have any way to know if these OH scavengers were removed before or during illumination? Similarly, guaiacol

shouldn't undergo direct photochemical loss under illumination above 300 nm, so the apparent decay measured in the dark could be evaporation during purging. If the purging was slow enough, each bubble would achieve Henry's law equilibrium with the solution, which would allow you to estimate the rates of IPA and bicarbonate (lost as CO₂) from the rate constant for GUA loss and the ratio of Henry's law constants for GUA and OH scavenger. For GUA, which can be measured by HPLC, the authors should report the fraction of the initial concentration (0.1 mM) that was lost after the 30 min of purging in the dark and the fraction then lost in the dark control for the illumination experiment. Then for IPA and bicarbonate, some estimate of their fraction lost during purging would be helpful. At the very least, this issue needs to be raised and addressed.

5. Section 3.1.2. Are VL (and GUA) decay rate constants normalized for photon fluxes? Given the variability in kinetic decays, are the relative small differences in decay rate constants between pH 2.5 and 4 statistically different? Do the authors have a good measure of the variability of the kinetics, e.g., the standard deviation of $j(\text{VL})$ based on triplicate experiments? Given that the decays are not first order, it is more difficult to discern differences in rate constants, so I would be cautious.

6. Lines 283-289. I would be surprised if deprotonation of phenols is responsible for the higher absorbance of the aqSOA at pH 4 compared to pH 3 and 2.5. For one, the pK_a values of methoxy-substituted phenols are near 10, so there's no appreciable phenolate at pH 4. Nitro-substituted phenols can have much lower pK_as, but absorbance of the aqSOA formed in the presence of nitrate is nearly the same as in the absence of nitrate, so it seems nitrophenols are a minor part of the light absorption. Another possibility is that different products are made at pH 2.5 compared to pH 4. Measuring the pH dependence of the aqSOA formed at pH 2.5 and 4 would allow you to determine whether the pH dependence is rooted in acid-base chemistry of the products or of the reactions.

7. Section 3.5. This section repeats what has been stated before. I would delete this section, show Figure 4 the first time discussing possible mechanisms, then refer to the Figure throughout the discussion of mechanisms (which is hopefully much shorter in the revised version).

Minor Comments

Line 25. This notion of "efficiency" (i.e., which reaction path is faster) depends on the concentrations of the two oxidant precursors, VL and nitrate. Thus it's not a universally true statement.

L. 42. "respectively" doesn't serve a purpose in this sentence.

Section 2.1. What was the initial volume of solution illuminated? Were solutions stirred? What was the flow rate of gas (N₂ or air) through the solution before and during the experiment?

L. 100. Was there a difference in the temperature between the illuminated and dark solutions?

L. 106. If the authors are going to abbreviate 2-propanol as IPA, it would be better to call it isopropyl alcohol to help readers remember the name of the abbreviation. NaBC is a poor choice for an abbreviation for sodium bicarbonate since BC stands for black carbon typically. Better to simply use its chemical formula, NaHCO₃ or HCO₃⁻, depending on the context.

L. 111. 2-propanol and bicarbonate were added in some experiments, but the description of why is odd. Their primary role will be OH scavengers, so it's strange to call them a VOC

and inorganic anion, respectively. 2-propanol is not a common atmospheric gas, so it's a poor choice of model VOC. Similarly, calling bicarbonate an "inorganic anion" is a poor choice of words, since sulfate and nitrate are the classic inorganic ions. Better to refer to 2-propanol and bicarbonate as "OH scavengers" since that is their main role.

L. 113. What does it mean that the OH scavengers were not added "in excess"? Since they're reacting with OH (which will have a very low concentration) they are technically in excess. Better to avoid this discussion, as it's not fruitful. If you want to dive more into the OH scavengers, you could calculate the fraction of OH each intercepts in their respective solutions or the amount that they suppress the OH concentration. (But, again, this depends on if the species were purged from solution.)

L. 151. The disproportionation of HO₂/O₂⁻ is the same as the reaction of HO₂ with O₂⁻, so this sentence repeats itself.

L. 163. It's unclear what the authors mean by "...a minimal role for 3VL* in VL photo-oxidation". Do they mean that 3VL* + VL is an unimportant reaction (but see above about this) or that the direct photodegradation of VL doesn't proceed through the triplet state?

L. 167. It is not true that 1O₂* has a much longer lifetime than 3C*; rather, the lifetimes are approximately the same. In cloud and fog drops, the lifetime of 1O₂* is controlled by water deactivation and is approximately 5 us (see Bilski et al., 1997). The lifetime of 3C* is controlled by reaction with dissolved O₂ and is approximately $1/((2E9 M^{-1} s^{-1}) * (250 \mu M)) \sim 2$ us. Also, rather than the oxidant lifetime, it is the product of the oxidant concentration times its second-order rate constant that determines the relative importance of a given oxidant.

Page 7. This whole page is one paragraph. It should be trimmed to reduce speculative discussions of mechanisms, then broken into smaller pieces, focused on certain themes/points.

L. 196. The text here and elsewhere discusses the abundance of specific products (not just the normalized product abundance). The abundance of each product should be added to Table S3, along with some estimate of the relative uncertainty of these values.

L. 224. How much lower are OS(C) values here compared to previous work on aqSOA? Compare these values.

L. 240. Is there any evidence that 3VL* + O₂ directly makes OH? This would seem energetically unfavorable and also to be minor compared to energy transfer to make 1O₂*.

L. 242. In the presence of O₂, the ketyl radical is probably too short lived (it reacts with O₂ to make an alpha-hydroxy peroxy radical) to combine appreciably with a phenoxy radical. But the phenoxy radical is in resonance with a carbon-centered cyclohexadienyl radical that is longer lived; these two species can couple (Yu et al., ACP, 2014).

L. 261. The rate constant for H₂O₂ formation is fastest near the pK_a of HO₂, i.e., pH 4.8, so one wouldn't expect greater H₂O₂ formation at pH 2.5 compared to pH 4. But this also depends on the pH dependence of the HO₂/O₂⁻ sources and sinks.

L. 264. This discussion of the pH dependence of N(III) photolysis doesn't seem applicable since the addition of nitrate makes a negligible contribution to VL decay. Just because N(III) photolysis is pH dependent doesn't mean it matters here.

L. 299. Why would the presence of HO₂ lead to more dimer formation? HO₂ (and O₂⁻) are

too weak to oxidize phenols at any significant rate.

Lines 298-301: This argument is circular: IPA cannot make more OH by scavenging OH and turning it into HOOH, which then photolyzes to make OH. Think of the associated stoichiometry. IPA will suppress [OH] because it is an OH sink, thus rendering OH an insignificant oxidant for VL. The observation that IPA has a negligible impact on VL decay (Fig. S3c) indicates that OH is not important as an oxidant for VL (with or without IPA) or that the IPA was mostly purged from the system.

L. 310. IPA makes no difference in the VL kinetics, whether nitrate is present or not. So please don't make sweeping statements such as "...the role of nitrate in VL photo-oxidation is enhanced in the presence of IPA...". And don't suggest that OH is an important intermediate in the formation of a product in the presence of IPA (e.g., line 311), since IPA will greatly suppress the OH concentration.

L. 313-322. It is hard to believe that 1 mM of IPA can significantly disrupt the structure of 55 M water. In any case, there is no increase in light absorption by the aqSOA formed in the presence of IPA (Fig. 2), so the Berke mechanism seems unimportant. Most of this should be deleted.

L. 327. It is difficult to imagine that carbonate radical is a significant oxidant in these experiments: carbonate rate constants are relatively slow (compared to triplets or OH) and VL photodegradation is very fast. If the authors want to propose carbonate radical as an important sink, they need to do some calculations of its steady-state concentration and estimate the corresponding rate of VL loss. Again, the qualitative normalized abundance of products is driving these uncertain statements, while the quantitative photodecay rates and light absorption are showing there is no significant effect of bicarbonate. Lead with the latter observations, as they are more robust.

L. 336. 1 mM IPA or bicarbonate is not high enough to reduce the cage effect from nitrate photolysis. In any case, IPA or bicarbonate are OH sinks, so they will suppress, not enhance, the OH concentration.

L. 376. If this proposed mechanism was true, then VL decay would be significantly faster in the presence of nitrate, but this is not the case. It's not clear what the authors are trying to explain here - is it the increase in oligomerization at higher [VL]? The explanation for this is probably that the concentrations of phenoxy radicals (and the related, carbon-centered cyclohexadienyl radicals) increase with [VL], making radical-radical recombination to form oligomers a more significant fate.

L. 405. GUA should not undergo any direct photochemistry, so its decay in the absence of VL or AN suggests either that there is an oxidant-making contaminant in the system (that is consumed within a few hours) or that GUA is evaporating during illumination. But there is no GUA loss in the dark: is this because the temperature was cooler in the dark?

L. 498. This sentence mentions "Further enhancement of VL photo-oxidation...in the presence of nitrate...", but VL photo-oxidation (i.e., photodegradation) was not enhanced in the presence of nitrate.

L. 1004. The author order is incorrect on the Tinel et al. ref.

Table 1. The quantum yield for Rxn 3 is not 0.001. This is a misperception based on the O(3P) result of Warneck and Wurzinger (J Phys Chem, 1988); their paper shows a value of ~0.01 for more direct (nitrite) measurements. Benedict et al. (Env Sci Technol., 2017) confirmed this higher value. This error doesn't affect the current work, but it would be a shame to propagate the misperception.

Figure 4. (a) The resolution of the figure is poor, so it's fuzzy and hard to read. (b) Scheme 1 suggests that oligomers are only formed at pH < 4, which isn't true, as past work has shown oligomer formation in similar phenol systems at pH 5. (c) Ketyl radicals formed by $^3C^* + \text{phenol}$ typically are shown as phenoxy OH group (a result of the triplet abstracting a hydrogen) and no double bond between the C and O. As stated earlier, their lifetimes are short in the presence of O₂, so they're unlikely to do the coupling as shown here.

Supplemental Material Notes

General note – it would have been helpful to have line numbers in the supplement.

Text S3. Were calibration curves only made once? Were they actually used in quantifying VL and GUA? (I don't see the need since absolute values are not needed in the kinetic plots.)

Text S6. (a) It's unclear what is meant by "Then, the average relative intensity absorbed by 2NB solution as a function of wavelength was calculated." Can you show this with an equation? (b) How much did the photon flux vary between experiments? Was this determined? If not, this variation is a source of variability in the kinetic measurements.

Table S2. (a) VL (and GUA) decays are rate constants, not decay rates. (b) For reference, it would be helpful to give the OS(C) of VL. (c) What is pH of expt. A19?

Figure S1. The vanillin spectrum has a problem around 305 nm - a large discontinuity that is probably caused by lamp switch. Either reacquire the spectrum or replace with a published value.

Figure S3. Were the decays ever determined multiple times for the same condition? It would be helpful to show these results and derive a relative uncertainty for decay rate constants.

Figure S6. How can we tell that the imidazole formed in the AN experiment was not formed in the SN experiment? It would be helpful to put a marker on the two plots of Fig. S6 to show where the imidazole showed up in the AN experiment.

Recommendation

I recommend that the manuscript be majorly revised and then reconsidered.