Responses to reviewer

Reviewer comments are in **bold**. Our responses are labelled with [R] and authors' actions with [A]. Line numbers in the responses correspond to the revised manuscript with track-changes. Modifications to the manuscript are in blue.

Reviewer 3

This manuscript describes studies of aqueous phase oxidation of sulfur dioxide by three photosensitizers, and for comparison, a non-photosensitizing organic compound and the nitrate ion. The organic compounds are common components of biomass burning plumes, including some phenolic and some non-phenolic species. The authors show that photosensitizer-mediated oxidation of SO₂ is much faster than by nitrate photolysis. Pure N2 is also substituted for air in some experiments to provide some clues about the reaction mechanism. These results suggest that SO2 oxidation by the secondary oxidants (singlet oxygen (¹O2), superoxide (O2 ⁻), hydroperoxyl radical (HO2), and OH) produced by reaction of the triplet species with O2 is much more significant than direct reactions between ³C + SO₂. These results are of interest especially to those studying the puzzle of rapid sulfur oxidation in polluted regions, which is especially notable in humid areas with high aerosol loading. I recommend publication after minor revision to address the following comments and questions.

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

The manuscript cites two earlier studies of photosensitizer-induced S(IV) oxidation (Wang et al. 2020 and 2021). Looking at these earlier studies, it appears that Wang et al. (2020) studied humic acid, ambient aerosol particles, and 4-benzoyl benzoic acid, while Wang et al. (2021) studied naphthalene-derived secondary compounds, so this manuscript advances our knowledge of photosensitizer-induced S(IV) oxidation by testing three photosensitizing aldehyde species, both phenolic and non-phenolic, plus a non-photosensitizing acid species for comparison. However, readers would benefit from a clearer explanation of how the current study builds on these earlier works in the introduction. This would also help readers to better understand the statement (page 8 line 188) where the authors try to rationalize the conflicting results about the importance of secondary oxidant species between the current study and that of Wang et al. (2020).

[R1] Thanks for the suggestions.

[A1] We have added more related background information in the introduction as follows (lines 62-69): "However, only limited studies focused on the role of biomass burning-derived photosensitizers in S(IV) oxidation. Wang et al. (2020) reported that photosensitized chemistry involving the humic fraction of aerosols during Chinese haze events could explain a significant fraction of the observed sulfate formation, which highlighted the potential photosensitizing properties played by biomass burning particles. Naphthalene, emitted primarily from fossil fuel combustion and biomass burning, can be oxidized by hydroxyl radicals to form secondary organic aerosol (SOA), which was observed to possess interfacial photosensitizing properties (Wang et al., 2021). These recent studies have advanced our understanding of the photosensitized processes, but the types of photosensitizers from biomass burning are diverse and their properties are complex, limiting us from further assessing the importance of photosensitized sulfate formation in the dynamic ambient atmosphere. In this study, we investigate sulfate formation via aerosol phase SO₂ oxidation by biomass burning-derived aromatic carbonyl photosensitizers, including both nonphenolic (3,4-dimethoxybenzaldehyde, DMB) and phenolic photosensitizers (vanillin, VL and syringaldehyde, SyrAld) with similar molar absorptivity at atmospheric relevant wavelengths (Figure S1, Supporting information), in an oxidation flow reactor (OFR) utilizing a single particle aerosol mass spectrometer (SPAMS). Nitrate photolysis has been reported as a typical sulfate formation pathway initiated by particulate photoactive compounds, similar to photosensitization (Gen et al., 2022). The objectives of this study are to semi-quantitatively evaluate the extent of sulfate formation in photosensitizer particles and qualitatively compare the relative atmospheric importance of particulate photosensitization and nitrate photolysis in sulfate formation."

It would be helpful to have the chemical structures of the studied compounds given somewhere in the manuscript or SI along with a listing of which compounds are photosensitizers and which are phenolic. Currently, the latter bits of information are split between the Introduction and the Methods sections, making it difficult for readers to notice or understand the close structural relationships between the different VOCs selected for study.

[R2] Thanks for the suggestions.

[A2] We have added after line 85 in the method that: "The structures of the chemicals used are provided in Table S2.", and added Table S2 in the supporting information.

Table S2 Chemical formula, structure, molar mass and property of the chemicals used in this study.

| Chemical compound Formula Structure Molar mass (g mol ⁻¹) | |
|--|--|
|--|--|



^aThe Photosensitizing properties are derived from the literature (Smith et al., 2015, 2016; Smith et al., 2014).

p. 8 line 188: This sentence is the authors' only attempt at resolving the significant differences in results between Wang et al. 2020 and the current work. Yes, they studied different photosensitizing compounds. However, given what is known about triplet carbon states and photosensitization, does it make sense that the aldehyde photosensitizers in the current work reacted with SO2 mostly via secondary oxidants, while the carboxylic acid photosensitizers in the earlier study reacted directly with SO2? Some further discussion here could be very valuable.

[R3] Figure 3 compared the distribution of RPA for DMB-, VL- and SyrAld-coated particles under air and N_2 conditions, and it is clear that replacing air by pure N_2 substantially shifted the distribution of RPA for DMB- and VL-coated particles toward the lower end, while SyrAld-coated particles exhibited slight changes. Our results suggested the involvement of O_2 and the potential important role of secondary oxidants in sulfate formation and also the lower ability of direct $3C^*$ oxidation of SO₂ to produce large sulfate RPA. The relative importance of the direct $3C^*$ and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system. In addition to the aldehyde functional group, the effects of other different functional groups should still be considered (Mabato et al., 2023). For instance, the phenolic structure and the number of methoxy groups, etc. Therefore, we think that our understanding of the effects of different functional groups of the photosensitizer on the reactivity of

3C* is far from being generalized. In any case, future studies on the physicochemical properties of photosensitizers are required to better understand the impact of photosensitized reactions.

[A3] We modified the sentence on line 224: "Upon the increase of UV intensity (from I₁ to I₄), the number fraction of particles with sulfate RPA larger than 0.2 only slightly increased in N₂-saturated conditions, and particles with RPA of 0-0.2 dominated the population, indicating the lower ability of direct ${}^{3}C^{*}$ oxidation of SO₂ to produce large sulfate RPA. The relative importance of the direct ${}^{3}C^{*}$ and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system."

We have also added after line 186 that: "Specifically, DMB has a higher quantum yield and longer lifetime of ${}^{3}C^{*}$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the ${}^{3}C^{*}$ is needed."

p. 9 lines 195 – 199: This argument about solubility, phase, and reactivity is confusing. The authors note that vanillic acid and syringic acid have no measurable hygroscopic growth due to water uptake at 90% RH, and that the three aldehyde photosensitizers are less hygroscopic than these two acids, suggesting that they may therefore be solid or semi-solid phase aerosol particles at the range of RH used in this study. From the preceding parts of the paragraph, the authors appear to be using this aerosol phase argument as a possible explanation of the lower reactivity of vanillin and syringaldehyde. However, DMB is clearly less hygroscopic than vanillin or syringaldehyde, and by this argument it should be the least reactive of the three. In any case, how this aerosol hygroscopicity information ties in to the rest of the paper is not spelled out.

[R4] [A4] The purpose of this sentence is to describe the probable phase states of photosensitizer-coated particles instead of explaining the observed discrepancy in sulfate production for the three photosensitizers. To explain the lower sulfate formation efficiency for VL and SyrAld than DMB, we have added after line 186: "Specifically, DMB has a higher quantum yield and longer lifetime of ${}^{3}C^{*}$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of

SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the ${}^{3}C^{*}$ is needed."

The original lines 195-199, which better fit the method part, have been moved to line 100. In addition, we have added after line 99 that "Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N_2 through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as –CHO may have even lower hygroscopicity than –COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013)."

Supplement p 2 line 23: Was the transmission of the quartz glass vial measured through just one wall, or all the way through the vial (both walls)? If the latter, the transmission of light to the inside of the vial may be closer to 95%, necessitating a smaller photon flux correction factor.

[R5] [A5] The transmission of the quartz glass vial was measured through one wall. This information has been added to SI.

Technical corrections

p. 7 line 146: this sentence is unclear. What "considerable difference" is being referred to, that between average RPA and NP, between different VOCs, between dark and UV conditions, or between one of those things and the SO2 consumption? The context of surrounding sentences does not fully resolve the meaning of this sentence.

[R6] [A6] We have deleted "a considerable difference in" to make the sentence clear and it is revised as follows: "Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-

containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO₂, and the corresponding SO₂ consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses)."

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