This manuscript provides evidence that OH oxidation of phenyl sulfate can regenerate inorganic sulfate, and that OH oxidation of aromatic OSs can form BrC products. These are important scientific questions relevant to this journal; however, many claims are made without data to back them despite it being collected. Most notably, products detected with mass spectrometry are only reported for 1 of 5 experiments for which UPLC/LC-MS/MS data was obtained, and ion chromatography data is also only provided for 1 experiment.

I found numerous (>20) grammatical and syntactical errors, and thus I recommend that the authors review the language with a more critical eye and double check their revisions with a grammar checking software. Awkward transition word choices obscured the meaning of many sentences, particularly in the introduction and results & discussion.

Overall, I have many significant concerns about the quality control and experimental methods that need to be addressed before I can recommend this manuscript for publication.

We gratefully thank for your comments and suggestions to improve the manuscript. We have revised the manuscript by carefully considering the comments. The major revisions are specified as follows:

(1) We have added additional details regarding sample collection and analysis.
(2) We have provided further evidences to demonstrate that the observed signals of products originate from the reactions rather than from analytical artifacts.
(3) We have added discussion about the conversion of p-tolyl sulfate and 4-ethylphenyl sulfate to inorganic sulfate and provided the related evidence to support the discussion.
(4) We have reconstructed the discussion on the mechanism underlying changes in optical properties at the molecular-level.
(5) We have added the discussion about the potential influence of ionic strength on the rate constants of aromatic OSs.
(6) We have rewritten the vague sentences, and corrected the typos and grammatical errors of the manuscript.

More details about the revisions can be found in the revised manuscript and in our response below.

(Q1) *Line 24: It is inaccurate to state that organosulfates constitute "~30% of particulate organic mass," please rephrase as "up to 30%" or cite specific regions where this mass concentration was measured.*

Response: We have changed "~30% of particulate organic mass" to "up to 30% of particulate organic mass" in the revised manuscript.

(Q2) *Line 31: "except for isoprene and monoterpenes derived OSs" – confusing wording; were these OSs also detected? Please clarify.*

Response: Yes, isoprene and monoterpenes derived OSs can also be detected in the aerosol collected in urban areas. In the revised manuscript, we have rephrased this sentence as "In urban areas, in addition to isoprene and monoterpenes derived OSs,

other OSs containing an aromatic ring (e.g., phenyl sulfate, benzyl sulfate) were also observed in collected aerosols.".

(Q3) *Line 64: A key citation is missing: Xu et al. Environ. Sci. Technol., 2024. (DOI:10.1021/acs.estlett.4c00451) This paper is a critical study providing evidence for inorganic sulfate formation from OH-initiated decomposition of IEPOX-OS referenced earlier in the text. This should also be discussed in Section 3.2 (line 207).*
Response: Thank you for the suggestion. In the revised manuscript, we have cited this paper in Introduction, and added the brief description about the mechanism of inorganic sulfate through $\bullet SO_3^-$ resulting from the decomposition of β-OSO_3^- alkoxy radical [-C(O•)–C(OSO_3^-)-] in Section 3.2.

(Q4) *Line 88: If aliquots were removed at a specific time interval for analysis, this should be specified, as well as whether they were diluted prior to analysis with UPLC.*
Response: For kinetic experiments, aliquots (1 mL) were withdrawn from the solution during the reaction at specific time intervals (every 30 minutes over a 2-hour period). These aliquots were directly injected into the UPLC system for analysis without any dilution. We have clarified these details in the revised manuscript.

(Q5) *Line 163: Please quantify the "high reactivity" of aromatic OSs compared with alkyl OSs, citing specific examples of rate constants.*
Response: In the revised manuscript, the detailed literature results of second-order reaction rate constant (k_{OS}) of alkyl OSs were described as the comparison. "Previous study has reported the k_{OS} values of typical alkyl OSs (e.g., methyl sulfate, ethyl sulfate, and propyl sulfate) ranged from 1.03×10^8 to 1.23×10^9 M^{-1} s^{-1}, which is lower than the k_{OS} values measured for the aromatic OSs in our study, falling between 4.29×10^9 and 6.38×10^9 M^{-1} s^{-1}."

(Q6) *Line 170: The reported errors should be specified as calculated from the regression fit. It is unclear whether repeats were performed and propagated to yield this value.*
Response: The reported errors represent the standard deviations calculated from experimental replicates. We have claimed it in the revised manuscript.

(Q7) *Line 179: What are the ionic strengths of the solutions in your reactor at pH 3 and pH 8? Please calculate (using approximations as needed) to provide a reference for the difference in ionic strength that could be affecting kinetics.*
Response: In this study, the ionic strengths of the solution at pH 3 and pH 8 were calculated as ~1×10^{-3} and 6.9×10^{-3} M, respectively. Gweme and Styler (2024) observed that the rate constant of phenyl sulfate at ~0 M ionic strength is about ten times higher than that at 6.5 M. Thus, although the ionic strength at pH 8 is higher than that at pH 3, this difference is unlikely to have a significant effect on the rate constants of aromatic OSs. We have added a discussion on the potential influence of ionic strength in the revised manuscript.

(Q8) *Section 3.2: Results from LC-MS analysis of dark experiments should be included to eliminate the possibility that any reported products are analytical artifacts. Line 212: The observed peak for m/z 97 is discussed multiple times in this section, but there is no figure showing a mass spectrum with this peak. It is also very important to show that this is not an artifact of the mass spectrometric analysis or a fragment ion. A mass spectrum from a dark/0 min/standard sample showing the absence (or extremely low signal) of m/z 97 is important to demonstrate this. The extracted ion chromatogram (EIC) for m/z 97 should also be compared with the EICs of identified organosulfate products (such as those listed in Table S1 for phenyl sulfate) to see if their peaks align, as this would suggest fragmentation in the MS to form m/z 97.*

Response: Thanks for your suggestion. Mass spectra of samples from reactions without illumination under the same experimental conditions were also collected. The possibility that the peak at m/z 97 originates from fragmentation of aromatic OSs during electrospray ionization can be ruled out, because its intensity is substantially higher than that of m/z 97 in the EIC spectra of the organosulfate standard and of the same reactions performed in the dark. In addition to m/z 97, signals from other potential analytical artifacts were also excluded. In the revised manuscript, we have included these mass spectra in the Supporting Information to demonstrate that the observed products signals arise from the reactions rather than from analytical artifacts.

(Q9) *Line 200: Please clarify that this work does not disprove isoprene as a source of this m/z 139, but rather this work provides an additional source.*

Response: We have rephrased the sentence as "For example, previous studies inferred that *m/z* 139 ($C_2H_3O_5S^-$) is produced from isoprene and its derivates related reactions (Cai et al., 2020; Wang et al., 2022). In this study, it is found that this compound can also be formed through the oxidation of phenyl sulfate by OH radicals, providing the additional pathway for its formation in the atmosphere." in the revised manuscript.

(Q10) *Section 3.2: Since conversion of OSs to inorganic sulfate is purported as a main finding of this paper in the abstract (line 15), evidence supporting this should be high-quality enough to include in the main text.*

Response: Based on the IC and mass spectrometry results, it can be concluded that phenyl sulfate can revert to inorganic sulfate during its liquid-phase reaction with OH radicals. In the revised manuscript, we have reconstructed the discussion about the observation of inorganic sulfate formed during the reactions and provided additional evidence including IC results, mass spectra of reactions with/without illumination, and extracted ion chromatogram (EIC) comparison results to support this conclusion.

(Q11) *Line 224: There is no discussion of inorganic sulfate quantification using ion chromatography, and thus a mass yield is very confusing to report. With all the uncertainties related to the inorganic sulfate peak in the chromatogram, this should not be included in the manuscript.*

Response: We have reconstructed the discussion about the formation of inorganic sulfate during the reactions. The discussion about its yield is now deleted in the revised

manuscript.

(Q12) *Line 225: The peak of inorganic sulfate does not appear negligible based on Figure S6 – please provide the chromatogram from a blank/dark/0 min sample to support this claim. This is especially important since it is claimed earlier that the existence of a m/z 97 peak in mass spectra implies conversion of OSs to inorganic sulfate. If small amounts of sulfate are detected with IC without OH oxidation, m/z 97 is likely to appear in the mass spectrum at 0 min as well.*

Response: Although a small SO_4^{2-} peak was observed in IC prior to illumination, originating from impurities in the water blank and the aromatic OS commercial standards, the gradual increase of SO_4^{2-} peak with reaction time after illumination indicates that SO_4^{2-} was formed through the oxidation of phenyl sulfate by OH radicals. This is further supported by mass spectrometry results. A peak at *m/z* 97, which can be assigned to HSO_4^-, was observed in the mass spectra of phenyl sulfate reacting with OH radicals. The possibility that this signal resulted from fragmentation of phenyl sulfate during electrospray ionization can be ruled out, as its intensity was substantially higher than that of the *m/z* 97 signal in the extracted ion chromatogram (EIC) of the organosulfate standard, as well as in the same reactions performed under dark conditions. The pronounced signal of m/z 97 (HSO_4^-) observed in the mass spectra provides robust evidence for the formation of inorganic sulfate during the reactions. Based on the IC and mass spectrometry results, it can be concluded that phenyl sulfate can revert to inorganic sulfate during the liquid-phase reaction with OH radicals. In the revised manuscript, we have reconstructed the discussion about the observation of inorganic sulfate formed during the reactions and provided additional evidence including IC results, mass spectra of reactions with/without illumination, and extracted ion chromatogram (EIC) comparison results to support this conclusion.

(Q13) *Line 237: The products from the two other OSs in this study are glossed over very quickly here. Please report relevant mass spectrometry results to support these claims, including molecular formulas similarly to Table S2. If this is not possible, then this discussion should not be included and the section should be reframed to ONLY discuss phenyl sulfate; Two key datasets are missing to support the claims of this paper: (1) mass spectrometry characterization of OH oxidation products from p-tolyl sulfate and 4-ethylphenyl sulfate and (2) ion chromatography data showing formation of inorganic sulfate OH oxidation of p-tolyl sulfate and 4-ethylphenyl sulfate. If these cannot be included, then the scope of claims in the abstract should be narrowed. In its current form, there is only evidence of phenyl sulfate conversion to inorganic sulfate, not multiple aromatic OSs (line 15). Additionally, the characterization of multiphase OH oxidation products of only phenyl sulfate is shown, not multiple aromatic OSs (line 13).*

Response: In addition to phenyl sulfate, the products from the reactions of p-tolyl sulfate and 4-ethylphenyl sulfate with OH radicals were also measured by LC-MS. The *m/z* values, molecular formulas, and possible structures of the identified products are summarized and are now provided in the Supporting Information in the revised

manuscript. The mechanism for the formation of functionalized and fragmented OSs from either p-tolyl sulfate or 4-ethylphenyl sulfate is elucidated as being similar to that of phenyl sulfate.

In this study, the formation of inorganic sulfate in the reaction of phenyl sulfate with OH radicals was verified by combining mass spectrometry and ion chromatography data. Analogous to phenyl sulfate, the formation of inorganic sulfate via the reaction of p-tolyl sulfate with OH radicals can be also inferred based on IC and mass spectrometry results. However, for 4-ethylphenyl sulfate, SO_4^{2-} peak in IC was found to overlap with that of the compound itself. The inference that 4-ethylphenyl sulfate converts to inorganic sulfate is supported by comparing the intensity of the *m/z* 97 peak in the EIC spectra of illuminated versus dark reactions. These results suggest that phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate revert to inorganic sulfate during liquid-phase OH radical oxidation. However, whether the proposed mechanism also applies to other types of aromatic OSs warrants further investigations. In the revised manuscript, we have added a discussion on the conversion of p-tolyl sulfate and 4-ethylphenyl sulfate to inorganic sulfate and have provided the related evidence to support it. We have also clarified that inorganic sulfate can be generated from the liquid-phase OH radical oxidation of the specific aromatic OSs (i.e., phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate) studied here rather than from multiple aromatic OSs that were not investigated.

(Q14) *Section 3.3: Throughout this section, differing absorbance/fluorescence is justified with speculations about chemical composition without evidence. This includes speculations about the formation of oligomers/HULIS (line 254, 274) and products with more expanded conjugated systems (line 271), as well as changes in the products formed at different pH (line 291). These claims should be supported with UPLC/LC-MS/MS data, which they have collected for these experiments. It is not sufficient to reference other publications, especially when these compounds should be observable with the analytical technique used.*

Response: Thanks for your comment. In addition to the absorption spectra obtained by UV–vis spectrophotometry, we have identified the molecular composition of the main chromophores generated in the liquid-phase reactions of aromatic OSs with OH radicals and characterized their optical properties using UPLC-PDA-HRMS. The characteristic absorption peaks of the three aromatics were located at 262 nm for phenyl sulfate, 266 nm for p-tolyl sulfate, and 266 nm for 4-ethylphenyl sulfate. After OH radical oxidation, the newly formed chromophores contributing most to light absorption were $C_6H_5O_5S^-$ (characteristic absorption peak at 274 nm), $C_7H_5O_5S^-$ (characteristic absorption peak at 258 nm), and $C_8H_7O_5S^-$ (characteristic absorption peak at 254 nm), respectively. The formation of these new OSs indeed significantly alters the optical properties of the solution. Additionally, the light absorption properties of other products were characterized. Hydroxylated products exhibited a red shift in their characteristic absorption peaks due to the electron-donating effect of the hydroxyl group, whereas the formation of carbonyl functional groups results in a blue shift. Multi-hydroxylated products are likely responsible for the enhanced light absorption and the red shift of the

fluorescence band observed in the reaction system. In the revised manuscript, we have reconstructed the discussion on the mechanism underlying the changes in optical properties at the molecular-level.

(Q15) *Technical corrections: Multiple instances where "Oss" rather than "OSs" was used to refer to organosulfates in the text, please double check all abbreviations; Line 67: There is no reference to Gweme and Styler, although it is the "recent study" discussed through the end of the paragraph; Line 74: It is unclear why He et al., 2022 is cited here – please clarify; Line 118: Were these products quantified using IC? Line 122: "ocus" should be "Focus"?; Line 134: "em" and "ex" should be subscripted; Line 150: Superscript is missing from scientific notation; Line 153: Reference to Table 1 is missing; Table S2 does not specify that these results are for pH 3, as mentioned in the main text (Line 187). Additionally, negative charges are missing from all molecular formulas in the table, although they are included when referenced in the main text; Colors in Figure S5 are difficult to distinguish from each other.*

Response: The reference cited here is to illustrate the three aromatic OSs were selected in our study have been observed in the field observation or the isomer which were observed. We have checked and corrected the typos or grammatical errors of the manuscript.

References

Gweme, D. T., and Styler, S. A.: OH radical oxidation of organosulfates in the atmospheric aqueous phase, J. Phys. Chem. A, 128, 9462–9475, https://doi.org/10.1021/acs.jpca.4c02877, 2024.