Response to Reviewer's comments

For clarity, the reviewers' comments are listed below in *black italics* type, our responses are in black normal type, and changes in the revised version are highlighted in blue.

Reviewer #1:

Yang et al. investigated the multiphase reaction of aromatic organosulfates with OH radicals, providing pH dependent rate constants, organosulfate products, and produced inorganic sulfate. The authors additionally show evidence for increased absorbance in OS reaction products. The main kinetically related goals of this manuscript are closely related to that of Gweme and Styler (2024) (referenced by the authors). And indeed, these authors find good agreement between their kinetic results and those from Gweme and Styler (2024). But at least as worded in the introduction, the authors suggest that the novelty and necessity of their new study here is to investigate the possibility of inorganic sulfate as a product (something Gweme and Styler did not provide evidence for, at least for aromatic organosulfates). I have concerns about the experimental design and quality control related to their observation of inorganic sulfate as described below. Recent work from their own institution on inorganic sulfate products is also not referenced (https://acp.copernicus.org/articles/25/8575/2025/). I have listed my concerns below, which largely pertain to novelty and need for increased experimental evidence in some cases. Overall, I believe that my concerns should be addressed before I can recommend 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 provided additional evidences to support the finding of inorganic sulfate formation in the reactions of the studied aromatic OSs with OH radicals, and the related discussion has been revised accordingly.
(2) We have reconstructed the discussion about the reliability of the method employed for kinetic studies.
(3) We have added the discussion about the mechanism for the changes in optical properties at the molecular-level.
(4) 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) *Recent work from their own institution on inorganic sulfate products is also not referenced (https://acp.copernicus.org/articles/25/8575/2025/).*

Response: We have briefly introduced and cited this work in Section 1 (Introduction) in the revised manuscript.

Page 2: In addition to laboratory experiments, Tsona et al. (2025) employed quantum chemical calculations based on density functional theory to confirm the formation of inorganic sulfate from the gas-phase and aqueous-phase reactions of OSs with •OH.

(Q2) *Line 35-36: This statement is unsupported and too speculative for an introduction.*

Response: We have reconstructed the introduction about aromatic OSs in the atmosphere. This sentence is now deleted in the revised manuscript.

Page 1: In urban areas, in addition to isoprene and monoterpenes derived OSs, other OSs containing an aromatic ring were also observed in collected aerosols (Kundu et al., 2013; Huang et al., 2018; Wang et al., 2021; He et al., 2022). He et al. (2022) identified four kinds of aromatic OSs (i.e., phenyl sulfate, methylphenyl sulfate, benzyl sulfate and phenethyl sulfate) with concentrations ranging from 0.04 ± 0.08 to 2.37 ± 3.59 ng m^{-3} in $PM_{2.5}$ collected in Chengdu, China. Previous study observed that aromatic OSs can account for up to 63.5% of the total identified OSs in a megacity in China (Ma et al., 2014).

(Q3) *Line 51: No need to say 'potential' – Hydrolysis is indeed known to removed OSs.*

Response: We have deleted it in the revised manuscript.

(Q4) *Line 54: …radicals that reacted…*

Response: We have corrected this typo and rephrased this sentence in the revised manuscript.

Page 2: Lai et al. (2024) investigated the kinetics of reactions of methyl sulfate and ethyl sulfate with •OH.

(Q5) *Line 57: "border kind" is at least an unfamiliar term to me, consider using something else.*

Response: We have changed it to "more kinds of" in the revised manuscript.

Page 2: This observation was also verified in more kind of aliphatic OSs

(Q6) *Line 63: "… the partial of OSs…" is confusing as written.*

Response: We have rewritten this sentence in the revised manuscript.

Page 2: During the oxidation of some OSs (e.g., methyl sulfate, ethyl sulfate, 2-methyltetrol sulfate, and α-pinene derived OSs) by •OH, it is interesting to find that OSs can also return to inorganic sulfate except for new OS formation (Kwong et al., 2018; Xu et al., 2020, 2024).

(Q7) *Lines 65 – 70: No reference is given for this. Please correct, as the authors seem to use this evidence as the paramount motivation for their study here. Presumably this is Gweme and Styler (2024), but it isn't confirmed.*

Response: Yes, this reference is Gweme and Styler (2024). We have added this citation at the end of sentence.

Page 2: A very recent study investigated the aqueous-phase •OH oxidation of phenyl sulfate other than aliphatic OSs (Gweme and Styler, 2024),

(Q8) *Line 88: Is this a summed concentration? Or for each individual component?*

Response: The value of 0.05 mM is the initial concentration of each aromatic OS.

(Q9) *Line 96 – 97: This statement needs experimental or referenced support. Even though I appreciate that hydrolysis of aromatic organosulfates is slow, it is critical that the authors make it defensible beyond doubt that hydrolysis isn't a kinetically meaningful contributor to their aqueous phase analyses.*

Response: The assumption that aromatic OS and the reference compound are just consumed due to •OH oxidation is one of important principles in measuring reaction rate constant using the competition kinetics method. We agree well with reviewer that it is essential to preclude interference from other reactions, such as hydrolysis, during kinetic measurements. In this study,

control experiments were conducted for the reactions of aromatic OS, BA, and H_2O_2 in the absence of illumination. The results show that hydrolysis of aromatic OS has a negligible effect on the rate constant measurement. Additionally, we performed experiments on the direct photolysis of each aromatic OS in the presence of H_2O_2 to confirm that photodegradation of OSs cannot interfere with kinetic measurements either. In the revised manuscript, we have reconstructed the discussion about the reliability of method employed.

Page 4: The second-order rate constant of each aromatic OS with •OH was measured by the competition kinetics methods using 0.05 mM sodium benzoate as the reference compound (Smith et al., 2015). It is noted that one of important principles of this method is that aromatic OS and the reference compound are consumed only by OH radical oxidation in the aqueous phase. Control experiments of the direct photolysis of each aromatic OS without the addition of H_2O_2 as well as the reactions of each aromatic OS, BA, and 10 mM H_2O_2 without illumination were carried out to preclude the interference of other reactions. Figs. S2 and S3 show that the influences of either hydrolysis or photodegradation on the kinetic measurements of these three aromatic OSs are negligible, verifying that the decay of reactants resulted from •OH oxidation. Therefore, in this study, the second-order rate constant for aromatic OS (k_{OS}) can be calculated using the equation E1 based on the following reactions (R1 and R2).

(Q10) *Line 122: Change 'spectrometry' to 'spectrometer'*; *Line 150: Missing superscript formatting*; *Line 196: Typo for 'radical'*

Response: We have corrected these typos in the revised manuscript.

(Q11) *Line 202-203: This is more interesting to me than the motivation that was framed in the introduction.*

Response: Thanks for your suggestion. In addition to phenyl sulfate, fragmented OSs can be observed in the liquid-phase •OH oxidation of either p-tolyl sulfate or 4-ethylphenyl sulfate. Therefore, in the revised manuscript, we have moved this conclusion statement to Section 4 (Atmospheric implications and conclusions).

Page 13: Fragmented OS formation resulting from ring-opening pathway during •OH oxidation of aromatic OSs has not reported previously. Several fragmented OSs (e.g., $C_2H_3O_5S^-$, $C_5H_7O_8S^-$, $C_4H_5O_7S^-$, and $C_5H_5O_6S^-$) detected in our study have been previously identified in ambient aerosols (Kuang et al., 2016; Cai et al., 2020; Wang et al., 2022; Yang et al., 2023), suggesting that aromatic OSs may serve as a potential source for aliphatic OSs in the atmosphere.

(Q12) *Line 213: Did the authors conduct any full scan mass spectrometry acquisitions of individual organosulfate standards? The detection of m/z 97 does not exclusively indicate inorganic sulfate, as it may also be the result of in-source fragmentation of their organosulfate standards. While electrospray ionization is soft, is still doesn't eliminate the possibility of such byproduct fragments formed from organic precursors. This needs to be clarified in detail. Line 228: I'm not sure this is true as written. Again, I need to see more quality control experiments of the standards themselves to be sure of what the exact origin is of the author's inorganic sulfate peak.*

Response: The mass spectra of samples from reactions without illumination under the same experimental conditions were also collected as the comparison. 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. 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 more evidences including IC results, mass spectra of reactions with/without illumination and EIC comparison results to support this conclusion.

Page 9: In this study, the formation of inorganic sulfate during the reaction of phenyl sulfate with •OH was also examined. Figure S7a shows that the SO_4^{2-} peak in IC increased progressively with reaction time. The formation of inorganic sulfate was further supported by the evidence of the observed prominent HSO_4^- peak at *m/z* 97, which is assigned to HSO_4^-, in the mass spectra (Fig. S6b), the intensity in the extracted ion chromatograms (EIC) was substantially higher than in dark controls (Fig. S8a), ruling out in-source fragmentation or hydrolysis as the source of HSO_4^-. The results of IC and mass spectrometry suggest that in addition to the new OSs, inorganic sulfate can also be formed during the reaction.

In addition to new OSs formed, the formation of inorganic sulfate was also observed during the process of either p-tolyl sulfate or 4-ethylphenyl sulfate oxidized by •OH. For p-tolyl sulfate, the gradual increase of SO_4^{2-} peak with reaction time in IC as well as the pronounced signal of *m/z* 97 (HSO_4^-) observed in the mass spectra provide robust evidence for the formation of inorganic sulfate during the reaction (Figs. S7b and S8b). For 4-ethylphenyl sulfate, SO_4^{2-} peak in IC was found to overlap with that of the compound itself (Fig. S7c). The inference that 4-ethylphenyl sulfate converts to inorganic sulfate is supported by comparing the intensity of HSO_4^- (*m/z* 97) peak of samples collected from illumination and dark conditions (S8c).

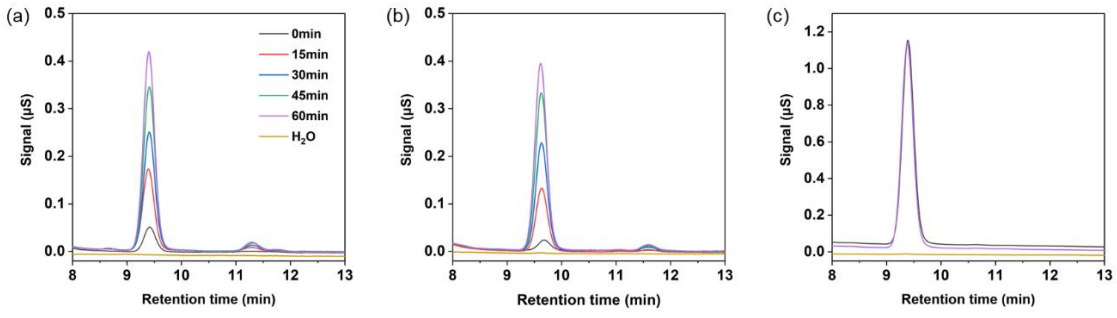


Figure S7. Time profile of SO_4^{2-} peak in ion chromatograms in the reactions of 0.05 mM (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate with •OH at pH 3. IC result of water blank was shown as the comparison.

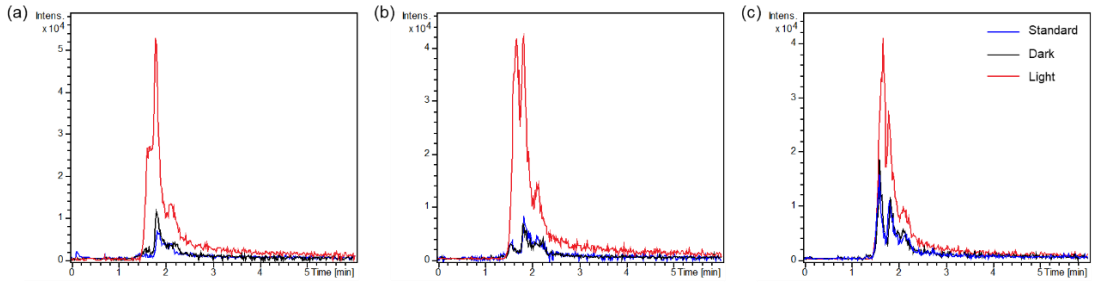


Figure S8. EIC of HSO_4^- (*m/z* 97) obtained from standards (blue line) of (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate, and from their liquid-phase reactions under dark (black line) and illumination (red line) conditions.

(Q13) *Line 225 – 227: If the authors cannot adequately defend their observations (especially for a chemical product that is so important to their studies motivations and novelty), then it should not be included in the manuscript.*

Response: We have reconstructed the discussion about the formation of inorganic sulfate during the reactions. This sentence is now deleted in the revised manuscript.

(Q14) *Line 243 – 244: This is vague and unspecific. Statements such as this are best introduced in the introduction with referenced support.*

Response: We have moved this statement to Section 1 (Introduction) to introduce the aim of our work in the revised manuscript.

Page 9: Moreover, given that the oxidation of aromatic organic compounds often induces significant alterations in the optical properties of the reaction system (Li et al., 2021; Arciva et al., 2024), the change of optical properties was also examined.

(Q15) *Line 250: This is just my opinion, but descriptors like 'remarkable' don't offer much for a scientific observation. What exactly makes it 'remarkable?*

Response: We have reconstructed the discussion on optical property changes, this sentence is now deleted it in the revised manuscript.

(Q16) *Section 3.3: The authors talk about the formation of brown carbon species. They do not provide molecular-level data to better defend this observation despite having the capability to do so (i.e., a high-resolution mass spectrometry system). There are indeed interesting and exciting observations reported in this paragraph. But while they do have the absorbance data, some molecular-level evaluation of these formed compounds would be much more convincing and comprehensive to defend/prove these observations. This type of data, if acquired, should then also be featured in a key manuscript figure.*

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 and characterized their optical properties using UPLC-PAD-MS. 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 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. In the revised manuscript, we have reconstructed the discussion on the mechanism underlying the changes in optical properties at the molecular-level.

Page 10: Kinetic and mechanism results show that aromatic OSs can undergo rapid •OH oxidation to form a series of functionalized and fragmented compounds. The changes of optical properties resulting from the formation of these compounds were also investigated. Figure S9 shows the time-dependent absorption spectra of aromatic OSs during •OH oxidation at pH 3. As the reaction progressed, the consume of reactants accompanied with the increase in absorbance across 250–400 nm. To establish the relationship between light absorption and organic compounds, chromophores formed in the reaction were identified by correlating UV absorption bands with the retention time based on UPLC-PAD-MS analysis. For phenyl sulfate, Figure 3a displays that phenyl sulfate (*m/z* 173) was the prominent chromophore with the retention time of 5.67–6.16 min at the beginning of the reaction, exhibiting a characteristic absorption peak at 262 nm (Fig. S9a). After the liquid-phase •OH oxidation, five major chromophores were observed as shown in Fig. 3c. Chromophore #4 was assigned to the unreacted phenyl sulfate. Figure 3c shows that Chromophore #1, #2, and #3 eluted at 3.47–3.72 min, 4.00–4.18 min, and 5.46–5.60 min, respectively. These newly formed chromophores exhibit red-shifted absorption peaks (Fig. 10a), likely due to the electron-donating effect of hydroxyl groups increasing aromatic ring electron density (Hems and Abbatt, 2018). The results of EIC suggest that these chromophores correspond to co-eluting mixtures containing $C_6H_5O_5S^-$ isomers (*m/z* 189), along with $C_6H_5O_6S^-$ (*m/z* 205), $C_6H_5O_7S^-$ (*m/z* 221) and $C_6H_7O_8S^-$ (*m/z* 239) (Fig. 3d). Among these compounds, $C_6H_5O_6S^-$ exhibited the highest intensity. Chromophore #5, eluting at 14.98–15.67 min, remained unidentified. Its later elution time suggests a larger molecular structure and lower polarity (Fleming et al., 2020). Additionally, there may exist other chromophores unidentified since these five chromophores can not fully explain the total light adsorption as shown in Fig. 10a.

For p-tolyl sulfate, the increase in absorbance, contributing by the formation of chromophores, was also observed after OH oxidation. The primarily newly formed chromophore (Chromophore #1), eluting at 5.23–5.78 min, was identified as $C_7H_5O_5S^-$ (*m/z* 201) based on the corresponding EIC (Figs. S11c and d). A blue-shift peak at 258 nm was observed upon the formation of $C_7H_5O_5S^-$, which is associated with the generation of a carbonyl (C=O) functional group (Fig. S10b). Other newly formed chromophores were characterized as Chromophore #2 and Chromophore #3. Chromophore #2 corresponded to a mixture of $C_7H_7O_5S^-$ (*m/z* 203), $C_7H_7O_5S^-$ (*m/z* 217), and $C_7H_7O_6S^-$ (*m/z* 219) with absorption band at 274 nm, and Chromophore #3 was assigned to $C_7H_7O_5S^-$ (*m/z* 203) with the absorption band at 266 nm (Figs. S10b and S11). Figures S10c and S12 show the characterization of chromophores formed from liquid-phase reaction of 4-ethylphenyl sulfate with OH radicals. After reactions, Chromophore #2 ($C_8H_7O_5S^-$, *m/z* 215) with a characteristic absorption peak at 254 nm was the dominant contributor to total light absorption. Four additional chromophores were also identified: Chromophore #1, a mixture of $C_7H_7O_5S^-$ (*m/z* 201), $C_8H_9O_5S^-$ (*m/z* 217), $C_8H_7O_6S^-$ (*m/z* 231), and $C_8H_9O_6S^-$ (*m/z* 233), with absorption peak at 258 nm; Chromophore #3, an isomer of

$C_8H_7O_6S^-$, with absorption peak at 262 nm; Chromophore #4, an isomer of $C_8H_9O_5S^-$ (*m/z* 217), with absorption peak at 274 nm; and Chromophore #5, another isomer of $C_8H_9O_5S^-$, also with a characteristic absorption peak at 274 nm.

Furthermore, fluorescence evolutions during liquid-phase •OH oxidation of aromatic OSs were investigated as shown in Fig. 4. The initial maximum excitation/emission (Ex/Em) wavelengths of phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate at pH 3 were Ex/Em = 255/275 nm, 260/284 nm, and 260/284 nm, respectively. The different initial fluorescence intensity among these three aromatic OSs may be attributed to the substituent effect of the compound. Compared to phenyl sulfate, p-tolyl sulfate and 4-ethylphenyl sulfate contain additional methyl and ethyl groups, respectively. These electron-donating substituents extend the conjugation system, lowering the $\pi \rightarrow \pi^*$ transition energy and resulting in both emission redshift and fluorescence enhancement (Cao et al., 2023). During the reaction, the fluorescence intensity initially decreased due to phenyl sulfate consumption, followed by a subsequent increase from fluorescent product formation. After 8 h of illumination, a redshifted fluorescence peak emerged at Ex/Em = 260/283 nm, implying the formation of products with expanded conjugated systems (e.g., $C_6H_5O_5S^-$, $C_6H_5O_6S^-$ and $C_6H_5O_7S^-$) (Tang et al., 2020). The fluorescence intensity of p-tolyl sulfate and 4-ethylphenyl sulfate monotonically decreased with the reaction time and showed a redshift in the fluorescence band at Ex/Em = (250–300)/(400–500). Previous studies uncovered that the emission wavelengths of 400–500 nm are the indicative of humic-like substances (HULIS), which can significantly contribute to the light-absorbing properties of organic aerosols (Bianco et al., 2014). Previous studies revaled that the oxidation of non-photolyzable phenolics by •OH can yield HULIS-like fluorescent products (Tang et al., 2020; Chang et al., 2010). Here, multi-hydroxy products from p-tolyl sulfate (e.g., $C_7H_7O_5S^-$, $C_7H_7O_6S^-$ and $C_7H_7O_7S^-$) and 4-ethylphenyl sulfate (e.g., $C_8H_9O_5S^-$, $C_8H_9O_6S^-$ and $C_8H_9O_7S^-$) may exhibit spectral features resembling aerosol HULIS.

Employing phenyl sulfate as the representative, spectral changes at pH 8 were also examined. Previous studies have demonstrated that the light absorption properties of carbonyl compounds (e.g., aldehydes) and nitrophenols exhibit pronounced pH-dependence owing to protonation-deprotonation equilibria (Calvert and Schnitzler, 2023; Chen et al., 2020b). In this study, the phenyl sulfate remains deprotonated across the pH range of 3–8, resulting in negligible spectral variations in the initial solution (Figs. S9 and S13). However, the temporal evolution of the reaction revealed substantially enhanced absorbance at pH 3 compared to pH 8, particularly within the 300–400 nm range. Figure S14 shows the molecular composition of chromophores from the reaction of phenyl sulfate with •OH at pH 8. Chromophores #1–3 were identical to those at pH 3 but exhibited stronger absorption due to their higher concentrations. An additional chromophore #4, eluting at 4.99–5.23 min, contributed significantly to absorption but the detailed composition of this chromophore is unknown. Compared to pH 3, solution of pH 8 exhibited an enhanced peak intensity at 4.99–5.23 min, while the peak at 14.98–15.67 min was reduced, which corresponded to distinct changes in the relative contributions to total absorption. For fluorescence spectra, phenyl sulfate exhibited an initial maximum fluorescence peak at Ex/Em = 255/279 nm at pH 8 (Fig. S15), displaying minimal variation from the pH 3 conditions (Fig. 4a). However, the temporal evolution of its fluorescence spectrum differs obviously at different pH values. Under basic conditions (pH 8), fluorescence decreased monotonically without recovery, and no red shift occurred even after 8 h.

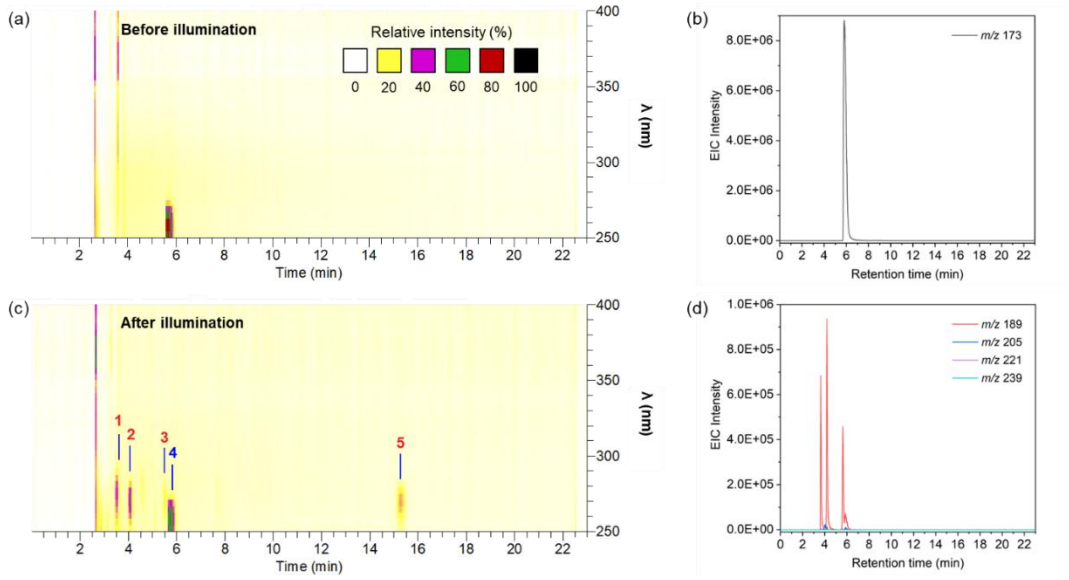


Figure 3. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of phenyl sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) phenyl sulfate and (d) the compositions of chromophores.

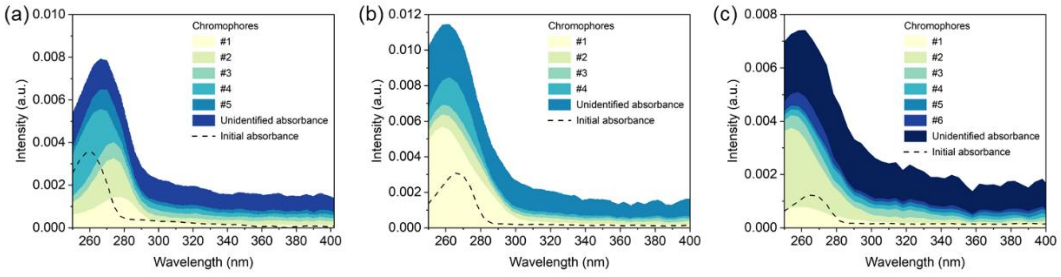


Figure S10. Contributions of the main absorbing chromophores to the total light absorption from the liquid-phase reactions of (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate with •OH at pH 3. The dotted line indicates the initial absorbance of phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate at pH 3.

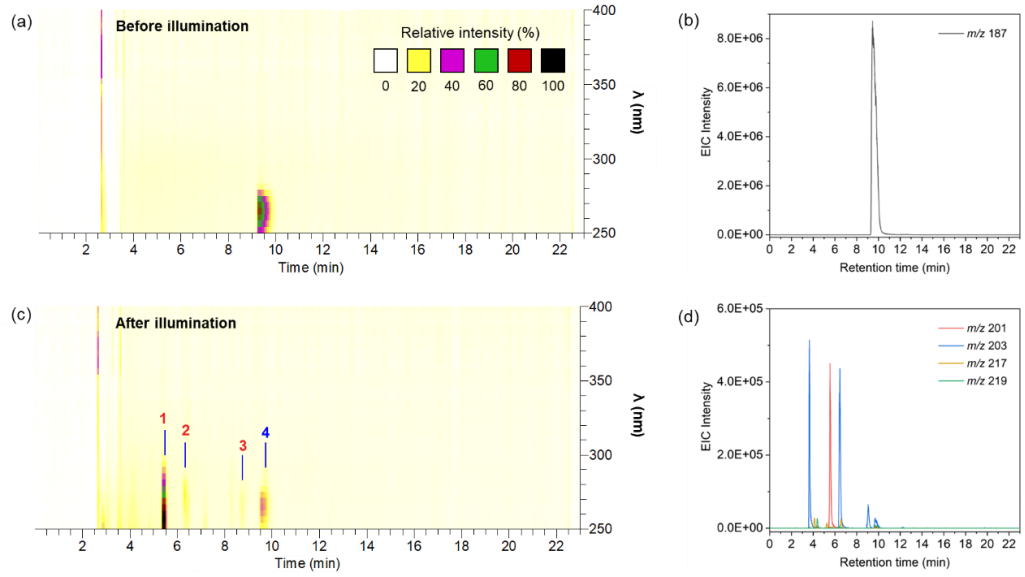


Figure S11. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of p-toly sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) p-toly sulfate and (d) the compositions of chromophores.

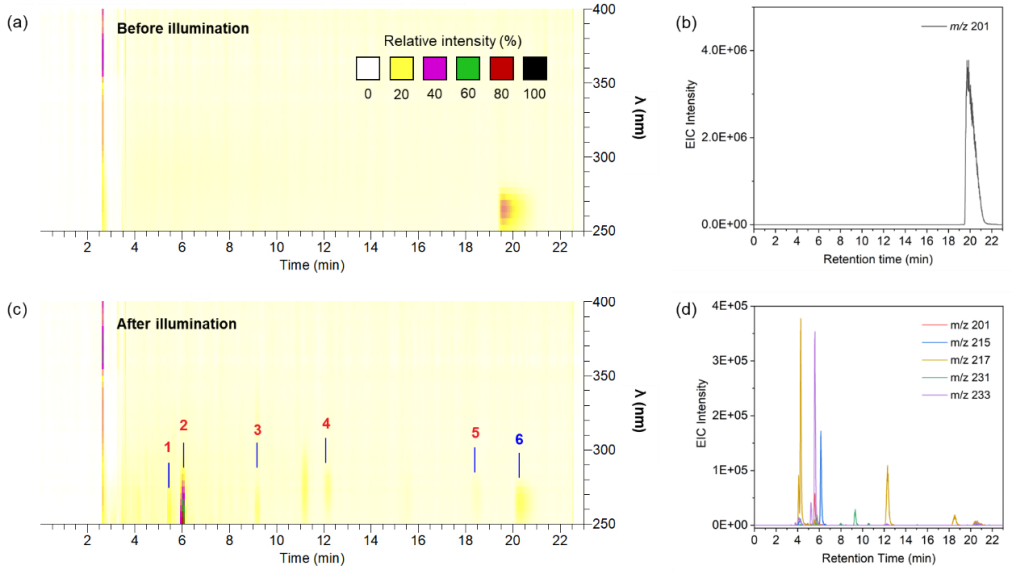


Figure S12. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of 4-ethylphenyl sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) 4-ethylphenyl sulfate and (d) the compositions of chromophores.

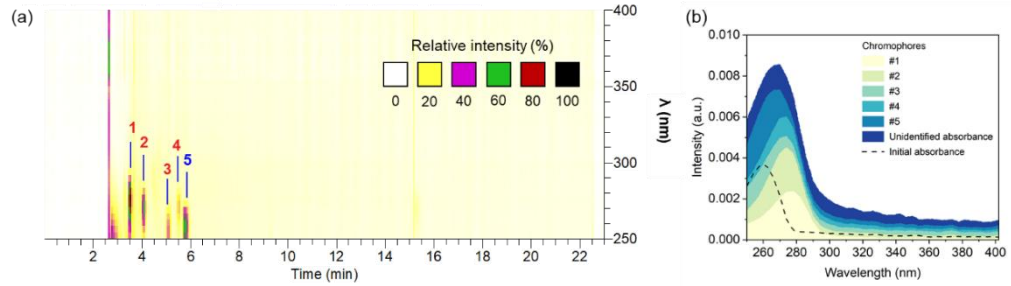


Figure S14. UPLC-PAD-MS chromatograms of sample collected (a) after the liquid-phase •OH oxidation of phenyl sulfate at pH 8. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. (b) Relative contribution of the main absorbing chromophores to the total light absorption from the liquid-phase reaction of phenyl sulfate with •OH at pH 8. The dotted line represents the initial absorbance of phenyl sulfate.

(Q17) *Figure 4: Please be more descriptive (i.e., avoid acronyms) whenever possible in figure captions and axes. While I hope that most don't just look at figures, many inevitably do, so it is best to avoid acronyms as much as possible.*

Response: We have replaced the abbreviations with their corresponding full name in figure captions and axes.

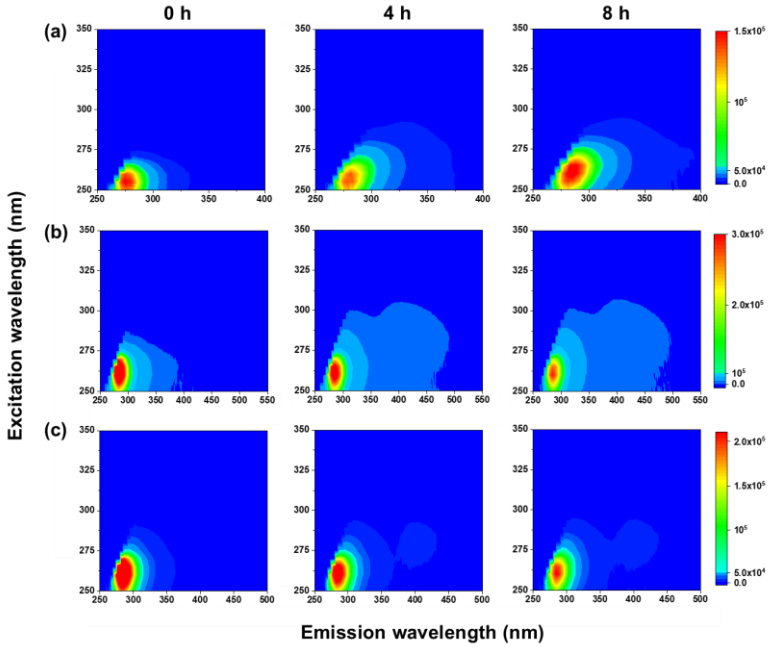


Figure 4. Time profile of excitation–emission matrix (EEM) fluorescence spectra during the processes of (a) phenyl sulfate, (b) p-tolyl sulfate and (c) 4-ethylphenyl sulfate reacting with •OH at pH 3.

Reviewer #2:

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. We have rephrased this sentence in the revised manuscript.

Page 1: In urban areas, in addition to isoprene and monoterpenes derived OSs, other OSs containing an aromatic ring were also observed in collected aerosols (Kundu et al., 2013; Huang et al., 2018; Wang et al., 2021; He et al., 2022).

(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 Section 1 (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.

Page 1: During the oxidation of some OSs (e.g., methyl sulfate, ethyl sulfate, 2-methyltetrol sulfate, and α-pinene derived OSs) by •OH, it is interesting to find that OSs can also return to inorganic sulfate except for new OS formation (Kwong et al., 2018; Xu et al., 2020, 2024).

Page 9: Additionally, a recent study proposed an alternative mechanism for the formation of inorganic sulfate, proceeding via sulfite radicals ($\bullet SO_3^-$) (Xu et al., 2024). In this pathway, a β-OSO_3^- alkoxy radical [-C(O•)–C(OSO_3^-)-] undergoes C–C bond cleavage, yielding an α-OSO_3^- alkyl radical, subsequently generating non-sulfate products and $\bullet SO_3^-$.

(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.

Page 3: Reaction progress was tracked by withdrawing 1 mL aliquots at 30-minute intervals for direct analysis via either ultrahigh-performance liquid chromatography (UPLC, Agilent 1260) or ion chromatography (Dionex ICS-600), without any intermediate process or dilution.

(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.

Page 6: Lai et al. (2024) reported that k_{OS} of ethyl sulfate ($3.8 \pm 0.1 \times 10^8$ M^{-1} s^{-1}) was approximately five times higher than that of methyl sulfate ($7.5 \pm 0.1 \times 10^7$ M^{-1} s^{-1}). Gweme and Styler (2024) also found that k_{OS} value increased with increasing carbon chain length for methyl sulfate ($1.03 \pm 0.21 \times 10^8$ M^{-1} s^{-1}), ethyl sulfate ($4.07 \pm 0.17 \times 10^8$ M^{-1} s^{-1}), and propyl sulfate ($1.22 \pm 0.03 \times 10^9$ 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.

Page 3: All experiments were performed at 298 K in at least duplicate.

(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 lower 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.

Page 7: It should be noted that different matrices (HCl *vs* phosphate buffer) were used to adjust the solution pH, and the ionic strength of the solution is different at different pHs. The ionic strengths of solution at pH 3 and pH 8 were estimated as 1 × 10^{-3} M and 6.9 × 10^{-3} M, respectively. Previous study reported that a substantial increase in ionic strength from ca. zero to 6.5 M only resulted in a tenfold decrease in k_{OS} value of phenyl sulfate (Gweme and Styler, 2024). Therefore, the relatively low ionic strength variation between pH conditions in this study may not account for the observed differences in the k_{OS} values of aromatic OSs

(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.*

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: 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 of aromatic OSs 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.

Page 7: The observation that product intensities were substantially higher under illumination conditions than in dark controls confirms that these products arise from •OH oxidation, not from analytical artifacts or hydrolysis (Fig. S6).

Page 9: In this study, the formation of inorganic sulfate during the reaction of phenyl sulfate with •OH was also examined. Figure S7a shows that the SO_4^{2-} peak in IC increased progressively with reaction time. The formation of inorganic sulfate was further supported by the evidence of the observed prominent HSO_4^- peak at *m/z* 97, which is assigned to HSO_4^-, in the mass spectra (Fig. S6b), the intensity in the extracted ion chromatograms (EIC) was substantially higher than in dark controls (Fig. S8a), ruling out in-source fragmentation or hydrolysis as the source of HSO_4^-. The results of IC and mass spectrometry suggest that in addition to the new OSs, inorganic sulfate can also be formed during the reaction.

In addition to new OSs formed, the formation of inorganic sulfate was also observed during the process of either p-tolyl sulfate or 4-ethylphenyl sulfate oxidized by •OH. For p-tolyl sulfate, the gradual increase of SO_4^{2-} peak with reaction time in IC as well as the pronounced signal of *m/z* 97 (HSO_4^-) observed in the mass spectra provide robust evidence for the formation of inorganic sulfate during the reaction (Figs. S7b and S8b). For 4-ethylphenyl sulfate, SO_4^{2-} peak in IC was found to overlap with that of the compound itself (Fig. S7c). The inference that 4-ethylphenyl sulfate converts to inorganic sulfate is supported by comparing the intensity of HSO_4^- (*m/z* 97) peak of samples collected from illumination and dark conditions (S8c).

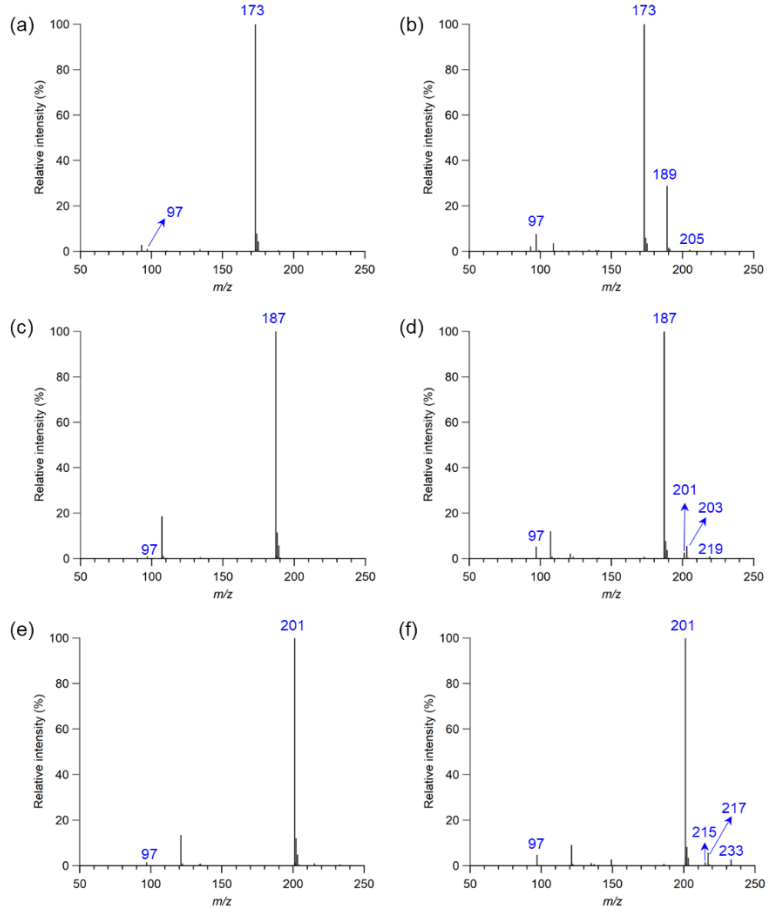


Figure S6. Mass spectra collected from the liquid-phase reactions of 0.05 mM (a, b) phenyl sulfate, (c, d) p-tolyl sulfate, and (e, f) 4-ethylphenyl sulfate with 10 mM H_2O_2 under dark (left panels) and illumination (right panels) conditions.

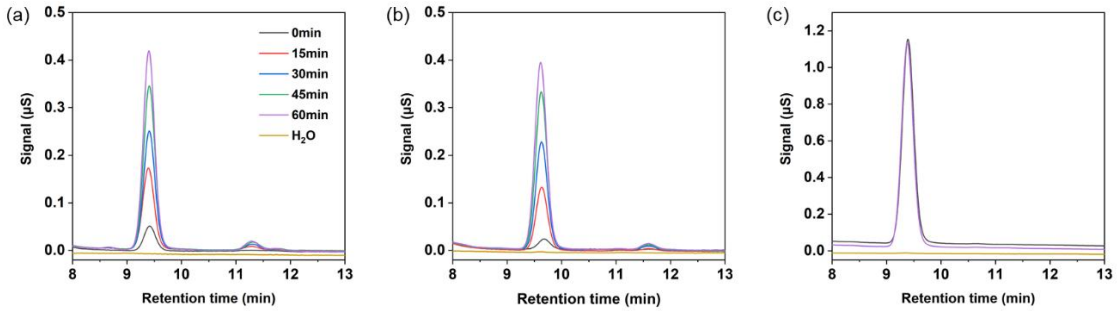


Figure S7. Time profile of SO_4^{2-} peak in ion chromatograms in the reactions of 0.05 mM (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate with •OH at pH 3. IC

result of water blank was shown as the comparison.

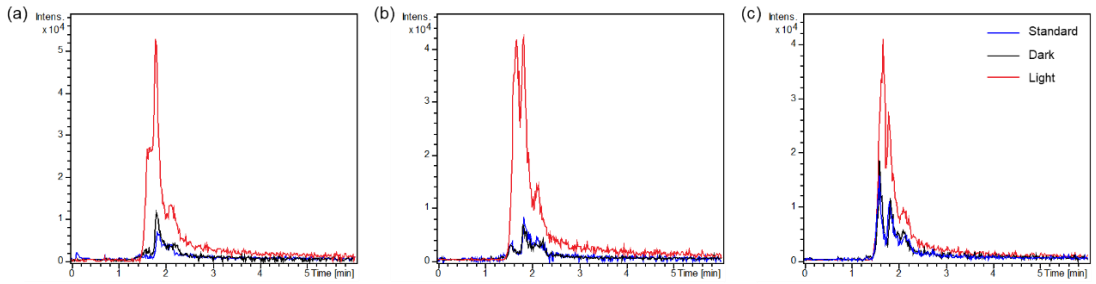


Figure S8. EIC of HSO_4^- (*m/z* 97) obtained from standards (blue line) of (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate, and from their liquid-phase reactions under dark (black line) and illumination (red line) conditions.

(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 this sentence in the revised manuscript.

Page 8: 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, we found that this compound can also be formed through the oxidation of phenyl sulfate by •OH, providing the additional pathway for its formation in the atmosphere.

(Q10) *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.

(Q11) *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. 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. 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 EIC comparison results to support this conclusion. More details can be seen in the Response of (Q8).

(Q12) *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 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 was verified by combining mass spectrometry and ion chromatography data. In analogous to phenyl sulfate, the formation of inorganic sulfate via the reaction of p-tolyl sulfate with •OH 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 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 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.

Page 9: Tables S3 and S4 summarize the identified products from the liquid-phase reactions of p-tolyl sulfate and 4-ethylphenyl sulfate with •OH, respectively. The mechanism of p-tolyl sulfate and 4-ethylphenyl sulfate oxidized by •OH is similar to that of phenyl sulfate as mentioned above. Similar to phenyl sulfate, the addition of •OH to the aromatic ring predominantly yields phenolic compounds, such as $C_7H_5O_5S^-$, $C_7H_7O_5S^-$, $C_8H_9O_5S^-$, and $C_8H_9O_6S^-$. Further oxidation initiated by hydrogen abstraction can also generate fragmented products, such as $C_5H_5O_6S^-$ and $C_4H_5O_7S^-$ (Tables S2 and S3). Moreover, the presence of alkyl

substituents for p-tolyl sulfate and 4-ethylphenyl sulfate can enable additional hydrogen abstraction pathways (Forstner et al., 1997; Baltaretu et al., 2009; Liu et al., 2017), leading to the formation of aromatic aldehydes (e.g., $C_7H_5O_5S^-$, $C_8H_7O_5S^-$). In addition to new OSs formed, the formation of inorganic sulfate was also observed during the process of either p-tolyl sulfate or 4-ethylphenyl sulfate oxidized by •OH. For p-tolyl sulfate, the gradual increase of SO_4^{2-} peak with reaction time in IC as well as the pronounced signal of *m/z* 97 (HSO_4^-) observed in the mass spectra provide robust evidence for the formation of inorganic sulfate during the reaction (Figs. S7b and S8b). For 4-ethylphenyl sulfate, SO_4^{2-} peak in IC was found to overlap with that of the compound itself (Fig. S7c). The inference that 4-ethylphenyl sulfate converts to inorganic sulfate is supported by comparing the intensity of HSO_4^- (*m/z* 97) peak of samples collected from illumination and dark conditions (Fig. S8c).

Table S3. Products from liquid-phase •OH oxidation of p-tolyl sulfate.

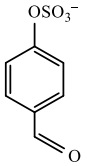
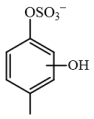
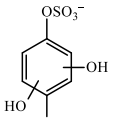
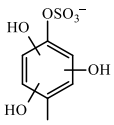
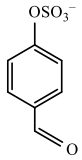
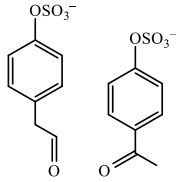
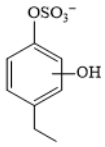
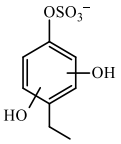
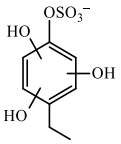
m/z **[M-H]**	**Error (ppm)**	**Formula**	**Structure**
192.9807	-2.756	$C_5H_5O_6S^-$	
200.9863	-0.235	$C_7H_5O_5S^-$	
203.0020	0.013	$C_7H_7O_5S^-$	
208.9760	-0.701	$C_5H_5O_7S^-$	
216.9816	1.697	$C_7H_5O_6S^-$	
218.9968	-0.465	$C_7H_7O_6S^-$	
234.9917	-0.368	$C_7H_7O_7S^-$	
253.0021	-1.032	$C_7H_9O_5S^-$	

Table S4. Products from liquid-phase •OH oxidation of 4-ethylphenyl sulfate.

m/z [M-H]	Error (ppm)	Formula	Structure
196.9762	0.272	$C_4H_5O_7S^-$	
200.9862	-0.583	$C_7H_5O_5S^-$	
215.0013	-3.104	$C_8H_7O_5S^-$	
217.0172	-1.923	$C_8H_9O_5S^-$	
230.9961	-3.385	$C_8H_7O_6S^-$	
233.0120	-2.283	$C_8H_9O_6S^-$	
246.9914	-1.605	$C_8H_7O_7S^-$	
249.0068	-2.597	$C_8H_9O_7S^-$	
267.0173	-2.664	$C_8H_{11}O_8S^-$	

(Q13) *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: 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 and characterized their optical properties using UPLC-PAD-MS. 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 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. In the revised manuscript, we have reconstructed the discussion on the mechanism underlying the changes in optical properties at the molecular-level.

Page 10: Kinetic and mechanism results show that aromatic OSs can undergo rapid •OH oxidation to form a series of functionalized and fragmented compounds. The changes of optical properties resulting from the formation of these compounds were also investigated. Figure S9 shows the time-dependent absorption spectra of aromatic OSs during •OH oxidation at pH 3. As the reaction progressed, the consume of reactants accompanied with the increase in absorbance across 250–400 nm. To establish the relationship between light absorption and organic compounds, chromophores formed in the reaction were identified by correlating UV absorption bands with the retention time based on UPLC-PAD-MS analysis. For phenyl sulfate, Figure 3a displays that phenyl sulfate (*m/z* 173) was the prominent chromophore with the retention time of 5.67–6.16 min at the beginning of the reaction, exhibiting a characteristic absorption peak at 262 nm (Fig. S9a). After the liquid-phase •OH oxidation, five major chromophores were observed as shown in Fig. 3c. Chromophore #4 was assigned to the unreacted phenyl sulfate. Figure 3c shows that Chromophore #1, #2, and #3 eluted at 3.47–3.72 min, 4.00–4.18 min, and 5.46–5.60 min, respectively. These newly formed chromophores exhibit red-shifted absorption peaks (Fig. 10a), likely due to the electron-donating effect of hydroxyl groups increasing aromatic ring electron density (Hems and Abbatt, 2018). The results of EIC suggest that these chromophores correspond to co-eluting mixtures containing $C_6H_5O_5S^-$ isomers (*m/z* 189), along with $C_6H_5O_6S^-$ (*m/z* 205), $C_6H_5O_7S^-$ (*m/z* 221) and $C_6H_7O_8S^-$ (*m/z* 239) (Fig. 3d). Among these compounds, $C_6H_5O_6S^-$ exhibited the highest intensity. Chromophore #5, eluting at 14.98–15.67 min, remained unidentified. Its later elution time suggests a larger molecular structure and lower polarity (Fleming et al., 2020). Additionally, there may exist other chromophores unidentified since these five chromophores can not fully explain the total light adsorption as shown in Fig. 10a.

For p-tolyl sulfate, the increase in absorbance, contributing by the formation of chromophores, was also observed after OH oxidation. The primarily newly formed chromophore (Chromophore #1), eluting at 5.23–5.78 min, was identified as $C_7H_5O_5S^-$ (*m/z* 201) based on the corresponding EIC (Figs. S11c and d). A blue-shift peak at 258 nm was observed upon the formation of $C_7H_5O_5S^-$, which is associated with the generation of a carbonyl (C=O) functional group (Fig. S10b). Other newly formed chromophores were characterized as Chromophore #2 and Chromophore #3. Chromophore #2 corresponded to a mixture of $C_7H_7O_5S^-$ (*m/z* 203),

$C_7H_7O_5S^-$ (*m/z* 217), and $C_7H_7O_6S^-$ (*m/z* 219) with absorption band at 274 nm, and Chromophore #3 was assigned to $C_7H_7O_5S^-$ (*m/z* 203) with the absorption band at 266 nm (Figs. S10b and S11). Figures S10c and S12 show the characterization of chromophores formed from liquid-phase reaction of 4-ethylphenyl sulfate with OH radicals. After reactions, Chromophore #2 ($C_8H_7O_5S^-$, *m/z* 215) with a characteristic absorption peak at 254 nm was the dominant contributor to total light absorption. Four additional chromophores were also identified: Chromophore #1, a mixture of $C_7H_7O_5S^-$ (*m/z* 201), $C_8H_9O_5S^-$ (*m/z* 217), $C_8H_7O_6S^-$ (*m/z* 231), and $C_8H_9O_6S^-$ (*m/z* 233), with absorption peak at 258 nm; Chromophore #3, an isomer of $C_8H_7O_6S^-$, with absorption peak at 262 nm; Chromophore #4, an isomer of $C_8H_9O_5S^-$ (*m/z* 217), with absorption peak at 274 nm; and Chromophore #5, another isomer of $C_8H_9O_5S^-$, also with a characteristic absorption peak at 274 nm.

Furthermore, fluorescence evolutions during liquid-phase •OH oxidation of aromatic OSs were investigated as shown in Fig. 4. The initial maximum excitation/emission (Ex/Em) wavelengths of phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate at pH 3 were Ex/Em = 255/275 nm, 260/284 nm, and 260/284 nm, respectively. The different initial fluorescence intensity among these three aromatic OSs may be attributed to the substituent effect of the compound. Compared to phenyl sulfate, p-tolyl sulfate and 4-ethylphenyl sulfate contain additional methyl and ethyl groups, respectively. These electron-donating substituents extend the conjugation system, lowering the $\pi \rightarrow \pi^*$ transition energy and resulting in both emission redshift and fluorescence enhancement (Cao et al., 2023). During the reaction, the fluorescence intensity initially decreased due to phenyl sulfate consumption, followed by a subsequent increase from fluorescent product formation. After 8 h of illumination, a redshifted fluorescence peak emerged at Ex/Em = 260/283 nm, implying the formation of products with expanded conjugated systems (e.g., $C_6H_5O_5S^-$, $C_6H_5O_6S^-$ and $C_6H_5O_7S^-$) (Tang et al., 2020). The fluorescence intensity of p-tolyl sulfate and 4-ethylphenyl sulfate monotonically decreased with the reaction time and showed a redshift in the fluorescence band at Ex/Em = (250–300)/(400–500). Previous studies uncovered that the emission wavelengths of 400–500 nm are the indicative of humic-like substances (HULIS), which can significantly contribute to the light-absorbing properties of organic aerosols (Bianco et al., 2014). Previous studies revaled that the oxidation of non-photolyzable phenolics by •OH can yield HULIS-like fluorescent products (Tang et al., 2020; Chang et al., 2010). Here, multi-hydroxy products from p-tolyl sulfate (e.g., $C_7H_7O_5S^-$, $C_7H_7O_6S^-$ and $C_7H_7O_7S^-$) and 4-ethylphenyl sulfate (e.g., $C_8H_9O_5S^-$, $C_8H_9O_6S^-$ and $C_8H_9O_7S^-$) may exhibit spectral features resembling aerosol HULIS.

Employing phenyl sulfate as the representative, spectral changes at pH 8 were also examined. Previous studies have demonstrated that the light absorption properties of carbonyl compounds (e.g., aldehydes) and nitrophenols exhibit pronounced pH-dependence owing to protonation-deprotonation equilibria (Calvert and Schnitzler, 2023; Chen et al., 2020b). In this study, the phenyl sulfate remains deprotonated across the pH range of 3–8, resulting in negligible spectral variations in the initial solution (Figs. S9 and S13). However, the temporal evolution of the reaction revealed substantially enhanced absorbance at pH 3 compared to pH 8, particularly within the 300–400 nm range. Figure S14 shows the molecular composition of chromophores from the reaction of phenyl sulfate with •OH at pH 8. Chromophores #1–3 were identical to those at pH 3 but exhibited stronger absorption due to their higher concentrations. An additional chromophore #4, eluting at 4.99–5.23 min, contributed significantly to absorption but the

detailed composition of this chromophore is unknown. Compared to pH 3, solution of pH 8 exhibited an enhanced peak intensity at 4.99–5.23 min, while the peak at 14.98–15.67 min was reduced, which corresponded to distinct changes in the relative contributions to total absorption. For fluorescence spectra, phenyl sulfate exhibited an initial maximum fluorescence peak at Ex/Em = 255/279 nm at pH 8 (Fig. S15), displaying minimal variation from the pH 3 conditions (Fig. 4a). However, the temporal evolution of its fluorescence spectrum differs obviously at different pH values. Under basic conditions (pH 8), fluorescence decreased monotonically without recovery, and no red shift occurred even after 8 h.

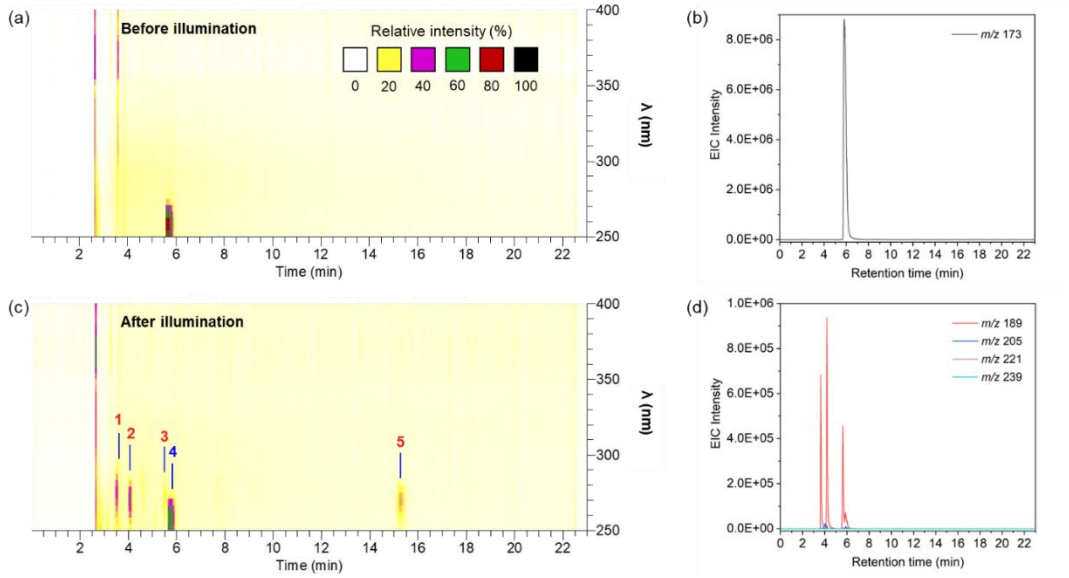


Figure 3. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of phenyl sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) phenyl sulfate and (d) the compositions of chromophores.

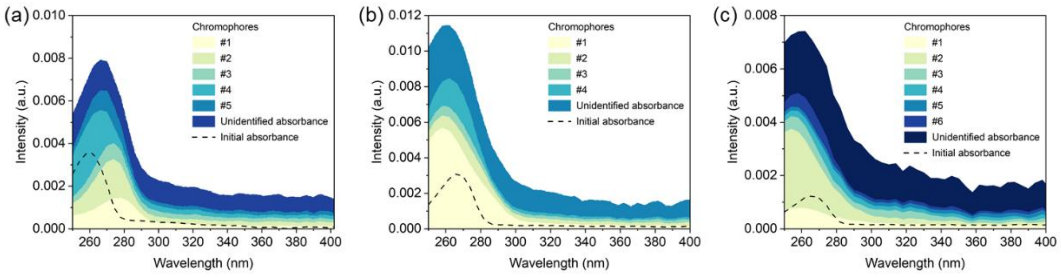


Figure S10. Contribution of the main absorbing chromophores to the total light absorption from the liquid-phase reactions of (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate with •OH at pH 3. The dotted line indicates the initial absorbance of phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate at pH 3.

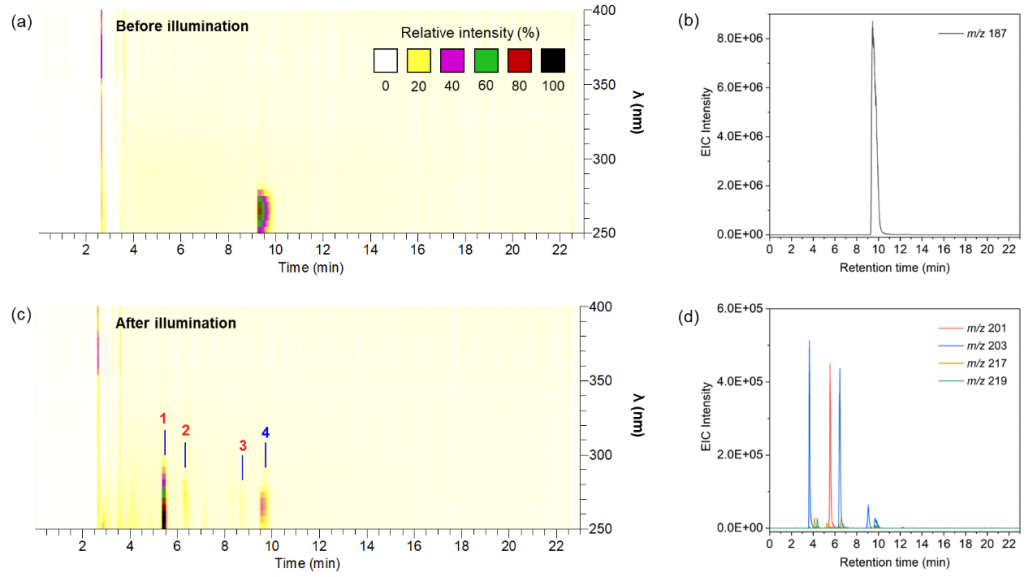


Figure S11. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of p-toly sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) p-toly sulfate and (d) the compositions of chromophores.

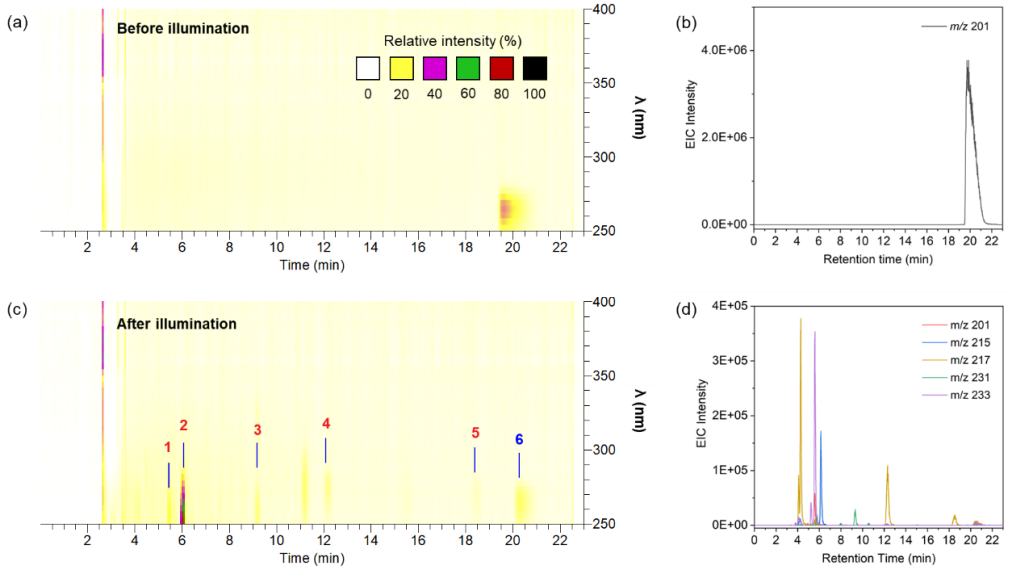


Figure S12. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase •OH oxidation of 4-ethylphenyl sulfate at pH 3. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) 4-ethylphenyl sulfate and (d) the compositions of chromophores.

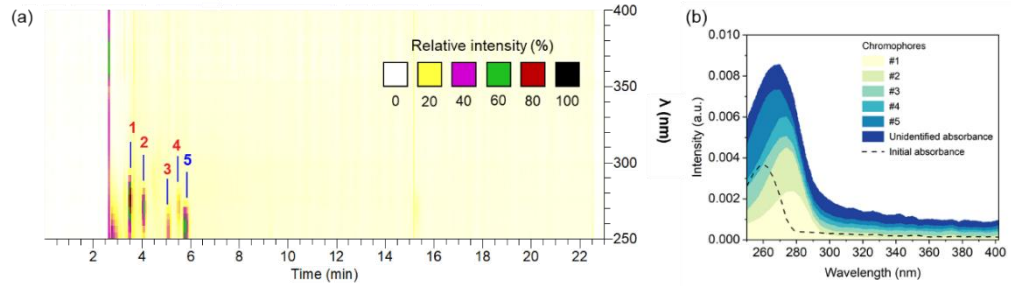


Figure S14. UPLC-PAD-MS chromatograms of sample collected (a) after the liquid-phase •OH oxidation of phenyl sulfate at pH 8. The y-axis and color map represents the wavelength and corresponding UV-vis absorbance, respectively. (b) Relative contribution of the main absorbing chromophores to the total light absorption from the liquid-phase reaction of phenyl sulfate with •OH at pH 8. The dotted line represents the initial absorbance of phenyl sulfate.

(Q14) *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.

Reviewer #3:

The article by Yang et al. investigates the kinetics and products of liquid-phase OH radical oxidation of three aromatic organosulfates (OSs), namely phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate. The authors employed a batch reactor containing an aqueous solution of aromatic OSs, H_2O_2, and dissolved O_2 under xenon lamp irradiation to study OH radical oxidation processes. Concentrations of the OSs were quantified using LC–MS analysis, while UV–visible absorption and fluorescence spectra were also measured. The results and conclusions provide new insights into this field, including faster OH oxidation rates under more alkaline conditions, the formation of inorganic sulfate, and the production of brown carbon–like species. Incorporation of these findings into atmospheric models could improve understanding of the atmospheric impacts of aromatic OS oxidation. However, the manuscript would benefit from additional work and refinement prior to publication in an EGU journal, particularly through the inclusion of missing references, more detailed discussion of the results, and a clearer overall structure.

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 changed the title of the manuscript.
(2) We have revised the discussion about the possible explanations for the difference in rate constant at different pH values.
(3) We have reconstructed the discussion about atmospheric lifetime of aromatic OSs under different environmental conditions.
(4) We have provided more details about the quantitation method of three aromatic OSs and benzoic acid.
(5) We have cited the related references, 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) *Change "multiphase" to "liquid-phase" or delete "multiphase" from the title, the whole manuscript and supplement. In atmospheric science, the "multiphase reaction" generally means heterogeneous reactions happening between different phases (e.g., gas and liquid). To study multiphase reactions, people generally react gas-phase VOCs or oxidants with liquid-phase aerosol inside a chamber. All papers with titles including "multiphase" the authors cited used a chamber to study the aerosol-gas reaction. This study used a water solution containing reactants in batch reactor and studied liquid-phase reactions.*

Response: We have changed the title of manuscript to "Liquid-phase reactions of aromatic organosulfates with OH radicals: Kinetics, mechanisms, and environmental effects".

(Q2) *In Section 2.3, explain in more detail the quantification of OSs compounds and do a mass closure calculation. The authors said that the concentration was detected by LCMS analysis. However, the specific quantification process was unclear in the paper. Two essential questions the reader may ask: What standards the authors used to quantify OSs and their oxidation products? What percentage of total compounds quantified using both IC and LC/MS (a mass closure calculation)?*

Response: Thanks for your comment. In this study, for kinetic studies, the concentrations of aromatic OS and benzoic acid were simultaneously quantified by their corresponding commercial standards using UPLC. For mechanism studies, due to the lack of authentic standards, qualitative rather than quantitative measurements of new OSs formed during the reaction of aromatic with OH radicals were carried out using LC-MS. Moreover, it is noted that inorganic sulfate species can also be in the form of SO_4^{2-} (*m/z* 48) in addition to HSO_4^- (*m/z* 97) in the mass spectra. Peak at *m/z* 48 is below the mass range of the instrument (50–500), and the distribution of different forms of inorganic sulfate species is significantly affected by the solution pH. Therefore, it seems that accurately measuring inorganic sulfate concentration via LC-MS using the external standard method is not feasible. In the revised manuscript, we have provided further details regarding the quantitation method for the three aromatic OSs (i.e., phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate) and for benzoic acid.

Page 5: The concentration of aromatic OSs and BA was detected using an ultrahigh-performance liquid chromatography (UPLC, Agilent 1260) coupled with a UV detector operating at 254 nm. Chromatographic separation was performed on a ZORBAX Eclipse Plus C18 column (4.6 mm × 250 mm, 5 μm) maintained at 40 °C. The mobile phase consisted of acetonitrile and 0.1% formic acid aqueous solution (20:80, v/v) delivered at a flow rate of 0.8 mL min^{-1}, with an injection volume of 10 μL. Quantification of aromatic OSs and BA was achieved by external calibration using commercial standards (Fig. S5), based on their corresponding peak areas in the chromatogram.

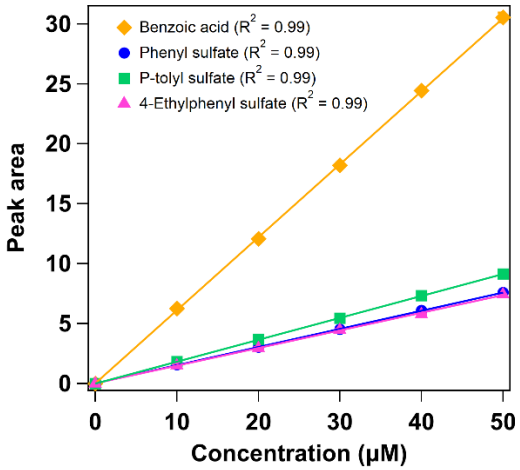


Figure S5. Calibration curves of benzoic acid, phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate.

(Q3) *The authors observed that aromatic OSs reacting with OH radical more rapidly in alkaline solution (pH 8) compared to acidic solution (pH 3). However, I am not entirely convinced that the acidity is the reason for this change in OH oxidation kinetics. As the solution at pH 3 contains HCl and the solution at pH 8 contains phosphate buffer (Na_2HPO_4 and NaH_2PO_4). These additional compounds in solutions may affect the OH radical oxidation kinetics. The authors need to prove that the change in oxidation kinetics is indeed caused by acidity change. The authors also need to explain why they chose phosphate buffer to adjust the pH, as phosphate is not a ubiquitous species in atmosphere.*

Response: The acidity of the solution increased slightly after the reactions for kinetic studies.

This increase is negligible at an initial pH of 3 but becomes significant at an initial pH of 8. Therefore, although phosphate is not a ubiquitous species in the atmosphere, a phosphate buffer was still used to maintain the pH at 8 throughout the reactions. Phosphate buffers have also been employed in similar kinetic studies in previous work (Witkowski et al., 2019).

Previous studies have shown that even though methoxyphenols, benzene-diols, and highly substituted phenols exist predominantly in protonated form within the pH range of 2 to 6, their second-order reaction rate constants with •OH at pH 2 are generally lower than those at pH 5 or 6. (Smith et al., 2015; Arciva et al., 2022). Moreover, we observed variations in product distributions at different pH values, suggesting the involvement of distinct reaction mechanisms, thereby affecting the kinetics of •OH oxidations. Other possible reasons for the difference in rate constants at different pH values may include uncertainty in the rate constant of the reaction of reference with •OH, as well as differences in the reaction matrix (HCl *vs* phosphate buffer) as noted by the reviewer (Arciva et al., 2022). In the revised manuscript, we have revised the discussion about the possible explanations for the difference in the rate constant at different pH values.

Page 7: It should be noted that different matrices (HCl *vs* phosphate buffer) were used to adjust the solution pH, and the ionic strength of the solution is different at different pHs. The ionic strengths of solution at pH 3 and pH 8 were estimated as 1×10^{-3} M and 6.9×10^{-3} M, respectively. Previous study reported that a substantial increase in ionic strength from ca. zero to 6.5 M only resulted in a tenfold decrease in k_{OS} value of phenyl sulfate (Gweme and Styler, 2024). Therefore, the relatively low ionic strength variation between pH conditions in this study may not account for the observed differences in the k_{OS} values of aromatic OSs. Gweme and Styler (2024) measured the k_{OS} of phenyl sulfate at pH 2 and pH 9, observing that it was pH independence. They attributed this pH independence to phenyl sulfate remaining fully deprotonated (pKa = –2.2) across the entire experimental pH range. However, previous studies demonstrated that even though methoxyphenol, benzene-diols, and highly substituted phenol mainly exist in their protonated form within the pH range of 2 to 6, their second-order reaction rate constants with OH radicals at pH 2 were generally lower than those at pH 5 or 6 (Arciva et al., 2022). On possible explanation is that the acidic condition could hinder OH radical attack on aromatic systems or reduce the lifetime of hydroxyl-cyclohexadienyl radical intermediates, slowing irreversible diol formation (Smith et al., 2015). Another possible explanation is the uncertainty of the second-order rate constant of the reaction of reference with the OH radical (Arciva et al., 2022). Therefore, the difference and uncertainty of the rate constant of the reference may also explain the discrepancy between that reported by Gweme and Styler (2024) and our study.

(Q4) *Add a section specifically explaining the calculation of the lifetime of OSs against OH radical oxidation. The authors could include more information on the ambient OH concentrations. Ambient OH concentrations [•OH] could fluctuate greatly from remote to urban environments, the authors could discuss a little more about the ambient OH concentrations across different regions, especially on the urban sites. Moreover, in Lines 298-299, the authors mentioned that "The lifetime of aromatic OSs is significantly shorter than those of aliphatic OSs (Gweme and Styler, 2024; Lai et al., 2025)." However, the authors didn't further explain why. Also, the cited studies reported oxidation kinetics in liquid-phase. There are other laboratory studies (listed below) reported the heterogeneous OH oxidation kinetics*

of aliphatic OSs. The authors may also want to include these studies in the discussion of aerosol lifetimes.

Response: Thanks for your suggestion. In the revised manuscript, we have added the discussion on the atmospheric lifetime of aromatic OSs under different environmental conditions and improved the comparative analysis of the lifetimes of various OSs, including heterogeneous •OH oxidation.

Page 13: As shown in Table S5, using the *k* value coupled with modeled •OH concentrations (Herrmann et al., 2005, 2010), the corresponding lifetime ($\tau=1/k_{OS}\times[\bullet OH]$) of aromatic OSs was calculated. In urban areas, the concentrations of •OH in cloud and aerosol are estimated as 3.5×10^{-15} and 4.4×10^{-13} M, respectively. In contrast to urban areas, remote areas exhibit higher •OH concentrations both in cloud (2.2×10^{-14} M) and aerosol (3.0×10^{-12} M) (Herrmann et al., 2005, 2010). Concentrations of •OH are consistently higher in aerosol than in cloud water across different environments. Consequently, the lifetime of aromatic OSs ranges from approximately 1 min in remote aerosols to up to 16 h in urban cloud water (Table S5), highlighting the significant influence of environmental conditions on their persistence. Previous studies reported that the lifetime of aliphatic OSs in such varied environments ranges from several minutes to dozen days (Gweme and Styler, 2024; Lai et al., 2025). The substantially shorter lifetimes of aromatic OSs can be attributed to their higher reactivity toward OH radicals compared to aliphatic OSs. Given the high abundance of aromatic OSs and their fast reactivity with •OH in urban environments, aromatic OSs likely play a significant role in both the atmospheric sulfur cycle and environmental effects. In addition to lifetimes in aqueous environments, previous studies also estimated the atmospheric lifetimes of several aliphatic OSs via heterogeneous •OH oxidation based on measured uptake coefficients (Kwong et al., 2018; Lam et al., 2019; Xu et al., 2022). For instance, the atmospheric lifetime of methyl sulfate ranges from 53 min to 32 days via liquid-phase OH radical oxidation, compared to approximately 20 days via heterogeneous •OH oxidation (Gweme and Styler, 2024; Kwong et al., 2018). The results indicate that the atmospheric lifetimes of these OSs differ between liquid-phase and heterogeneous •OH oxidation pathways. However, experiments of heterogeneous reactions of aromatic OSs with •OH were not conducted in this study. Thus, we cannot directly compare the lifetime of aromatic and aliphatic OSs through heterogeneous •OH oxidation, and need further investigations.

Table S5. Calculated lifetimes of OS via liquid-phase •OH oxidation in different scenarios.

Species	*k* (M^{-1} s^{-1})	Aerosol		Cloud		Reference
		Urban	Remote	Urban	Remote	
Phenyl sulfate	5.09×10^{9}[a]	7 min	1 min	16 h	2 h	This study
p-Tolyl sulfate	5.37×10^{9}[a]	7 min	1 min	15 h	2 h	
4-Ethylphenyl sulfate	5.40×10^{9}[a]	7 min	1 min	15 h	2 h	
Methyl sulfate	1.05×10^{8}	6 h	53 min	32 day	5 day	(Gweme and Styler, 2024)
Ethyl sulfate	3.93×10^{8}	2 h	14 min	8 day	1 days	

Propyl sulfate	1.22×10^{9}	31 min	5 min	3 day	10 h	
Hydroxyacetone sulfate	1.52×10^{8}	4 h	37 min	22 day	4 days	
α-Pinene-derived organosulfate	2.2×10^{9}		3min	2 day		(Lai et al, 2025)

k value represents the average value under the pH 3 and pH 8 conditions in this study.

•OH concentrations are obtained from CAPRAM model (Herrmann et al., 2005, 2010). $[\bullet OH]_{urban\ aerosol} = 4.4 \times 10^{-13}$ M; $[\bullet OH]_{remote\ aerosol} = 3 \times 10^{-12}$ M; $[\bullet OH]_{urban\ cloud} = 3.5 \times 10^{-15}$ M; $[\bullet OH]_{urban\ cloud} = 2.2 \times 10^{-14}$ M

(Q5) *The first row of the Table S3 lists the concentration of OH radicals while other rows list the lifetimes (days). It would be better to put the concentration of OH radicals as a note at the end of the table or on the title.*

Response: We have put the concentration of OH radical as a note at the end of the table.

(Q6) *Lines 21-25: Cite study Hu, W. W., P. Campuzano-Jost, B. B. Palm, et al. "Characterization of a Real-Time Tracer for Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA) from Aerosol Mass Spectrometer Measurements." Atmospheric Chemistry and Physics 15, no. 20 (2015): 11807–33. https://doi.org/10.5194/acp-15-11807-2015.; Lines 41-42: Add references to "previous studies revealed that the addition of sulfate radicals on the C=C bond can result in the formation of OSs in aqueous aerosols". Lines 85-86: add reference Pye et al., 2020 review paper on aerosol acidity, focus more on the aerosol in the urban sites; Lines 154-155: I recommend the authors also cite following laboratory studies (listed below) on the heterogeneous OH radical oxidation of isoprene epoxy diol-derived secondary organic aerosol (IEPOX-SOA). These two studies also suggest that reaction rate is faster for aliphatic OSs with longer carbon chain length: a. Yan, J.; Zhang,Y.; Chen,Y.; Armstrong, N.C.; Buchenau, N. A.; Lei, Z.; Xiao,Y.; Zhang, Z.; Lambe, A. T.; Chan,M.N. Kinetics and Products of Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-Derived Secondary Organic Aerosol. ACS Earth Space Chem. 2023, 7, 1916. b. Armstrong, N. C.; Chen, Y.; Cui, T.; Zhang,Y.; Christensen, C.; Zhang, Z.; Turpin, B. J.; Chan, M. N.; Gold, A.; Ault, A. P. Isoprene Epoxydiol-Derived Sulfated and Nonsulfated Oligomers Suppress Particulate Mass Loss during Oxidative Aging of Secondary Organic Aerosol. Environ. Sci.Technol. 2022, 56, 16611; Lines 207-208: add references to the "previous studies"; Lines 222-224: add references on "benzoic acid can undergo decarboxylation reactions", and "the elimination of the sulfate group from phenyl sulfate".*

Response: Thanks for your suggestion. We have cited related references in the revised manuscript.

(Q7) *Lines 34-35: The focus of the study is on the aromatic OSs, I would suggest the authors focus more on the introduction of aromatic OSs in urban sites. The authors could lists more studies which detected aromatic OSs in the urban atmosphere (Huang et al.,2020; Li et al., 2023). Then mention the Ma et al., 2025 study to show their contributions to ambient aerosol. a. Huang, Liubin, Tongshan Liu, and Vicki H. Grassian. Radical-Initiated Formation of Aromatic Organosulfates and Sulfonates in the Aqueous Phase. Environmental Science & Technology 54, no. 19 (2020): 11857–64. https://doi.org/10.1021/acs.est.0c05644. b. Li, Ailin,*

Xiaodi Shi, Xinghua Qiu, et al. "Organosulfur Compounds in Ambient Fine Particulate Matter in an Urban Region: Findings of a Nontargeted Approach." Science of The Total Environment 887 (August 2023): 164114. https://doi.org/10.1016/j.scitotenv.2023.164114.

Response: Thanks for your suggestion. We have reconstructed the introduction about aromatic OSs in the atmosphere.

Page 1: In urban areas, in addition to isoprene and monoterpenes derived OSs, other OSs containing an aromatic ring were also observed in collected aerosols (Kundu et al., 2013; Huang et al., 2018; Wang et al., 2021; He et al., 2022). He et al. (2022) identified four kinds of aromatic OSs (i.e., phenyl sulfate, methylphenyl sulfate, benzyl sulfate and phenethyl sulfate) with concentrations ranging from 0.04 ± 0.08 to 2.37 ± 3.59 ng m^{-3} in $PM_{2.5}$ collected in Chengdu, China. Previous study observed that aromatic OSs can account for up to 63.5% of the total identified OSs in a megacity in China (Ma et al., 2014).

(Q8) *Lines 54-55: I don't see the point of stating the effects of carbon chain length on the OH oxidation kinetics in the introduction part, as the authors later explains the chain length effects in Section 3.1. So I would recommend the authors to just summarize the oxidation kinetics reported from previous studies for aliphatic OSs in introduction part.*

Response: In the revised manuscript, we have shortened the discussion about chain length effects in Section 1 (Introduction) and added more details about this effect in Section 3.1.

Page 2: Lai et al. (2024) investigated the kinetics of reactions of methyl sulfate and ethyl sulfate with •OH, finding that the rate constant (k) may be significantly affected by the carbon chain length. This observation was also verified in more kind of aliphatic OSs (methyl sulfate, ethyl sulfate, and propyl sulfate) (Gweme and Styler, 2024).

Page 6: This observation is quite different from that for the alkyl OSs, which shows that k_{OS} is strongly dependent on the carbon number of OS molecule contained (Armstrong et al., 2022; Yan et al., 2023; Lai et al., 2024; Gweme and Styler, 2024). Lai et al. (2024) reported that k_{OS} of ethyl sulfate ($3.8 \pm 0.1 \times 10^8$ M^{-1} s^{-1}) was approximately five times higher than that of methyl sulfate ($7.5 \pm 0.1 \times 10^7$ M^{-1} s^{-1}). Gweme and Styler (2024) also found that k_{OS} value increased with increasing carbon chain length for methyl sulfate ($1.03 \pm 0.21 \times 10^8$ M^{-1} s^{-1}), ethyl sulfate ($4.07 \pm 0.17 \times 10^8$ M^{-1} s^{-1}), and propyl sulfate ($1.22 \pm 0.03 \times 10^9$ M^{-1} s^{-1}). This distinct behaviour may be ascribed to the different mechanism for aromatic OSs and alkyl OSs oxidized by •OH. For aromatic OSs, the OH radical predominantly attacks the aromatic ring with multiple addition sites and has high reactivity (Bloss et al., 2005; Garmash et al. 2020). While alkyl OSs react primarily through hydrogen abstraction, the increasing carbon chain length can enhance reactivity through the inductive effect of $-CH_x$ groups, the increasing electron density at the hydrogen abstraction site, and the stabilization of resulting alkyl radicals (Monod and Doussin, 2008; Dorfman and Adams, 1973).

(Q9) *Line 67. The author mentioned that "a very recent study…". However there is no reference to this study.*

Response: We have cited the related reference in the revised manuscript.

Page 2: A very recent study investigated the aqueous-phase •OH oxidation of phenyl sulfate other than aliphatic OSs (Gweme and Styler, 2024),

(Q10) *Lines 72-74: The sentence "In this study, we investigated the multiphase reaction of atmospherically relevant aromatic OSs (i.e., phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl*

sulfate) with OH radicals (He et al., 2022)" is somewhat confusing, as the reference (Hu et al., 2022) appears to support the present study rather than the atmospheric relevance of the compounds. I suggest separating this into two sentences. For example, the authors could write: "Phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate have been observed as atmospherically relevant aromatic OSs in Chengdu, an urban environment during winter (He et al., 2022). In this study, we investigated their liquid-phase reactions with OH radicals."

Response: Thanks for your suggestion. We have rephrased this sentence in the revised manuscript.

Page 1: He et al. (2022) identified four kinds of aromatic OSs (i.e., phenyl sulfate, methylphenyl sulfate, benzyl sulfate and phenethyl sulfate) with concentrations ranging from 0.04 ± 0.08 to 2.37 ± 3.59 ng m^{-3} in $PM_{2.5}$ collected in Chengdu, China.

Page 3: In this study, we investigated the liquid-phase reactions of atmospherically relevant aromatic OSs (i.e., phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate) with •OH (He et al., 2022).

(Q11) *Line 88: the authors could explain more why choose the initial concentration of aromatic OSs to be 0.05 mM? How is this value compared to that in ambient aerosol?*

Response: The typical concentrations of aromatic OSs in aerosols range from a few hundredths to several ng m^{-3} (Kundu et al. 2013; He et al., 2022). Assuming an aerosol liquid water content (ALWC) of 1–100 μg m^{-3} (Guo et al., 2015; Su et al., 2022), the corresponding concentration in aerosols is estimated to be on the order of several μM to several mM. In this study, the concentration of aromatic OSs (50 μM) used falls within this atmospherically relevant range.

(Q12) *Lines 89-90: "additional experiments with elevated concentrations of OSs (0.5 or 1 mM) were carried out in order to observe obvious product signals and optical change characteristics." Does the high concentration of OSs change the oxidation kinetics determined using lower concentration (0.05mM)? The authors could report both the oxidation kinetics (k) for low and high concentration experiments if possible.*

Response: Unlike studies that directly determined the rate constants of reactants with oxidants based on pseudo first-order assumption, our study employed a competition kinetics method using BA as the reference to measure the second-order rate constants for the oxidation of aromatic OSs by •OH. Therefore, we did not investigate the effect of concentration on the rate constants. Although experiments were also performed at elevated OS concentrations to observe obvious changes in optical properties, BA was not added to the solution for these experiments to avoid interference with product analysis. Consequently, despite having decay curves of aromatic OSs under high-concentration conditions, we could not calculate their reaction rate constants due to the absence of BA.

(Q13) *Line 212: change "sulfate anions ($•SO_4^-$)" to "sulfate radical anions ($•SO_4^-$)" assuming the "•" means "Radicals"*

Response: We have corrected this typo in the revised manuscript.

(Q14) *Lines 230-231: the author wrote "Figure S7 reveals that $C_6H_5O_5S^-$ exists as three isomeric forms: ortho, meta, and para hydroxyphenyl sulfate, exhibiting distinct distribution patterns at different pH values." However, Figure S7 only shows the abundance peak of $C_6H_5O_5S^-$ including all structures proposed in Figure 2 mechanism. Figure S7 can only tell us*

that the OH oxidation happened much faster in alkaline environment (pH 8) compared to more acidic environment (pH 3). I suggest the author don't mention the three isomeric forms, and reword the sentence.

Response: Thanks for your suggestion. In the revised manuscript, we have deleted the discussion of the effects of pH on the products from the OH radical oxidation of phenyl sulfate.

(Q15) *Line 304: In ambient air, a compound with "shorter lifetime" generally considered not as important as the "long lifetime" species regarding their climate impacts. You could reword this to be "the high abundance of aromatic OSs and their fast reactivity with OH radicals in urban environments further underscores their potentially significant role…".*

Response: Thanks for your suggestion. We have changed this expression in the revised manuscript.

Page 13: The substantially shorter lifetimes of aromatic OSs can be attributed to their higher reactivity toward OH radicals compared to aliphatic OSs. Given the high abundance of aromatic OSs and their fast reactivity with •OH in urban environments, aromatic OSs likely play a significant role in both the atmospheric sulfur cycle and environmental effects.

(Q16) *In section 4, the author didn't mention the formation of sulfate anions, which is directly related to the sulfur cycle.*

Response: We have added the related discussion about the implication of inorganic sulfate formation in Section 4 (Atmospheric implications and conclusions) in the revised manuscript.

Page 13: Furthermore, the observation of inorganic sulfate formation, for the first time, indicates that aromatic OSs can also be converted into inorganic sulfate in analogy to aliphatic OSs (Kwong et al., 2018; Xu et al., 2022, 2024; Lai et al., 2025), potentially contributing to the atmospheric sulfur cycle. Further investigations are warranted to examine whether the proposed mechanism can be also applied to other types of aromatic OSs in the atmosphere.

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