



*Supplement of*

## **Liquid-phase reactions of aromatic organosulfates with OH radicals: kinetics, mechanisms, and environmental effects**

**Yu Yang et al.**

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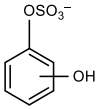
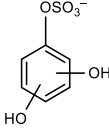
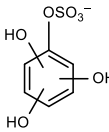
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**Table S1.** Summary of experiments conducted in this study.

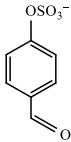
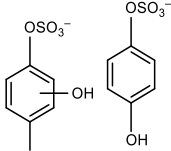
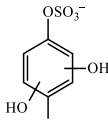
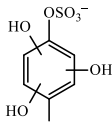
<b>Exp no.</b>	<b>Aromatic OSs</b>	<b>Conc. (mM)</b>	<b>BA (mM)</b>	<b>H<sub>2</sub>O<sub>2</sub> (mM)</b>	<b>UV conditions</b>	<b>pH</b>	<b>Method</b>
1	Phenyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC
2	Phenyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC
3	Phenyl sulfate	0.05	0.05	–	Xe lamp	3	UPLC
4	Phenyl sulfate	0.05	0.05	–	Xe lamp	8	UPLC
5	Phenyl sulfate	0.05	0.05	10	dark	3	UPLC
6	Phenyl sulfate	0.05	0.05	10	dark	8	UPLC
7	Phenyl sulfate	0.05	–	10	Xe lamp	3	UPLC-Q-TOF-MS
8	Phenyl sulfate	0.05	–	10	Xe lamp	8	UPLC-Q-TOF-MS
9	Phenyl sulfate	0.05	–	10	dark	–	UPLC-Q-TOF-MS
10	Phenyl sulfate	0.05	–	–	–	–	UPLC-Q-TOF-MS
11	Phenyl sulfate	0.5	–	10	Xe lamp	3	UPLC-PAD-MS
12	Phenyl sulfate	0.5	–	10	Xe lamp	8	UPLC-PAD-MS
13	Phenyl sulfate	1	–	10	Xe lamp	3	UV-vis, EEM
14	Phenyl sulfate	1	–	10	Xe lamp	8	UV-vis, EEM
15	p-Tolyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC
16	p-Tolyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC
17	p-Tolyl sulfate	0.05	0.05	–	Xe lamp	3	UPLC
18	p-Tolyl sulfate	0.05	0.05	–	Xe lamp	8	UPLC
19	p-Tolyl sulfate	0.05	0.05	10	dark	3	UPLC
20	p-Tolyl sulfate	0.05	0.05	10	dark	8	UPLC
21	p-Tolyl sulfate	0.05	–	10	Xe lamp	3	UPLC-Q-TOF-MS
22	p-Tolyl sulfate	0.05	–	10	Xe lamp	8	UPLC-Q-TOF-MS
23	p-Tolyl sulfate	0.05	–	10	dark	–	UPLC-Q-TOF-MS
24	p-Tolyl sulfate	0.05	–	–	–	–	UPLC-Q-TOF-MS
25	p-Tolyl sulfate	0.5	–	10	Xe lamp	3	UPLC-PAD-MS
26	p-Tolyl sulfate	0.5	–	10	Xe lamp	8	UPLC-PAD-MS
27	p-Tolyl sulfate	1	–	10	Xe lamp	3	UV-vis, EEM
28	4-Ethylphenyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC
29	4-Ethylphenyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC
30	4-Ethylphenyl sulfate	0.05	0.05	–	Xe lamp	3	UPLC
31	4-Ethylphenyl sulfate	0.05	0.05	–	Xe lamp	8	UPLC
32	4-Ethylphenyl sulfate	0.05	0.05	10	dark	3	UPLC
33	4-Ethylphenyl sulfate	0.05	0.05	10	dark	8	UPLC
34	4-Ethylphenyl sulfate	0.05	–	10	Xe lamp	3	UPLC-Q-TOF-MS
35	4-Ethylphenyl sulfate	0.05	–	10	Xe lamp	8	UPLC-Q-TOF-MS
36	4-Ethylphenyl sulfate	0.05	–	10	dark	–	UPLC-Q-TOF-MS
37	4-Ethylphenyl sulfate	0.05	–	–	–	–	UPLC-Q-TOF-MS

38	4-Ethylphenyl sulfate	0.5	–	10	Xe lamp	3	UPLC-PAD-MS
39	4-Ethylphenyl sulfate	0.5	–	10	Xe lamp	8	UPLC-PAD-MS
40	4-Ethylphenyl sulfate	1	–	10	Xe lamp	3	UV-vis, EEM

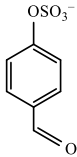
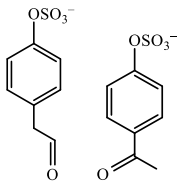
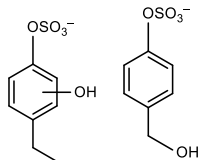
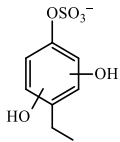
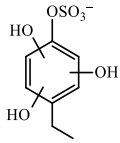
**Table S2.** Products from liquid-phase  $\bullet\text{OH}$  oxidation of phenyl sulfate.

<i>m/z</i> [M-H]	Error (ppm)	Formula	Structure
138.9711	3.114	$\text{C}_2\text{H}_3\text{O}_5\text{S}^-$	
188.9864	0.438	$\text{C}_6\text{H}_5\text{O}_5\text{S}^-$	
204.9813	0.332	$\text{C}_6\text{H}_5\text{O}_6\text{S}^-$	
208.9765	1.692	$\text{C}_5\text{H}_5\text{O}_7\text{S}^-$	
220.9766	2.052	$\text{C}_6\text{H}_5\text{O}_7\text{S}^-$	
226.9869	0.832	$\text{C}_5\text{H}_7\text{O}_8\text{S}^-$	
238.9866	-0.465	$\text{C}_6\text{H}_7\text{O}_8\text{S}^-$	
254.9811	-2.062	$\text{C}_6\text{H}_7\text{O}_9\text{S}^-$	
256.9971	-0.684	$\text{C}_6\text{H}_9\text{O}_9\text{S}^-$	

**Table S3.** Products from liquid-phase  $\bullet\text{OH}$  oxidation of p-tolyl sulfate.

<i>m/z</i> [M-H]	Error (ppm)	Formula	Structure
192.9807	-2.756	$\text{C}_5\text{H}_5\text{O}_6\text{S}^-$	
200.9863	-0.086	$\text{C}_7\text{H}_5\text{O}_5\text{S}^-$	
203.0020	0.161	$\text{C}_7\text{H}_7\text{O}_5\text{S}^-$	
208.9760	-0.701	$\text{C}_5\text{H}_5\text{O}_7\text{S}^-$	
216.9816	1.697	$\text{C}_7\text{H}_5\text{O}_6\text{S}^-$	
218.9968	-0.374	$\text{C}_7\text{H}_7\text{O}_6\text{S}^-$	
234.9917	-0.411	$\text{C}_7\text{H}_7\text{O}_7\text{S}^-$	
253.0021	-1.032	$\text{C}_7\text{H}_9\text{O}_8\text{S}^-$	

**Table S4.** Products from liquid-phase  $\bullet\text{OH}$  oxidation of 4-ethylphenyl sulfate.

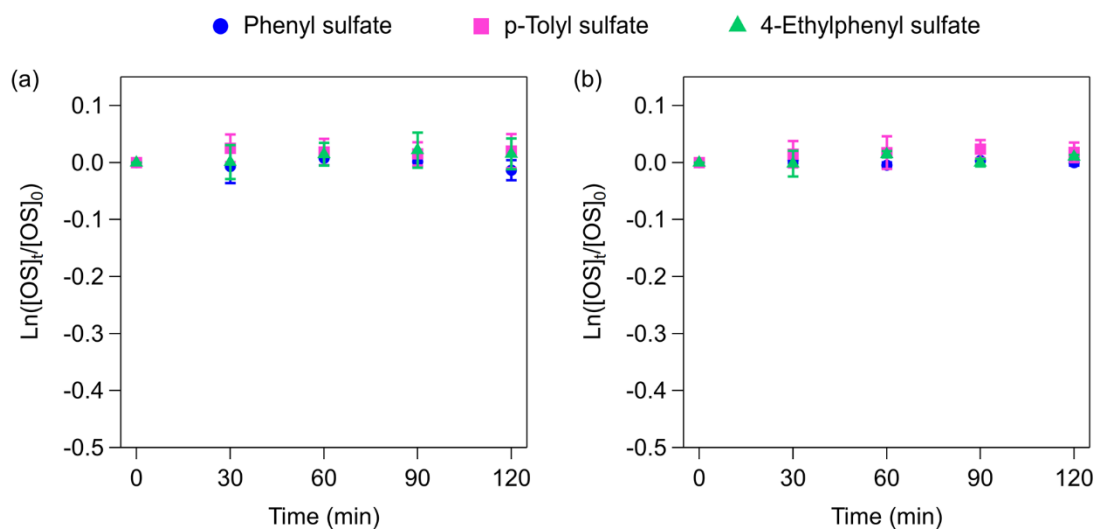
$m/z$ [M-H]	Error (ppm)	Formula	Structure
196.9762	0.272	$\text{C}_4\text{H}_5\text{O}_7\text{S}^-$	
200.9862	-0.583	$\text{C}_7\text{H}_5\text{O}_5\text{S}^-$	
215.0013	-3.104	$\text{C}_8\text{H}_7\text{O}_5\text{S}^-$	
217.0172	-1.923	$\text{C}_8\text{H}_9\text{O}_5\text{S}^-$	
230.9961	-3.385	$\text{C}_8\text{H}_7\text{O}_6\text{S}^-$	
233.0120	-2.283	$\text{C}_8\text{H}_9\text{O}_6\text{S}^-$	
246.9914	-1.605	$\text{C}_8\text{H}_7\text{O}_7\text{S}^-$	
249.0068	-2.597	$\text{C}_8\text{H}_9\text{O}_7\text{S}^-$	
267.0173	-2.664	$\text{C}_8\text{H}_{11}\text{O}_8\text{S}^-$	

**Table S5.** Calculated lifetimes of OS via liquid-phase  $\bullet\text{OH}$  oxidation in different scenarios.

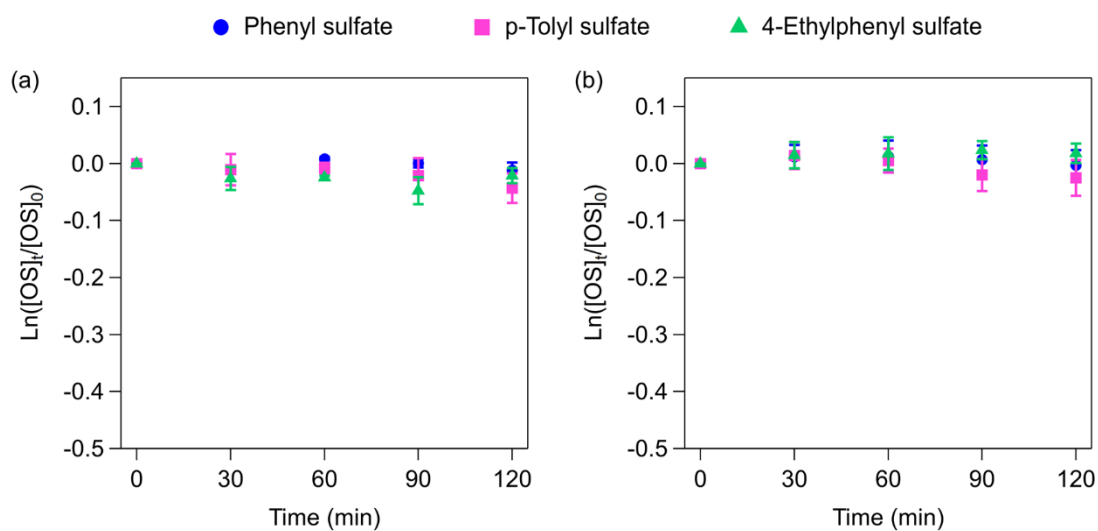
Species	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )	Aerosol		Cloud		Reference
		Urban	Remote	Urban	Remote	
Phenyl sulfate	$5.1 \times 10^9$	7 min	1 min	16 h	2 h	
p-Tolyl sulfate	$5.4 \times 10^9$	7 min	1 min	15 h	2 h	This study
4-Ethylphenyl sulfate	$5.4 \times 10^9$	7 min	1 min	15 h	2 h	
Methyl sulfate	$1.05 \times 10^8$	6 h	53 min	32 day	5 day	
Ethyl sulfate	$3.93 \times 10^8$	2 h	14 min	8 day	1 day	(Gweme and Styler, 2024)
Propyl sulfate	$1.22 \times 10^9$	31 min	5 min	3 day	10 h	
Hydroxyacetone sulfate	$1.52 \times 10^8$	4 h	37 min	22 day	4 day	
$\alpha$ -Pinene-derived organosulfate	$2.2 \times 10^9$		3min	2 day		(Lai et al, 2025)

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

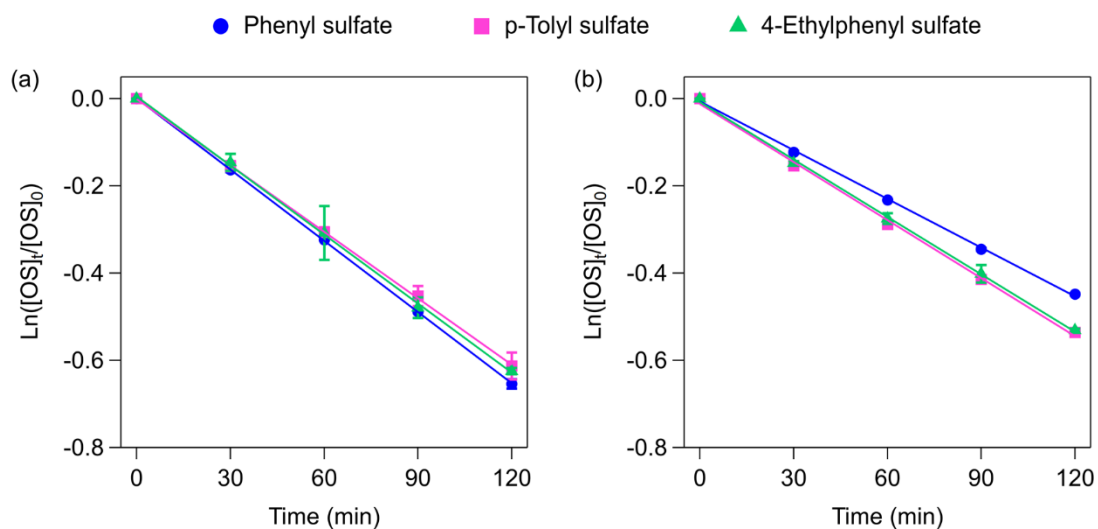
$\bullet\text{OH}$  concentrations are obtained from CAPRAM model (Herrmann et al., 2005, 2010).  $[\bullet\text{OH}]_{\text{urban aerosol}} = 4.4 \times 10^{-13} \text{M}$ ;  $[\bullet\text{OH}]_{\text{remote aerosol}} = 3.0 \times 10^{-12} \text{M}$ ;  $[\bullet\text{OH}]_{\text{urban cloud}} = 3.5 \times 10^{-15} \text{M}$ ;  $[\bullet\text{OH}]_{\text{remote cloud}} = 2.2 \times 10^{-14} \text{M}$ .



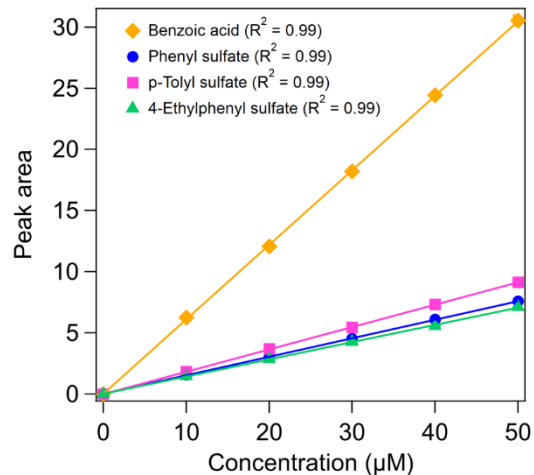
**Figure S1. Kinetics of aromatic OSs from control experiments performed at (a) pH 3 and (b) pH 8 under dark conditions.**



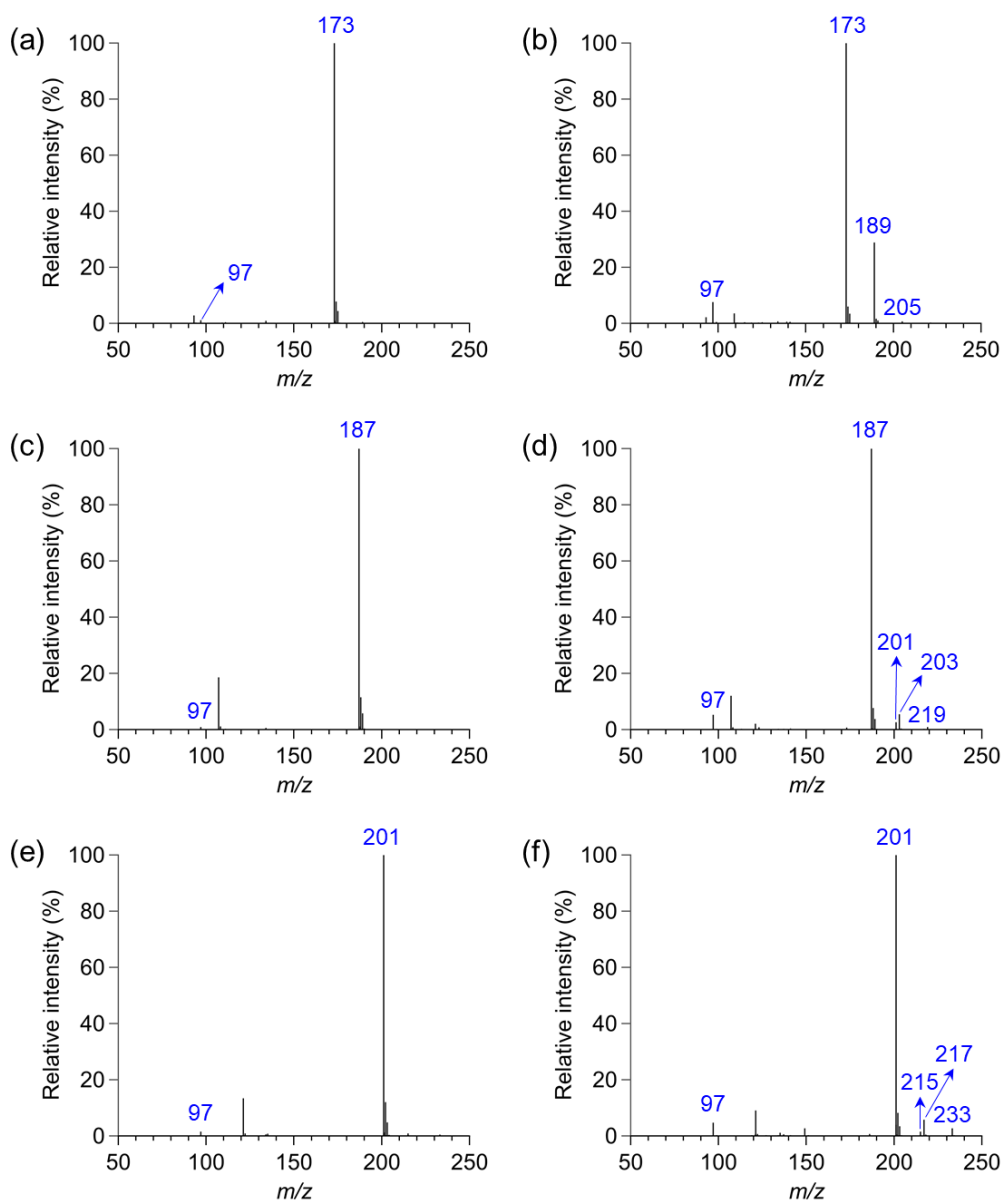
**Figure S2. Kinetics of aromatic OSs from control experiments performed at (a) pH 3 and (b) pH 8 under illumination in the absence of  $\text{H}_2\text{O}_2$ .**



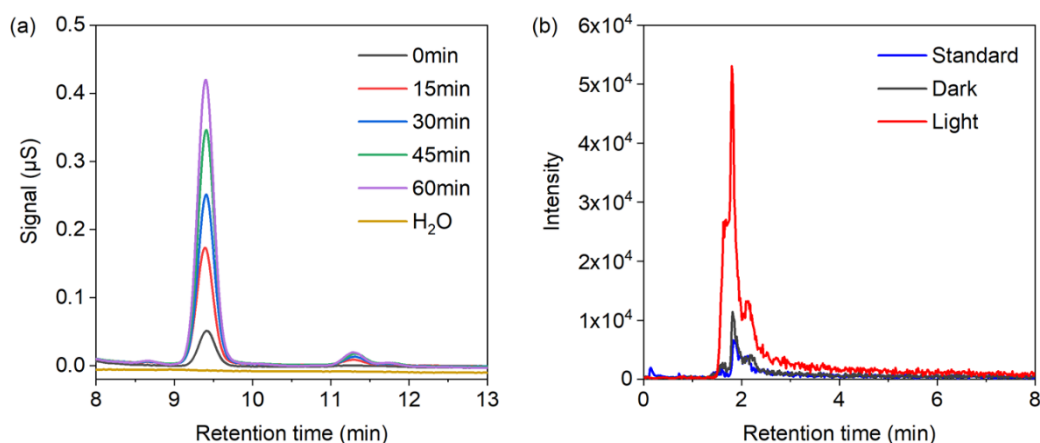
**Figure S3. Time dependence of aromatic OS consumption during the processes of  $\bullet\text{OH}$  oxidation at (a) pH 3 and (b) pH 8.**



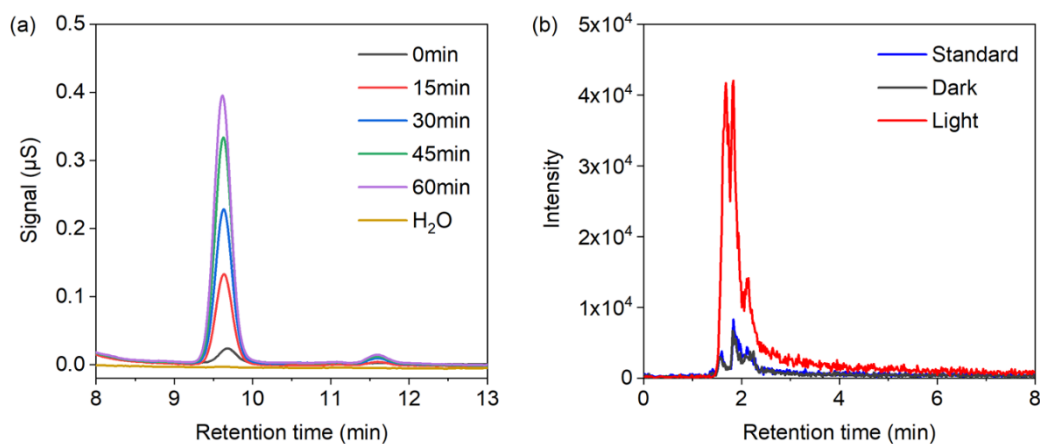
**Figure S4. Calibration curves of benzoic acid, phenyl sulfate, p-tolyl sulfate, and 4-ethylphenyl sulfate.**



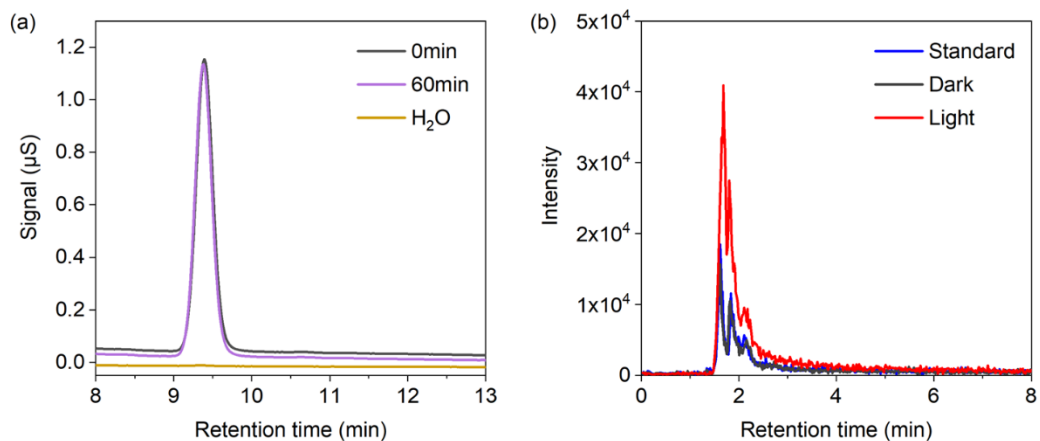
**Figure S5. Mass spectra collected from the liquid-phase reactions of 0.05 mM (a, b) phenyl sulfate, (c, d) p-tolyl sulfate, and (e, f) 4-ethylphenyl sulfate with 10 mM H<sub>2</sub>O<sub>2</sub> under dark (left panels) and illumination (right panels) conditions.**



**Figure S6. (a)** Time profile of  $\text{SO}_4^{2-}$  peak in ion chromatograms (IC) in the reactions of 0.05 mM phenyl sulfate with  $\bullet\text{OH}$  at pH 3. **(b)** Extracted ion chromatogram (EIC) of  $\text{HSO}_4^-$  ( $m/z$  97) obtained from phenyl sulfate standard (blue line) and from their liquid-phase reactions under dark (black line) and illumination (red line) conditions.



**Figure S7. (a)** Time profile of  $\text{SO}_4^{2-}$  peak in ion chromatograms (IC) in the reactions of 0.05 mM p-tolyl sulfate with  $\bullet\text{OH}$  at pH 3. **(b)** Extracted ion chromatogram (EIC) of  $\text{HSO}_4^-$  ( $m/z$  97) obtained from p-tolyl sulfate standard (blue line) and from their liquid-phase reactions under dark (black line) and illumination (red line) conditions.



**Figure S8. (a)** Time profile of  $\text{SO}_4^{2-}$  peak in ion chromatograms (IC) in the reactions of 0.05 mM 4-ethylphenyl sulfate with  $\bullet\text{OH}$  at pH 3. **(b)** Extracted ion chromatogram (EIC) of  $\text{HSO}_4^-$  ( $m/z$  97)

obtained from 4-ethylphenyl sulfate (blue line) and from their liquid-phase reactions under dark (black line) and illumination (red line) conditions.

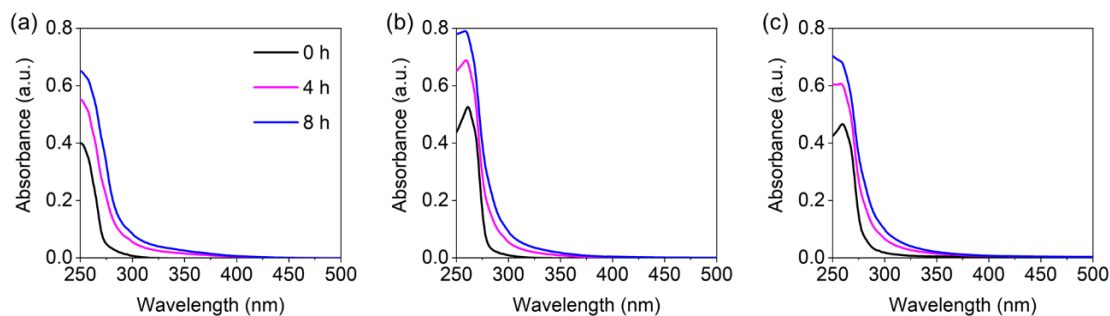


Figure S9. Time profile of UV-vis light absorption spectra during the liquid-phase  $\bullet\text{OH}$  oxidation of (a) phenyl sulfate, (b) p-tolyl sulfate and (c) 4-ethylphenyl sulfate at pH 3.

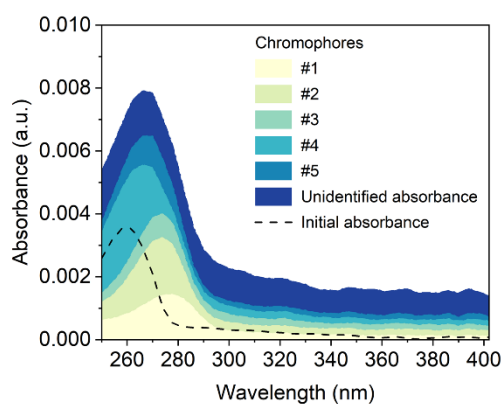


Figure S10. Contributions of the main absorbing chromophores to the total light absorption from the liquid-phase reactions of phenyl sulfate with  $\bullet\text{OH}$  at pH 3. The dotted line indicates the initial absorbance of phenyl sulfate at pH 3.

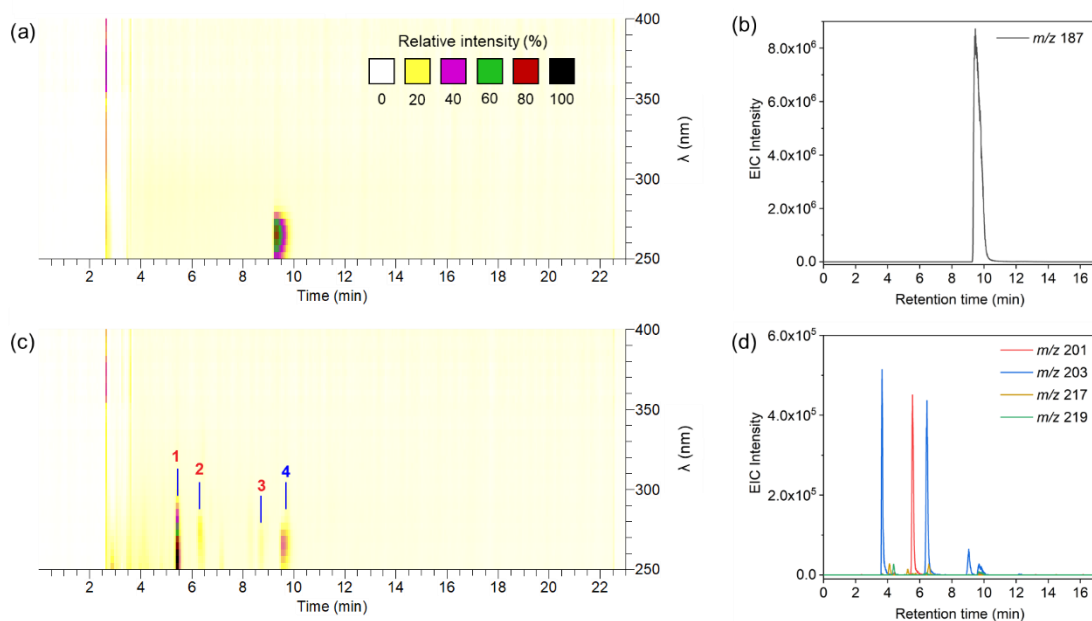


Figure S11. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-

phase  $\bullet\text{OH}$  oxidation of p-tolyl sulfate at pH 3. The y-axis and color map represent the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) p-tolyl sulfate and (d) the compositions of chromophores.

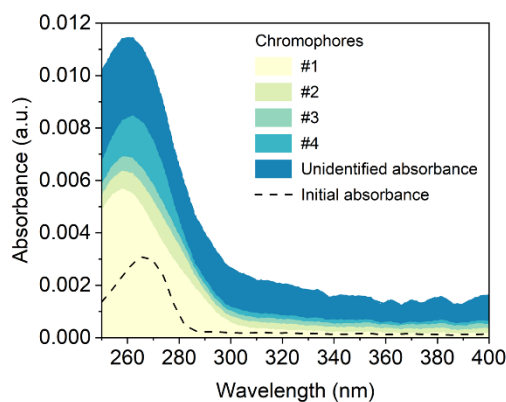


Figure S12. Contributions of the main absorbing chromophores to the total light absorption from the liquid-phase reactions of p-tolyl sulfate with  $\bullet\text{OH}$  at pH 3. The dotted line indicates the initial absorbance of p-tolyl sulfate at pH 3.

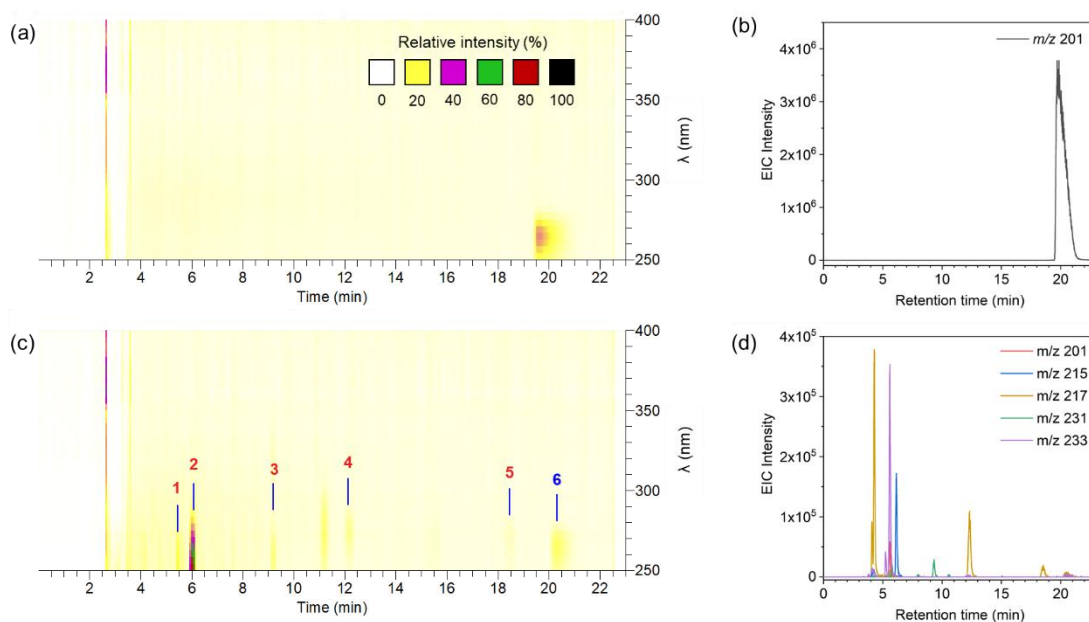
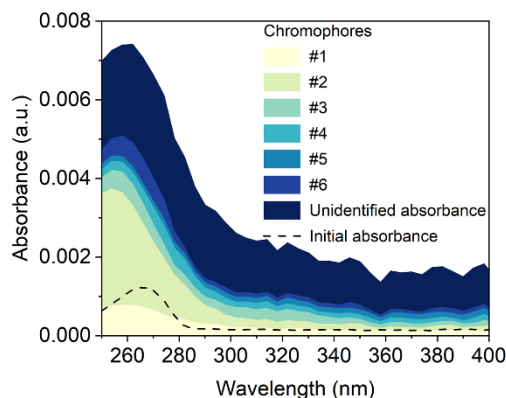
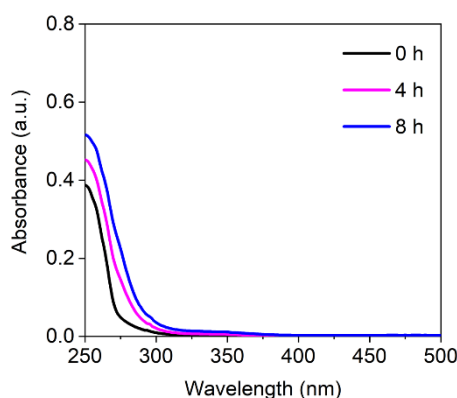


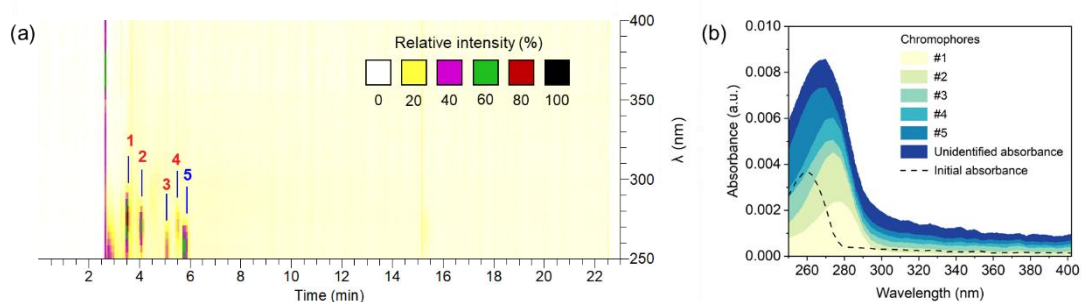
Figure S13. UPLC-PAD-MS chromatograms of samples collected (a) before and (c) after the liquid-phase  $\bullet\text{OH}$  oxidation of 4-ethylphenyl sulfate at pH 3. The y-axis and color map represent the wavelength and corresponding UV-vis absorbance, respectively. Extracted ion chromatograms (EIC) of (b) 4-ethylphenyl sulfate and (d) the compositions of chromophores.



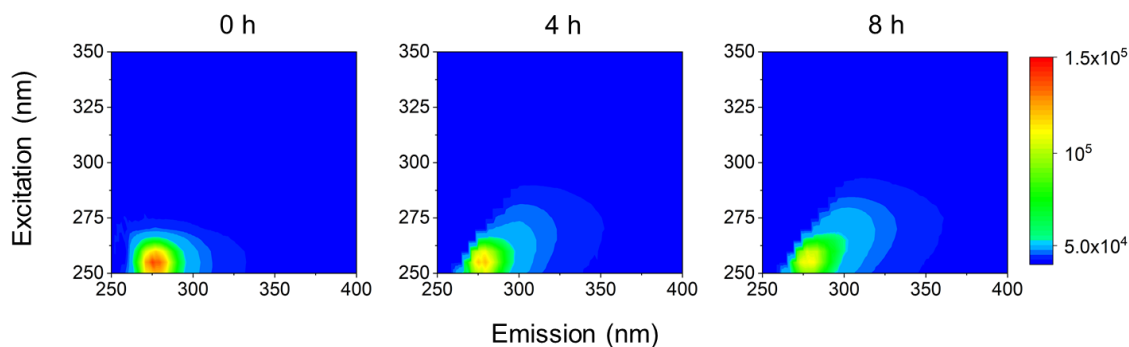
**Figure S14.** Contributions of the main absorbing chromophores to the total light absorption from the liquid-phase reactions of 4-ethylphenyl sulfate with  $\bullet\text{OH}$  at pH 3. The dotted line indicates the initial absorbance of 4-ethylphenyl sulfate at pH 3.



**Figure S15.** Time profile of UV-vis light absorption spectra during the process of phenyl sulfate reacting with  $\bullet\text{OH}$  at pH 8.



**Figure S16.** UPLC-PAD-MS chromatograms of sample collected (a) after the liquid-phase  $\bullet\text{OH}$  oxidation of phenyl sulfate at pH 8. The y-axis and color map represent 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  $\bullet\text{OH}$  at pH 8. The dotted line represents the initial absorbance of phenyl sulfate.



**Figure S17. Time profile of excitation-emission matrix (EEM) fluorescence spectra during the process of phenyl sulfate reacting with  $\bullet\text{OH}$  at pH 8.**

## References

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