

Supplement of

Multiphase reactions of aromatic organosulfates with OH radicals: Kinetics, mechanisms, and environmental effects

5 Yu Yang¹, Caiqing Yan¹, Ruyu Yuang¹, Ping Liu¹, Hanyuan Zhang¹, Haibiao Chen¹,
Yujiao Zhu¹, Hengqing Shen¹, Yan Wu², Likun Xue¹ and Liubin Huang^{1*}

¹Environment Research Institute, Shandong University, Qingdao, Shandong 266237, China

²School of Environmental Science and Engineering, Shandong University, Qingdao, Shandong 266237, China

Correspondence to: Liubin Huang (hliubin@sdu.edu.cn)

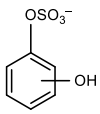
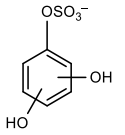
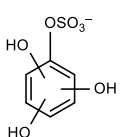
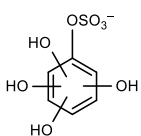
Table S1. Summary of the different experiments conducted in this study.

Exp no.	Aromatic OSs	Conc. (mM)	BA (mM)	H ₂ O ₂ (mM)	UV conditions	pH	Method
1	Phenyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC/LC-MS/MS
2	Phenyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC/LC-MS/MS
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	p-Tolyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC/LC-MS/MS
8	p-Tolyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC/LC-MS/MS
9	p-Tolyl sulfate	0.05	0.05	-	Xe lamp	3	UPLC
10	p-Tolyl sulfate	0.05	0.05	-	Xe lamp	8	UPLC
11	p-Tolyl sulfate	0.05	0.05	10	dark	3	UPLC
12	p-Tolyl sulfate	0.05	0.05	10	dark	8	UPLC
13	4-Ethylphenyl sulfate	0.05	0.05	10	Xe lamp	3	UPLC/LC-MS/MS
14	4-Ethylphenyl sulfate	0.05	0.05	10	Xe lamp	8	UPLC/LC-MS/MS
15	4-Ethylphenyl sulfate	0.05	0.05	-	Xe lamp	3	UPLC
16	4-Ethylphenyl sulfate	0.05	0.05	-	Xe lamp	8	UPLC
17	4-Ethylphenyl sulfate	0.05	0.05	10	dark	3	UPLC
18	4-Ethylphenyl sulfate	0.05	0.05	10	dark	8	UPLC
19	Phenyl sulfate	0.5	-	10	Xe lamp	3	LC-MS
20	Phenyl sulfate	0.5	-	10	Xe lamp	8	LC-MS
21	p-Tolyl sulfate	0.5	-	10	Xe lamp	3	LC-MS
22	p-Tolyl sulfate	0.5	-	10	Xe lamp	8	LC-MS
23	4-Ethylphenyl sulfate	0.5	-	10	Xe lamp	3	LC-MS
24	4-Ethylphenyl sulfate	0.5	-	10	Xe lamp	8	LC-MS
25	Phenyl sulfate	1	-	10	Xe lamp	3	UPLC/UV-vis/EEM
26	Phenyl sulfate	1	-	10	Xe lamp	8	UPLC/UV-vis/EEM
27	p-Tolyl sulfate	1	-	10	Xe lamp	3	UPLC/UV-vis/EEM
28	p-Tolyl sulfate	1	-	10	Xe lamp	8	UPLC/UV-vis/EEM
29	4-Ethylphenyl sulfate	1	-	10	Xe lamp	3	UPLC/UV-vis/EEM
30	4-Ethylphenyl sulfate	1	-	10	Xe lamp	8	UPLC/UV-vis/EEM

LC-MS: an ultra-high performance liquid chromatography (UltiMate 3000) coupled to a Q Exactive locus Hybrid Quadrupole-Orbitrap mass spectrometry (Thermo Scientific, USA).

MS: a quadrupole time-of-flight mass spectrometry (Q-TOF-MS, Bruker Impact HD, Germany).

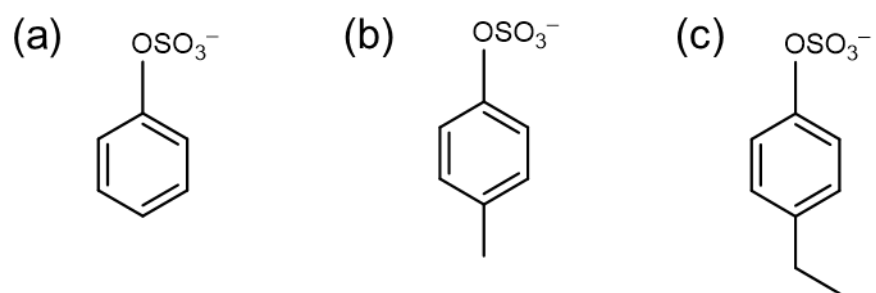
15 **Table S2.** Products of the multiphase reaction of phenyl sulfate with OH radicals.

<i>m/z</i> [M-H]	Error (ppm)	Formula	Structure
188.9864	0.385	C ₆ H ₅ O ₅ S	
204.9813	-0.284	C ₆ H ₅ O ₆ S	
220.9766	1.871	C ₆ H ₅ O ₇ S	
236.9703	-3.127	C ₆ H ₅ O ₈ S	
206.9966	-1.362	C ₆ H ₇ O ₆ S	—
222.9915	-1.330	C ₆ H ₇ O ₇ S	—
238.9866	-0.465	C ₆ H ₇ O ₈ S	—
254.9811	-2.062	C ₆ H ₇ O ₉ S	—
192.9815	1.390	C ₅ H ₅ O ₆ S	—
208.9765	1.692	C ₅ H ₅ O ₇ S	—
224.9715	1.951	C ₅ H ₅ O ₈ S	—
226.9869	0.832	C ₅ H ₇ O ₈ S	—
136.9908	-4.399	C ₃ H ₅ O ₄ S	—
155.0017	-1.725	C ₃ H ₇ O ₅ S	—

138.9711	3.114	$\text{C}_2\text{H}_3\text{O}_5\text{S}$	—
110.9757	-0.474	$\text{CH}_3\text{O}_4\text{S}$	
96.9602	1.418	HSO_4	—

Table S3. Calculated lifetimes of OS by the multiphase OH radical oxidation in urban aerosols and cloud scenarios.

Species	k ($\text{M}^{-1} \text{s}^{-1}$)	Aerosols	Cloud	Reference
[•OH] (M)		4.40×10^{-13}	3.50×10^{-15}	
Phenyl sulfate	5.09×10^9	7 min	16 h	this study
p-Tolyl sulfate	5.37×10^9	7 min	15 h	
4-Ethylphenyl sulfate	5.40×10^9	7 min	15 h	
Methyl sulfate	1.05×10^8	6 h	32 day	(Gweme and Styler, 2024)
Ethyl sulfate	3.93×10^8	2 h	8 day	
propyl sulfate	1.22×10^9	31 min	3 day	
Hydroxyacetone sulfate	1.52×10^8	4 h	22 day	
Phenyl sulfate	5.42×10^9	7 min	15h	
α -pinene-derived organosulfate	2.2×10^9		2 day	(Lai et al, 2025)



20

Figure S1. Structures of (a) phenyl sulfate, (b) p-tolyl sulfate, and (c) 4-ethylphenyl sulfate.

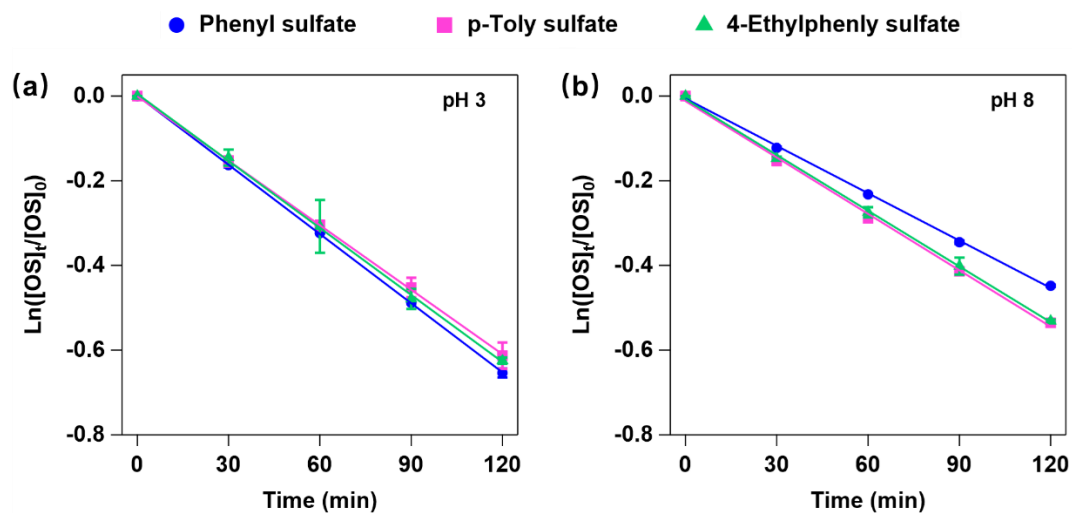


Figure S2. Time dependence of aromatic OS consumption during the processes of OH radical oxidation at (a) pH 3 and (b) pH 8.

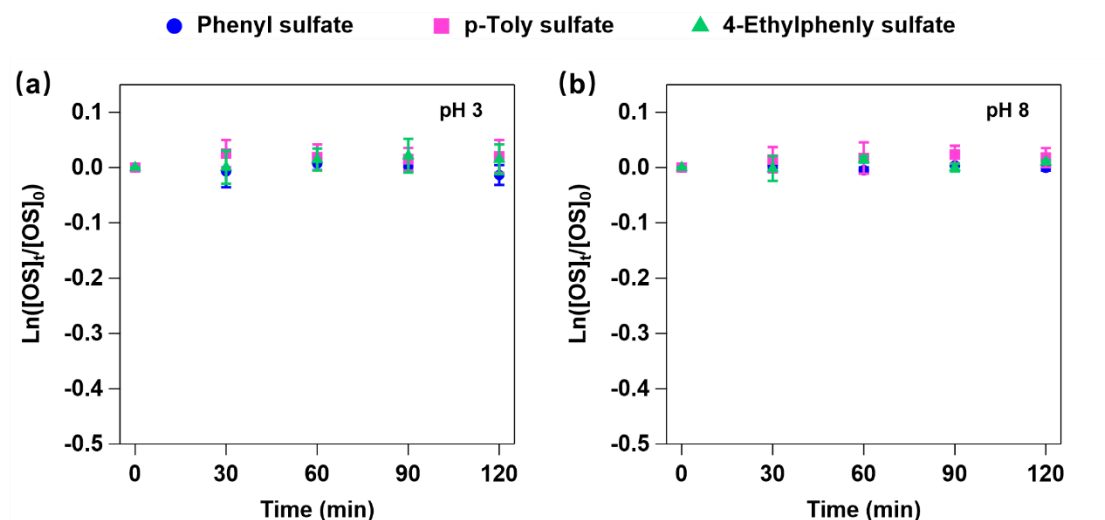


Figure S3. Kinetics of aromatic OSs for control experiments performed at pH 3 and pH 8 under dark conditions.

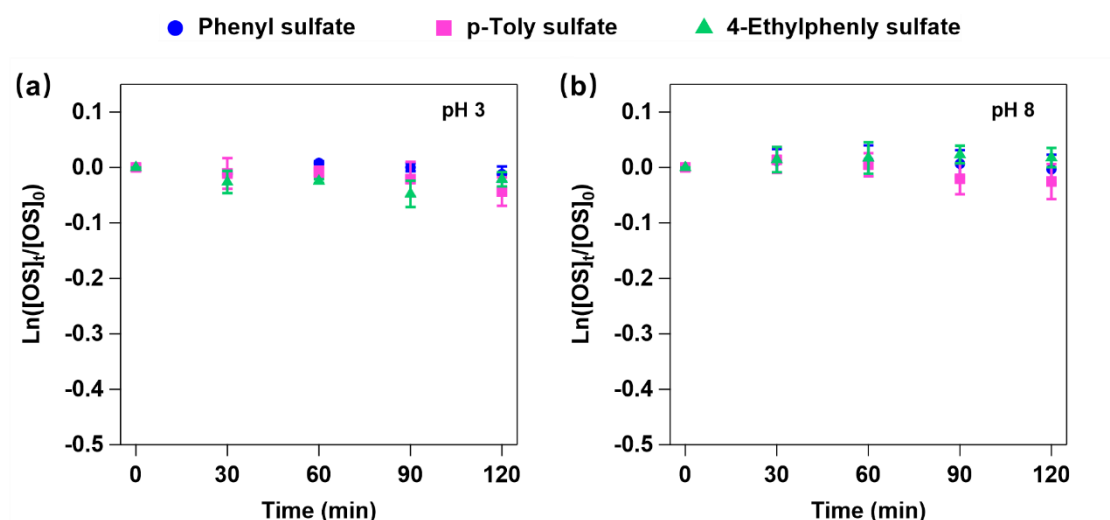
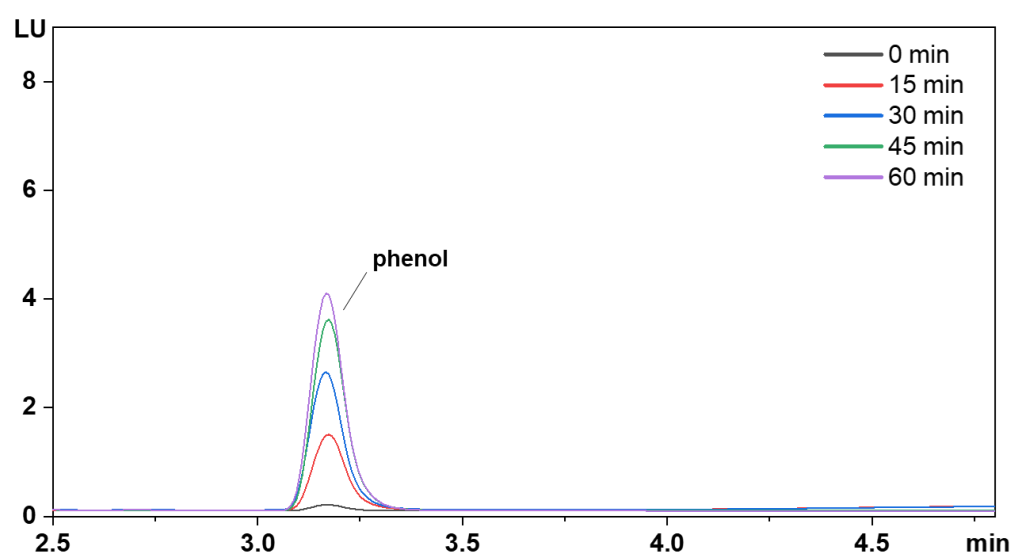


Figure S4. Kinetics of aromatic OSs for control experiments performed at pH 3 and pH 8 under UV conditions in the absence of H_2O_2 .



35

Figure S5. The production of phenol during the multiphase reaction of phenyl sulfate (0.05mM) and OH radicals.

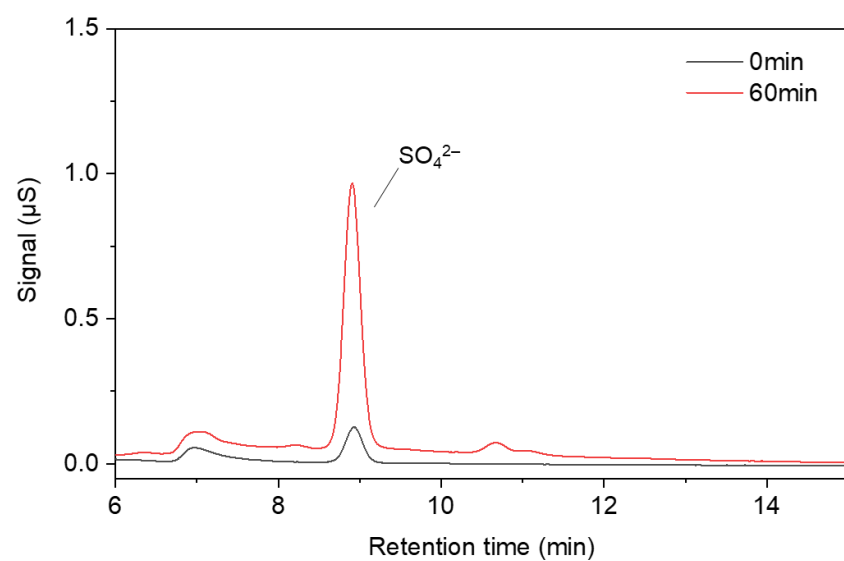


Figure S6. Ion chromatograms of SO_4^{2-} during the multiphase reaction of phenyl sulfate (0.05 mM) and OH radicals at pH 3.

40

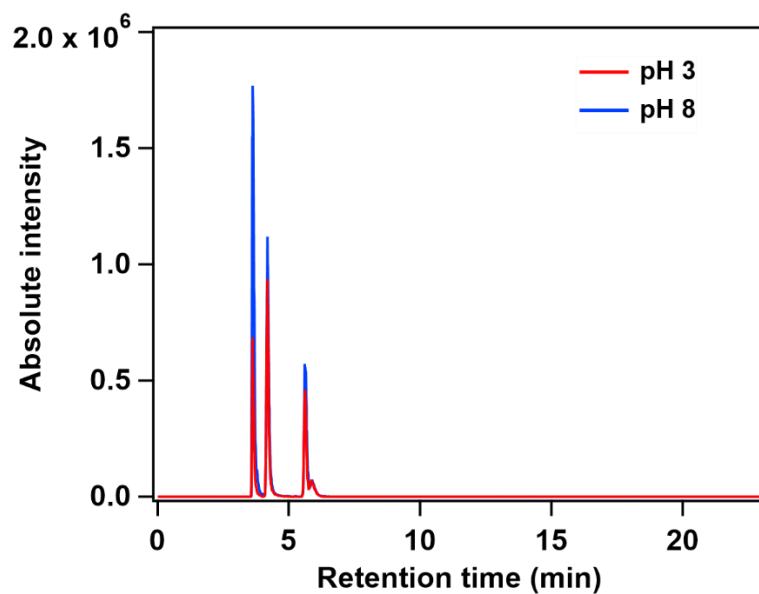


Figure S7. Extracted ion chromatograms (EICs) for m/z 189 ($\text{C}_6\text{H}_5\text{O}_5\text{S}^-$) obtained from the multiphase reaction of phenyl sulfate (0.5 mM) with OH radicals.

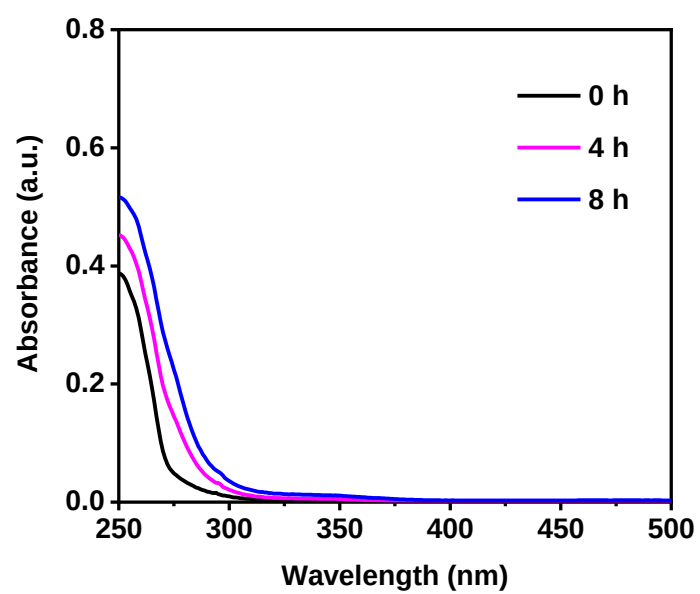


Figure S8. Time profile of UV-vis light absorption spectra during the process of phenyl sulfate reacting with OH radicals at pH 8.

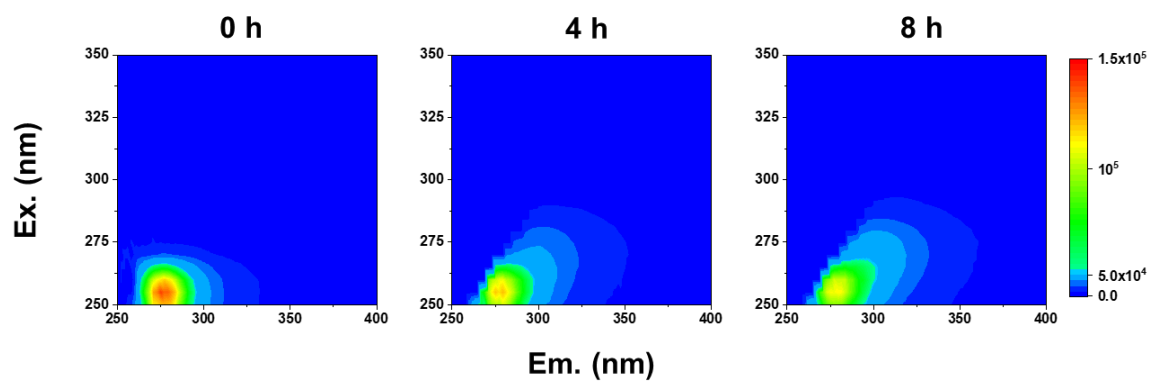


Figure S9. Time profile of EEM fluorescence spectra during the process of phenyl sulfate reacting with OH radicals at pH 8.

References

- Gweme, D. T., and Styler, S. A.: OH radical oxidation of organosulfates in the atmospheric aqueous phase, 55 J. Phys. Chem. A, 128, 9462–9475, <https://doi.org/10.1021/acs.jpca.4c02877>, 2024.
- Lai, D., Bai, Y., Zhang, Z., So, P.-K., Li, Y. J., Tse, Y.-L. S., Yeung, Y.-Y., Schaefer, T., Herrmann, H., Yu, J. Z., Wang, Y., and Chan, M. N.: Rapid aqueous-phase oxidation of an α -pinene-derived organosulfate by hydroxyl radicals: a potential source of some unclassified oxygenated and small organosulfates in the atmosphere, Atmos. Chem. Phys., 25, 12569–12584, 60 <https://doi.org/10.5194/acp-25-12569-2025>, 2025.