Supplementary Information (SI) for RSC Advances.

Supplementary Information

Degradation of bisphenol A during heat-activated peroxodisulfate treatment: Kinetics, mechanism, and transformation products

Chunyu Wang[a], Juan Yan[a], Jia Yuan[a], Ling Zhang[a], Wei Qian[b], Guochen Bian[b], Yunhong Song[a], Xu Gao[a, *], Han Mao[c, **]

[a] Chaohu Regional Collaborative Technology Service Center for Rural Revitalization of Anhui Province, School of Biological and Environmental Engineering, Chaohu University, Hefei, 238000, China

[b] Anhui Green Energy Technology Institute Co., Hefei, 238088, China

[c] South China Institute of Environment Sciences, Ministry of Ecology and Environment, Guangdong, 510655, China

[*]Corresponding author: E-mail: gaoxun@chu.edu.cn

[**]Co-Corresponding author: E-mail: maohan@scies.org

Telephone: +86-0551-82369184

3 Texts, 1 Tables, 5 Figures

Text S1. Chemicals.

Bisphenol A (BPA, ≥ 98.5%), sodium peroxydisulfate ($Na_2S_2O_8$, ≥ 99.0%), sodium hydroxide (NaOH, ≥ 98.5%), and sodium sulfite (Na_2SO_3, ≥ 99.0%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Sodium bicarbonate ($NaHCO_3$, ≥ 99.0%), sodium nitrate ($NaNO_3$, ≥ 98.0%), potassium dihydrogen phosphate (KH_2PO_4, ≥ 98.5%), and sodium chloride (NaCl, ≥ 99.5%) were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). Methanol (MeOH), tert-butanol (TBA), isopropanol (IPA), and formic acid were of chromatographic grade and obtained from Sigma-Aldrich (St. Louis, MO, USA). Suwannee river NOM (#1R101F) from was supplied by the International Humic Substance Society (Minnesota, USA). All experimental solutions were prepared by ultra-pure water (18.25 MΩ/cm). Balanced Reverse Polymer (BRP) cartridges (60 mg/3 cm^3, #00522-20009) were obtained from Welch Materials. Inc.

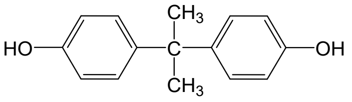
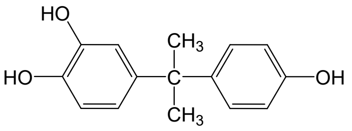
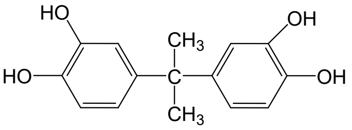
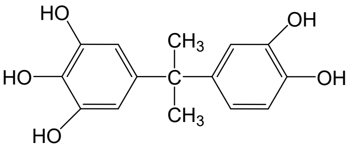
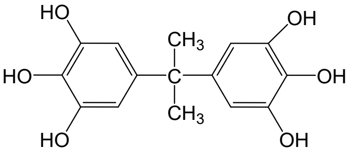
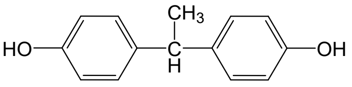
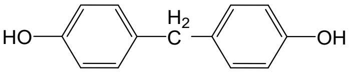
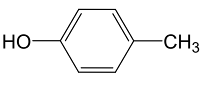
Text S2. SPE procedures.

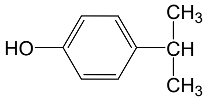
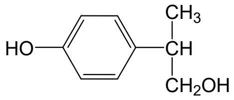
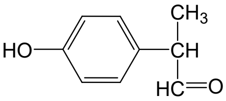
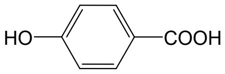
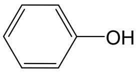
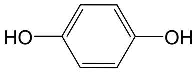
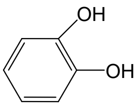
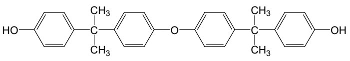
Immediately after incubation, the reaction solutions of BPA were adjusted to pH < 2 by 98% sulfuric acid before SPE. BRP cartridges were conditioned with 5 mL MeOH and 5 mL water (pH 3) sequentially, followed by sample loading. Approximately 50 mL sample was loaded onto each cartridge, then rinsed with 2 mL water and 2 mL 3% MeOH-water and blown to dryness under vacuum. The cartridge was then eluted with 2 mL MeOH.

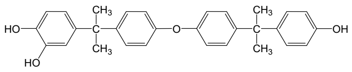
Text S3. Instrumental setup of HRMS.

Transformation products of BPA in the samples were identified by a Thermo Fisher Scientific Q-Exactive HRMS (Waltham, MA, USA) equipped with an ZORBAX SB-C18 column (Agilent, 5 μm, 2.1 × 100 mm). Elution was performed at a flow rate of 0.2 mL min^{-1} with H_2O + 0.1% formic acid (v/v) (eluent A) and MeOH + 0.1% formic acid (v/v) (eluent B), employing a linear gradient as follows: 95% A, 0-3 min; 95% to 5% A, 3-7 min; 5% A, 7-12 min; 5% to 95% A, 12-12.1 min; 95% A, 12.1-15 min. The sample injection volume was 2 μL. Mass analyses were conducted in negative mode using electrospray ionization (ESI) source. The instrument parameters used for sample analysis were as follows: ion transfer tube temperature of 350 °C; source temperature of 300 °C; sheath gas pressure of 35 arb, auxiliary gas pressure of 10 arb, spray voltage of 3500 V. Mass spectrometric data was collected at full scan mode over a mass range of *m/z* 60-900 to identify the transformation products.

Table S1. Mass spectrum data and proposed molecular structures for the transformation products generated from BPA in heat/PDS system.

Transformation Products	Retention time	Measured exact mass	Formula of derived molecule	Proposed structure
BPA	3.06	227.12741 [M-H]$^-$	$C_{15}H_{16}O_2$	
P1	4.46	243.11685 [M-H]$^-$	$C_{15}H_{16}O_3$	
P2	2.45	258.91504 [M-H]$^-$	$C_{15}H_{16}O_4$	
P3	1.46	277.09781 [M+H]$^+$	$C_{15}H_{16}O_5$	
P4	0.83	290.90201 [M-H]$^-$	$C_{15}H_{16}O_6$	
P5	7.16	213.01425 [M-H]$^-$	$C_{14}H_{14}O_2$	
P6	0.64	199.90761 [M-H]$^-$	$C_{13}H_{12}O_2$	
P7	1.89	109.02868 [M+H]$^+$	C_7H_8O	

P8	7.514	135.04716 $[M-H]^-$	$C_9H_{12}O$	
P9	6.95	153.09103 $[M-H]^-$	$C_9H_{12}O_2$	
P10	2.29	149.02335 $[M-H]^-$	$C_9H_{10}O_2$	
P11	3.04	137.02303 $[M-H]^-$	$C_7H_6O_3$	
P12	6.17	95.06091 $[M+H]^+$	C_6H_6O	
P13	6.85	111.05555 $[M+H]^+$	$C_6H_6O_2$	 Or 
P14	8.00	439.30029 $[M+H]^+$	$C_{30}H_{30}O_3$	

P15	7.66	455.27890 $[M+H]^+$	$C_{30}H_{30}O_4$	

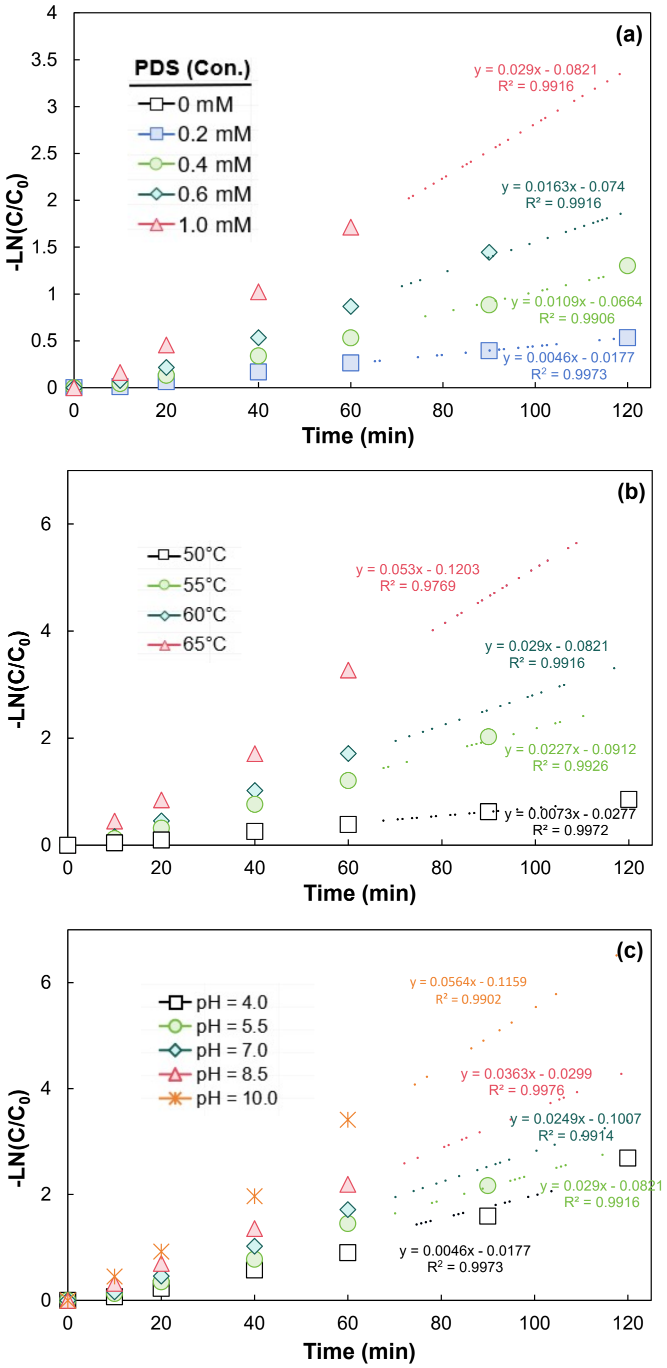


Fig. S1. Effects of (a) initial PDS dosage at 60°C , (c) reaction temperature, (d) solution pH on the observed pseudo-first-order rate constant (k_{obs}) of BPA degradation in heat/PDS system. Experimental conditions: $[\mathrm{BPA}]_0$ = 40 μM, $[\mathrm{PDS}]_0$ = 1.0 mM, pH 7.0 ± 0.1 maintained by 10.0 mM phosphate buffer.

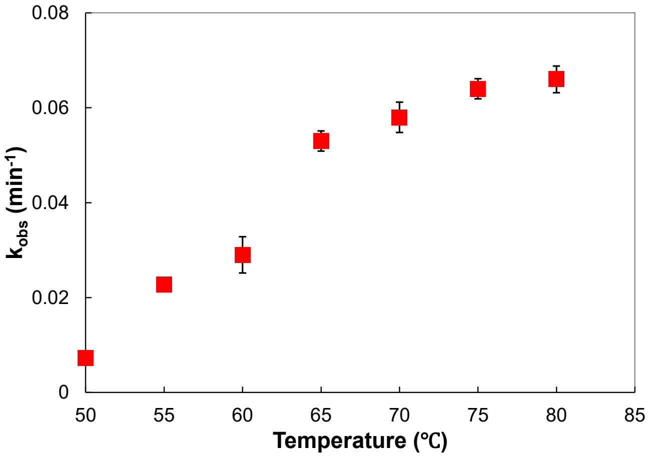


Fig. S2. Relationship between the k_{obs} of BPA degradation and reaction temperature. Experimental conditions: $[\text{BPA}]_0 = 40$ µM, $[\text{PDS}]_0 = 1.0$ mM, pH 7.0 ± 0.1 maintained by 10.0 mM phosphate buffer.

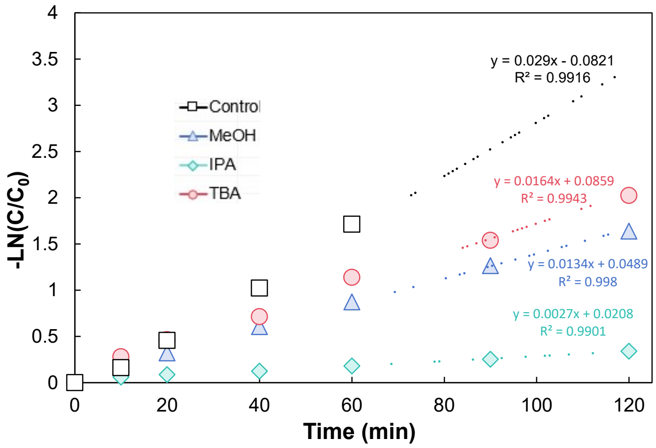


Fig. S3. Effects of MeOH, TBA, and IPA on the k_{obs} of BPA degradation in heat/PDS system. Experimental conditions: $[BPA]_0$ = 40 μM, $[PDS]_0$ = 1.0 mM, $[MeOH]_0$ = 10 mM, $[TBA]_0$ = 10 mM, $[IPA]_0$ = 10 mM, pH 7.0 ± 0.1 maintained by 10.0 mM phosphate buffer.

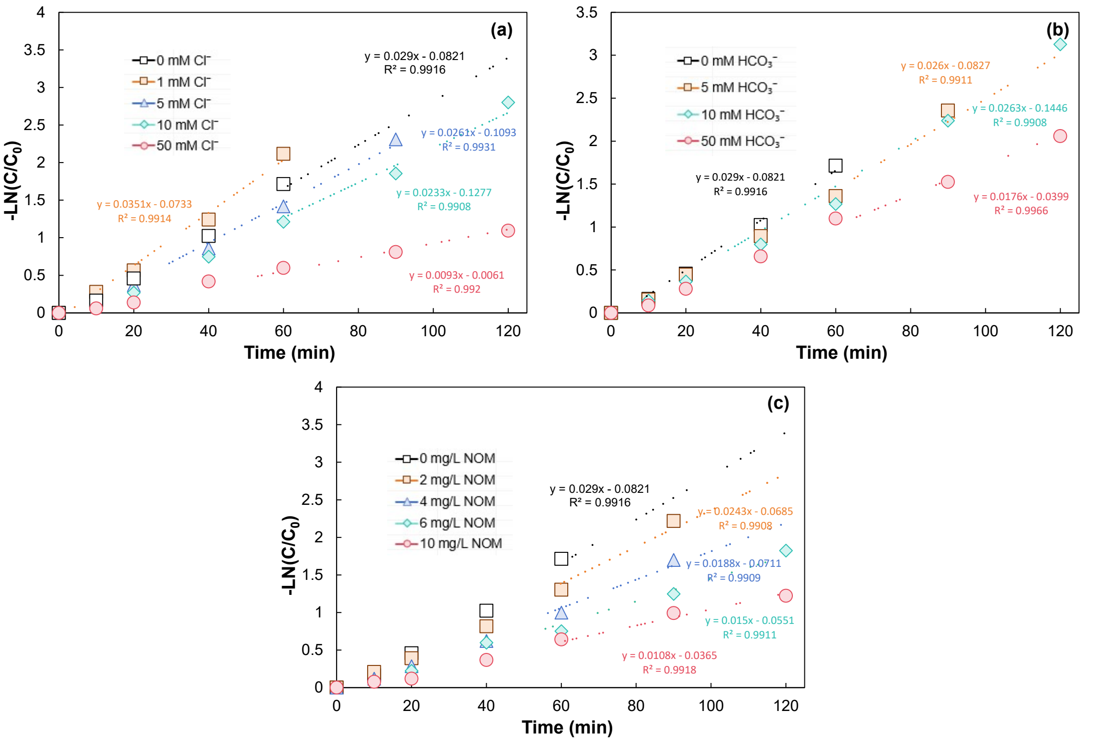


Fig. S4. Effects of (a) Cl^-, (b) HCO_3^-, and (c) NOM on the k_{obs} of BPA degradation in heat/PDS system. Experimental conditions: $[BPA]_0$ = 40 µM, $[PDS]_0$ = 1.0 mM, $[Cl^-]_0$ = 0-50 mM, $[HCO_3^-]_0$ = 0-50 mM, $[NOM]_0$ = 0-10 mg/L, pH 7.0 ± 0.1 maintained by 10.0 mM phosphate buffer.

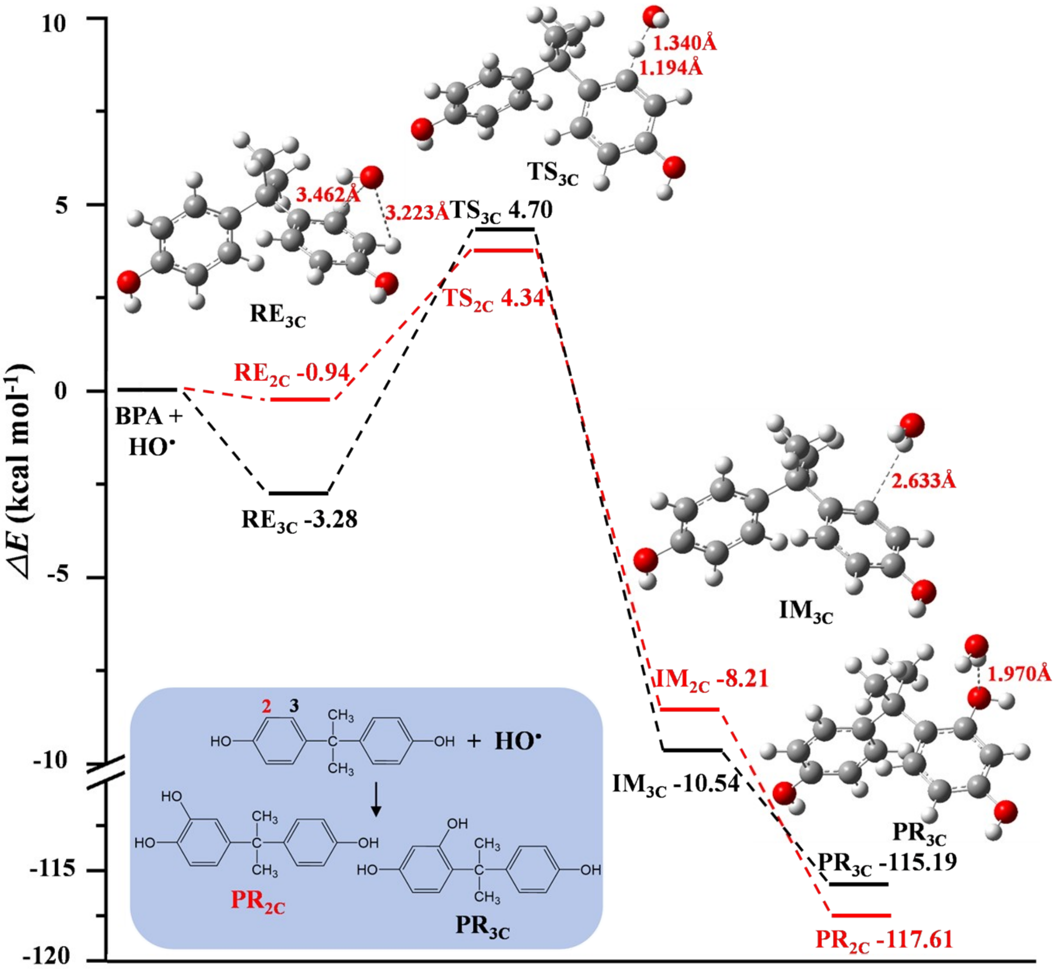


Fig. S5. Calculation of the *ΔE* value for HO$^\bullet$ addition reactions at different C sites of BPA molecule.