Comparison of the Oxidation of Halogenated Phenols in UV/PDS and UV/H_2O_2 Advanced Oxidation Processes

Junxin Liu†, Yongze Liu†, Yajun Tian†, Liqiu Zhang†, Li Feng†*

†Beijing Key Laboratory for Source Control Technology of Water Pollution, Engineering Research Center for Water Pollution Source Control and Eco-remediation, Beijing Forestry University, Beijing 100083, China

Corresponding Authors: Prof. Li Feng

E-mail: fengli_hit@163.com (Li Feng)

Text S1 Effects of photodegradation on kinetics

The overall k_{obs} in solutions was comprised of direct photolysis (k_{uv}) and indirect oxidation by $k_{radicals}$, as described in Eq. 1.

$$k_{obs} = S \times k_{uv} + k_{radicals} \quad (1)$$

In Eq. 1, S is screening correction calculated with Eq. S1, α is the absorption coefficient of the solutions, the α was the absorbance of the solution at the wavelength of UV light at 254nm, l is the light path length of the reactor (l = 4 cm, vertical path length of the solutions). (Mangalgiri, et al., 2017)

$$\frac{k'_{uv}}{k_{uv}} = S \cong \frac{1 - e^{-2.303\alpha l}}{2.303\alpha l} \quad (S1)$$

Text S2 Product analysis method

The flow rate of the mobile phase was 0.2 mL/min. The mobile phase (i.e., acetonitrile (A) and 0.1% formic acid in water (B)) eluted following gradient pattern: (i) 90% B, 0 to 2 min; (ii) from 2 to 42 min, B decreased linearly from 90% to 0%; (iii) from 42 to 50 min, B increased linearly from 0% to 90%; and (iv) from 50 to 55 min, the mobile phase returned to its initial composition. The mass spectrometers were performed in negative electron-spray ionization (ESI-) mode.

Figure S1. Degradation of BPs and CPs under UV light at pH 7

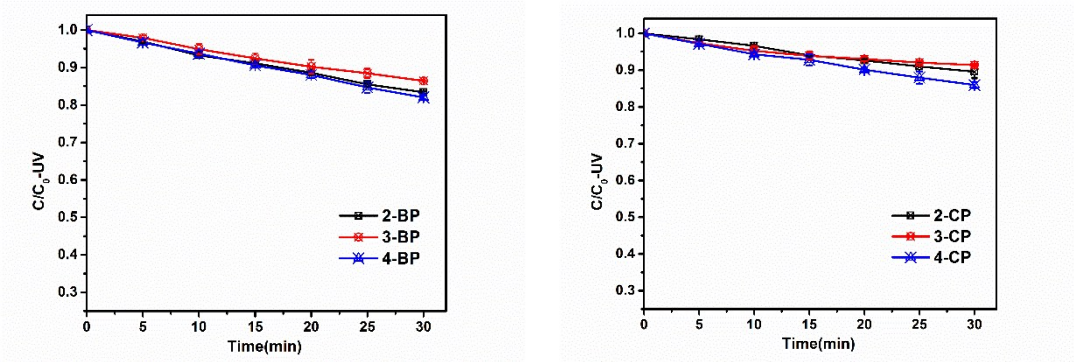


Fig. S1 Degradation of BPs and CPs under UV light

Environmental conditions: [BPs]= [CPs] = 10 μM; 10 mM phosphate buffer (pH 7.0); [PDS] = [H_2O_2] = 0.5 mM.

Figure S2. The HOMO orbital composition of 2-BP

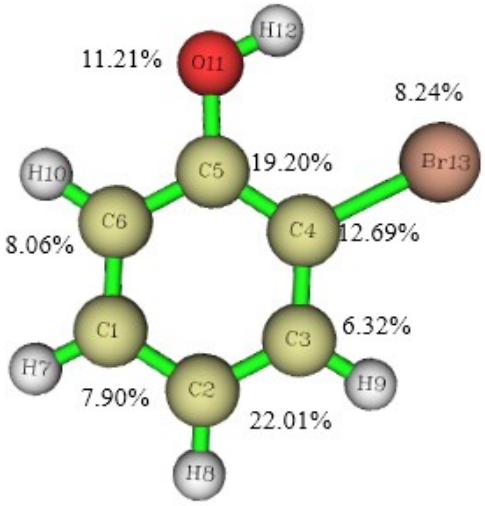


Fig. S5 The HOMO orbital composition of 2-BP

Figure S3. The variation of TOC of 2-BP in UV/PDS and UV/H_2O_2 systems.

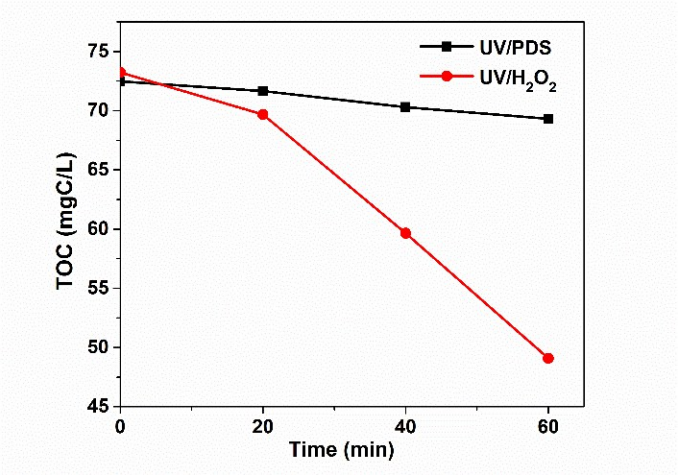


Fig. S6 The variation of TOC of 2-BP in UV/PDS and UV/H_2O_2 systems. Environmental conditions: [2-BP]= 1 mM; 10 mM phosphate buffer (pH 7.0); [PDS] = [H_2O_2] = 20 mM.

Table S1. Optical properties of six HPs

Table S1 Optical properties of six HPs.

Parameter	Screening factor (S)	
	UV/PDS	UV/H_2O_2
2-BP	0.94	0.96
3-BP	0.93	0.96
4-BP	0.94	0.96
2-CP	0.94	0.96
3-CP	0.94	0.95
4-CP	0.95	0.95

Table S2. Optical properties of pH 4 ~ 8

Table S2 Optical properties of pH (4 ~8).

pH	Screening factor (S)	
	UV/PDS	UV/H_2O_2
4	0.95	0.96
5	0.95	0.96
6	0.96	0.97
7	0.96	0.97
8	0.93	0.95

Table S3. Optical properties of Cl^-, HCO_3^- and NOM

Table S3 Optical properties of Cl^-, HCO_3^- and NOM

Parameter	Screening factor (S)				
	1 mg/L	5 mg/L	10 mg/L	100 mg/L	500 mg/L
UV/PDS-Cl^-	0.93	0.92	0.91	0.87	0.82
UV/H_2O_2-Cl^-	0.96	0.95	0.93	0.90	0.85
UV/PDS-HCO_3^-	0.94	0.93	-	-	-
UV/H_2O_2-HCO_3^-	0.96	0.95	-	-	-

Parameter	Screening factor (S)		
	1 mgC/L	5 mgC/L	10 mgC/L
UV/PDS-NOM	0.87	0.59	0.39
UV/H_2O_2- NOM	0.91	0.61	0.41

Table S4. The k_{obs}, k_{UV} and $k_{radicals}$ of six HPs.

Table S4 The k_{obs}, k_{UV} and $k_{radicals}$ of six HPs.

Compounds	k_{UV}	UV/PDS (min^{-1})			UV/H_2O_2 (min^{-1})		
		k_{obs}	S×k_{UV}	$k_{SO4\bullet-}$	k_{obs}	S×k_{UV}	$k_{HO\bullet}$
2-BP	0.0060	0.04714	0.00564	0.0415	0.03006	0.00576	0.0243
3-BP	0.0049	0.02825	0.00455	0.0237	0.03480	0.00470	0.0301
4-BP	0.0066	0.05420	0.00620	0.0480	0.03794	0.00634	0.0316
2-CP	0.0038	0.03447	0.00357	0.0309	0.02385	0.00365	0.0202
3-CP	0.0029	0.02553	0.00273	0.0228	0.03296	0.00276	0.0302
4-CP	0.0050	0.03865	0.00475	0.0339	0.03605	0.00475	0.0313

Table S5. The k_{obs}, k_{UV} and $k_{radicals}$ of 2-BP under pH 4 ~ 8.

Table S5 The k_{obs}, k_{UV} and $k_{radicals}$ of 2-BP under pH 4 ~ 8.

pH	k_{UV}	UV/PDS (min^{-1})			UV/H_2O_2 (min^{-1})		
		k_{obs}	S×k_{UV}	$k_{SO4\bullet-}$	k_{obs}	S×k_{UV}	$k_{HO\bullet}$
4	0.0038	0.0699	0.00361	0.06629	0.0415	0.00365	0.03785
5	0.0032	0.05755	0.00304	0.05451	0.0378	0.00307	0.03473
6	0.0038	0.02945	0.00365	0.02580	0.02375	0.00369	0.02006
7	0.006	0.04735	0.00576	0.04159	0.03155	0.00582	0.02573
8	0.0204	0.06205	0.01897	0.04308	0.0579	0.01938	0.03852

Table S6. The $k_{radicals}$ of 2-BP with different background matrix.

Table S6 The $k_{radicals}$ of 2-BP with different background matrix.

Parameter	$k_{radicals}$ (min^{-1})				
	1 mM	5 mM	10 mM	100 mM	500 mM
UV/PDS-Cl^-	0.0217	0.0185	0.0145	0.0286	0.0514
UV/H_2O_2-Cl^-	0.0191	0.0179	0.0176	0.0168	0.0167
UV/PDS-HCO_3^-	0.0208	0.0118	-	-	-
UV/H_2O_2-HCO_3^-	0.0148	0.0122	-	-	-

Parameter	$k_{radicals}$ (min^{-1})		
	1 mgC/L	5 mgC/L	10 mgC/L
UV/PDS-NOM	0.0197	0.0141	0.0113
UV/H_2O_2- NOM	0.0197	0.0154	0.0128

Table S7. Summary of identified intermediates determined by LC/MS-MS of 2-BP in UV/PDS system

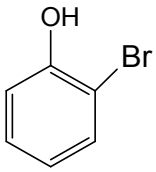
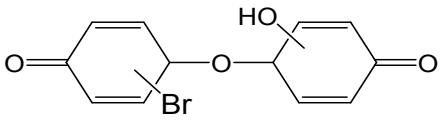
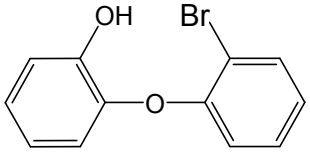
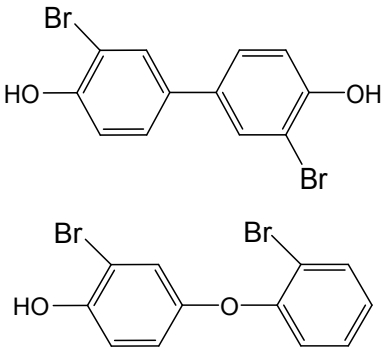
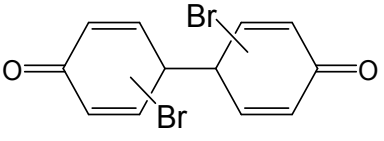
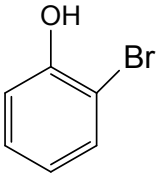
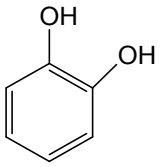
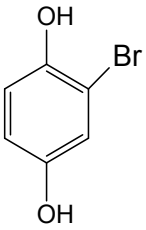
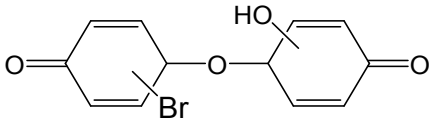
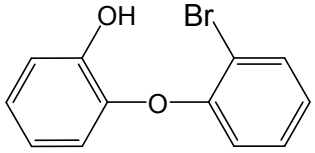
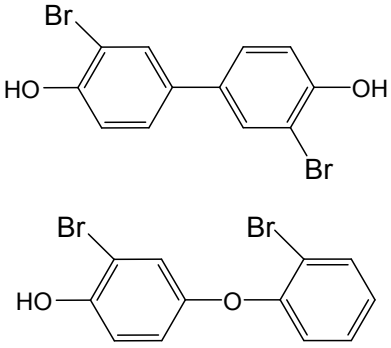
Compound	Retention Time (RT, min)	Molecular Weight (MW)	Formula	Structural Formula
2-BP	15.73	170.94	C_6H_5BrO	
P1	9.72	145.05	$C_6H_{10}O_4$	
P2	14.80	292.95	$C_{12}H_7BrO_4$	
P3	18.70	262.97	$C_{12}H_9BrO_2$	
P4	20.02	340.88	$C_{12}H_8Br_2O_2$	
P5	22.57	338.87	$C_{12}H_6Br_2O_2$	

Table S8. Summary of identified intermediates determined by LC/MS-MS of 2-BP in UV/H_2O_2 system

Compound	Retention Time (RT, min)	Molecular Weight (MW)	Formula	Structural Formula
2-BP	15.73	170.94	C_6H_5BrO	
P1	9.92	109.03	$C_6H_6O_2$	
P2	12.70	186.94	$C_6H_5BrO_2$	
P3	14.80	292.95	$C_{12}H_7BrO_4$	
P4	18.70	262.97	$C_{12}H_9BrO_2$	
P5	20.02	340.88	$C_{12}H_8Br_2O_2$	

P6	20.97	354.86	$C_{12}H_6Br_2O_3$