

Supplementary Information

**Distinct photoproducts of hydroxylated polybromodiphenyl ethers
from different photodegradation pathways: A case of 2'-HO-BDE-68**

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Contents: 7 pages that include 1 text, 5 figures and 3 tables.

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Abbreviations in the figures and tables of this supporting information

Abbreviation	Full name
2,4-DBP	2,4-dibromophenol
di-HO-DBB	dihydroxylated dibromobenzene
1,3,8-TBDD	1,3,8-tribromodibenzo- <i>p</i> -dioxin
di-HO-TBDE	dihydroxylated tribromodiphenyl ether
BSTFA+TMCS	1% trimethylchlorosilane (TMCS) in N,O-bis(trimethylsilyl)trifluoroacetamide (TMCS)
tri-HO-DBB	trihydroxylated dibromobenzene
di-HO-TeBDE	dihydroxylated tetrabromodiphenyl ether
2,4,6-TBP	2,4,6-tribromophenol

Text 1 GC/MS conditions

An Agilent 6890GC/5975MS equipped with a DB-XLB column (30 m × 0.25 mm, 0.25 μm film thickness, J&W Scientific) were used for the product analysis. The injector temperature was 280 °C. 1 μL sample was auto injected into inlet at the splitless mode. Helium was used as the carry gas at a flow rate of 1 mL/min. The GC oven temperature was programmed as follows: start from 90 °C for 2min, increase to 200 °C at a rate of 15 °C/min, then to 270 °C at the rate of 2.5 °C/min, thereafter to 310 °C at 20 °C/min and kept for 1.5 min. The temperatures of interface, EI source and NCI source were set at 280 °C, 230 °C and 150 °C, respectively. The scan mode was operated at the *m/z* range of 60-800. Selected ion monitoring of *m/z* = 79 and 81 with the NCI source was adopted for quantification of the brominated compounds.

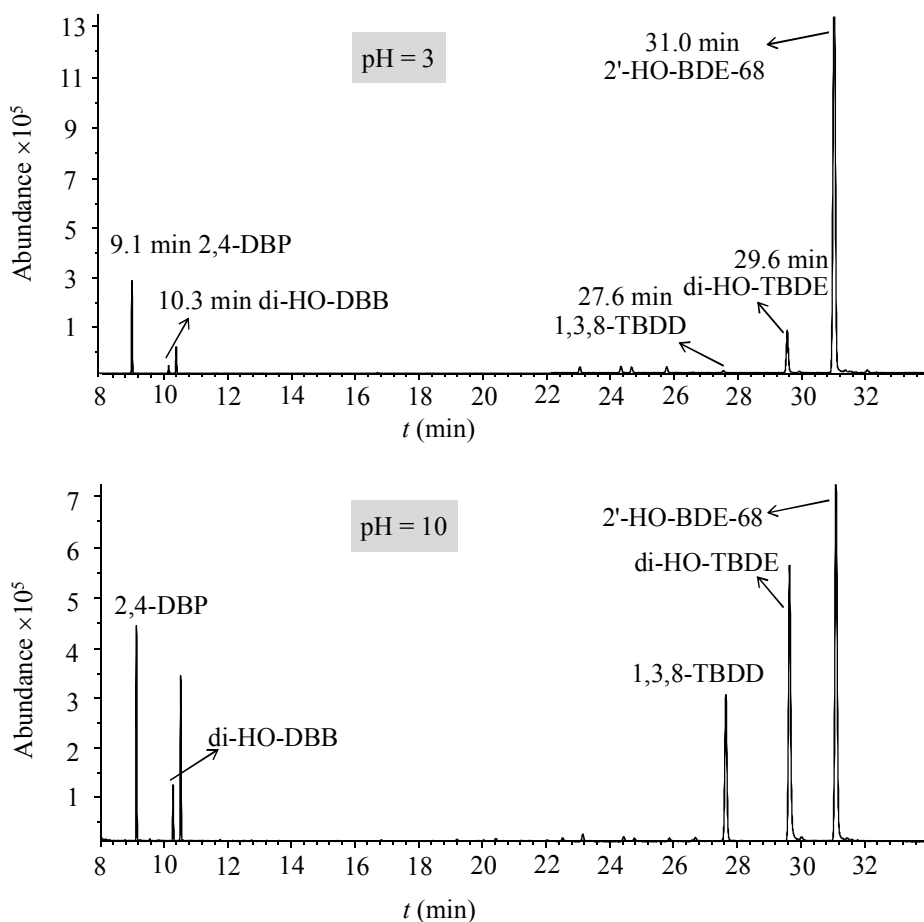
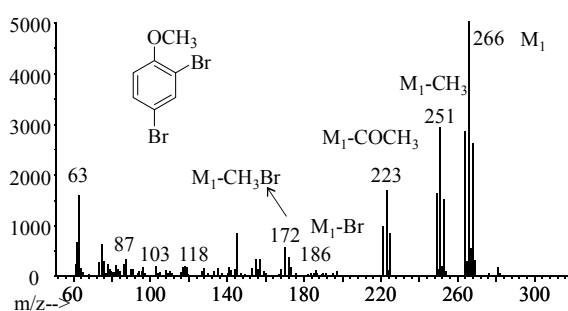
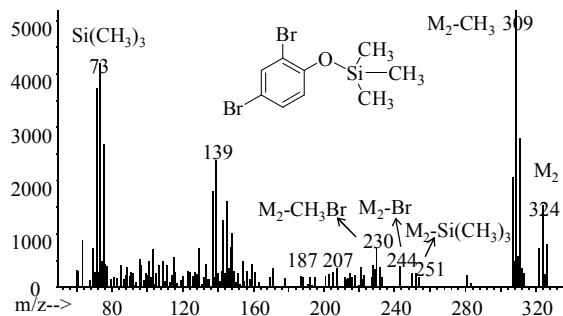


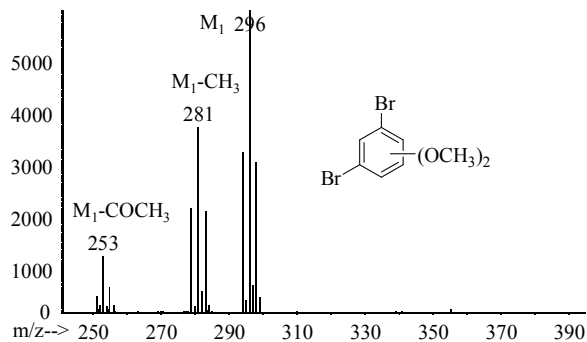
Fig. S1 Total ion chromatograms of the products from direct photolysis of 2'-HO-BDE-68 when 68.4% (pH =3) and 89.0% (pH =10) of it photolyzed (The samples were derivatized by diazomethane and the chromatograms were obtained by GC-MS with a negative chemical ionization source at the selective ion monitoring mode with $m/z = 79$ and 81).



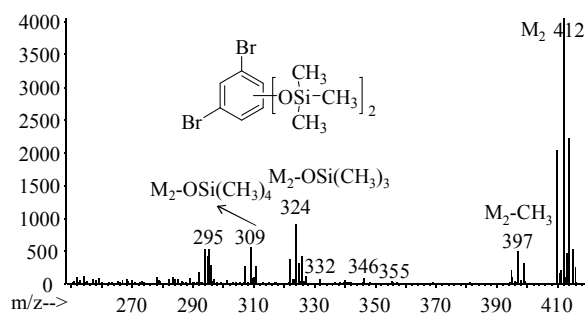
(A) diazomethane derivatized 2,4-DBP



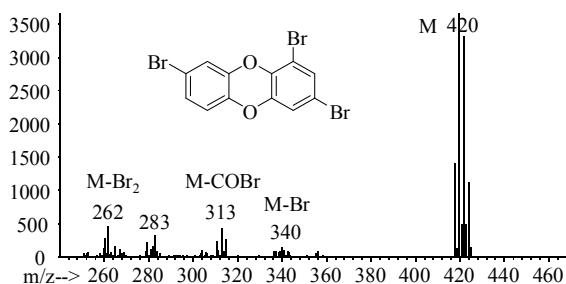
(B) BSTFA+TMCS derivatized 2,4-DBP



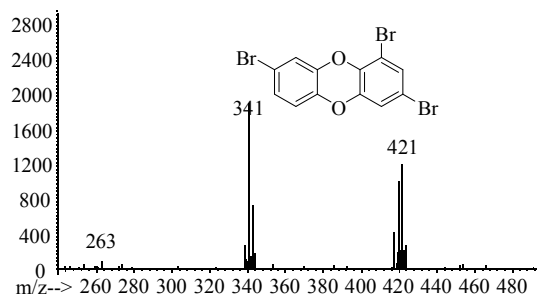
(C) diazomethane derivatized di-HO-DBB



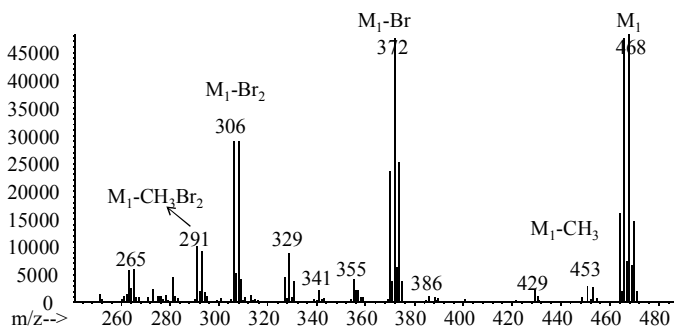
(D) BSTFA+TMCS derivatized di-HO-DBB



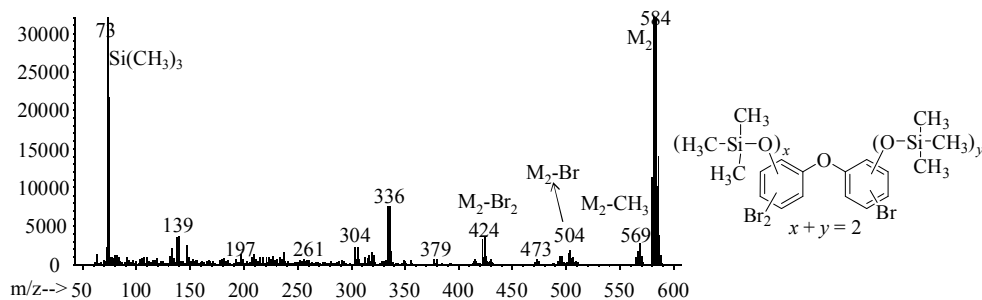
(E) Underivatized 1,3,8-TBDD



(F) Underivatized 1,3,8-TBDD



(G) diazomethane derivatized di-HO-TBDE



(H) BSTFA+TMCS derivatized di-HO-TBDE

Fig. S2 Mass spectra for the derivatized and underivatized products generated from direct photolysis of 2'-HO-BDE-68, obtained with electron-impact ionization source (A, B, C, D, E, G and H) and negative chemical ionization source (F).

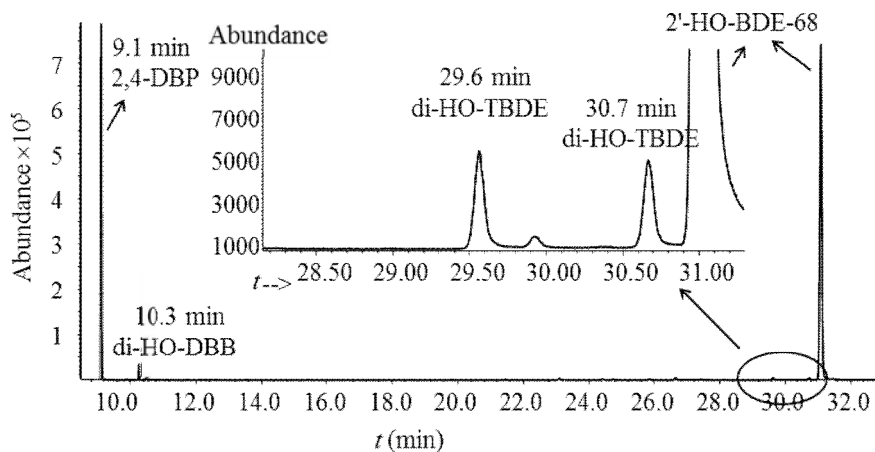


Fig. S3 Total ion chromatogram obtained by GC-MS with a negative chemical ionization source at the selective ion monitoring mode ($m/z = 79$ and 81) for the diazomethane derivatized products generated from reaction of 2'-HO-BDE-68 with $^1\text{O}_2$ (pH = 10) when 64.8% of 2'-HO-BDE-68 degraded.

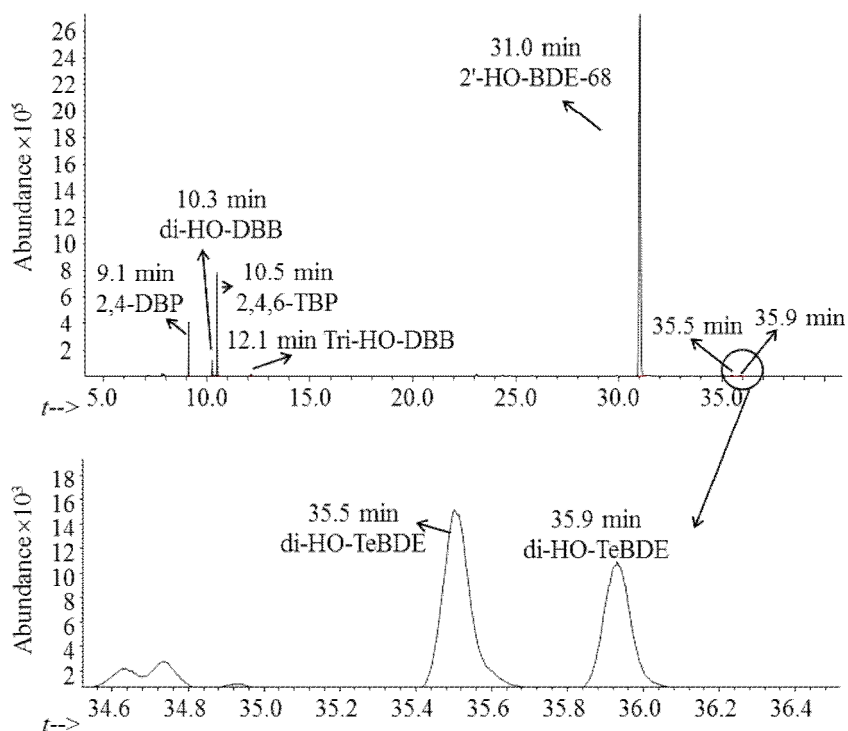


Fig. S4 Total ion chromatogram obtained by GC-MS with a negative chemical ionization source at the selective ion monitoring mode ($m/z = 79, 81$) for the diazomethane derivatized products generated from reaction of 2'-HO-BDE-68 with $\cdot\text{OH}$ (pH = 3) when 31.6% of 2'-HO-BDE-68 degraded.

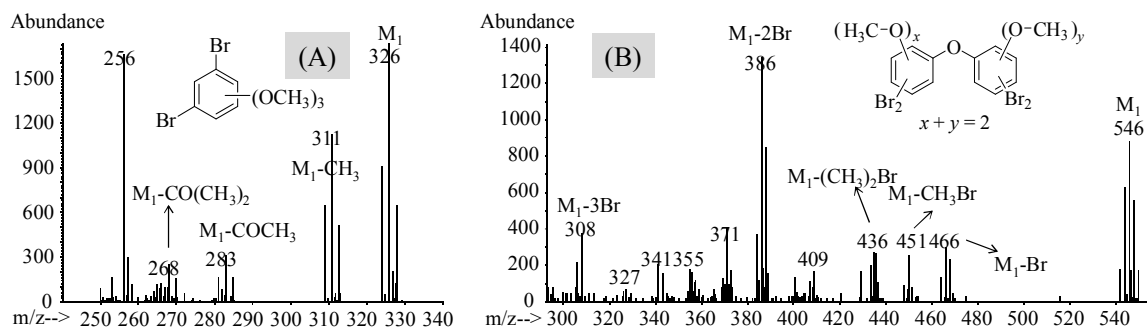


Fig. S5 Mass spectra (electron-impact ionization source) for the diazomethane derivatized tri-HO-DBB (A) and di-HO-TeBDE (B) generated from reaction of 2'-HO-BDE-68 with ·OH.

Table S1. Formation and degradation rate constants (k_p and k_p), yields (Y) of the products generated from direct photolysis of 2'-HO-BDE-68.

Product	pH = 3			pH = 10		
	k_p (min ⁻¹)	k_p (min ⁻¹)	Y (%)	k_p (min ⁻¹)	k_p (min ⁻¹)	Y (%)
2,4-DBP	$(8.9 \pm 3.2) \times 10^{-4}$	$(5.2 \pm 3.8) \times 10^{-3}$	35 ± 13	$(6.6 \pm 2.7) \times 10^{-2}$	$(3.3 \pm 1.8) \times 10^{-1}$	43 ± 18
di-HO-DBB	<i>l</i> *	<i>l</i> *	<i>l</i> *	$(3.0 \pm 0.9) \times 10^{-3}$	<i>l</i> *	1.9 ± 0.6
1,3,8-TBDD	$(2.2 \pm 0.5) \times 10^{-5}$	$(7.9 \pm 4.1) \times 10^{-3}$	0.86 ± 0.20	$(9.1 \pm 1.6) \times 10^{-3}$	$(6.7 \pm 4.0) \times 10^{-2}$	5.9 ± 1.1
di-HO-TBDE	$(1.3 \pm 0.2) \times 10^{-4}$	$(1.2 \pm 1.0) \times 10^{-3}$	5.0 ± 0.6	$(1.8 \pm 0.3) \times 10^{-2}$	$(7.6 \pm 2.7) \times 10^{-2}$	12 ± 2

* The data were not obtained, as the detected concentrations were very low and with high uncertainties.

Table S2. Formation and degradation rate constants (k_p and k_{-p}), and yields (Y) of the products generated from $^1\text{O}_2$ and $\cdot\text{OH}$ reaction of 2'-HO-BDE-68.

	Product	k_p (min^{-1})	k_{-p} (min^{-1})	Y
$^1\text{O}_2$ reaction	2,4-DBP	$(5.4 \pm 1.9) \times 10^{-2}$	$(6.8 \pm 4.0) \times 10^{-2}$	$(70 \pm 25)\%$
	di-HO-DBB	$(1.2 \pm 0.1) \times 10^{-3}$	$(1.4 \pm 1.3) \times 10^{-2}$	$(1.5 \pm 0.2)\%$
	di-HO-TBDEs	$(2.5 \pm 0.3) \times 10^{-4}$	$(5.6 \pm 1.4) \times 10^{-2}$	$(0.32 \pm 0.03)\%$
$\cdot\text{OH}$ reaction	2,4-DBP	$(9.3 \pm 1.8) \times 10^{-1}$	4.7 ± 1.9	$(75 \pm 15)\%$
	di-HO-TBDEs	$(3.0 \pm 0.9) \times 10^{-2}$	3.1 ± 1.4	$(2.4 \pm 0.8)\%$

Table S3. Apparent product yields (Y_{app}) of the products from the reaction of 2'-HO-BDE-68 with $\cdot\text{OH}$.

Degradation percentage of 2'-HO-BDE-68	12.0%	19.0%	31.6%	62.8%	84.1%
di-HO-DBB	8.0%	11.0%	15.2%	6.8%	0.4%
2,4,6-TBP	1.8%	2.6%	2.5%	1.1%	0.0%
tri-HO-DBB	0.0%	4.7%	4.5%	2.4%	0.0%