Supporting Information

Oxidative Destruction of Chlorinated Persistent Organic Pollutants by Hydroxyl Radicals *via* Ozone and UV Light Irradiation

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Experimental section

(a) General Procedure:

All reactions were conducted under an ozone atmosphere using oven-dried glass wares. A 100 W Hg lamp was used as a light source without any filter. Ozone was generated by an ozone generator (C-labsky series, model no. c-l010-DT)) using pure oxygen gas as the source of oxygen with a flow rate of 0.45 mL/ min. Starting materials (Aldrich) are commercially available and were used as received. NMR spectra were recorded in $CDCl_3$, DMSO or $CDCl_3$-DMSO mixture. ^1H NMR at 600 MHz and ^{13}C NMR at 150 MHz were used to determine the structures of products. Data were reported as: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet, b= broad.

(b) General procedure for dechlorination of chlorobenzene to oxalic acid:

A dry test tube of 20 mL capacity was charged with chlorobenzene (5 mL) mixed with 6 mL of CH_3CN-H_2O (4:2) solvent system with neutral medium and equipped with a Teflon septum and a magnetic stirrer bar. Ozone gas was bubbled into the chlorobenzene solution and simultaneously irradiated under a 100 W Hg lamp (200 mW/cm^2 at 310 nm) for 10 h at room temperature. Upon irradiation, white solid was slowly formed and precipitated. The white solid was further dispersed in ethyl acetate-hexane (80:20) solution. Pure oxalic acid solid was obtained by centrifugation. The structure of the solid product oxalic acid was determined by ^1H NMR, ^{13}C NMR and confirmed by x-ray crystallography. All experiments were repeated at least 3 times.

Procedure for determination of conversion, and mass balance [1].
After ozone-UV irradiation, a known amount (in mole) of external standard, 1,4-dicyanobenzene, was added to the final crude products solution. Once the external standard was added, the molar ratios of all products relative to the external standard in the final solution are fixed irrespective of the later experimental procedure. Then, the absolute amounts of all products in the final solution can be determined by multiplication of the relative molar ratios of all crude products to the external standard (determined by ^1H NMR peak area ratio) with the mole of the external standard added. The mass balance was determined by the sum of all products (in moles, including unreacted starting substrate) divided by the initial mole of starting material. The conversion percentage was determined by the total moles of all crude products divided by the initial mole of the starting material.

EPR measurements of hydroxyl radicals[1,2]:

EPR spectra (X band, 9.8 GHz, room temperature) were taken from samples of cyclopentylchloride (95%) with 5% of water and ACN mixture under photoirradiation or dark condition in the presence a radical trapping reagent, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 2.5 x 10^{-2} M). The parameters used in the simulation are the followings: g= 2.0073, coupling constant A_N= 7.2 G (1N) and A_{rH}= 4.1 G (2H). All measurements were done at room temperature. By using DMPO as a spin trapping reagent, we have detected the presence of hydroxyl radical (see the EPR spectra shown below in Fig. S1) in both dark and photo conditions in the case of chlorobenzene-neutral water-ozone system. The observed EPR spectrum for both conditions is the same as those reported in the literature.
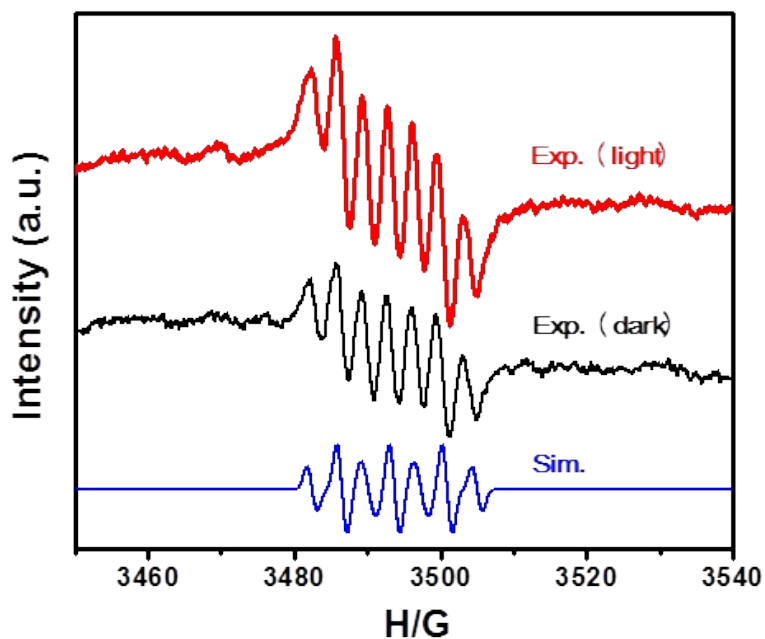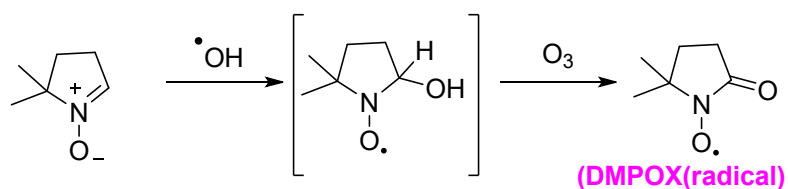

Figure S1: EPR spectra detected from a chlorobenzene –neutral water-ozone system under uv light irradiation (top) and in dark (middle). The bottom EPR spectrum is a simulated one using the following parameters: g= 2.0073, coupling constant A_N= 7.2 G (1N) and A_{rH}= 4.1 G (2H). The top equation

illustrates the reaction of a spin trapping reagent, DMPO (5,5-Dimethyl-1-pyrroline N-oxide), with hydroxyl radical, followed by ozone oxidation of the DMPO-OH adduct to become stable DMPOX radical, which is corresponding to the observed EPR signal.

Spectroscopic Data:

bis (4-chlorophenyl) methanone (5a)
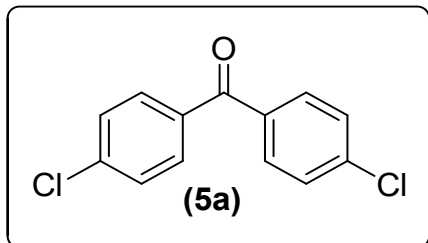
White solid; **¹H NMR** (600 MHz, CDCl$_3$): **δ** 7.69(d, J= 8.50 Hz, 2 H), 7.43(d, J= 8.34 Hz, 2 H). **¹³C NMR** (150 MHz, CDCl$_3$): δ 194.0, 139.0, 135.4, 131.2, and 128.7.

ppm

7.70015
7.68594
7.44240
7.42851

(5a)

Integral

2.0000
2.0294

ppm   10   8   6   4   2   0

ppm
194.035

139.092
135.485
131.249
128.721

77.225
77.003
76.791

(5a)

ppm   180   160   140   120   100   80   60   40   20
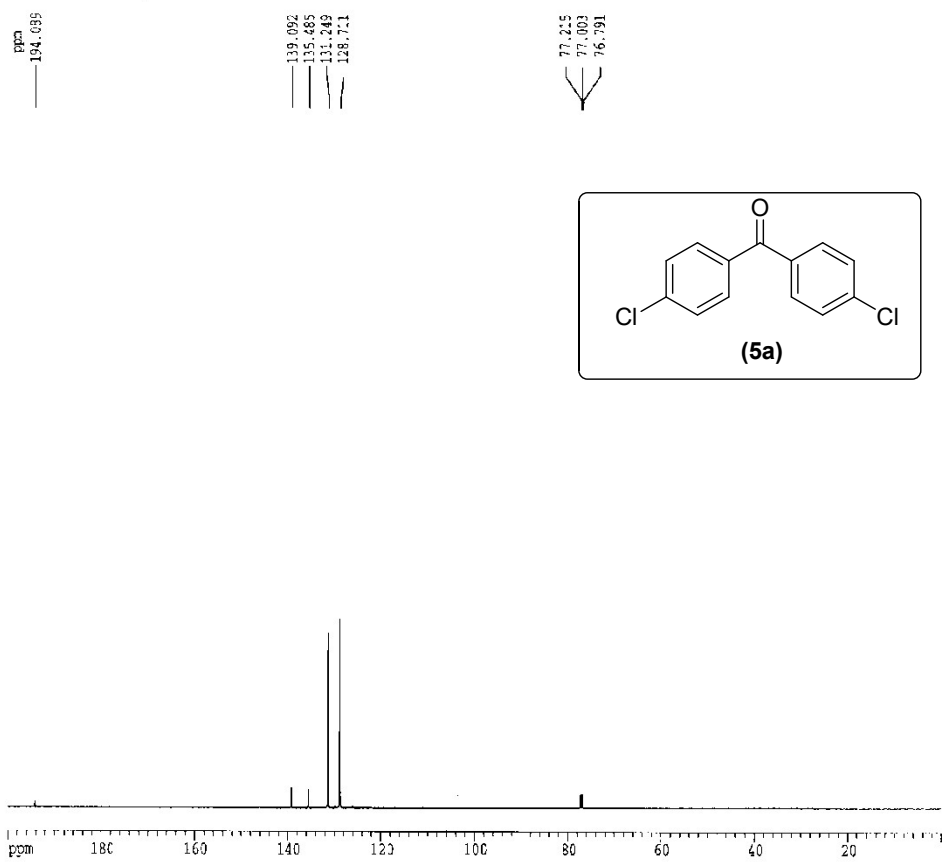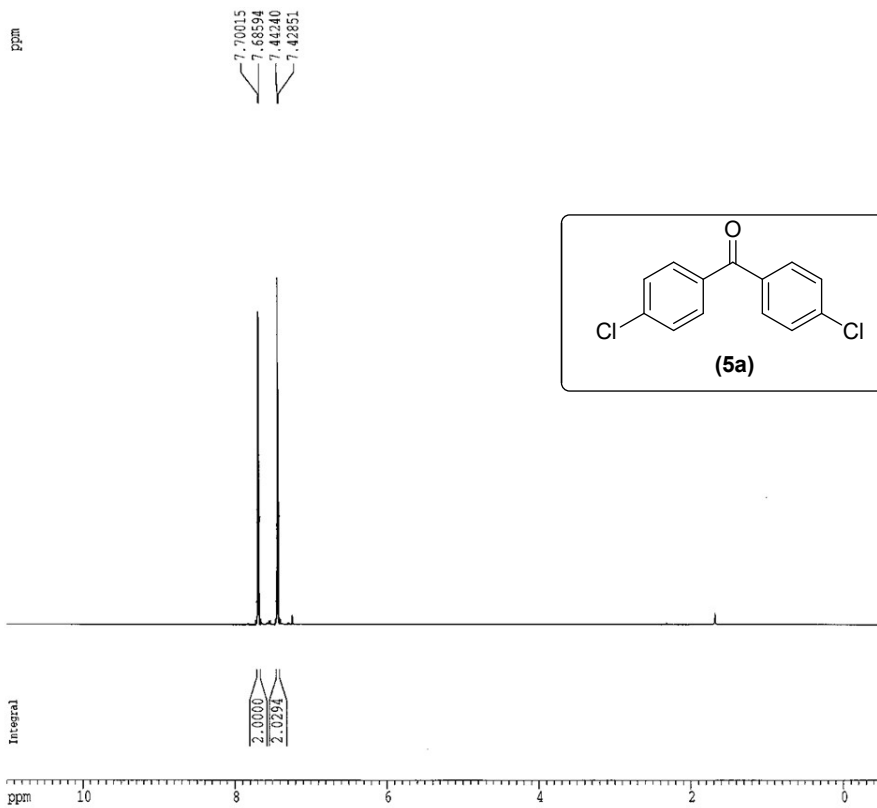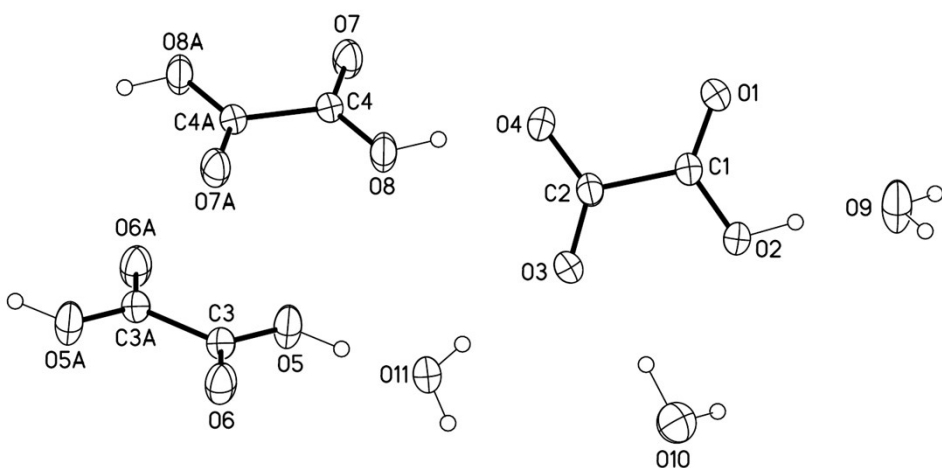
Figure S2: ORTEP diagram of compound **2b (CCDC No. 1940531)**

Table S1. Crystal data and structure refinement for mo_150605_0m_a.

Identification code	mo_150605_0m_a
Empirical formula	C4 H9 O11
Formula weight	233.11
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 6.3450(6) Å a= 94.218(2)°.
	b = 7.2323(7) Å b= 100.280(2)°.

| | c = 10.5606(10) Å | g = 97.907(2)°. |

Volume	469.90(8) $Å^3$
Z	2
Density (calculated)	1.648 Mg/m^3
Absorption coefficient	0.174 mm^{-1}
F(000)	242
Crystal size	0.28 x 0.25 x 0.08 mm^3
Theta range for data collection	1.970 to 26.407°.
Index ranges	-7<=h<=7, -9<=k<=8, -13<=l<=13
Reflections collected	7231
Independent reflections	1906 [R(int) = 0.0185]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9485 and 0.8899
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1906 / 0 / 136
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1211
R indices (all data)	R1 = 0.0535, wR2 = 0.1274
Extinction coefficient	n/a
Largest diff. peak and hole	0.543 and -0.423 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_150605_0m_a. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(1)	7555(3)	3239(3)	5781(2)	24(1)
C(2)	7250(3)	4363(3)	4580(2)	24(1)
C(3)	5813(3)	10093(3)	642(2)	25(1)
C(4)	4934(3)	4525(3)	630(2)	24(1)
O(1)	7267(3)	1539(2)	5676(1)	35(1)
O(2)	8158(3)	4302(2)	6862(1)	39(1)
O(3)	7620(3)	6091(2)	4775(1)	36(1)
O(4)	6668(3)	3377(2)	3514(1)	35(1)
O(5)	5017(2)	9231(2)	1519(1)	34(1)
O(6)	7617(2)	10977(2)	761(1)	34(1)

O(7)	3385(2)	3351(2)	680(1)	32(1)
O(8)	6577(3)	5100(2)	1536(1)	35(1)
O(9)	9439(3)	2540(3)	8745(2)	44(1)
O(10)	8421(3)	8450(2)	7244(2)	44(1)
O(11)	7678(3)	9289(2)	3544(1)	32(1)

Table S3. Bond lengths [Å] and angles [°] for mo_150605_0m_a.

C(1)-O(1)	1.211(2)
C(1)-O(2)	1.294(2)
C(1)-C(2)	1.553(3)
C(2)-O(3)	1.234(2)
C(2)-O(4)	1.254(2)
C(3)-O(6)	1.213(2)
C(3)-O(5)	1.291(2)
C(3)-C(3)#1	1.536(4)
C(4)-O(7)	1.219(2)
C(4)-O(8)	1.281(2)
C(4)-C(4)#2	1.551(4)
O(2)-H(1)	0.9346
O(5)-H(2)	0.9612
O(8)-H(3)	0.8895
O(9)-H(4)	0.8391
O(9)-H(5)	0.8904
O(10)-H(6)	0.9863
O(10)-H(7)	1.0311
O(11)-H(8)	0.7166
O(11)-H(9)	0.8812
O(1)-C(1)-O(2)	125.14(17)
O(1)-C(1)-C(2)	121.75(17)
O(2)-C(1)-C(2)	113.11(16)
O(3)-C(2)-O(4)	127.77(18)
O(3)-C(2)-C(1)	117.35(17)
O(4)-C(2)-C(1)	114.87(17)
O(6)-C(3)-O(5)	126.62(18)

O(6)-C(3)-C(3)#1	121.0(2)				
O(5)-C(3)-C(3)#1	112.3(2)				
O(7)-C(4)-O(8)	126.66(17)				
O(7)-C(4)-C(4)#2	120.3(2)				
O(8)-C(4)-C(4)#2	113.1(2)				
C(1)-O(2)-H(1)	108.8				
C(3)-O(5)-H(2)	113.2				
C(4)-O(8)-H(3)	111.2				
H(4)-O(9)-H(5)	105.9				
H(6)-O(10)-H(7)	107.5				
H(8)-O(11)-H(9)	105.5				

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z   #2 -x+1,-y+1,-z

Table S4. Anisotropic displacement parameters (Å^2x 10^3) for mo_150605_0m_a. The anisotropic displacement factor exponent takes the form: $-2p^2\,[h2\,a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U^{11}
C(1)	28(1)	24(1)	20(1)	6(1)	3(1)	4(1)
C(2)	27(1)	24(1)	21(1)	7(1)	3(1)	5(1)
C(3)	27(1)	24(1)	22(1)	4(1)	1(1)	5(1)
C(4)	31(1)	20(1)	19(1)	4(1)	3(1)	3(1)
O(1)	56(1)	22(1)	25(1)	7(1)	2(1)	3(1)
O(2)	70(1)	26(1)	18(1)	4(1)	0(1)	7(1)
O(3)	62(1)	22(1)	24(1)	6(1)	4(1)	5(1)
O(4)	55(1)	28(1)	18(1)	4(1)	-2(1)	1(1)
O(5)	31(1)	44(1)	23(1)	12(1)	0(1)	-1(1)
O(6)	28(1)	41(1)	28(1)	9(1)	-2(1)	-4(1)
O(7)	34(1)	34(1)	24(1)	10(1)	4(1)	-5(1)
O(8)	41(1)	35(1)	23(1)	12(1)	-5(1)	-8(1)
O(9)	33(1)	62(1)	32(1)	23(1)	-3(1)	-9(1)
O(10)	52(1)	40(1)	38(1)	6(1)	9(1)	1(1)
O(11)	43(1)	30(1)	23(1)	8(1)	3(1)	8(1)

Table S 5.   Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3 for mo_150605_0m_a.

H(8)	7719	8416	3820	50
H(9)	7507	10096	4171	50
H(4)	8750	1972	9245	50
H(6)	7494	7879	7813	50
H(5)	10785	2885	9189	50
H(7)	8279	7500	6445	50
H(2)	6024	9325	2326	50
H(1)	8580	3560	7522	50
H(3)	6543	4435	2210	50

References:

1. K. C. Hwang and A. Sagadevan, *Science,* 2014, **346,** 1495.
2. E. Finkelstein, G. M. Rosen and E. J. Rauckman, *Arch. Biochem. Biophys.,* 1980*,* **200**, 1.