Photochemical Rearrangement of Chlorinated Dibenzo-*p*-dioxins. Regioselective Carbon–Oxygen Bond Homolysis from the Singlet Excited State, and Carbon–Chlorine Bond Homolysis from the Triplet Excited State

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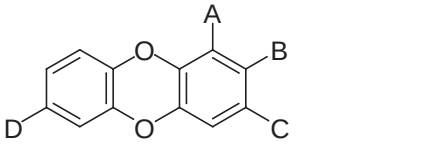
UV light irradiation of 1-chloro-, 2-chloro-, 1,2-dichloro-, 2,3-dichloro-, and 2,7-dichlorodibenzo-*p*-dioxin in methanol leads to regioselective homolysis of carbon–oxygen bond from the singlet excited state to undergo rearrangement into chlorinated 2,2′-biphenols. On the contrary, reaction from the triplet excited state of chlorinated dioxins results in selective formation of dechlorinated congeners without altering the dioxin skeleton.

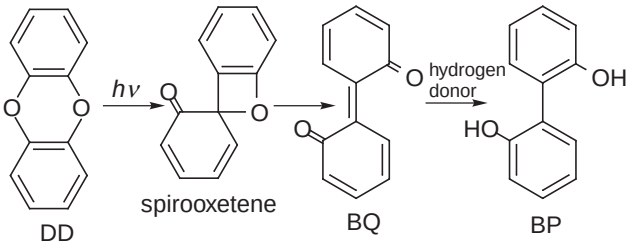
Chlorinated dibenzo-*p*-dioxins (CDDs) are well known as a highly toxic group of anthropogenic compounds for environment. Photochemical transformation of CDDs has been mainly focused on reductive dechlorination of highly chlorinated CDDs leading to less toxic congener.[1] On the basis of previous studies on photochemical rearrangement of diphenyl ethers into 2- and 4-hydroxybiphenyls initiated by carbon–oxygen bond homolysis,[2] it is anticipated that not only carbon–chlorine bond but also carbon–oxygen bond may be homolyzed. A few studies have paid attention to photochemical transformation of dioxin skeleton. It has been surely shown that rearrangement of unsubstituted[3] and substituted dibenzo-*p*-dioxins[3,4] gives 2,2′-biphenols by carbon–oxygen bond homolysis. Our attention has directed to factor controlling priority between carbon–oxygen and carbon–chlorine bond scission of excited CDDs.[5] We now wish to demonstrate that the singlet excited state ($^*S_1$) of monochloro- and dichlorodibenzo-*p*-dioxins in Chart 1 including 1-chloro- (1-CDD), 2-chloro- (2-CDD), 1,2-dichloro- (1,2-DCDD), 2,3-dichloro- (2,3-DCDD), and 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD) undergoes preferential carbon–oxygen bond homolysis to give chlorinated 2,2′-biphenols (CBPs), whereas selective carbon–chlorine bond homolysis from the triplet excited state ($^*T_1$) affords dechlorinated dioxins. To the best of our knowledge, this is the first finding that multiplicity of the excited state controls regioselectivity of photochemical transformation of CDDs.

Excitation of CDDs[6] was done in methanol (1.3×10^{-3} M) under argon atmosphere on irradiation with light of wavelength longer than 300 nm.[7,8] Determination of products was achieved by repeated chromatographic isolation followed by instrumental analyses. As shown in Table 1, most CDDs afforded CBPs as a major product except 1,2-DCDD. Unsubstituted dioxin (DD) and 2-CDD were also produced in the case of 2-CDD and 2,3-DCDD, respectively. Similarly, 1-CDD and 1,2-DCDD gave unsubstituted 2,2′-biphenol (BP). Formation of CBPs from CDDs is in accord with the mechanism proposed by Wan et al. (Scheme 1).[3] Homolytic carbon–oxygen bond scission of DD produces spirooxetene by concerted [1,3] sigmatropic rearrangement or by a stepwise process via a biradical. Electrocyclic reaction involving 4π-electron system can facilely convert this



1-CDD (A = Cl, B = C = D = H)
2-CDD (A = H, B = Cl, C = D = H)
1,2-DCDD (A = B = Cl, C = D = H)
2,3-DCDD (A = H, B = C = Cl, D = H)
2,7-DCDD (A = H, B = Cl, C = H, D = Cl)

Chart 1.



Scheme 1.

spirooxetene into 2,2′-biphenylquinone (BQ) with relatively long lifetime, which is then reduced to BP by hydrogen donation from solvent via a semiquinone radical.[9]

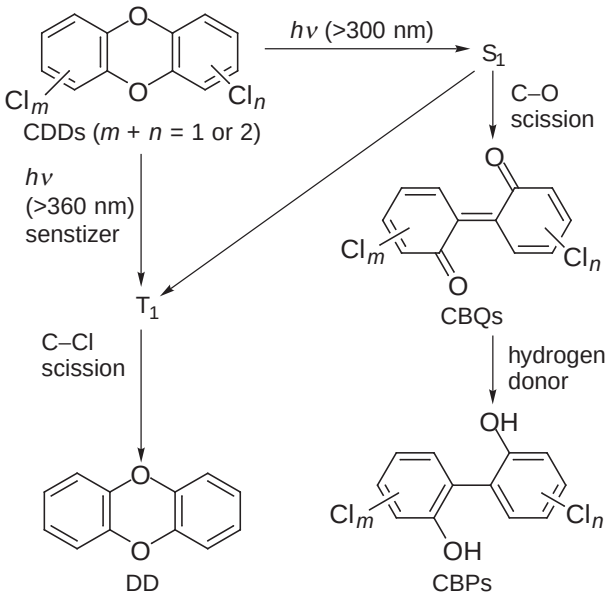
Quenching of $^*T_1$ by oxygen molecule, a triplet quencher, discloses reaction from $^*S_1$ of CDDs. On irradiation of CDDs (1.3×10^{-3} M) with >300 nm light in oxygen-saturated solution, formation of CBPs was increased concomitant with decrease of BP and DD. For example, in the case of 2-CDD, yield of 5-CBP increased from 16.6 to 28.8% in oxygen-saturated methanol accompanied by decrease of DD from 11.6 to 0%. It is evident that CBPs should necessarily come from $^*S_1$ of CDDs. Exclusive production of CBPs and absence of DD under oxygen atmosphere indicate that the major pathway from $^*S_1$ of CDDs is rearrangement of the dioxin skeleton initiated by carbon–oxygen bond homolysis, during which chlorine atoms are left intact on the aromatic ring (Scheme 2).

In order to identify the role of $^*T_1$ of CDDs, sensitization by acetophenone was performed.[10] Thus, upon excitation of acetophenone (5.0×10^{-3} M) in the presence of CDDs (1.3×10^{-3} M) in methanol with >360 nm light led to production of DD and/or CDDs with less chlorine atoms than the parent CDDs (Table 1). No other products such as CBPs were produced. In contrast with $^*S_1$ of CDDs, it is clear that $^*T_1$ of CDDs exclusively undergoes reductive dechlorination of chlorine substituents on the aromatic ring without transformation of the dioxin

Table 1. Products and yields of photochemical transformation of chlorinated dibenzo-*p*-dioxins in methanol

CDDs	Condition[a]	Time[b]	Yield/%[c]			
			CDDs	DD	CBPs	BP
1-CDD	A	3 h	—	0	11.7[d]	18.8
1-CDD	B	3 h	—	0	21.4[d]	trace
1-CDD	C	3 h	—	87.4	0	0
2-CDD	A	5 min	—	11.6	16.6[e]	0
2-CDD	B	5 min	—	0	28.8[e]	0
2-CDD	C	10 min	—	95.7	0	0
1,2-DCDD	A	1 h	0	0	0	13.0
1,2-DCDD	B	1 h	0	0	13.0[f]	0
1,2-DCDD	C	1 h	78.9[g]	trace	0	0
2,3-DCDD	A	10 min	24.3[h]	0	13.0[i]	0
2,3-DCDD	B	10 min	0	0	12.0[i]	0
2,3-DCDD	C	3 h	55.9[h]	19.9	0	0
2,7-DCDD	A	10 min	0	0	9.5[j]	0
2,7-DCDD	B	10 min	0	0	15.2[j]	0
2,7-DCDD	C	60 min	40.2[h]	49.1	0	0

[a]A: >300 nm, Ar; B: >300 nm, O_2; C: >360 nm, Ar, acetophenone (5.0×10^{-3} M). [b]Irradiation time was controlled so that conversion of CDDs may be in the range of 15–50%. [c]Yields based on CDDs consumed. [d]6-CBP. [e]5-CBP. [f]5,6-DCBP. [g]1-CDD (58.5%) and 2-CDD (20.5%). [h]2-CDD. [i]4,5-DCBP. [j]5,5′-DCBP.



Scheme 2.

framework (Scheme 2). Occurrence of reductive dechlorination from $^*T_1$ of CDDs, despite higher bond dissociation energy of carbon–chlorine bond than the triplet energy of CDDs, may be ascribed to the contribution from the mechanism that involves electron transfer from solvent molecule to CDDs to give radical anion of CDDs.[11] Production of DD on irradiation of 2-CDD and 2,3-DCDD with >300 nm light in the absence of oxygen can be rationalized in terms of intersystem crossing from $^*S_1$ to $^*T_1$ of these CDDs.

Formation of BP was observed on irradiation of 1-CDD and 1,2-DCDD with >300 nm light. In each case, BP was absent in oxygen-saturated solution. These results can be attributed to secondary photochemical reaction from $^*T_1$ of 6-CBP and 5,6-DCBP produced from 1-CDD and 1,2-DCDD, respectively. Reductive dechlorination from $^*T_1$ is a general process of chlorinated aromatics.[12] Another possibility for the pathway leading to BP is secondary photochemical rearrangement of DD produced by dechlorination of CDDs. This route can be ruled out, because DD was absent under the condition where BP was produced (Table 1).

In conclusion, it has been revealed that the singlet excited state of CDDs in methanol undergoes regioselective homolysis of carbon–oxygen bond leading to CBPs, while reductive dechlorination of the dioxin skeleton is dominant process for the triplet excited state. Investigation on photolysis of other CDDs is in progress. Details of this study will be published elsewhere in the near future.

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5 Bond dissociation energy of carbon–chlorine (chlorobenzene) and carbon–oxygen bond (diphenyl ether) is 398[13] and 368 kJ mol^{-1},[13] respectively, which is expected to be competitively homolyzed upon excitation.
6 1-CDD, 2-CDD, and 2,3-DCDD were synthesized according to the literature.[14] Preparation of 1,2-DCDD[15] and 2,7-DCDD[16] was successfully achieved by a modified method of the literature.
7 The energy of $^*S_1$ of CDDs estimated from the edge (λ with ε of 2 cm^{-1} M^{-1}) of UV–vis spectrum is as follows: 377 kJ mol^{-1} (1-CDD); 371 kJ mol^{-1} (2-CDD); 361 kJ mol^{-1} (1,2-DCDD); 347 kJ mol^{-1}(2,3-DCDD); 369 kJ mol^{-1} (2,7-DCDD). These values are lower than the energy of 302.5 nm light from the Hg lamp that corresponds to 395 kJ mol^{-1}.
8 A methanol solution of CDDs was irradiated in a cylindrical irradiation flask (Pyrex, 200 mL or 500 mL) using a 400 W high-pressure mercury lamp (RIKO UVL-400-HA, internal irradiation type) with a Pyrex jacket. Argon or oxygen gas was bubbled before and throughout the irradiation. Evaporation of solvent and isolation by repeated chromatography (silica gel, hexane–acetone as a developing solvent) of the residual photolysate afforded products to allow instrumental analysis (EI-MS, ^{1}H and ^{13}C NMR) as listed in Table 1.
9 Formation of CBPs was dramatically enhanced when irradiation was performed in the presence of $NaBH_4$ as a hydride donor, by which CBQs is facilely reduced to CBPs.[3]
10 Triplet energy of CDDs estimated by phosphorescence spectra is 278, 284, 275, and 257 kJ mol^{-1} for 1-CDD, 2-CDD, 2,3-DCDD, and 2,7-DCDD, respectively,[14,17] which is lower than that of acetophenone (311 kJ mol^{-1}).
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