

Photodegradation of tetra- and hexachlorodibenzo-*p*-dioxins

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Abstract

This study examined the direct photolysis and photocatalytic processes for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,6,7,8-HxCDD). The photocatalytic procedure was performed on the TiO₂ film under irradiation with 365 nm UV and the compounds were immobilized on TiO₂/solid phase. No 2,3,7,8-substituted PCDD/Fs products were detected in photocatalytic process under the experimental conditions. The reaction rate constants were 0.3256 h⁻¹ for 2,3,7,8-TCDD (2000 ng) in UV/TiO₂ reaction, 0.2474 h⁻¹ for 1,2,3,6,7,8-HxCDD (2000 ng) in UV/TiO₂ reaction and 0.0666 h⁻¹ for 1,2,3,6,7,8-HxCDD (50 ng) under direct UV irradiation. For 1,2,3,6,7,8-HxCDD (50 ng) in a UV/TiO₂ reaction, the degradation is too fast to determine the reaction rate. The photocatalytic process was faster than direct photolysis for the same chlorinated PCDDs, and the rate decreased with increasing PCDDs quantity. The photocatalytic rate of the PCDDs decreased with increasing chlorination extent. The confirmed intermediates of 1,2,3,6,7,8-HxCDD in direct photolysis, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD both were formed by the loss of a longitudinal chlorine nearest the oxygen atom. The quantity of 1,2,3,7,8-PeCDD and toxic equivalency quantity (TEQ) declined after 10 h of UV irradiation. The proposed dechlorination pathway of 1,2,3,6,7,8-HxCDD was via 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD. Formation of trace concentrations of 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (1,2,3,4,7,8-HxCDD) and 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (1,2,3,7,8,9-HxCDD) from 1,2,3,6,7,8-HxCDD appears to be a minor side reaction.

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1. Introduction

There are 75 different polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 different polychlorinated dibenzo-*p*-furans (PCDFs). PCDDs, especially those with at least four and more chlorine atoms in the 2, 3, 7, and 8 positions, are generally extremely resistant to biological degradation [1]. PCDDs enter the environment in ultra-trace amounts from various combustion sources, particularly municipal waste incineration. The total concentration of seventeen 2,3,7,8-substituted congeners of ambient air in northern Taiwan was detected from 0.056 to 0.348 pg-TEQ/m³ [2]. Cheng et al. [3] showed that PCDD/Fs levels measured in soil in Taiwan range from 0.524

to 5.02 pg-TEQ/g. Generally, they are all poorly water soluble, possess high octanol–water coefficients, and tend to be strongly adsorbed on the surfaces of particulate matter. The values of log *K*_{ow} of TCDD and HxCDD are 6.4 and 7.3, and solubility of TCDD and HxCDD at 25 °C is 3.5 × 10⁻⁴ (mg/l) and 4.4 × 10⁻⁶ (mg/l), respectively. The water solubility of dioxins decreases and solubility in organic solvents and fats increases with increasing chlorine content [4]. Generally, elimination rates decrease and biological half-life increases with an increasing chlorine number in a molecule [1].

In Taiwan, incineration is becoming a dominant municipal waste treatment method. Due to the rapid increase in municipal waste incinerations, potential dioxin emissions from these sources have caused significant public concern in Taiwan. Wang et al. [5] investigated two crematories in southern Taiwan and their results revealed that the mean PCDD/Fs

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emissions from the stacks were 2.36 and 0.322 ng TEQ/N m³. The overall concentration in the stack flue gas of sinter plants with SCR (0.995–2.06 ng TEQ/N m³) is lower than that from sinter plant without SCR (3.10 ng TEQ/N m³) [6]. Dioxins are emitted into the environment via flue gases and incineration ashes. Activated carbon injection technology can effectively decrease flue gas dioxin concentration, but increases total dioxin emissions from municipal waste incinerations [7]. Fly ashes from municipal waste incinerations are considered hazardous in Taiwan, and are treated by solidifying with cement followed by landfill disposal. Leaching or perceived leaching of potentially toxic contaminants into the environment is a public concern. The coexistence of dissolved coloring constituents, could enhance the leachability of PCDD/Fs, thus contributing to the vertical movement and leaching behavior of PCDD/Fs in the landfill layers of the incineration residue [8]. Accordingly, an effective dioxin destruction method is required to solve this problem.

Several methods have been considered in the development of an efficient and economically feasible approach for destroying PCDD/Fs, including catalytic destruction [9,10], photolysis [11–16], photocatalysis [17], radiolysis [18], ozonolysis [19], and biodegradation [20,21]. Dechlorination is generally reported as the predominant reaction, and dechlorinated products have been identified in different solvents. Only a few studies claim that photodechlorination is not the major pattern of PCDD/Fs degradation and propose that C–O cleavage is an important photolysis route [14,17]. This is due to the differences between the photodegradation mechanisms of PCDD/Fs. Rayne et al. [16] examined the photochemical transformation of 2,3,7,8-TCDD in aqueous solution, using 302 nm light and indicated that the major primary product of 2,3,7,8-TCDD is 2,2'-dihydroxy-4,4',5,5'-tetrachlorobiphenyl (4,4',5,5'-TeCDHBP). The findings reveal that the photochemical conversion of PCDDs to chlorinated dihydroxybiphenyls may be the most important factor in determining the environmental fate of these compounds.

Although biological processes frequently are favorites for contaminated site remediation, advanced oxidation processes (AOPs) provide effective and rapid treatment. In the photocatalytic process, organic compounds are oxidized mainly to carbon dioxide when they make contact with TiO₂ powder illuminated with UV light. The capability of TiO₂ photocatalyst to decompose dioxins and dioxin-like compounds has been reported [17,22]. For soil remediation, the extracted PCDD/Fs from polluted soil can be dechlorinated using photolysis. The photolytic treatment herein not only destroyed PCDD/Fs and generated no 2,3,7,8-substituted chlorine PCDD/Fs. Additionally, photolytic treatment is more effective than photolysis; hence, this method is appropriate for soil remediation. This study investigated PCDD degradation by the direct photolysis process (UV) and the photocatalytic process (UV/TiO₂). The PCDDs included 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD. This study aims: (i) to investigate the reaction rate of different photolytic processes for 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD, (ii) to determine

the byproducts and the dechlorination of Cl atom positions of 1,2,3,6,7,8-HxCDD under direct UV irradiation, and (iii) to suggest possible reaction pathways of 1,2,3,6,7,8-HxCDD in the direct photolysis process.

2. Materials and methods

2.1. Materials

The non-labeled target compounds, 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD were obtained from Wellington Laboratories Inc. (concentration in nonane as 50 µg/ml) and used as supplied. The labeled compounds, [¹³C]-2,3,7,8-TCDF, [¹³C]-1,2,3,7,8-PeCDF, [¹³C]-2,3,4,7,8-PeCDF, [¹³C]-1,2,3,4,7,8-HxCDF, [¹³C]-1,2,3,6,7,8-HxCDF, [¹³C]-2,3,4,6,7,8-HxCDF, [¹³C]-1,2,3,7,8,9-HxCDF, [¹³C]-1,2,3,4,6,7,8-HpCDF, [¹³C]-1,2,3,4,7,8,9-HpCDF, [¹³C]-2,3,7,8-TCDD, [¹³C]-1,2,3,7,8-PeCDD, [¹³C]-1,2,3,4,7,8-HxCDD, [¹³C]-1,2,3,6,7,8-HxCDD, [¹³C]-1,2,3,4,6,7,8-HpCDD, and [¹³C]-OCDD, were also purchased from Wellington Laboratories Inc. The catalyst – TiO₂ sourced from Degussa P-25 (specific surface area = 50 m²/g).

2.2. Photolytic experiments

For direct photolysis processes, an aliquot 1 µl of 1,2,3,6,7,8-HxCDD (concentration in nonane as 50 µg/ml) was loaded on the quartz plates (20 mm × 20 mm), then the solvent was evaporated and exposed to UV light in the ambient air (*T* = 25 °C).

The UV light source was a 400 W medium-pressure Hg lamp, and had a spectrum mainly between 300 and 400 nm (HPA-400). For the photocatalytic processes, the PCDDs samples were dropped on a TiO₂ film. Coating TiO₂ film on the quartz plate was obtained by dipping the substrate into a 5 wt.% TiO₂ suspension and pulling it up manually at constant speed. The film then was dried in air for some time, and subjected to heat treatment under ambient atmosphere for 30 min at 400 °C. This process was repeated five times to obtain a film with uniform thickness [17]. The other procedures were same as for the direct photolysis experiments.

This work also performs the photocatalytic processes of 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD at high dosage (total dosage = 2000 ng), with all procedures being as above except for the dosage.

2.3. Analysis of PCDD/Fs

To extract dioxin compounds from the quartz plates, the quartz plates were first treated using 10 ml methanol, and the extractors were spiked with 10 µl labeled PCDD/Fs standard described USEPA M1613. The treated samples were further chromatographically purified through the silica gel column (70–130 mesh, Acme's) using 20 ml hexane. Extracted PCDD/Fs were analyzed in the Super Micro Mass

Research and Technology Center of Cheng-Shiu University of Technology. This center was the first lab certified by the Taiwan EPA to analyze PCDD/Fs, and has passed international intercalibration on PCDD/Fs in fly ash, sediment, mothers' milk, human blood, and cod liver. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/Fs analyses. The HRGC is a Hewlett Packard 6890 Series gas chromatograph, equipped with a DB-5MS (F&W Scientific, USA) fused silica capillary column (60 m, 0.25 mm ID, 0.25 μm film thickness), and splitless injection. The oven temperature program was set as follows: 150 $^{\circ}\text{C}$ held for 4 min, then increased to 220 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$, then increased at 1.5 $^{\circ}\text{C}/\text{min}$ to 260 $^{\circ}\text{C}$, then increased at 4 $^{\circ}\text{C}/\text{min}$ to 310 $^{\circ}\text{C}$ and finally held for 5 min at 310 $^{\circ}\text{C}$. The carrier gas was Helium, with a flow rate of 1.2 ml/min. The HRMS is a Micromass Autospec Ultima (UK) mass spectrometer with a positive electron ionization detector. The analyzer mode of the selected ion recording had resolution of 10 000 (10% valley definition). The electron energy was 35 eV, and the source temperature was 250 $^{\circ}\text{C}$.

3. Results and discussion

3.1. Characteristic of TiO_2 film

Fig. 1 displays the surface morphology of the film heated at 400 $^{\circ}\text{C}$. The scanning electron micrographic (SEM) figures are shown at two different magnifications (3000 and 60 000 multiple). Particle size is approximately 20 nm and typically falls within the range of nanosize particles. At 3000 multiple, the surface of the film exhibits textured uniform clusters of TiO_2 grains (Fig. 1(a)). Higher magnification reveals a highly porous sponge-like surface (Fig. 1(b)). The pattern for both powders and immobilized films is essentially the same for TiO_2 . The sintering temperature of 400 $^{\circ}\text{C}$ used in immobilization apparently did not alter the crystallization of the catalyst. The 2θ peaks at 25.4 $^{\circ}$, 37.8 $^{\circ}$ and 48.1 $^{\circ}$, elucidate the typical structure of anatase-type TiO_2 , and those at 27.6 $^{\circ}$ and 36.1 $^{\circ}$ are associated with rutile-type TiO_2 . The temperature affects the distribution between these two phases; the active anatase phase is most prevalent at 400 $^{\circ}\text{C}$ [22]. The crystallite size can be determined from the broadening of the diffraction peak, by applying the Scherrer equation, or $d = 0.89\lambda/\beta \cos \theta$, where d represents the crystal size of the photocatalyst; λ the X-ray wavelength; β the full width at half maximum value of the photocatalyst; θ the diffraction angle [23]. The diameter of the TiO_2 powders was thus calculated to be 24 nm. The diameter of TiO_2 by SEM observation was very close to the result of Scherrer equation calculation.

3.2. Photodegradation of 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD

Fig. 2 illustrated the photocatalytic process and direct photolysis of PCDDs under different concentrations.

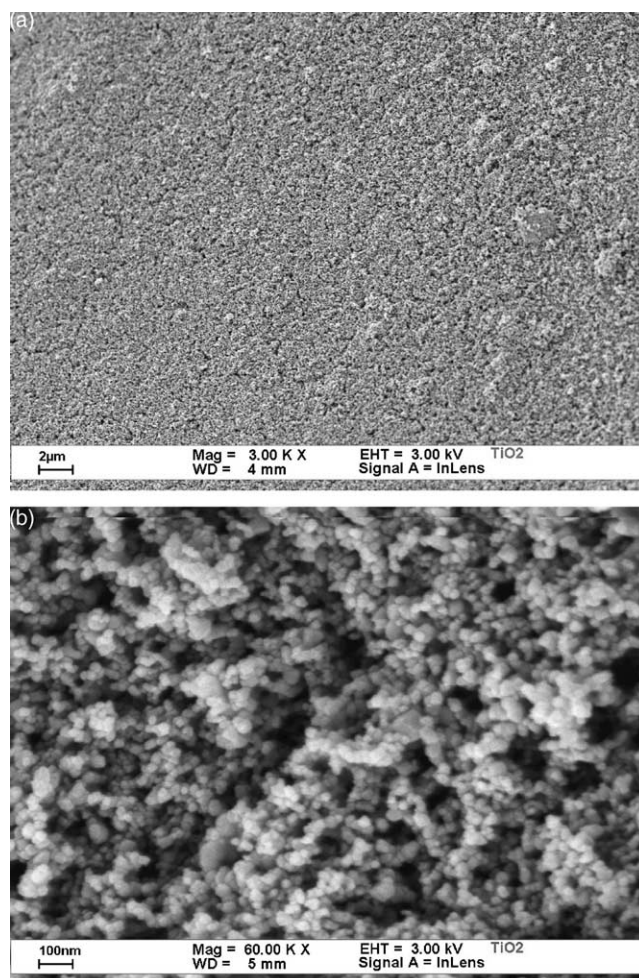


Fig. 1. SEM micrograph of the TiO_2 film at two different magnifications: (a) 3000 multiple, (b) 60 000 multiple.

Rapid photolytic transformation was noted for both 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD, with 99.86% conversion of 2,3,7,8-TCDD (2000 ng) in 4 h of UV/ TiO_2 reaction, 96.48% conversion of 1,2,3,6,7,8-HxCDD (2000 ng) in 4 h

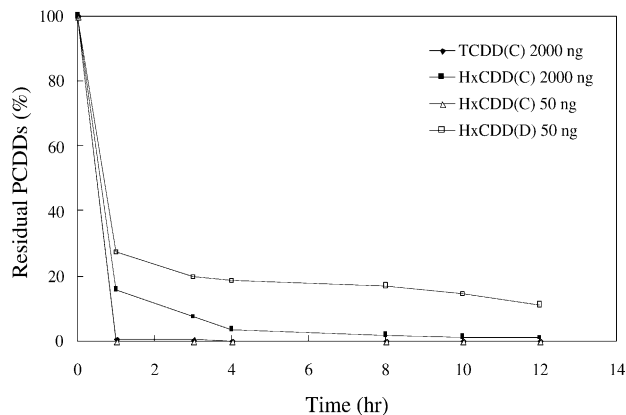


Fig. 2. Photodegradation of 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD. 'C' denotes the photocatalytic process and 'D' denotes the direct photolysis process.

of UV/TiO₂ reaction, 99.99% conversion of 1,2,3,6,7,8-HxCDD (50 ng) in 4 h of UV/TiO₂ reaction, and 81.57% conversion of 1,2,3,6,7,8-HxCDD (50 ng) in 4 h of direct UV irradiation. No 2,3,7,8-substituted PCDD/Fs products were detected in the photocatalytic process under experimental conditions. In contrast, several 2,3,7,8-substituted congener byproducts were obtained in the direct photolysis process (discussed in the subsequent section). The fact that the photoproduct could not be positively identified in the photocatalytic process implied that another pathway involving C–O cleavage might be more important than reductive dechlorination for PCDDs. Choi et al. [17] demonstrated that OH radical attack on the aromatic ring structure initiates photocatalytic degradation of all dioxin congeners, and neither stable intermediates nor dechlorinated PCDD were detected during the photocatalytic degradation, similar to this study.

The magnitudes of the rate of PCDDs followed the order 2,3,7,8-TCDD (2000 ng) (UV/TiO₂) > 1,2,3,6,7,8-HxCDD (2000 ng) (UV/TiO₂) > 1,2,3,6,7,8-HxCDD (50 ng) (UV). The reaction rate constants were 0.3256 h⁻¹ for 2,3,7,8-TCDD (2000 ng) in UV/TiO₂ reaction, 0.2474 h⁻¹ for 1,2,3,6,7,8-HxCDD (2000 ng) in UV/TiO₂ reaction and 0.0666 h⁻¹ for 1,2,3,6,7,8-HxCDD (50 ng) under direct UV irradiation. For 1,2,3,6,7,8-HxCDD (50 ng) in a UV/TiO₂ reaction, the degradation is too fast to determine the reaction rate. Rapid photodegradation of 2,3,7,8-TCDD compared to 1,2,3,6,7,8-HxCDD in the photocatalytic process indicated that the chlorine substitution pattern on the dibenzo-*p*-dioxin nucleus influenced the selectivity of environmental photocatalytic reactions. The photocatalytic rate of the PCDDs decreased with increasing chlorination. This result may contribute to the increased chlorines on PCDDs, the decreased electron density on the aromatic ring, and the decreased reaction rate of electrophilic OH addition. The results also indicated that high PCDDs caused low photodegradation rate, and the photocatalytic process was faster than the direct photolysis process. Decrease in photodegradation rate constants with increasing chlorination extent has been described previously for PCDD/Fs photodegradation experiments [11,13–15,17]. The results differed among studies but the order of the reaction rate constant was similar. Different results may result from differences in experimental conditions, including light source, light intensity and wavelength, the use of PCDDs in solvent or aqueous solution or nature water, PCDDs concentration, and whether or not PCDDs was degraded with catalyst.

3.3. Pathways of direct photolysis of 1,2,3,6,7,8-HxCDD

Fig. 3 illustrates the time profile for the photoproduct of 1,2,3,6,7,8-HxCDD by direct photolysis. The amount of 1,2,3,7,8-PeCDD increased to a maximum value and then fell. The amount of lower chlorinated dioxin, 2,3,7,8-TCDD gradually increased, implying that dechlorination of 1,2,3,6,7,8-HxCDD proceeded stepwise. This result was similar to that obtained by Buser [24] for the direct photolysis of

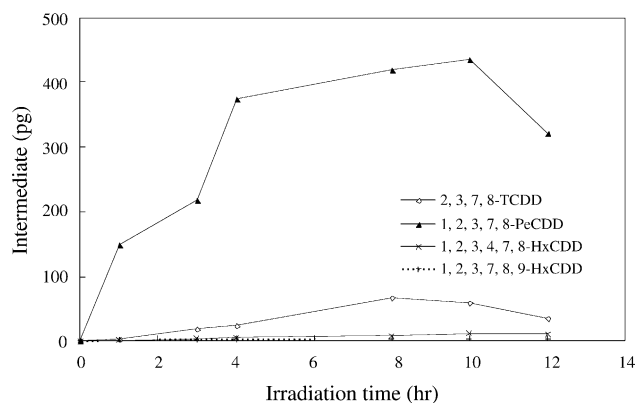


Fig. 3. 1,2,3,6,7,8-HxCDD photoproduct profiles from direct photolysis. Total 1,2,3,6,7,8-HxCDD is 50 ng.

1,2,3,6,7,8-HxCDD, and the photoproducts were identified as TCDDs and PeCDDs.

Several works have noted that dechlorination is a major route for PCDD/Fs decomposed by direct photolysis, photocatalytic process, and biologic treatment [9,11,12,14,15,18–21]. The confirmed intermediates in this research, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD are both formed by the loss of a longitudinal chlorine nearest the oxygen atom. Moreover, the dominant byproduct, 1,2,3,7,8-PeCDD, is formed by reductive dechlorination involving the loss of a longitudinal chlorine atom (from position 6) from 1,2,3,6,7,8-HxCDD. Several studies previously have observed this preferential loss of longitudinal chlorine atoms (from position 1,4,6,9) [9,11,25]. In contrast, some researchers indicated that the reductive dechlorination occurred mainly from the lateral positions (2,3,7,8) [14,19,26]. Significant differences have been demonstrated to exist in photoinduced dechlorination of PCDDs in the solution phase and on solid surfaces. Preferential chlorine loss occurred in the lateral positions in the solution phase, and from the longitudinal positions on adsorbent surfaces [25]. Since this study performed the photolysis of 1,2,3,6,7,8-HxCDD on the quartz surface, loss of longitudinal chlorine atoms was reasonable.

To demonstrate the toxicity variation during the direct photolysis process, the toxicity equivalency quantity (TEQ) was calculated based on the appropriate toxicity equivalent factor (TEF). After each of the congener classes was weighted by the appropriate TEF, Table 1 listed the TEQ concentrations of intermediate in different reaction times by direct photolysis. The 1,2,3,7,8-PeCDD was the largest contributor to the dioxin equivalents among these byproducts in this study. From Table 1, the quantities of 1,2,3,7,8-PeCDD and TEQ declined after 10 h of UV irradiation. For higher chlorinated PCDD/Fs, toxicity may increase if partially dechlorinated products are recovered after the dechlorination reaction. Accordingly, checking the dechlorination selectivity of higher chlorinated PCDD/Fs is important.

The proposed dechlorination pathways of 1,2,3,6,7,8-HxCDD, as displayed in Fig. 4, were established by concluding the byproducts formed during direct photolysis.

Table 1
Photodechlorination of toxic PCDDs congeners for 1,2,3,6,7,8-HxCDD by direct photolysis process

PCDDs	TEF ^a	Amount (pg)					
		1 h	3 h	4 h	8 h	10 h	12 h
1,2,3,6,7,8-HxCDD	0.1	13545	9810	9215	8545	7160	5525
2,3,7,8-TCDD	1	2.2	18.1	24.3	67.7	59.2	35.6
1,2,3,7,8-PeCDD	0.5	149.6	218.0	375.3	420.6	436.6	321.9
1,2,3,4,7,8-HxCDD	0.1	1.4	3.7	5.6	7.4	11.5	10.1
1,2,3,7,8,9-HxCDD	0.1	1.9	3.1	3.3	3.9	4.4	4.5
Total TEQ (pg TEQ)		1431.8	1108.8	1134.3	1133.6	995.1	750.5

^a McKay [4].

The assumed reaction routes are based only on analyses of 2,3,7,8-chlorinated PCDD/Fs. Formation of trace concentrations of 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD from 1,2,3,6,7,8-HxCDD appears to be a minor side reaction, since no typical product of further dechlorination was observed. Huang et al. [27] reported Gibbs free energy values and redox potentials for the reductive dechlorination of dioxins with hydrogen as the electron donor. The results postulated that a dechlorination pathway would follow the redox potential of the various couples, and that the couples that produced the highest energy yield would be proceeded preferentially. The redox potentials strongly favor the dechlorination of 1,2,3,6,7,8-HxCDD via 1,2,3,6,8-PeCDD to 1,3,6,8-TCDD. For 1,2,3,7,8-PeCDD, the theoretical primary dechlorination product was 1,3,7,8-TCDD. Based on the estimation method of Huang et al. [27], 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD were all second priority products in the dechlorination pathway of 1,2,3,6,7,8-HxCDD. Lynam et al. [26] explored the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap as an indicator of molecule stability, with larger gap indicating greater molecule stability. Restated, the larger amount of

Gibbs free energy released during the reaction results in a compound that is thermodynamically more stable, as it reflected by the larger HOMO–LUMO gap. These theoretical studies all indicated that dechlorination in the most thermodynamically favored pathway generally occurred in lateral chlorinated positions. This study demonstrated the dechlorination involving the loss of a longitudinal chlorine atom from 1,2,3,6,7,8-HxCDD, which differed from the theoretical prediction. The differences between the findings of this study and the theoretical prediction might contribute to the differences in assumption conditions. Huang et al. [27] and Lynam et al. [26] used anaerobic environment condition as a basis for deducing the reductive dechlorination pathways. Meanwhile, this study involved an open system, which was not an anaerobic environment. Because the non-2,3,7,8-substitute congeners and the lower-chlorinated dioxins were not detected in this work, the full byproduct production and the reaction mechanism cannot be confirmed and compared between the theoretical and experimental conditions. Future investigations could provide further insights into the dioxin photodegradation mechanism and compare the experimental and theoretical results.

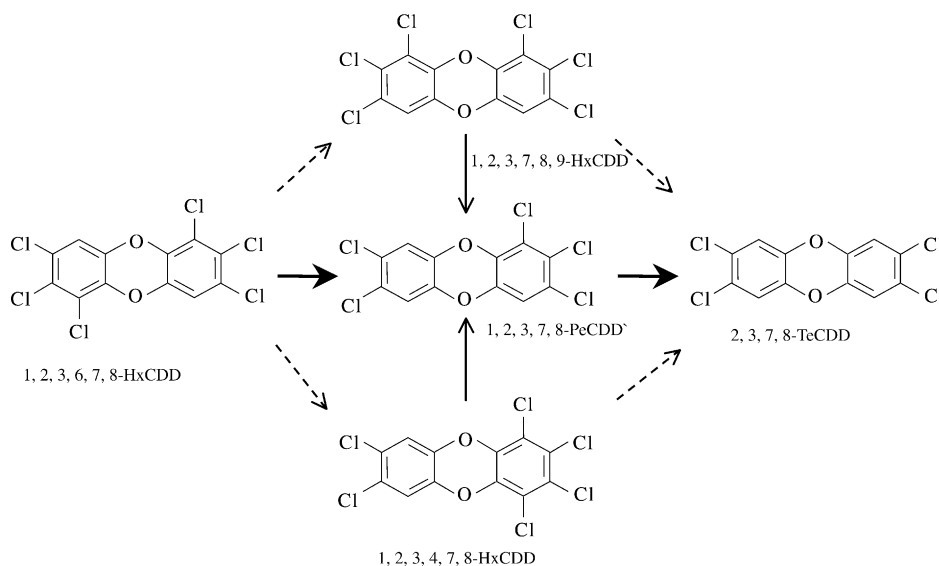


Fig. 4. Proposed dechlorination pathways of direct photolysis for 1,2,3,6,7,8-HxCDD. The solid lines denoted the major reaction routes and the dotted lines denoted the minor reaction routes.

4. Conclusions

No 2,3,7,8-substituted PCDD/Fs products were detected in photocatalytic process in this study. In contrast, several 2,3,7,8-substituted congener byproducts-1,2,3,4,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD were obtained in the direct photolysis process for 1,2,3,6,7,8-HxCDD. This study suggested that C–Cl cleavage could provide a major route for PCDDs in direct photolysis. The magnitudes of the rate of PCDDs were found to be followed the order 2,3,7,8-TCDD (2000 ng) (UV/TiO₂) > 1,2,3,6,7,8-HxCDD (2000 ng) (UV/TiO₂) > 1,2,3,6,7,8-HxCDD (50 ng) (UV). The decrease in photodegradation rate with increasing chlorination extent was similar to those in previous PCDD/Fs photodegradation experiments. The dominant byproduct, 1,2,3,7,8-PeCDD, is formed by reductive dechlorination involving the loss of a longitudinal chlorine atom (from position 6) from 1,2,3,6,7,8-HxCDD. For 1,2,3,6,7,8-HxCDD, this study noted that toxicity might increase if partially dechlorinated products are recovered following the dechlorination reaction. The proposed dechlorination pathways of 1,2,3,6,7,8-HxCDD in direct photolysis were 1,2,3,6,7,8-HxCDD → 1,2,3,7,8-PeCDD → 2,3,7,8-TCDD, and the formation of 1,2,3,4,7,8-HxCDD from 1,2,3,6,7,8-HxCDD appears to be a minor side reaction. Owing to the lack of detection of non-2,3,7,8-substitute congeners and lower chlorinated dioxins in this study, the fully reaction mechanism was unavailable for comparing the theoretical dechlorination pathways. Consequently, further studies should be undertaken to obtain more insights into the photodegradation mechanisms.

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