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Photocatalytic Degradation of Polychlorinated Dibenzo-*p*-dioxins on TiO₂ Film under UV or Solar Light Irradiation

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The photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins (PCDDs), which include mono-, tetra-, hepta-, and octachlorinated congeners (MCDD, TCDD, HpCDD and OCDD), was carried out on TiO₂ films under UV ($\lambda >$ 300 nm) or solar light irradiation in the air. All the dioxin congeners tested were successfully degraded on TiO₂ while the direct photolysis of them in the absence of TiO₂ was negligible. The photocatalytic degradation rates of PCDDs decreased with the number of chlorines and were described by the first-order reaction kinetics with half-lives of 5.8, 3.9, 0.71, and 0.38 h for OCDD, HpCDD, TCDD, and MCDD, respectively. The degradation rates increased with light intensity and TiO₂ coating weights up to 2 mW/cm² ($300 < \lambda < 400$ nm) and 200 μg of TiO₂/cm², respectively. Further increases in either the light intensity or the TiO₂ coating mass did not much affect the degradation rate. The natural solar light under clear sky conditions was as effective as a 200-W mercury lamp irradiation (filtered through a Pyrex filter) in degrading OCDD on TiO₂. The photocatalytic degradation of PCDDs seems to be initiated by OH radical attack and not by conduction band electron transfer. From a diffuse reflectance FTIR study, the degradation of OCDD was found to involve the cleavage of the aromatic ring. Neither stable intermediates nor dechlorinated PCDDs were detected during the photocatalytic degradation.

Introduction

The term dioxin, which refers to polychlorinated dibenzo-*p*-dioxins (PCDDs), has been a frequent topic in the public discourse due to its extreme toxicity and widespread occurrence in the environment. Public concerns about dioxins are related with their role as not only a potent carcinogen but also an extremely persistent endocrine disrupter that may have serious reproductive and developmental effects in humans and animals (*1*). Although some dioxins are formed as a result of some natural processes (e.g., volcanoes, forest fires), their major sources are municipal incinerators and combustion processes, chemical production processes of chlorinated aromatic compounds, and bleach processes in the paper industry (*2*).

Since dioxins are resistant to thermal, chemical, and biological degradation, they accumulate in natural environ-

ment (*2*). There has been growing interest in developing efficient and economically feasible methods that destroy these recalcitrant compounds, which include incineration and thermal treatment (*3, 4*), catalytic destruction (*5, 6*), photolysis (*7–15*), photocatalysis (*16–18*), ozonolysis (*19*), radiolysis (*20*), and biodegradation (*21, 22*). Among them, photocatalytic process is highly promising because it operates at ambient temperature and pressure with low energy photons ($\lambda < 388$ nm for anatase TiO₂), requires no chemical reagents except O₂ in the ambient air and no expensive catalysts, and utilizes natural sunlight. Therefore, the photocatalytic method can be developed into a safe and economically viable remediating system. Photocatalytic processes use light to generate conduction band (CB) electrons and valence band (VB) holes (e⁻ and h⁺) that are capable of initiating redox chemical reactions on semiconductors (*23*). TiO₂ has been predominantly used as a semiconductor photocatalyst. The VB holes of TiO₂ are powerful oxidants that initiate the degradation reactions of a wide variety of organic compounds (*24*).

The present paper reports the study of photocatalytic degradation of PCDDs on TiO₂ film under UV or solar irradiation. A few investigations on photocatalytic degradation of dioxins on TiO₂ have been performed in aqueous suspensions (*16, 18*) and soils (*17*). Complete disappearance of 2-chlorodibenzo-*p*-dioxin and 2,7-dichlorodibenzo-*p*-dioxin was observed after 2 and 90 h, respectively, in UV-illuminated aqueous TiO₂ suspension with no significant intermediates detected (*18*). However, the photocatalytic degradation of highly chlorinated dioxin congeners has not been reported, and their photocatalytic degradation mechanism is not understood. Investigations into the photocatalytic efficiency of PCDD degradation as a function of various experimental parameters and their mechanistic pathways are discussed.

Experimental Section

Chemicals. Octachlorodibenzo-*p*-dioxin (OCDD), 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TCDD), and 2-monochlorodibenzo-*p*-dioxin (MCDD) were supplied by Ultra Scientific as pure powder and used without any further purification. Toluene and other solvents (J. T. Baker) were of ultra analysis grade and used as received. The TiO₂ powder was Degussa P-25 (anatase:rutile 8:2, surface area 50 ± 15 m²/g). All glasswares were washed with the detergent solution followed by distilled water, methanol, acetone, methylene chloride, and toluene, in this order.

Sample Preparation and Photolysis. PCDD samples were loaded on TiO₂ film, which was coated on a glass plate, and subsequently exposed to UV light in the ambient air. The substrate glass plate (18 mm × 18 mm) was rinsed with a detergent solution, 1% HCl, and distilled water and dried at 100 °C. Coating the glass plate was performed by dipping it into a 5 wt % TiO₂ suspension, drying it at room temperature, then heating it at 400 °C for 30 min. The coating procedure was repeated five times. A typical coating mass of TiO₂ obtained by this method was ~600 μg/cm². The TiO₂ coating mass could be varied by dipping into a less concentrated suspension (0.5–5 wt %). A stock solution of 100 ppm by weight of each dioxin (OCDD, HpCDD, TCDD, and MCDD) in toluene was prepared and stored at 3 °C in the dark. An aliquot of 200 μL of the stock solution was dropped on the TiO₂-coated glass plate, then the solvent was evaporated to get a dioxin concentration of ~6.2 μg/cm², which corresponded to dioxin/TiO₂ ratio of 10 000 ppm by weight. A

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set of duplicate or triplicate samples was prepared for each photolysis experiment.

The light was irradiated from a 200-W mercury lamp through a Pyrex filter cover ($\lambda > 300$ nm) to the samples (dioxin adsorbed on TiO$_2$ film). The distance between the sample and the lamp was 12 cm. The light flux onto the sample was measured using a power meter (Newport 1815-C with a 818-UV silicon diode detector). The light intensity of the naked irradiation, I_{tot}, Pyrex-filtered irradiation ($\lambda > 300$ nm), $I_{>300}$, and 400-nm cutoff ($\lambda > 400$ nm) filtered irradiation from the lamp, $I_{>400}$, was 20.6, 12.6, and 9.5 mW/cm^2, respectively. The active portion of the light intensity (I_{act}, 300 $< \lambda <$ 400 nm) that can excite TiO$_2$ was estimated from $I_{>300}-I_{>400}$. The average I_{act} was about 3.1 mW/cm^2. The light intensity could be varied by using neutral density filters (Oriel). All experiments were carried out at ambient temperature (about 20−40 °C) and pressure. Dark control samples were carried along with the photolysis samples through the entire experimental procedure in order to check any loss from thermal degradation or evaporation. No such effects were detected.

Samples for solar photolysis experiments were prepared by the same procedure. The samples were placed on a solar panel (25 cm × 25 cm), which was adjusted to face the sun every 30 min. Solar light was also filtered through a Pyrex cover in order to ensure the same condition with the UV lamp experiment. Solar photolysis experiments were carried out on the roof of the Environmental Engineering Building at POSTECH (Pohang, Korea: 36° N latitude) in the mid-September days between 11 AM and 3 PM under clear or partly cloudy sky conditions. I_{act} varied between 1.8 and 2.5 mW/cm^2 with an average of 2.1 mW/cm^2.

Analysis. (a) GC/ECD. After irradiation, the residual parent PCDDs and any stable intermediates on the TiO$_2$ film were extracted with a Soxhlet extractor in toluene for 12 h and concentrated to 800 μL. A blank run under the same conditions ensured that 95 ± 5% could be recovered through this procedure. Extracted PCDDs and intermediates were analyzed by using a Hewlett-Packard (HP6890A) gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) and a HP-5 column (30 m × 0.32 mm × 0.25 μm). Duplicate injections were made for each sample analysis. Nitrogen was used as a carrier gas. The injector and detector temperatures were 250 °C. The oven temperature was held at 100 °C for 1 min, then increased at a rate of 15 °C/min up to 280 °C, and held at 280 °C for 15 min. The retention times under these conditions were 9.8, 13.8, 18.2, and 21.9 min for MCDD, TCDD, HpCDD, and OCDD, respectively.

(b) FTIR. Since the above extraction/GC analysis can detect only toluene-extractable stable species, in-situ spectroscopic evidences of OCDD degradation on TiO$_2$ were sought by using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). DRIFT spectra were recorded using a Bomem DA3 FTIR spectrometer equipped with a triglycine sulfate detector (DTGS) and a diffuse reflectance accessory of Harrick (model DRA-2CE). TiO$_2$ powder coated with OCDD was prepared and packed into a sample cup for DRIFTS analysis. A mirror was used as a reference in obtaining the DRIFT spectra. The pressure in the sample compartment of the spectrometer was kept at 1.8 ± 0.4 Torr. Spectra of TiO$_2$ and OCDD-coated TiO$_2$ powder were obtained before exposing to UV light. The photolysis was carried out by irradiating the surface of the sample cup packed with OCDD-coated TiO$_2$ powder under the 200-W mercury lamp. The DRIFT spectra of OCDD-coated TiO$_2$ were taken every hour after the photoirradiation began. The spectra were recorded by averaging 256 scans for each measurement at 4 cm^{-1} resolution. The IR spectrum of pure OCDD was obtained by an external reflection method with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The
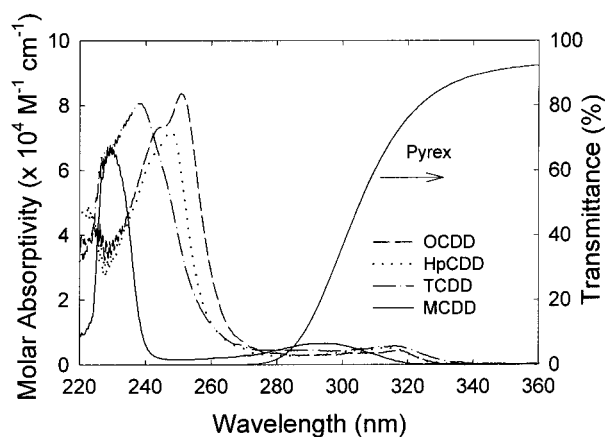

FIGURE 1. UV absorption spectra of OCDD, HpCDD, TCDD, and MCDD in methylene chloride solution. A light transmittance through a Pyrex filter that was used in the photodegradation experiment is compared along with the spectra.

pure OCDD was coated on a gold plate, and its spectrum was recorded with reference to a bare gold plate.

Results and Discussion

Absorption Spectra of PCDDs. Since light absorption is a prerequisite for photodegradation, UV−visible absorption spectra of PCDDs were obtained. The absorption spectra of MCDD, TCDD, HpCDD, and OCDD dissolved in methylene chloride are compared in Figure 1. All of them show a strong absorption band in the range of 230−260 nm, which arises from aromatic $\pi \rightarrow \pi^*$ transition. As the number of substituted chlorines increases, the absorption band shifts to longer wavelengths. The nonbonding electrons on Cl atoms interact with the π electrons of the aromatic ring, which apparently stabilizes the π^* state with a red shift (25). The weak absorption band extending over 280−340 nm is ascribed to n$\rightarrow \pi^*$ transition (26). Since the naked light from a mercury lamp can induce a direct photolysis of PCDDs through irradiation at $\lambda < 260$ nm, a Pyrex cover that transmitted $\lambda > 300$ nm was used in a typical photolysis experiment in order to inhibit direct photolytic degradation. The transmission spectrum of the Pyrex cover is compared along with the absorption spectra of PCDDs in Figure 1.

Photocatalytic Degradation of PCDDs. Figure 2a compares the direct photolytic and photocatalytic degradation of OCDD under a 200-W mercury lamp irradiation. Under naked UV lamp irradiation (without Pyrex filter), a significant photolytic degradation was observed. The strong absorption band of OCDD around 250 nm, which is coincident with a major mercury lamp emission at 254 nm, is responsible for the direct photolysis. However, the light with $\lambda > 300$ nm (with Pyrex filter) did not induce any noticeable direct photolytic degradation up to 15 h irradiation, although a small fraction of light in this wavelength range was absorbed by OCDD (see Figure 1). On the other hand, the photocatalytic degradation on TiO$_2$ with $\lambda > 300$ nm was greatly enhanced and resulted in 85% conversion within 15 h irradiation. Neither stable intermediates nor less chlorinated dioxin congeners from OCDD degradation were detected under the present analytical conditions where authentic less chlorinated dioxin was easily detected. Since PCDDs and their degradation products reside on TiO$_2$ surface in the air throughout the photoirradiation, stable degradation intermediates, if any, seemed to be volatilized into the air or not to be extracted by toluene from the TiO$_2$ surface. No further rigorous analysis for intermediates was attempted. Although the direct photolytic degradation of PCDDs in organic solvents has been reported to form less chlorinated dioxin byproducts through
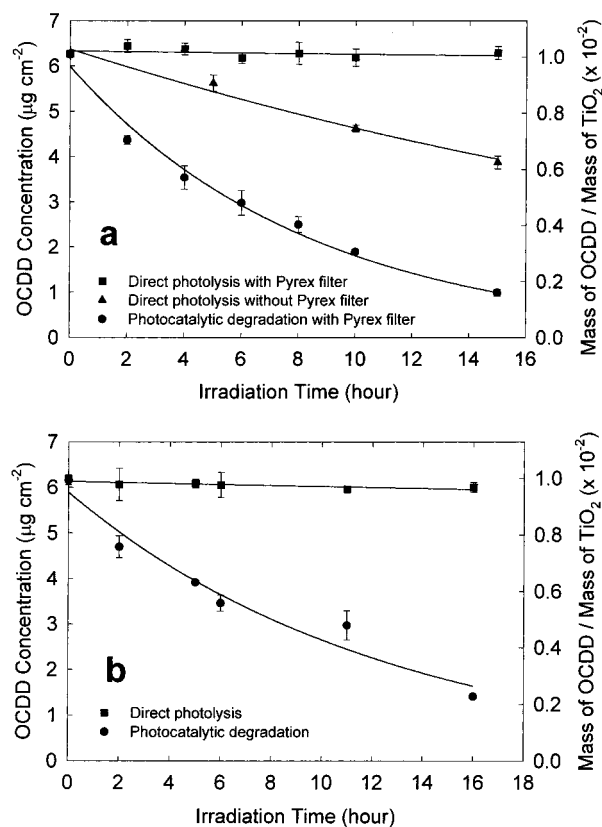
FIGURE 2. Direct photolytic and photocatalytic degradation of OCDD as a function of irradiation time (a) under a 200-W mercury lamp and (b) under natural solar light irradiation. The UV light from the lamp was directly irradiated or filtered through a Pyrex cover. The experimental conditions were as follows: I_{act}(300 $< \lambda <$ 400 nm) of 4.0 and 2.1 mW/cm^2 for Pyrex-filtered UV light and solar light, respectively; [OCDD]$_0$ = 6.3 μg/cm^2; TiO$_2$ coating mass of 610 $\pm$ 10 μg/cm^2. The solid lines are first-order fit.
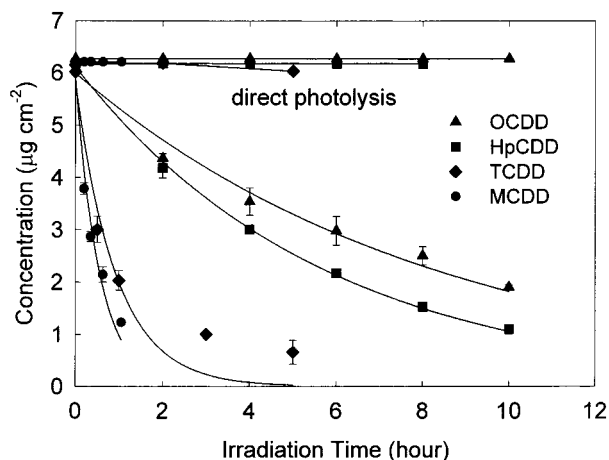

FIGURE 3. Comparison of the photocatalytic degradation of four dioxin congeners as a function of irradiation time under a 200-W mercury lamp irradiation ($\lambda >$ 300 nm). Direct photolysis was negligible for all congeners. The experimental condition was the same to that of Figure 2 except for I_{act} = 3.1 mW/cm^2. The solid lines are first-order fit.
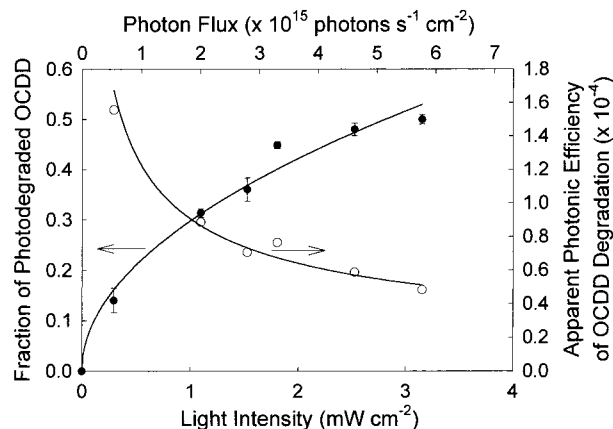

FIGURE 4. Light intensity effect on the photocatalytic degradation of OCDD on TiO$_2$. The fraction of photodegraded OCDD was measured after 5 h irradiation. The experimental condition was the same to that of Figure 2, and the light intensity from a 200-W mercury lamp was varied by using neutral density filters. The solid lines are fitted to $I^{1/2}$ function for the photodegraded OCDD and $I^{-1/2}$ for the photonic efficiency.

C−Cl bond cleavage (7−15), the absence of them in this photocatalytic degradation implies different mechanistic pathways, which are discussed in a later section.

The feasibility of using natural solar light in degrading PCDDs was tested by performing the photolysis of OCDD on TiO$_2$ under sunlight illumination. All the experimental conditions were the same as those of laboratory experiments except for the source of light. The direct photolytic and photocatalytic degradation of OCDD under sunlight are compared in Figure 2b. The irradiation time is the cumulative hours of solar exposure during 4-day experiment (4 h of exposure per day). The solar experiment showed little difference from the UV lamp experiment. Although I_{act} was about half of the UV lamp intensity, the overall photodegradation efficiency was similar.

Similar photolytic and photocatalytic behaviors were observed for HpCDD, TCDD, and MCDD: no direct photolytic degradation and a greatly enhanced photocatalytic degradation on TiO$_2$ under $\lambda >$ 300 nm irradiation for all of them. Their photocatalytic degradation rates are compared in Figure 3, which shows the first-order photodegradation kinetics with the rate constants (k_{ph}) of 1.81, 0.98, 0.18, and 0.12 h^{-1} for MCDD, TCDD, HpCDD, and OCDD, respectively.

Effect of Light Intensity. The effect of light intensity on OCDD photocatalytic degradation was investigated by adjusting the UV intensity in the range of 0.3−3.15 mW/cm^2 with a combination of neutral density filters. The fraction of photodegraded OCDD on TiO$_2$, which was measured after 5 h irradiation, is plotted along with its apparent photonic efficiency (Ψ) as a function of I_{act} in Figure 4. The photonic

efficiencies of OCDD degradation were calculated based on an assumption that all incident photons have the energy of $\lambda =$ 365 nm and that 80% of them are absorbed by TiO$_2$ since the diffuse reflectance UV spectrum of TiO$_2$ showed 20% reflectance at this wavelength. The initial photonic efficiencies of the photocatalytic degradation of PCDDs (from Figure 3), which were calculated in the same way, were 1.93 $\times$ 10^{-3}, 7.09 $\times$ 10^{-4}, 9.83 $\times$ 10^{-5}, and 6.06 $\times$ 10^{-5} for MCDD, TCDD, HpCDD, and OCDD, respectively. The values of Ψ decrease with increasing I_{act}. The solid lines are fitted to $I^{1/2}$ function for the photodegraded OCDD and to $I^{-1/2}$ for the photonic efficiency. Such nonlinear behavior is frequently observed in typical photocatalytic reactions where higher light intensity induces even faster recombination of charge pairs rather than the interfacial charge transfer (27). The UV intensities (2∼3 mW/cm^2) in the natural solar light are in the saturation region where further increase in light intensity has little effect in enhancing the photodegradation rates of PCDDs.

Effect of TiO$_2$ Coating Weight. Figure 5 shows the effect of TiO$_2$ coating mass on the photocatalytic degradation of OCDD. The photocatalytic conversion was measured after 5 h irradiation. The film thickness at 600 μg/cm^2 corresponded
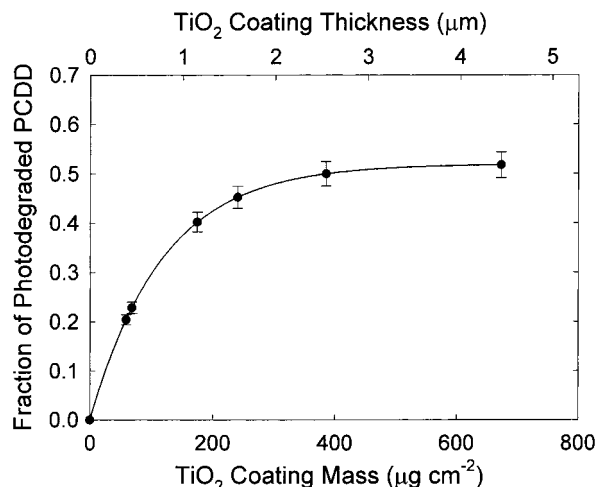
FIGURE 5. Photocatalytic degradation of OCDD as a function of the TiO_2 coating mass with $I_{act} = 3.1$ mW/cm² and $[OCDD]_0 = 6.2 \mu g/cm²$. The fraction of photodegraded OCDD was measured after 5 h irradiation. The solid line is a fit to eq 2.

FIGURE 6. Reflectance and diffuse reflectance FTIR spectra of OCDD on a gold plate, pure TiO_2 powder, and OCDD adsorbed on TiO_2 powder are compared. In situ DRIFT spectra of photodegrading OCDD on TiO_2 powder that were recorded at a time of 1, 2, 3, and 5 h photoirradiation ($\lambda > 300$ nm) are shown as well.

to 4.0 μm, which was determined from scanning electron micrographic (SEM) analysis. The degradation efficiencies rapidly increased with TiO_2 mass up to 200 $\mu g/cm²$, above which point they started to level off. Similar TiO_2 mass dependence was commonly observed in photocatalytic studies employing aqueous suspension phases (28). The steeply rising part is ascribed to increasing surface area. Further increase in surface area (or coating thickness) is not efficient in enhancing the photoreactivity largely because the light penetration is exponentially extinguished along the depth:

$$I_p = I_i \exp(-\alpha l) \qquad (1)$$

where I_i is the incident light intensity, I_p is the penetrated light intensity at a depth of l, and α is the absorption coefficient of TiO_2 coating. Since the photocatalytic degradation rates are proportional to the absorbed light intensity (I_a):

$$I_a = I_i - I_p = I_i[1 - \exp(-\alpha l)] \qquad (2)$$

the saturating efficiency with increasing the coating thickness can be explained. Data in Figure 5 were fitted to eq 2 to give the α value of 1.29×10^4 cm⁻¹, which corresponded to a light penetration depth of 0.78 μm. Considering a reported α value of 10^5 cm⁻¹ at 348 nm for polycrystalline TiO_2 (29), the present TiO_2 coating film that was estimated to have a porosity factor of 0.6 allowed a much larger penetration depth (0.78 vs 0.1 μm).

In-Situ Monitoring of OCDD Photodegradation on TiO_2 Using DRIFTS. The in-situ DRIFT spectra of degrading OCDD on TiO_2 were taken intermittently during the photoirradiation and were shown along with the pre-irradiation spectra in Figure 6. The reflectance IR spectrum of pure OCDD on a gold plate showed four major peaks at 1554.3, 1446.3, 1007.6, and 847.6 cm⁻¹. The first two were ascribed to the aromatic ring vibration modes, and the other two (not shown in the spectra) were ascribed to C−O−C symmetric stretching modes (30). The IR peaks of OCDD adsorbed on TiO_2 were noticeably shifted from those on gold surface. While the peak at 1554 cm⁻¹ remained the same, one at 1446 cm⁻¹ was significantly shifted to a lower wavenumber and split into a doublet. The π electrons in the aromatic ring of dioxin and nonbonding electrons on oxygen interact with Lewis acid sites on TiO_2 surface to form a weakly bound complex (31). The interaction could lead to a conformational change in
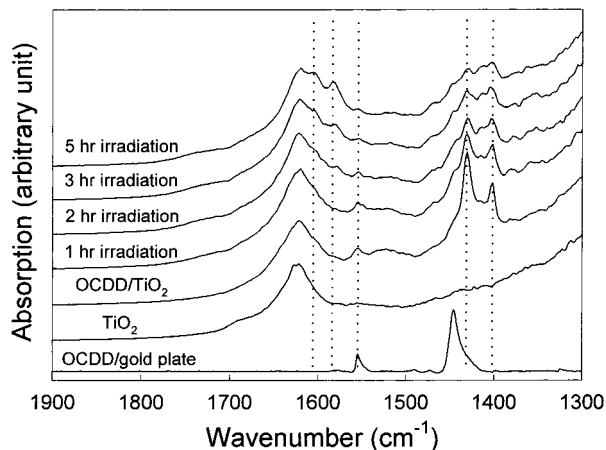
the OCDD structure, which results in the change of vibrational frequencies and intensities. Similar IR frequency shift has been reported from 4-chlorocatechol adsorbed on TiO_2 (32). The IR bands of C−O−C stretching vibration could not be detected due to the strong absorption background from TiO_2 below 1200 cm⁻¹. In-situ DRIFT spectra of OCDD on TiO_2 showed that the intensities of the aromatic peaks at 1557, 1431, and 1402 cm⁻¹ decreased with the irradiation time, which meant that the aromatic ring of OCDD was destroyed. The diminishing peaks were accompanied by the appearance of unidentified double peaks at 1583 and 1607 cm⁻¹.

Mechanistic Pathways of Photocatalytic Degradation of PCDDs. The degradation pathways of organic compounds on illuminated TiO_2 surface in general involve a series of electron or hole transfer reactions (24). Although the degradation of most organic compounds on TiO_2 is initiated by an oxidative path (hole transfer or ·OH radical attack), a reductive dechlorination through CB electron transfer is the only feasible initial pathway for destroying perhalogenated hydrocarbons such as CCl_4 and CFCs (33).

Among 75 congeners of dioxin, OCDD, which is a common impurity of the widely used biocide pentachlorophenol, is the most recalcitrant for degradation and the most thermodynamically stable (34). Accordingly, dioxin homologues found in the environment showed a strong predominance of OCDD since atmospheric oxidation processes preferentially remove the lower chlorinated dioxins (35). The degradation of OCDD on TiO_2 could be initiated by two paths: OH radical attack vs CB electron transfer

$$C_6Cl_4O_2C_6Cl_4 + \text{·OH} \rightarrow [C_6Cl_4O_2C_6Cl_4OH]\text{·} \qquad (3)$$

$$C_6Cl_4O_2C_6Cl_4 + e^-_{cb} \rightarrow [C_6Cl_4O_2C_6Cl_3]\text{·} + Cl^- \qquad (4)$$

Although the reaction with OH radical is known to be a major sink of dioxin in the atmosphere (35), the reductive path could be possible in the photocatalytic system. A cyclic voltammetry was performed in toluene solution to show a reduction peak of OCDD at −1.42 V (vs SCE). This value is comparable to a reported polarographic halfwave potential (−1.44 V vs SCE) of hexachlorobenzene (similar to OCDD in that all carbons are chlorinated) measured in 75% p-dioxane− 25% water (36). Compared with the TiO_2 CB edge potential (−0.74 V vs SCE at pH7), the reduction of OCDD by a CB electron is not thermodynamically feasible. Furthermore, less chlorinated dioxin congeners that commonly resulted from the reductive C−Cl bond cleavage were not found as

SCHEME 1. Pathways of OH Radical Addition on HpCDD and OCDD To Form a Hydroxycyclohexadienyl Radical
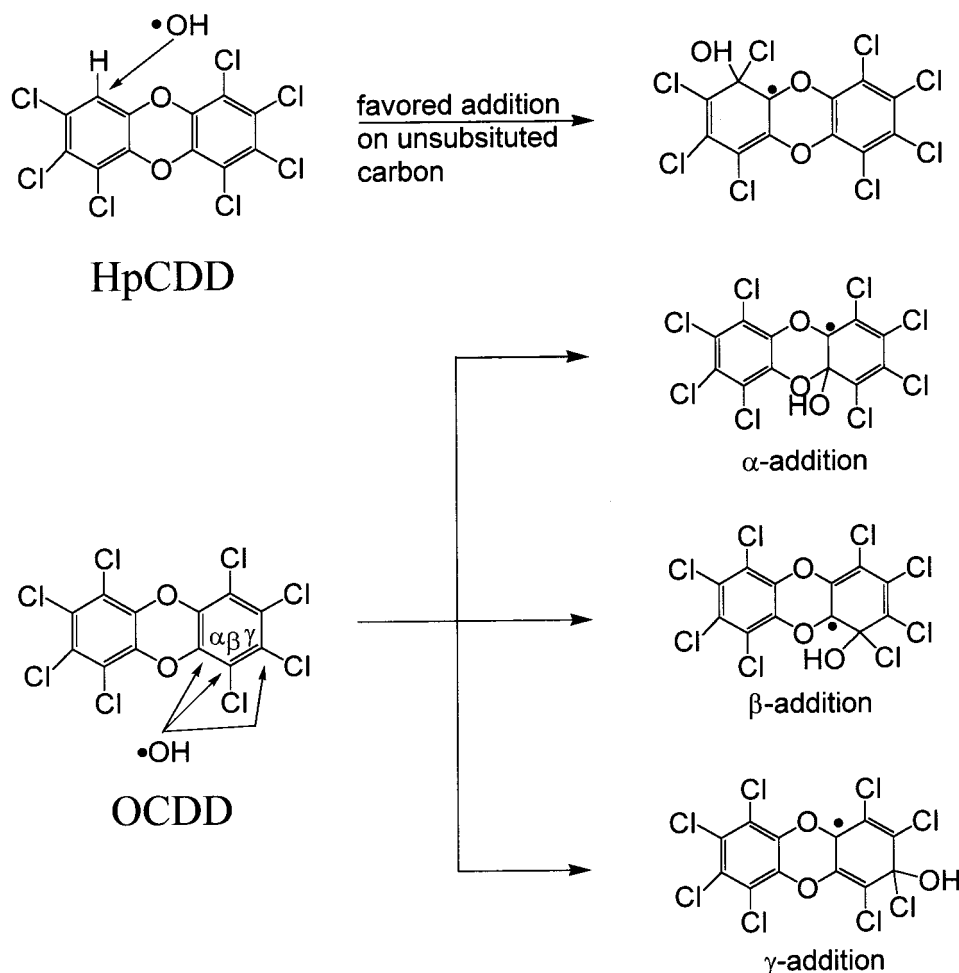
byproducts in this study. Therefore, the photocatalytic degradation of all dioxin congeners should be initiated by an OH radical attack on the aromatic ring structure.

The addition of OH radical to the aromatic ring of dioxin seems to take place preferentially at an unsubstituted carbon since the photocatalytic degradation rates of dioxins were in the order of MCDD > TCDD > HpCDD > OCDD. As the number of electron-withdrawing chlorines on PCDDs increases, the electron density on the aromatic ring decreases, and then the reaction rate of electrophilic OH addition decreases. The presence of bulky chlorine substituents on the aromatic ring may sterically hinder the approach of the OH radical to some extent. Atkinson (37) estimated that the rate constant of OH addition on PCDDs in the gas phase logarithmically decreased with increasing the number of chlorines. Although a similar trend was observed in this work, further study is needed to confirm the quantitative logarithmic dependence in photocatalytic oxidation. A reductive mechanism (reaction 4) would have shown the opposite trend in the degradation rate since the more highly chlorinated dioxin congeners are more susceptible to dechlorination reactions (38). Scheme 1 compares initial photocatalytic oxidation pathways of OCDD and HpCDD on TiO2. The photocatalytic oxidation begins with the addition of OH radicals, which leads to the formation of a hydroxycyclohexadienyl radical. The preferred position of OH radical attack on dioxin seems to be dependent on the number and the position of chlorines. When there are unsubstituted carbons as in HpCDD, the OH radicals preferentially add on them. However, with all carbons substituted in OCDD, the OH radical has no other choice but to add on one of three

substituted positions (α, β, and γ) of the aromatic ring. The hydroxycyclohexadienyl radical immediately reacts with O_2 in the air, and then the cleavage of the aromatic ring follows, which was suggested from the DRIFT analysis of OCDD degradation. Further mechanistic investigation on photocatalytic degradation of dioxin homologues is under progress.

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