## PREDICTION FOR PHOTODEGRADATION PATHWAYS OF PCDDS USING THE SEMI-EMPIRICAL MOLECULAR ORBITAL METHOD

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### Introduction
Photolytic transformation of toxic polychlorodibenzo-p-dioxins (PCDDs) to lower toxic ones or other compounds is one of the degradation methods for PCDDs. There are many studies on the photodegradation of PCDDs[1-10]. However, the majority of these studies are concerned Chlorine(Cl)–Hydrogen(H) photochemical substitution of some tetrachlorodibenzo-p-dioxins (TCDDs) and octachlorodibenzo-p-dioxin (OCDD). PCDDs consist of 75 compounds, but photoreactions for all of PCDDs have not been examined. We predicted the Cl–H photochemical substitution reactivity of PCDDs using the semi-empirical molecular orbital method. As for OCDD, after irradiation of ultraviolet (UV) -ray to OCDD in solution, the formed PCDDs were experimentally confirmed and compared with the results of calculation.

### Methods and Materials
*Enthalpy change of reaction*
Geometry optimizations of PCDDs were carried out using the semi-empirical molecular orbital method with PM3 hamiltonian[11,12]. The formation enthalpies ($\Delta H_f$) of chlorine radical ($Cl\cdot$), hydrogen radical ($H\cdot$) and PCDDs were also calculated using the same method. The enthalpy change ($\Delta H_r$) of Cl–H photochemical substitution of a PCDD was obtained as difference of formation enthalpies as shown in Eq. (1).

$$PCDD_{(Cl=n)} + H\cdot \rightarrow PCDD_{(Cl=n-1)} + Cl\cdot \qquad (1)$$
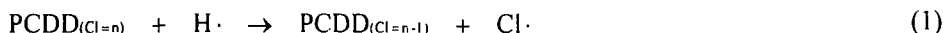
$$\Delta H_r = -H_f(PCDD_{(Cl=n)}) - H_f(H\cdot) + H_f(PCDD_{(Cl=n-1)}) + H_f(Cl\cdot)$$

*Electron spectrum*
Geometry optimizations of PCDDs were carried out using the semi-empirical molecular orbital method with PM3 hamiltonian[11,12]. Wavelength and oscillator strength with absorption bands of electron spectra of PCDDs were calculated using the semi-empirical molecular orbital method with INDO/S hamiltonian[11,13].

*Reaction of OCDD with UV-ray*
Ten $cm^3$ hexane solution of ten ng OCDD in a quartz beaker (diameter: 50 mm) was irradiated by UV-ray (mercury lamp, main wavelength: 254 nm, UV-ray strength: 5.56 mW/cm$^2$) for one minute. Resulting solution, added with internal standard compounds, was concentrated. The concentrations of OCDD, heptachlorodibenzo-p-dioxins (HpCDDs), hexadibenzo-p-dioxins (HxCDDs), pentachlorodibenzo-p-dioxins (PeCDDs) and TCDDs in the resulting solution were determined with HRGC/HRMS.

## Results and Discussion

### *Cl–H photochemical substitution reactivity of PCDDs*

### *Cl–H photochemical substitution of 2,3,7-trichlorodibenzo-p-dioxin (2,3,7-TrCDD)*

Cl–H photochemical substitution of 2,3,7,8-TCDD yields only 2,3,7-TrCDD. Cl–H photochemical-substitution of 2,3,7-TrCDD yields 2,7-dichlorodibenzo-p-dioxin (2,7-DiCDD) as a main product, and yields 2,8-DiCDD as a byproduct[1,2,5]. 2,3-DiCDD was not formed. Enthalpy changes of these reactions ($\Delta H_r$) were obtained from the values of $\Delta H_f$ that were calculated by the semi-empirical molecular orbital method with PM3 hamiltonian. The values of $\Delta H_r$ for formations of 2,7-DiCDD, 2,8-DiCDD and 2,3-DiCDD are –74.9 kJ/mol, –74.8 kJ/mol and –70.3 kJ/mol, respectively. Thus, it is suggested that the reaction with a larger value of $-\Delta H_r$ is carried out more easily.

### *Photodegradation of TCDDs*

The photodegradation half-life times[1,2,4] of 2,3,7,8-TCDD, 1,3,6,8-TCDD and 1,2,3,4-TCDD under UV-ray at 252.6 nm and 313.0 nm are shown in Table 1. The values of oscillator strength of absorption band near 252.6 nm and 313.0 nm are also shown in Table 1. The values of oscillator strength were obtained by the semi-empirical molecular orbital method with PM3 hamiltonian. Half-life times at 252.6 nm were 2,3,7,8-TCDD > 1,3,6,8-TCDD > 1,2,3,4-TCDD, and those at 313.0 nm were 2,3,7,8-TCDD < 1,3,6,8-TCDD < 1,2,3,4-TCDD[1,2]. The values of calculated oscillator strength of absorption band near 252.6 nm were 2,3,7,8-TCDD < 1,3,6,8-TCDD < 1,2,3,4-TCDD, those of absorption band near 313.0 nm were 2,3,7,8-TCDD > 1,3,6,8-TCDD > 1,2,3,4-TCDD. Thus, it is suggested that the reactivity increased with increase in the value of oscillator strength of absorption band near the wavelength of the mercury lamp.

Table 1  Half-life times[1,2] of photodegradation and oscillator strength of TCDDs.

| TCDD | 252.6 nm | | 313.0 nm | |
|---|---|---|---|---|
| | half-life time/min | oscillator strength, $O_s$ | half-life time/min | oscillator strength, $O_s$ |
| 2,3,7,8-TCDD | 72.6 | 0.196 (235.4nm) | 38.1 | 0.0504 (296.0nm) |
| 1,3,6,8-TCDD | 68.1 | 0.258 (234.0nm) | 294.0 | 0.0232 (294.5nm) |
| 1,2,3,4-TCDD | 37.0 | 0.886 [a] | 963.3 | 0.0112 (306.6nm) |

a) Sum of the oscillator strengths 0.880 (at 234.6nm) and 0.006 (at 270.0nm).

### *Reactivity of PCDDs*

For photoreaction, frequency factor $A$ in the Arrhenius's equation $k = A\exp(-E_a / RT)$ increases with increase in the value of oscillator strength $O_s$ of the concerned absorption band ( $k$ is kinetic constant, $E_a$ is activation energy,). As $E_a$ is expressed approximately the Polanyi–Evans's equation $B + C \Delta H_r$, so decrease of enthalpy change $\Delta H_r$ in the reaction increases with decrease in the value of activation energy $E_a$ ($B$, $C$ are constants) on analogous reactions[14]. Therefore, the kinetic constant $k$ is expressed approximately by Eq. (2) ( $D$ is constant).

$$k = O_s \cdot D\exp\left(-\frac{B + C\Delta H_r}{RT}\right) \qquad (2)$$

The kinetic constant approximately increases with increase in both the values of oscillator strength $O_s$ and $\exp(-\Delta H_r)$. This relation is consistent with the above-mentioned results of Cl–H photochemical substitution of 2,3,7-TrCDD and photodegradations of TCDDs. Without regarding photodecompositions of the dibenzo-$p$-dioxin structure in PCDDs, it may be concluded that the value of $O_s \cdot \exp(-\Delta H_r)$ shows the reactivity of Cl–H photochemical substitution.

## Decomposition of OCDD with UV-ray

### PCDDs formation from OCDD with irradiation of UV-ray

When the hexane solution of OCDD was irradiated by UV-ray at wavelength of 254 nm for one minute, OCDD was not detected in the solution, showing OCDD was almost decomposed completely. After irradiation of UV-ray, the concentrations of HpCDDs in resulting solution was 1,2,3,4,6,7,9-HpCDD > 1,2,3,4,6,7,8-HpCDD. The concentrations of HxCDDs were (1,2,3,4,6,8-HxCDD, 1,2,4,6,7,9-HxCDD, 1,2,4,6,8,9-HxCDD) > (1,2,3,6,7,9-HxCDD, 1,2,3,6,8,9-HxCDD), 1,2,3,4,6,9-HxCDD >> 1,2,3,4,6,7-HxCDD >> 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD ≈ zero. The concentrations of PeCDDs were (1,2,4,6,9-PeCDD, 1,2,3,4,7-PeCDD) >> (1,2,4,6,8-PeCDD, 1,2,4,7,9-PeCDD) > 1,2,3,6,9-PeCDD > 1,2,4,6,7-PeCDD, 1,2,4,8,9-PeCDD > 1,2,4,7,8-PeCDD > 1,2,3,6,8-PeCDD, 1,2,3,7,9-PeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,6-PeCDD, 1,2,3,6,7-PeCDD, 1,2,3,8,9-PeCDD ≈ zero. The concentrations of TCDDs were (1,2,7,8-TCDD, 1,4,6,9-TCDD) >> (1,3,6,9-TCDD, 1,2,4,7-TCDD, 1,2,4,8-TCDD) >> 1,2,6,9-TCDD > 1,3,6,8-TCDD, 1,3,7,9-TCDD, 1,3,7,8-TCDD, 1,2,6,8-TCDD, 1,4,7,8-TCDD, 2,3,7,8-TCDD, 1,2,3,7-TCDD, 1,2,3,4-TCDD, 1,2,4,6-TCDD, 1,2,4,9-TCDD, 1,2,3,8-TCDD, 1,2,3,9-TCDD, 1,2,6,7-TCDD, 1,2,8,9-TCDD ≈ zero.

### Proposed pathways of Cl–H photochemical substitution of OCDD

The values of $O_s \cdot \exp(-\Delta H_r)$, which indicate reactivity, were calculated as Cl–H photochemical substitution of PCDDs by UV-ray irradiation at wavelength 254 nm (main wavelength of the mercury lamp). We inferred the pathways of Cl–H photochemical substitution of OCDD to dibenzo-$p$-dioxin as shown in Fig. 1. The solid line showed the main pathway for each compound. The line-width is proportional to the value of $O_s \cdot \exp(-\Delta H_r)$. As shown in Fig. 1, PCDDs produced through the largest pathway of $O_s \cdot \exp(-\Delta H_r)$ are generally detected in the solution after irradiation of UV-ray. However, PCDDs having the largest pathway of $O_s \cdot \exp(-\Delta H_r)$ are not detected in the solution after irradiation of UV-ray as a rule. These results support the pathways predicted from the value of $O_s \cdot \exp(-\Delta H_r)$.