

# The study on the dechlorination of OCDD with Pd/C catalyst in ethanol–water solution under mild conditions

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## Abstract

Dechlorination of octachlorodibenzo-*p*-dioxin (OCDD) was carried out in ethanol–water (*v/v* = 1:1) solution of NaOH in the presence of Pd/C catalysts with the use of H<sub>2</sub>. The substrate was dechlorinated with Pd/C under mild conditions (atmospheric pressure and <100 °C) to give a chlorine-free product, dibenzo-*p*-dioxin (DD), in high yields. After reaction of 3 h at 50 °C, 95.9% OCDD was degraded to low dechlorinated congeners and the yield of DD was 77.4%. We have also studied the dechlorination selectivity of chlorine atoms on the different substituted positions and postulated the dechlorination pathway of OCDD. For OCDD, the 2-position has higher reactivity than 1-position, but the difference is very small. From the distribution statistics of the intermediates during the reaction, we postulate that the steric effect plays an important role during the reaction and affect the dechlorination pathway of OCDD.

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## 1. Introduction

Dioxins (PCDDs, PCDFs, and co-PCBs) are chlorinated organic compounds with high toxicity. Because of the high toxicity and stability, the degradation of dioxins attracts great attention of the researchers all over the world. Many methods for the decomposition of PCDD/Fs and PCBs have been consequently developed. For example, the techniques of using V<sub>2</sub>O<sub>5</sub>-based catalysts for decomposition of PCDD/Fs (Ide et al., 1996), oxidative treatment using supercritical water (Sako et al., 1997) and dehalogenation by hydroxide using KOH in DMI with heating (De Pava and Battistel, 2005) seemed to present some success for detoxification. However, these methods, which involve high temperature and/or high pressure conditions, have some disadvantages in recovering the vaporized dioxins, in driving up operating costs, and in incurring the high risk of de novo synthesis of dioxins. On the other hand, a few

methods, such as photolytic degradation (Mcpeters and Overcash, 1993; Hilarides et al., 1994), bioremediation method (Nam et al., 2005), electrochemical reduction (Miyoshi et al., 2004) and mechanochemical treatment (Nomura et al., 2005) were proposed. However, these methods also present some unfavorable aspects concerning the use UV-light, low decomposition rates, throughput, or efficiency.

Noble-metal catalysis becomes an effective tool for the dechlorination of a variety of chlorinated organic compounds for its mild reaction conditions, high degradation reaction speed and promising conversion. In recent years, a number of noble-metal catalysts including Pd/C, Pt/C and Rh/C were used for the dechlorination of PCDD/Fs. In this field, Ukisu and co-workers have performed many significant studies including dechlorination of di-, tri- and tetrachlorinated congeners of PCDD/Fs in 2-propanol solution (Ukisu and Miyadera, 2002, 2003, 2004). This method used 2-propanol as a hydrogen source instead of molecular hydrogen. The dechlorination of PCDD/Fs in the fly ash form MSW incinerators has been studied in

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the 2-propanol solution with the use of noble metal catalysts, which was suggested can be used as a practical disposal method for dioxins (Ukisu and Miyadera, 2004). Recently, in several methods, metallic calcium was used as a mild reducing reagent to degrade dioxin and dioxin-like compounds in the alcoholic solution under atmospheric pressure and at room temperature. Mitoma et al. (2004, 2006) used calcium to promote catalytic degradation of PCDD/Fs and PCBs in alcoholic solution and achieved good results.

In the previous reports of dioxin detoxification, most investigators paid more attention on the efficiency of the reaction. Few of them attached importance to the pathway of the dechlorination of the PCDD/Fs, especially to the higher chlorinated congeners. Because of the complex reaction process and the multitudinous dechlorination products, it is difficult to study the dechlorination routes of higher chlorinated PCDD/Fs. For higher chlorinated PCDD/Fs, it has been noted that the toxicity may increase if partially dechlorinated products are produced during the reaction. For example, OCDD may convert into the most toxic compound, 2,3,7,8-TCDD, when the dechlorination reaction is incomplete. Therefore, it is necessary to study the dechlorination pathway of the higher chlorinated PCDD/Fs.

In this work, we investigated the dechlorination of OCDD, whose dechlorination products is the most complex among the congeners of PCDDs. In the ethanol–water solution, with the flow of  $H_2$ , OCDD was degraded on the surface of noble-metal catalyst. Pd/C catalyst can be kept stable under reaction conditions and can be used repeatedly for the reaction. Moreover, ethanol–water, which is one of the safest solvents for humans, acts not only as a solvent but also as an accelerator due to its ability to clean the surface of catalyst (Xia et al., 2003). This decomposition method is one of the most environmentally friendly detoxification methods. The conversion of substrate and the yield of chlorine-free product DD were promising. From the distribution statistics of PCDD congeners formed during the reaction, the potential dechlorination pathway was postulated. Compared with the results of theoretical study and the thermal dechlorination of PCDD/Fs in incinerator, the difference and similarities were discussed.

## 2. Experimental

### 2.1. Materials

The following  $^{13}C_{12}$ -labeled compounds spiking solution (EDF-8999-4) and injection internal standard solution ( $^{13}C_{12}$ -1,2,3,4-TCDD) for EPA 1613 were purchased from Cambridge Isotope Laboratory (Andover, MA, USA). OCDD, DD were obtained from Accustandard. All the organic solvents were pesticide residue grade. Silica gel and basic alumina used in experiment were from ICN Medical, Germany. Anhydrous sodium sulfate (Aldrich, reagent grade) was rinsed with hexane and then dried. All

the pesticide residue solvents were obtained from Tedia (USA). The carbon-supported Pd-based catalyst in powdered form containing 5 wt% of Pd was obtained from Dalian Institute of Chemical Physics CAS. Prior to use, Pd/C was heated under the flow of  $N_2$  and  $H_2$ , at 200 °C for 1 h. All the chemicals and gases were high-purity grade and used without further purification. The water used in the experiment was deionized water.

### 2.2. Procedure for OCDD dechlorination

OCDD and NaOH were dissolved in the ethanol–water solution ( $v/v = 1:1$ ), and the final concentrations were 1 ppm and 400 ppm, respectively. Twenty-milliliter solution and 20 mg Pd/C catalyst were added into a 100 ml three-necked flask to start the dechlorination reaction. The reaction mixture was stirred vigorously with a magnetic stirrer under the flow of  $H_2$  and was kept at a desired temperature (30–80 °C) using a water bath. In the course of the reaction, an aliquot of solution was taken out for product analysis.

### 2.3. Extraction and analysis

After internal standard solution was added, 0.2 ml reaction mixture was centrifuged, lyophilized. The recovered catalyst was underwent Soxhlet extraction thoroughly by 250 ml toluene for 24 h. The toluene extraction was passed through a multilayer silica gel column then an alumina column for the pretreatment of PCDDs analysis. The incomplete degradation products, PCDDs, were analyzed using an Autospec Ultima high resolution mass spectrometer (Micromass, UK) interfaced with a Hewlett–Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph equipped with an Rtx-2330 capillary GC column (made by Restec) (60 m  $\times$  0.25 mm  $\times$  0.1  $\mu$ m). Samples were injected in splitless mode at an injector temperature of 280 °C and at an initial column temperature of 90 °C. After 1.5 min, the temperature was programmed at 25 °C  $min^{-1}$  to 180 °C, then at 3 °C  $min^{-1}$  up to 260 °C and held for 25 min. All

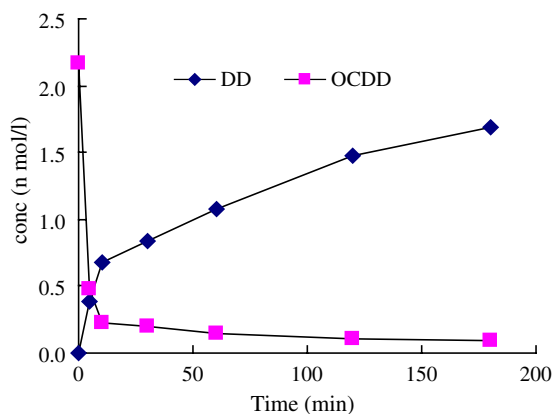


Fig. 1. Time profile for substrate and chlorine free product DD. Reaction conditions: substrate, 1 ppm; water-ethanol, 20 ml; Pd/C, 20 mg; 50 °C.

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