

# Complete dechlorination of DDT and its metabolites in an alcohol mixture using NaOH and Pd/C catalyst

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## Abstract

DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) was dechlorinated in 2-propanol/methanol (99:1 v/v) by means of stoichiometric reaction with NaOH and subsequent catalytic dechlorination over Pd/C catalyst. When DDT was treated with a molar excess of NaOH ( $[\text{NaOH}]/[\text{DDT}] = 9$ ) in the alcohol mixture at room temperature, DDT disappeared within 15 min. The reaction of DDT produced an equimolar amount of HCl to yield DDE (1,1-bis(4-chlorophenyl)-2,2-dichloroethylene). The produced DDE was successfully dechlorinated to a chlorine-free product (1,1-diphenylethane, 97% yield) by addition of Pd/C to the alkaline solution and heating at 40 °C for 4 h. DDD (1,1-bis(4-chlorophenyl)-2,2-dichloroethane) was also dechlorinated to 1,1-diphenylethane in a similar manner. Possible dechlorination pathways for DDT, DDE, and DDD were investigated by observation of the partially dechlorinated intermediates by means of gas chromatography/mass spectrometry (GC/MS). © 2007 Elsevier B.V. All rights reserved.

**Keywords:** DDT; DDE; DDD; Alkali; Catalytic dechlorination

## 1. Introduction

DDT has been used extensively worldwide as an insecticide for agricultural and residential purposes and in public health programs. Because of concerns about its toxicity and persistence, many developed countries restricted or banned the use of DDT in the 1970s, but in some tropical countries, DDT is still used for vector control. DDE and DDD are metabolites of DDT and are as stable and persistent in the environment as DDT. Although the use of DDT has declined, DDT and its metabolites are still found in environmental media [1] and in human tissues [2].

There are considerable stockpiles of DDT around the world; in Japan, for example, about 940 tonnes of unused DDT has been stored since 1972 [3]. DDT is one of 12 persistent organic pollutants (POPs) selected under the Stockholm Convention on POPs, and the disposal of stockpiles and wastes containing DDT was agreed internationally [4]. Therefore, the need for the development of efficient and economical techniques for the decomposition of DDT is urgent.

A number of methods for the chemical dechlorination of DDT under relatively mild conditions have been extensively studied, including photochemical, electrochemical, metal-catalyzed reactions and so on. In most cases, the main products are partially dechlorinated compounds. There are a few reports of complete dechlorination of DDT to chlorine-free hydrocarbons. Engelman et al. reported that DDT can be dechlorinated to 1,1-diphenylethane and minor products with Mg/Pd bimetallic particles in acetone/water at ambient temperature [5]. Schweizer et al. electrochemically reduced DDT to 1,1-diphenylethane (34% yield) in a microemulsion of surfactant, oil, and water [6]. Matsunaga et al. electrochemically transformed DDT into 1,1-diphenylethane (97% yield) with naphthalene radical anion as a mediator [7]. Zinovyev et al. dechlorinated DDT to 1,1-diphenylethane (100% yield) in a multiphase catalytic system composed of isooctane, aqueous KOH, a phase transfer agent (Aliquat 336), and a metal catalyst (Pd/C or Raney-Ni) under H<sub>2</sub> at atmospheric pressure at 50 °C [8]. Tabaei et al. dechlorinated DDT in 2-propanol containing NaBH<sub>4</sub>, 2-methoxyethanol, and NiCl<sub>2</sub>·6H<sub>2</sub>O at reflux (82–84 °C); diphenylmethoxymethane was obtained as the main product (80% yield) [9].

We previously reported that catalytic dechlorination of toxic chlorinated organic compounds such as polychlorinated biphenyls [10], chlorinated dioxins [11], and hexachlorocyclo-

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clohexanes [12] occurs efficiently in a solution of NaOH in 2-propanol in the presence of supported palladium catalysts such as Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub> under mild conditions (<82 °C) to yield chlorine-free products. This method does not use molecular hydrogen; instead, 2-propanol serves as the hydrogen source. We studied the reaction mechanism by using 2-propanol labeled with deuterium at several positions and found that the  $\alpha$ -hydrogen of 2-propanol is preferentially transferred to the organic chlorine compounds [13,14]. Dissolved NaOH is indispensable for the catalytic dechlorination because it scavenges released Cl<sup>-</sup> to form NaCl and also promotes the production of hydrogen from 2-propanol [15]. Recently, we found that dechlorination rates of aromatic chlorides with Pd/C are greatly increased by the addition of a small amount of methanol to the alkaline 2-propanol [16].

In this paper, we demonstrate that DDT, DDE, and DDD can be dechlorinated to a chlorine-free product (1,1-diphenylethane) in a liquid phase reaction at 40 °C. The process consists of treatment with NaOH and subsequent catalytic dechlorination with Pd/C catalyst. A mixture of 2-propanol and methanol was used as the solvent to enhance the catalytic activity of Pd/C. Furthermore, we identify dechlorination intermediates of DDT, DDE, and DDD and propose dechlorination pathways.

## 2. Experimental

### 2.1. Materials

The catalyst used in this study was palladium (5 wt%) supported on activated carbon in powdered form (Pd/C; N.E. Chemcat Corp., Japan, Lot No. 217-003331). The BET specific surface area and Pd dispersion (percentage exposed) were 1035 m<sup>2</sup>/g and 24%, respectively. The catalyst was pretreated under a flow of H<sub>2</sub> for 30 min at 200 °C and then under a flow of N<sub>2</sub> for 15 min at the same temperature. DDT (>98%; Tokyo Kasei Kogyo Co., Japan), DDE (99%; Aldrich, USA), and DDD (97%; Aldrich, USA) were used as the substrates. 1,1-Diphenylethane (>99%; ChemSampCo, USA) and DDMU (1,1-bis(4-chlorophenyl)-2-chloroethylene; AccuStandard Inc., USA) were used as analytical standards for the products. All other chemicals were high-purity grade and were used as obtained from the suppliers without further purification.

### 2.2. General procedure

DDT was dechlorinated in a glass test tube (i.d. = 13 mm, l = 120 mm) with a silicone rubber cap. DDT (18 mg) was added to a solution of NaOH (90 mmol/L) in 2-propanol/methanol (99:1 v/v, 5 mL). The mixture was stirred (ca. 900 rpm) with a stirring bar and a magnetic stirrer at room temperature for 15 min. Then a catalytic amount of Pd/C (10 mg) was added. The mixture was stirred and maintained at 40 °C by means of a water bath. Aliquots were removed several times and added to a toluene/water mixture (3:1 v/v, 2 mL). After the mixture was stirred for 15 min to extract the substrate and products adsorbed on Pd/C catalyst into the toluene phase and to transfer water-soluble compounds to the water phase, the toluene phase was

separated and diluted with isooctane containing *n*-dodecane as an internal standard for analysis by GC/MS. The concentrations of DDT and products were determined based on the responses of individual standards relative to the internal standard. DDD and DDE were dechlorinated in a similar manner.

DDT was titrated with NaOH as follows. DDT was dissolved in 2-propanol (10 mmol/L, 15 mL) in a flat-bottomed flask. Then a solution of NaOH in 2-propanol (100 mmol/L, 0.30 mL) was added. After the solution was magnetically stirred for 30 min at 40 °C, an aliquot was removed and diluted with isooctane for GC/MS analysis. Addition of NaOH and GC/MS analysis were repeated seven times.

### 2.3. GC/MS analysis

DDT, DDE, DDD, and dechlorinated organic products were analyzed using a Hewlett-Packard GC/MS instrument (GC: HP6890; MS: HP5973) equipped with an HP-5MS column (30 m × 0.25 mm, 0.25- $\mu$ m film thickness). The GC oven temperature was held at 40 °C for 1 min and then ramped at 10 °C/min to 270 °C. The injection port was utilized in splitless mode and maintained at 250 °C. The flow rate of carrier gas (He) was set at 1.2 mL/min. MS analyses were done in electron impact (EI) mode; the ion source temperature was set at 230 °C and the scan range was 50–550 amu. The unknown reaction products were identified by using a mass spectral database (Wiley 7th ed./NIST 05) and/or by referring to literature spectra [17,18].

## 3. Results and discussion

### 3.1. Dechlorination of DDT

The DDT dechlorination process was surveyed by monitoring the GC/MS total ion chromatogram (Fig. 1A–C). When DDT (10 mmol/L) was treated with NaOH (90 mmol/L) in 2-propanol/methanol (99:1 v/v) at room temperature for 15 min, the transparent solution became cloudy white; the peak for DDT disappeared completely, and a new intense peak was observed at shorter retention time (Fig. 1A and B). The mass spectrum of DDT showed major ions at  $m/z$  352, 282, 235, and 165. The new species and an authentic DDE standard gave identical retention times and mass spectra (major ions:  $m/z$  316, 246, 210, and 176). Quantitative analysis revealed that the mass balance between DDT and produced DDE was maintained within experimental error. Subsequent dechlorination of DDE was carried out by the addition of Pd/C to the alkaline solution. After reaction at 40 °C for 4 h, only one intense peak was observed (Fig. 1C). The retention time and mass spectrum (major ions:  $m/z$  182, 167, and 152) were identical to those of 1,1-diphenylethane (authentic standard), and the yield of 1,1-diphenylethane was estimated to be 97% from the quantitative analysis. Thus, DDT was dechlorinated to the chlorine-free product in a 2-propanol/methanol mixture by treatment with NaOH and catalytic reaction with Pd/C.

To study the reaction between DDT and NaOH in detail, we titrated a solution of DDT in 2-propanol with NaOH at

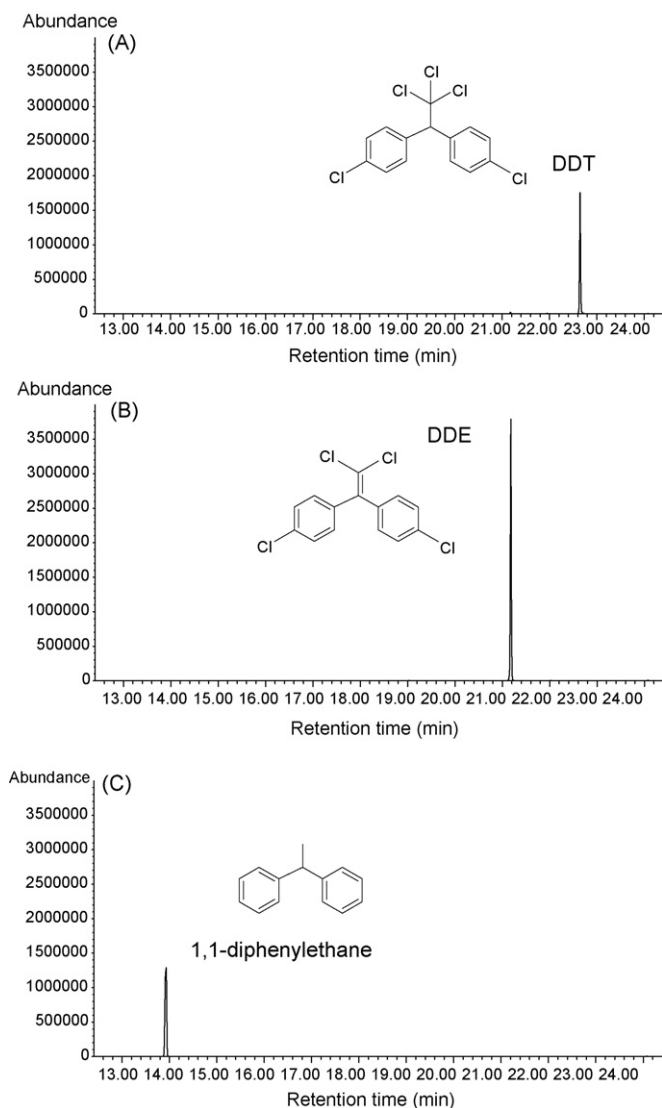


Fig. 1. GC/MS total ion chromatograms of (A) DDT, (B) product after reaction of DDT with NaOH at room temperature for 15 min, and (C) product after subsequent dechlorination with Pd/C at 40 °C for 4 h. Reaction conditions: DDT, 10 mmol/L; NaOH, 90 mmol/L; Pd/C, 10 mg; 2-propanol/methanol (99:1 v/v), 5 mL.

40 °C. Fig. 2 shows plots of the molar amounts of DDT consumed and DDE produced as functions of the molar amount of NaOH added. As more NaOH was added, the amount of DDT decreased. DDT disappeared almost completely when the molar ratio of added NaOH to initial DDT exceeded 1.0. The amount of DDE increased gradually as the amount of DDT decreased, and the yield of DDE reached almost 100% when DDT disappeared. These results indicate that DDT reacted with NaOH at a molar ratio of 1:1 and was quantitatively transformed into DDE. The released HCl was scavenged by the dissolved NaOH to give NaCl; because NaCl is insoluble in 2-propanol, the solution became cloudy white. The transformation rate was accelerated when an excess of NaOH was used. At a high initial molar ratio ( $[\text{NaOH}]/[\text{DDT}] = 9$ ), the reaction was complete within 15 min at room temperature, whereas at a lower initial molar ratio ( $[\text{NaOH}]/[\text{DDT}] = 2$ ), complete reaction took 30 min even

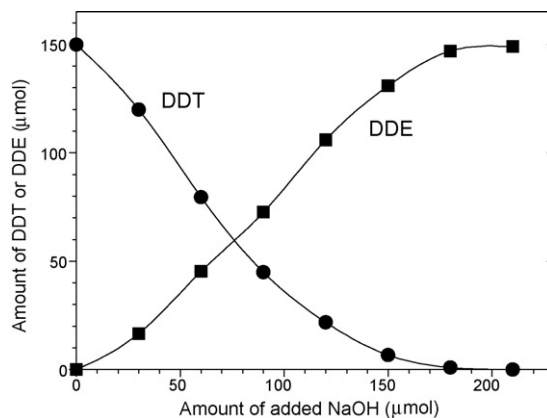


Fig. 2. Molar amounts of DDT and DDE during titration with NaOH.

at 40 °C. Addition of excess NaOH ( $[\text{NaOH}]/[\text{DDT}] > 5$ ) was necessary for complete dechlorination of DDT because subsequent catalytic dechlorination with Pd/C must be done in the presence of NaOH in excess than the amount of Cl contained in the substrate [13].

We previously reported that catalytic dechlorination of aromatic chlorides with Pd/C in a solution of NaOH in 2-propanol is enhanced greatly by the addition of a small amount of methanol (1%, v/v), probably because the Pd/C is activated by the added methanol [16]. Fig. 3A and B shows the time profiles for catalytic dechlorination of DDE (produced from

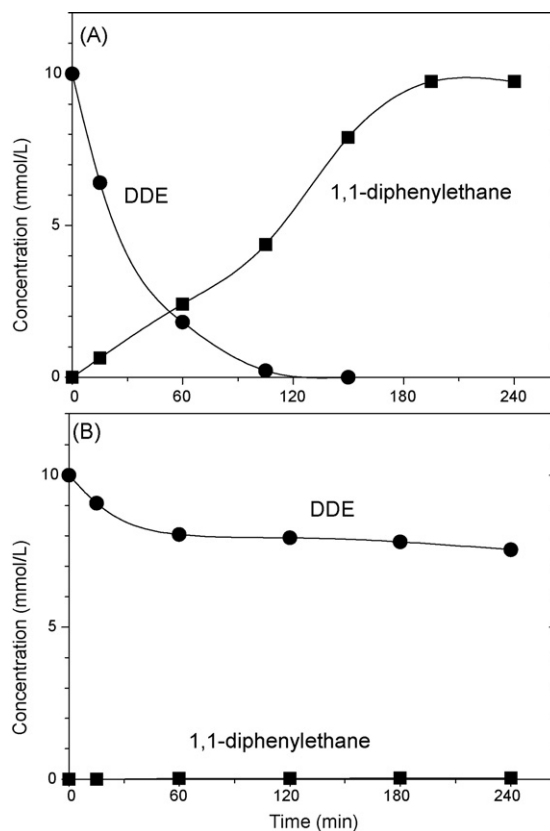
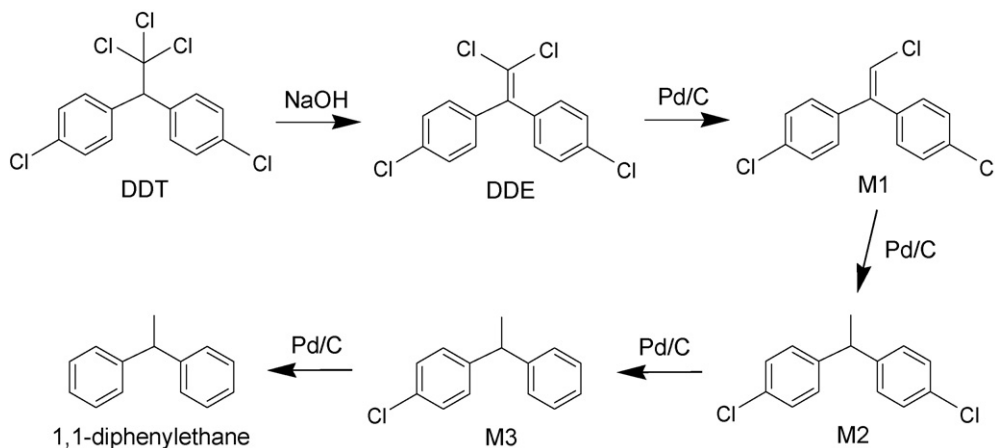


Fig. 3. Time profiles for catalytic dechlorination of DDE with Pd/C at 40 °C: (A) in 2-propanol/methanol (99:1 v/v); (B) in 2-propanol. DDE was produced by treating DDT with NaOH.



Scheme 1. Proposed dechlorination pathway of DDT.

DDT by NaOH treatment) over Pd/C in 2-propanol/methanol (99:1 v/v) and in 2-propanol alone, respectively. The dechlorination of DDE to 1,1-diphenylethane proceeded much faster in the 2-propanol/methanol mixture than in 2-propanol alone. Thus, the catalytic system including a small amount of methanol was effective for dechlorination of DDE.

In the GC/MS total ion chromatogram obtained during the catalytic reaction, three major peaks (denoted as M1, M2, and M3 in decreasing order of retention time) were observed between the peaks of DDE and 1,1-diphenylethane. The intensities of these peaks depended on the reaction time; each increased to a maximum and then decreased to zero, which implies that they were peaks for intermediate species in the dechlorination of DDE. The maximum intensities decreased in the order  $M3 > M1 > M2$ . M1 disappeared first, and then M2, followed by M3. The mass spectrum of M1 was almost the same as that of an authentic standard of DDMU (major ions:  $m/z$  282, 247, 212, and 176). The mass spectrum of M2 exhibited major ions at  $m/z$  250, 235, and 165; this compound was identified as a dichlorinated species, 1,1-bis(4-chlorophenyl)ethane, by using the mass spectral database. The mass spectrum of M3 was composed of the following major ions:  $m/z$  216, 201, and 166. This compound was identified as a monochlorinated species, 1-(4-chlorophenyl)-1-phenylethane, by referring to the literature [17].

Scheme 1 shows the proposed pathway for dechlorination of DDT by means of a stoichiometric reaction with NaOH and a catalytic reaction with Pd/C. The chlorine atoms bonded to aliphatic carbon are preferentially removed, followed by the chlorines bonded to aromatic carbons. In the catalytic reaction, the solvent serves as the hydrogen source in removal of chlorines and hydrogenation of a double bond between aliphatic carbons [13,16]. Zinovyev et al. proposed a similar reaction pathway for the dechlorination of DDT in a multiphase catalytic system with a metal catalyst (Pd/C or Raney-Ni) by analyzing the dechlorination intermediates [8].

### 3.2. Dechlorination of DDE

DDE was catalytically dechlorinated in a solution of NaOH in 2-propanol/methanol (99:1 v/v) with Pd/C at 40 °C. The reaction

proceeded to yield 1,1-diphenylethane, and the reaction rate was almost same as that observed for the catalytic dechlorination of DDE produced from DDT by treatment with NaOH. Mass spectral analysis of the reaction intermediates revealed that the dechlorination pathway was the same as that shown in Scheme 1 (from DDE to 1,1-diphenylethane).

### 3.3. Dechlorination of DDD

DDD was dechlorinated in the same manner as DDT. When DDD (10 mmol/L) was treated with NaOH (90 mmol/L) in 2-propanol/methanol (99:1 v/v) at room temperature for 15 min, the transparent solution became cloudy white, and a new species was detected in the GC/MS chromatogram. Unlike the mass spectrum of DDD (major ions:  $m/z$  318, 235, and 165), that of the new species exhibited major ions at  $m/z$  282, 247, 212, and 176. The new species was identified as DDMU by comparison with the authentic standard. Quantitative analysis revealed that DDD was converted entirely to DDMU, and the material balance was maintained. Then the produced DDMU was dechlorinated at 40 °C by addition of Pd/C to the alkaline solution. Fig. 4 shows the time profile for the catalytic dechlorination of the

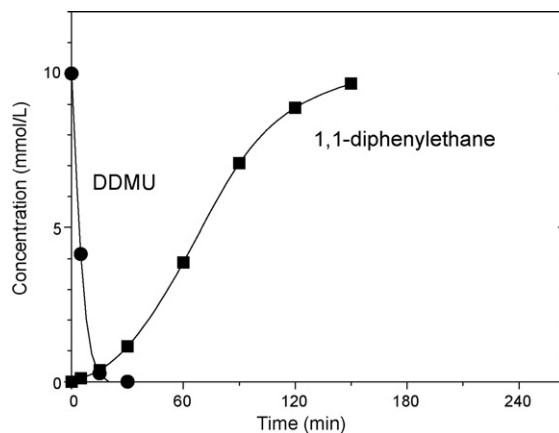
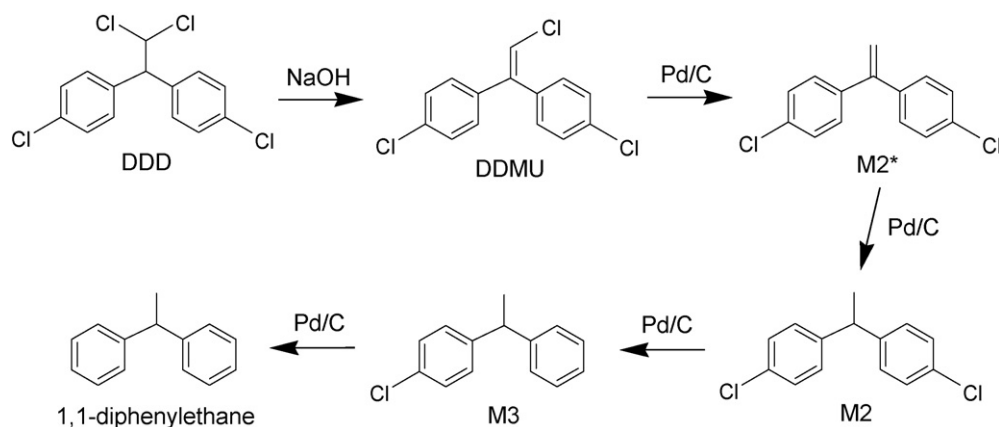


Fig. 4. Time profile for catalytic dechlorination of DDMU with Pd/C at 40 °C. DDMU was produced by treating DDD with NaOH. Reaction conditions were similar to those in Fig. 1.





Scheme 2. Proposed dechlorination pathway of DDD.

produced DDMU. The concentration of DDMU decreased rapidly, and the concentration of 1,1-diphenylethane increased gradually; after 2.5 h of reaction, the yield of dechlorinated product was 97%. The dechlorination rate of DDMU was faster than that of DDE (Fig. 3A) because DDMU has fewer Cl atoms than DDE. Thus, complete dechlorination of DDD was achieved to yield 1,1-diphenylethane by using an alkaline alcohol mixture and Pd/C catalyst.

Dechlorination intermediates M2 and M3 were observed in the GC/MS chromatogram during the catalytic dechlorination of DDMU. At the beginning of the reaction, an additional weak peak (denoted as M2\*) appeared at a slightly longer retention time than M2. As the intensity of the M2 peak increased, the intensity of the M2\* peak sharply decreased and the peak eventually disappeared, which implies that M2\* was a precursor of M2. The mass spectrum of M2\* exhibited major ions at  $m/z$  248, 212, and 178; this compound was identified as 1,1-bis(4-chlorophenyl)ethylene by using the mass spectral database and by referring to the literature [18]. Scheme 2 shows the proposed dechlorination pathway for DDD involving stoichiometric reaction with NaOH and catalytic reaction with Pd/C. The pathway from DDMU to 1,1-diphenylethane was observed in the dechlorination of both DDD and DDT, but M2\* was detected clearly only in the dechlorination of DDD because the concentration of DDMU (the source of M2\*) was as high as the initial concentration of the substrate (10 mmol/L). In the dechlorination of DDT, M2\* was hardly detected probably because the rate of M2\* hydrogenation was fast.

#### 4. Conclusions

We demonstrated that DDT, DDE, and DDD can be dechlorinated to a chlorine-free product (1,1-diphenylethane) at 40 °C in 2-propanol/methanol (99:1 v/v) in the presence of NaOH and Pd/C. DDT and DDD released an equimolar amount of HCl and were transformed to DDE and DDMU, respectively, by stoichiometric reaction with NaOH, and then these intermediate products were dechlorinated stepwise to 1,1-diphenylethane over Pd/C. In the catalytic dechlorination, methanol in the solvent greatly enhanced the catalytic activity. This method is simple and mild,

making it advantageous for practical disposal of DDT and related compounds.

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