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Facile and catalytic degradation method of DDT using Pd/C-Et₃N system under ambient pressure and temperature

Yasunari Monguchi, Akira Kume and Hironao Sajiki*

Laboratory of Medicinal Chemistry, Gifu Pharmaceutical University, 5-6-1 Mitahora-higashi, Gifu 502-8585, Japan

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Abstract—The catalytic degradation method of p, p'-DDT [1,1.1-trichloro-2,2-bis(p-chlorophenyl)ethane] and its regionsomer o, p'-DDT [1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane] using the Pd/C–Et₃N system under ambient hydrogen pressure and temperature was established. The presence of Et₃N was necessary for the quick and complete breakdown of DDT. The independent degradation study of two intermediates, p,p'-DDD [2,2-bis(p-chlorophenyl)-1,1-dichloroethane] and p,p'-DDE [2,2-bis(p-chlorophenyl)-1,1-dichloroethylene] using GC–MS let us to speculate the degradation pathway of $p_{,p'}$ -DDT. In the initial phase of the reaction, $p_{,p'}$ -DDT degradation splits into two ways: a dehydrochlorination pathway and a hydrodechlorination pathway. In each pathway, reaction starts from an aliphatic moiety and subsequent hydrodechlorination from the benzene moieties takes place in a stepwise manner. The former pathway leads to the formation of 1,1-diphenylethane and the latter leads to the formation of 1,1-dichloro-2,2-diphenylethane. These diphenylethane analogs, which are less toxic compared with $p_{p}p'$ -DDT, are terminal degradation products in our system. The distinctive features of our catalytic degradation method of DDTs are reliability, simplicity, efficiency, and inexpensiveness.

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1. Introduction

1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (p,p'-DDT)used to be employed worldwide as a broad-spectrum pesticide to protect crops from insects and to control insect-borne diseases such as malaria. But today the use of p,p'-DDT is banned in many countries because of its hydrophobic nature and of its persistence based on its chemical stability, leading to bioaccumulation and biomagnification in food chains. $^{1-3}$ p.p'-DDT affects the nervous system to cause tremors and convulsions.⁴ Both o,p'-DDT [1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane], a regioisomer of p,p'-DDT and p,p'-DDE [2,2-bis(p-chlorophenyl)-1,1-dichloroethylene], a metabolite of p, p'-DDT have been recognized as endocrine disruptors as a result of recent studies on DDT families.^{5,6} Despite such risks arising from p,p'-DDT and its related compounds, DDT (technical grade: a mixture of p,p'-DDT and its regionsomers) is still in use in some countries to combat disease-carrying insects because of the cost-efficiency of DDT. Furthermore, there is a fear of an accidental leak of a major fraction of DDTs, which was packed into drums and stored underground in 1970's especially in Japan due to the lack of suitable degradation methods of DDTs based on the high thermodynamic, chemical, and biological stability. As a global environmental issue, therefore, it is very important to monitor the pollution caused by the persistent insecticide^{7,8} and to develop

efficient degradation methods of DDT.9 Numerous studies for the development of DDT degradation methods reported to date include photoremediation, 10-16 bioremediation, 17-19mechanochemical remediation,²⁰ hydride reduction,²¹ hydrodechlorination,^{22–24} reductive dechlorination using metals,^{25,26} electrolysis,^{27–30} and supercritical water oxidation.³¹ Most processes require special and/or expensive equipment and facilities, large amounts of reagents, high heat, high pressure, radiation, and/or strong base conditions, and many of them do not complete degradation of DDT. Recently, Blum and co-workers reported a hydrodechlorination method using a combined Pd-Rh catalyst to achieve the complete removal of five chlorine atoms and saturation of aromatic rings of p,p'-DDT.²² Tundo and co-workers also succeeded in the complete dechlorination of p,p'-DDT by Pd/C or Raney-Ni-catalyzed hydrodechlorination method.24 These hydrodechlorinations were performed under relatively mild conditions, but still the former method requires heating (80-100 °C) and high pressure (27 atm) and the latter requires heating (50 °C) and continuous bubbling of hydrogen (10 mL/min).

We have reported that addition of a nitrogen-containing base such as NH₃, pyridine, and ammonium acetate to a Pd/Ccatalyzed hydrogenation system as a weak catalyst poison chemoselectively inhibited the hydrogenolysis of a benzyl ether with smooth hydrogenation of other reducible functionalities such as olefin, Cbz, benzyl ester, azide, and so on.^{32,33} During the course of our further study on the chemoselective hydrogenation using a Pd/C-Et₃N system, the catalytic activity of Pd/C towards the hydrodechlorination

^{*} Corresponding author. Tel.: +81 58 237 3931; fax: +81 58 237 5979; e-mail: sajiki@gifu-pu.ac.jp

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of aromatic chlorides was found to be remarkably and selectively enhanced by the addition of Et_3N^{34} and this system efficiently worked for the complete dechlorination of polychlorinated biphenyls (PCBs).³⁵ This method required only a catalytic amount of Pd/C and an almost stoichiometric amount of Et₃N (1.2 equiv vs chlorine atom) and did not require heating, high pressure of hydrogen, nor special equipment. In this paper, we discuss the application of this mild system to the degradation of *p*,*p*'-DDT and

o,p'-DDT and also propose the dechlorination pathways of p,p'-DDT in our system.

2. Results and discussion

2.1. Degradation of *p***,***p*[']**-DDT**

In accordance with our previous work for the hydrodechlorination of PCBs,³⁵ 10% Pd/C was used with 10% of the



Figure 1. Pd/C catalyzed degradation of p,p'-DDT (1) under ambient hydrogen pressure and temperature with Et₃N (1.2 equiv vs Cl).

substrate weight and 6 equiv of Et₃N (1.2 equiv to each chlorine atom of the substrate) was employed. The hydrodechlorination of p,p'-DDT 1 (CAS Registry Number 50-29-3) in MeOH using Pd/C-Et₃N system under ambient temperature and pressure is shown in Figure 1. p,p'-DDT 1 was completely consumed in the first 10 min and 1,1-bis(p-chlorophenyl)ethane 2 (CAS Registry Number 3547-04-4),³⁶ in which structure all aliphatic chlorine atoms of 1 were replaced with hydrogen atoms, and p,p'-DDD 3 (CAS Registry Number 72-54-8), in which structure an aliphatic chlorine atom of **1** was replaced with a hydrogen atom, were accordingly generated in the ratio of about 2:1. A trace amount of p, p'-DDE 4 (CAS Registry Number 72-55-9) was also detected during the initial phase (not shown in Fig. 1). After the formation of 2 and 3, the dechlorination of these compounds took place from their benzene rings step by step to generate mono-chlorophenyl compounds 5 (CAS Registry Number 60617-89-2)³⁷ and 6 (CAS Registry Number 6952-08-5)³⁸ and after 4 h the reaction was led to the formation of 1,1-diphenylethane 7 (CAS Registry Number 612-00-0)^{37,39} and 1,1-dichloro-2,2-diphenylethane 8 (CAS Registry Number 2387-16-8)⁴⁰ in the ratio of ca. 2:1. The reaction was monitored up to 24 h,

but further reduction was not observed and the material ratio of **7** and **8** was virtually the same.

On the other hand, the reaction of 1 in the absence of Et₃N did not completely consume 1 even after 72 h of the reaction (Fig. 2). The chlorine atoms on the benzene rings remained almost intact. Both the consumption of 1 and the formation of 2 and 3 were remarkably delayed, suggesting that the presence of Et₃N favorably affects the promotion of the dechlorination of alkyl chlorides as well as aromatic chlorides. Furthermore, methyl bis(*p*-chlorophenyl)acetate 9 (CAS Registry Number 5359-38-6),⁴¹ which is supposed to be formed via methanolysis of 1, 3, or 4, was generated as a by-product, whereas only a trace amount of the ester 9 was detected in the case of the reaction of 1 using Et₃N (not shown in Fig. 1). These results indicate that the presence of Et₃N in the catalytic degradation of *p*,*p'*-DDT 1 is crucial for increasing the efficiency of the reaction.

2.2. Degradation of $o_{,p'}$ -DDT

The application of the hydrodechlorination method using Pd/C and Et_3N was also investigated for the degradation



Figure 2. Pd/C catalyzed degradation of p,p'-DDT (1) under ambient hydrogen pressure and temperature without Et₃N.



Figure 3. Catalytic degradation of o,p'-DDT (10) using Pd/C-Et₃N system under ambient hydrogen pressure and temperature.

of o,p'-DDT 10 (CAS Registry Number 789-02-06) (Fig. 3). As we expected, 10 was degraded in a similar way to 1, although the reaction appeared somewhat more complicated than the reaction of p,p'-DDT 1 because of the asymmetrical structure of 10: (i) 10 completely disappeared within 30 min; (ii) the dechlorination started from aliphatic chlorides to generate 1-(o-chlorophenyl)-1-(p-chlorophenyl)ethane 11 (CAS Registry Number 77008-62-9)38,42 and 1-(o-chlorophenyl)-1-(p-chlorophenyl)-2,2-dichloroethane 12 (CAS Registry Number 53-19-0³⁸ as the first detectable intermediates; (iii) then mono-hydrodechlorination from the benzene rings proceeded to afford each regioisomeric mixture of monochlorides [5 and 13 (CAS Registry Number 76690-79-4)⁴³] and trichlorides [6 and 14 (CAS Registry Number 61693-87-6)³⁸]; (iv) finally the reaction resulted in the generation of 7 and 8, which are the same products from p,p'-DDT 1, with methyl diphenylacetate 15 (CAS Registry Number 3469-00-9),⁴⁴ which was structurally dechlorinated from 9.

2.3. Degradation of *p*,*p*'-DDD

As we mentioned above, in the early stage of the degradation of p,p'-DDT 1, a trace of p,p'-DDE 4 was detected with 2 and p,p'-DDD 3. We anticipated that both 3 and 4 were the first intermediates of the dechlorination of 1. To investigate the degradation pathway of p,p'-DDT by the hydrodechlorination using the Pd/C–Et₃N system, the reactions of p,p'-DDD 3 and p,p'-DDE 4 were independently monitored. As shown in Figure 4, 3 disappeared within 15 min and the chlorine atoms attached on the benzene rings were completely replaced with hydrogen atoms to generate 8 within 30 min. The reaction showed that the aliphatic chlorines of 3 were quite stable, but further dechlorination of 8 slowly proceeded to give 7 in about 30% yield after 24 h.

2.4. Degradation of *p*,*p*'-DDE

p,p'-DDE **4** was dechlorinated easily from both the aliphatic and aromatic portions (Fig. 5): **4** was completely consumed



Figure 4. Catalytic degradation of p,p'-DDD (3) using Pd/C-Et₃N system under ambient hydrogen pressure and temperature.

in 10 min; **2** and **5** were detected as intermediates; **7** was obtained as sole product after 30 min of the reaction; further reaction did not occur afterwards. If **4** had undergone the hydrogenation of its double bond before the dechlorination of its aliphatic chlorides, p,p'-DDD **3** would have been generated as an intermediate, leading to the formation of **8** as a final product as was expected from Figure 4. However, neither **3** nor **8** was detected at all, i.e., **4** was not a precursor of **3**. It is, therefore, reasonable to think that the aliphatic chlorine atoms of **4** underwent the hydrodechlorination first to afford 1,1-di-*p*-chlorophenylethylene **16** (CAS Registry Number 2642-81-1),³⁶ subsequent quick hydrogenation of the ethylene moiety gave **2**, and stepwise dechlorination from the benzene rings of **2** produced **7**.

2.5. Reductive degradation pathway of $p_s p'$ -DDT using Pd/C-Et₃N-H₂ system

Considering the degradation reactions of p,p'-DDD **3** and p,p'-DDE **4**, the degradation pathway of p,p'-DDT **1** was proposed in Figure 6. In the initial stage of the reaction, the aliphatic moiety of **1** was subjected, in two different manners, to a dehydrochlorination to afford p,p'-DDE **4** and to a hydrodechlorination to afford p,p'-DDD **3** in the

ratio of about 2:1, respectively. Two chlorine atoms attached with the alkene moiety of **4** were dechlorinated to generate **16** and subsequent hydrogenation of the alkene afforded **2**. Intermediates **2** and **3** underwent the successive dechlorination of their aromatic moieties to produce **7** and **8**, respectively. As we discussed above, **4** was not transformed to **3**. The dechlorination from the aliphatic moiety of **3** and **6** was so sluggish that no conversion from **3** to **2** nor from **6** to **5** was observed. After the complete dechlorination of the aromatic moieties of **3** and **6**, however, the resulting **8** could be transformed to **7** as shown in Figure 4, while the transformation of **8** to **7** were hardly observed in the reaction mixture starting from p,p'-DDT **1** (Fig. 1).

2.6. Dechlorination mechanism of trichloromethyl group of *p*₃*p*'-DDT using Pd/C–Et₃N–H₂ system

The hydrogenolysis of p,p'-DDT **1** over Pd/C without Et₃N (Fig. 2) gave **2** and **3** in the ratio of about 2:1, respectively, in which the ratio of **2** and **3** was almost same as the one in the reaction of **1** with Et₃N (Fig. 1). These results indicate that p,p'-DDE **4**, which is a precursor of **2**, was not formed via a simple base (Et₃N) promoted dehydrochlorination of **1**.^{45,46} The dechlorination of the trichloromethyl group of



Figure 5. Catalytic degradation of p,p'-DDE (4) using Pd/C–Et₃N system under ambient hydrogen pressure and temperature.

1 in our system would involve a single electron transfer (SET) process (Fig. 7), as we previously proposed in the hydrodechlorination of aromatic chlorides using Pd/C– Et_3N system, where Et_3N worked as an electron donor as well as an HCl scavenger.

According to the reported molecular orbital (CNDO/2) study, 98% of the electron density in the LUMO of p,p'-DDT is localized in aliphatic carbon–chlorine σ antibonding orbital.⁴⁷ Initial single electron transfer from Pd(0) to this orbital of **1** affords a chloride anion and an alkyl radical **A** since the reductive cleavage of aliphatic halides does not afford anion radicals as discrete intermediates.⁴⁸ In the hydrodechlorination pathway, **A** abstracts hydrogen to form p,p'-DDD **3**, whereas in the dehydrodechlorination pathway, **A** undergoes an abstraction of the hydrogen at the benzylic position by the chloride radical to form p,p'-DDE **4**, which undergoes successive hydrodechlorinations and subsequent hydrogenation of the double bond to afford **2**.

In a polarographic study reported by Rosenthal et al., the half-wave potential $(E_{1/2})$ on the first reduction wave of **1** (for the reaction from **1** to **3**) and the potential $E_{1/2}$ on the first reduction wave of **3** [for the reaction from **3** to 2,2-bis(*p*-chlorophenyl)-1-chloroethane] were -0.93 V and -2.31 V (vs a saturated calomel electrode), respectively.⁴⁹ This study suggests that **3** cannot readily accept an electron compared with **1** and it is rationale to think that in our system the SET initiated dechlorination of aliphatic moiety of **3** did not take place until the dechlorinations of aromatic moiety completed.

3. Conclusion

In summary, the hydrodechlorination method using the $Pd/C-Et_3N$ system accomplished the complete degradation of DDTs with the use of a catalytic amount of Pd/C under ambient pressure and temperature, generating much less



Figure 6. Proposed degradation pathway of p,p'-DDT under H₂ atmosphere using Pd/C–Et₃N system.

toxic 1,1-diphenylethane, 1,1-dichloro-2,2-diphenylethane, and triethylammonium chloride. The addition of Et_3N accelerated the dechlorination from the alkyl moiety as well as the phenyl moiety. All reagents and solvents used for the degradation reaction are commercially available and could be recovered and reused. The method is very simple, efficient, and does not require any expensive facilities. Further study to achieve the complete dechlorination of DDT under mild conditions is now ongoing in our laboratory.

4. Experimental

4.1. Chemicals

p,p'-DDT, p,p'-DDD [2,2-bis(p-chlorophenyl)-1,1-dichloroethane], p,p'-DDE, and o,p'-DDT were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan) and used without any purification prior to use. Pd/C (10%) and Et₃N were purchased from Sigma–Aldrich (St. Louis, MO) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan), respectively. MeOH (analytical grade) was purchased from Kanto Chemical Co. Inc. and used without any purification prior to use.

4.2. General procedure

After two vaccum/H₂ cycles to remove air from a roundbottom flask, a suspension of p,p'-DDT (50 mg, 0.14 mmol), 10% Pd/C (5.0 mg), and Et₃N (86 mg, 0.85 mmol) in MeOH (10 mL) was vigorously stirred using a stir bar under hydrogen atmosphere (balloon) at ambient temperature (ca. 20 °C). At a given time point, the reaction mixture (1 mL) was sampled using a syringe, filtered through a 0.2 µL Millipore membrane filter (Millipore, Billerica, MA), and concentrated in vacuo. The residue



Figure 7. Tentative dechlorination mechanism of aliphatic moiety of p,p'-DDT.

was partitioned between Et₂O (10 mL) and H₂O (10 mL) and the organic layer was washed with brine (10 mL), dried (MgSO₄), and filtered. An aliquot (2 mL) was taken from the filtrate, diluted with Et₂O (18 mL), and analyzed by a Hewlett Packard 5891 series II gas chromatograph equipped with a Hewlett Packard 5972 mass-selective detector (Hewlett Packard, Palo Alto, CA) and a Neutrabond-5 capillary column ($30 \text{ m} \times 0.25 \text{ m}$, $0.4 \mu \text{m}$ film thickness; GL Science, Tokyo, Japan). Helium was employed as carrier gas with a flow rate of 1.0 mL/min. Injector and detector temperatures were 230 and 250 °C, respectively. The column temperature was programed to ramp from 150 °C (5 min hold) to 250 °C (3 min hold) at a rate of 5 °C/min. Retention time and molecular ion peak and/or fragment peak of each compound are as follows: 1, 24.08 min, m/z352 (M+, 0.6%), 235 (M-CCl₃, 100%); 2, 16.10 min, m/z 250 (M+, 35%), 235 (M-CH₃, 100%); 3, 22.75 min, *m*/*z* 318 (M+, 1.4%), 235 (M-CHCl₂, 100%); 4, 21.19 min, m/z 316 (M+, 57%), 246 (M-Cl₂, 100%); 5, 11.39 min, m/z 216 (M+, 39%), 201 (M-CH₃, 100%); 6, 18.86 min, m/z 201 (M-CHCl₂, 100%); 7, 6.88 min, m/z 182 (M+, 35%), 167 (M-CH₃, 100%); 8, 14.68 min, m/z 178 (M-H₂Cl₂, 11%), 167 (M-CH₂Cl₂, 100%); 9, 20.40 min, *m/z* 294 (M+, 12%), 235 (M-CO₂CH₃, 100%); 10, 22.81 min, m/z 352 (M+, 0.9%), 235 (M-CCl₃, 100%); 11, 14.98 min, m/z 250 (M+, 40%), 235 (M-CH₃, 100%); 12, 21.45 min, m/z 318 (M+, 0.8%), 235 (M-CHCl₂, 100%); **13**, 10.45 min, *m*/*z* 216 (M+, 42%), 201 (M-CH₃, 100%); 14, 17.62 min, m/z 201 (M-CH₂Cl₂, 100%); **15** 12.49 min, *m/z* 226 (M+, 11%), 167 (M-CO₂CH₃, 100%).

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