



New insights into the effect of base on the dechlorination of DDT in isopropanol-water over Pd/C catalyst under mild conditions



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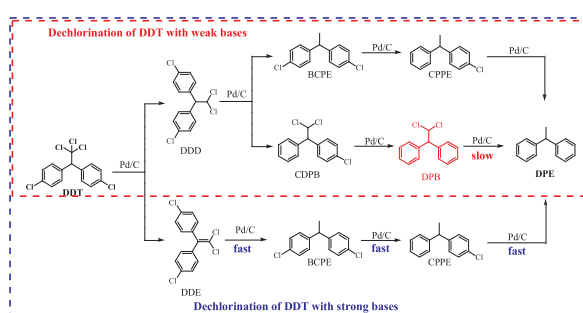
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HIGHLIGHTS

- The dechlorination pathway of DDT over Pd/C catalyst is studied and ascertained.
- The formation of DPB lead to the low dechlorination reactivity of DDT.
- The dechlorination rate of DDT with strong base is higher than that with weak base.
- Appropriate amount of strong base advances the formation of DDE.
- Appropriate amount of strong base improves the dechlorination reactivity of DDT.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic dechlorination of DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) over Pd/C catalyst under mild condition was carried out in 70% isopropanol-water (70/30, v/v). The dechlorination pathway of DDT over Pd/C catalyst and the reason for low dechlorination reactivity of DDT were investigated. It was found that there were three dechlorination pathways of DDT in the presence of NaOH: DDT-DDD-BCPE-DPE, DDT-DDE-BCPE-CPPE-DPE, and DDT-DDD-BCPE-CPPE-DPE. Notably, DPB, formed through the intermediate DDD molecule after losing two aromatic chlorines, led to the low dechlorination reactivity of DDT over Pd/C catalyst. Meanwhile, base could affect the dechlorination pathways of DDT, and thus influence the dechlorination reactivity of DDT over Pd/C catalyst. When strong bases were added, DDE and DDD were produced from the dehydrochlorination and hydrodechlorination of DDT, respectively. Yet, only DDD was formed when weak bases were added. When more NaOH was added, the dechlorination reactivity of DDT was apparently improved. And, NaOH addition also advanced formation of DDE, and affected the dechlorination pathways of DDT over Pd/C catalyst. On the basis of these results, we propose that DDT can be dechlorinated rapidly by means of altering the formation of DDE and DDD.

1. Introduction

DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) is a chlorinated pesticide once widely used for control of malaria, typhus, forest and agricultural pests, and other insect borne diseases since 1940s [1].

However, the use of DDT has recently been prohibited in most countries in the dirty dozen list of persistent organic pollutants (POPs) identified by the Stockholm Convention on POPs due to its serious health effects on wildlife and its ill effects on human life via the food chain [2]. The USEPA has classified DDT and its natural degradation products, DDE

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Nomenclature

DDT	1,1,1-trichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane
DDE	1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl)ethylene
DDD	1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane
DDMU	1,1-bis(4-chlorophenyl)-2-chloroethylene

BCPE	1,1-bis(chlorophenyl)ethane
CPPE	1-chlorophenyl-1-phenylethane
CDPB	1-chloro-4-(2,2-dichloro-1-phenylethyl)benzene
DPB	2,2-dichloro-1-phenylethyl)benzene
DPE	1,1-diphenylethane

(1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene), and DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane), as priority pollutants (commonly known as DDTr) [3]. Nevertheless, DDT is still allowed by the Stockholm Convention on POPs to use in some developing countries for essential public health purpose due to its effectiveness and low cost in controlling mosquito-borne malaria [4]. Because of the massive past use and extreme environmental persistence, DDT continues to be detected in environmental media and human tissues [4–6]. Thus, it is imperative to develop a practical and efficient remediation method for adequate decontamination of DDT.

A variety of treatment techniques, including physical treatment [7–9], biological treatment [10–12], incineration [13], advanced oxidation processes (AOPs) [14–16], zero-valent metal (ZVM) reduction [17–19], and catalytic dechlorination [20–22], have been explored to eliminate DDT. Among the approaches mentioned above, catalytic dechlorination was considered to be a promising detoxifying technology for its economic and environmental advantages and wide application for reducing dramatically toxicity without formation of chlorinated organic compounds (COCs) even more hazardous byproducts [23]. The main advantages of catalytic dechlorination are the ability to treat a wide range of concentrations, the mild operating conditions as well as the low reagent demand [24–27]. Moreover, catalytic dechlorination allows safe conversion of COCs regardless of their chlorine content into value added products, which can be recovered and further recycled, or safely disposed for further treatments [23].

Over the past decades, there has been intense research around the world to develop catalytic methods for the complete dechlorination of DDT. Zinovyev et al. found that quantitative dechlorination of DDT could be achieved in a multiphase catalytic system under atmospheric pressure at 50 °C [28]. Monguchi et al. reported that DDT could be dechlorinated to 1,1-diphenylethane (DPE) with Pd/C-Et₃N system under mild conditions [22]. Gautam et al. dechlorinated DDT to DPE with Mg/Pd bimetallic particles in water-biosurfactant phase [17]. Ukisu completely reduced DDT, DDE, and DDD to DPE in 2-propanol/methanol in the presence of NaOH and Pd/C [29]. We previously reported that a combined technique of solvent extraction and catalytic dechlorination was developed for the remediation of DDTr contaminated soil. The DDTr extract could be dechlorinated to DPE over Pd/C catalyst in 70% isopropanol-water (70/30, v/v) (70% IPA) under mild conditions [30]. However, application of these reaction systems for complete dechlorination of DDT required rather long reaction time, and rapid dechlorination of DDT is preferred.

Generally, base is a considerably important factor to influence the liquid-phase dechlorination reaction [31]. At present, it is widely accepted that base is used as a proton scavenger to eliminate the negative effect of HCl on the catalyst [31,32]. Besides, it was also found that base had participated in the dechlorination reaction. Cobo et al. proposed that an optimum amount of NaOH would be necessary to efficiently degrade dioxin to avoid poisoning and leaching of Pd and to reduce Na deposition over the active phase [33]. Monguchi et al. thought that, besides playing a role of a base in the dechlorination of aryl chlorides, Et₃N could also act as an electron donor for reactants and expedite the dechlorination reaction [22]. In our previous study, it was found that different existing species and action mechanisms of Et₃N in water and organic solvents possibly affected and determined the dechlorination reactivity or selectivity of chlorophenols over Raney Ni [34].

The aim of the presented study was to investigate precise

dechlorination pathway of DDT, and to elucidate the reason for low dechlorination reactivity of DDT. We studied the dechlorination reaction of DDT over Pd/C catalyst in 70% isopropanol-water (70/30, v/v). In order to ascertain the reaction pathway, the dechlorination pathway and reactivity of reaction intermediates of DDE and DDD were also investigated. Meanwhile, the effect of base on the dechlorination pathway and reactivity of DDT over 5% Pd/C were studied. We expected that the research results would give insight into the dechlorination pathway of DDT, which would be useful in designing catalytic dechlorination based DDT remediating method.

2. Experimental

2.1. Chemicals

The 5% Pd/C catalyst used in this study was purchased from C&P Chemical Co., China. The catalyst was not pre-treated before any experiment and was kept in desiccator before use. Physicochemical properties of the catalyst are given in Table 1. The content of Pd in the catalyst was measured via the ICP-MS (PE Elan DRC II). BET surface area, pore size distribution, and pore volume of the catalyst were characterized by the commercial Micrometrics ST2000B unit. Palladium particle size and morphology were characterized using transmission electron microscopy (TEM, a JEOL Model JEM-2011EM, Japan) at an accelerating voltage of 120 kV (TEM images of 5% Pd/C catalyst and its particle distribution are provided in Fig. S1 In Supplementary Data).

DDT, DDD, and DDE were purchased from Sigma-Aldrich, USA. The other reagents, such as isopropanol, sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), triethylamine (Et₃N), and ammonia (NH₄OH, 25%), were analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Deionized water used in the reaction was collected from an in-house water purification system. The purities of H₂ and N₂ used in the experiments were 99.99%.

2.2. Catalytic procedure

The liquid-phase dechlorination reactions were carried out in a three-neck flask, which was attached with a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter, three-way valve and a nitrogen cylinder). The reaction vessel (50 mL) was placed on a magnetic stirrer operating at 40 °C and 500 rpm. In a typical experiment, Pd/C catalyst and 40 mL of solution containing DDTr were charged and agitated under a N₂ flow (20 mL/min) for 5 min. Then, base was added into the flask and H₂ was

Table 1
The physicochemical properties of 5% Pd/C catalyst.

Property (units)	Value
Pd content (% w/w) ^a	5.0
BET surface area (m ² /g)	1325.0
Pore volume (m ³ /g)	0.78
Pd mean particle size (nm) ^b	5.77

^a Measured via the ICP.

^b Determined by TEM from more than 300 particles.

introduced at a constant flow rate of 10 mL/min (time $t = 0$ for dechlorination reaction). Three replicates of each dechlorination run were carried out, and the coefficient of variation was less than 4.0%. The intermediate products and the composition of the reaction system were determined by GC-FID and GC-MS. The carbon and chlorine balances in experiments matched are all above 96.0% and 98.5%, respectively (The data of carbon and chlorine balances are provided in Table S1 in Supplementary Data).

2.3. Analytical methods

The identification of DDTr and its dechlorination products was performed by GC-MS (Thermo Fisher ITQ-900) with a DB-5 ms column (30 m in length, 0.25 mm ID, 0.25 μ m film thickness). The quantification of DDTr and its dechlorination products was achieved by GC-FID (Agilent-7890A) with an HP-5 column (30 m in length, 0.32 mm ID, 0.25 μ m film thickness). It was well-established that DDT could be broken down during GC injection, so an analytical method was carefully chosen for DDT and intermediates measurements using GC-MS and GC-FID [35]. The GC temperature program was: started at 50 °C, held for 2.0 min; ramped at 10 °C/min up to 180 °C, held for 1.0 min; then, ramped at 5 °C/min up to the final temperature of 260 °C held for 6 min. The injection port was set at 220 °C. Mass spectrometry analysis was done in electron impact (EI) mode; the ion source temperature was set at 220 °C and the scan range was 50–550 amu. The intermediates and final product were identified by using the NIST 14 mass spectral database, and/or were verified via comparison with the ion chromatograms of reference standards.

Measurements of DDTr before and after the dechlorination reaction were divided into 9 groups on the basis of numbers of chlorine atoms on a molecular nucleus. The average chlorine atom number (ACN) was obtained as follows:

$$ACN = \sum_{i=1}^j iC_{DDTr_i} \quad (1)$$

where C_{DDTr_i} is the percentage of DDTr with i chlorine atom(s); i is the number of chlorine atom(s) on a molecular nucleus. And the chlorine atom removal efficiency was expressed as chlorine atom removal ratio, which was obtained as follows:

$$\text{chlorine atom removal ratio (\%)} = \frac{ACN_0 - ACN_t}{ACN_0} \times 100 \quad (2)$$

where ACN_0 and ACN_t represent the initial ACN of DDTr and the value at reaction time t , respectively.

The dechlorination reactivity was expressed as dechlorination rate, which was the average one within reaction time t here, as shown in the following equation:

$$\text{Dechlorination rate} = \frac{\text{chloride atom removal rate}}{n_{Pd/C} \times \text{Reaction time}} = \frac{n_{\text{organic-Cl}} \times \text{chloride atom removal ratio}}{n_{Pd/C} \times \text{Reaction time}} \quad (3)$$

where $n_{\text{organic-Cl}}$ is the total molar amount of chlorine atoms on DDTr; n_{Pd} is the total molar amount of palladium atoms in 5% Pd/C catalyst.

3. Results and discussion

3.1. Catalytic dechlorination of DDT over Pd/C catalyst in liquid-phase system

In our previous work, 70% IPA was used as the solvent system for the dechlorination of DDTr extract over Pd/C catalyst under mild conditions [30]. Moreover, water in the solvent system could prevent inorganic salt from accumulating on the surface of catalyst and thereby enabled the catalyst to keep high activity in the liquid-phase dechlorination [36]. Thus, the same solvent system was used in the

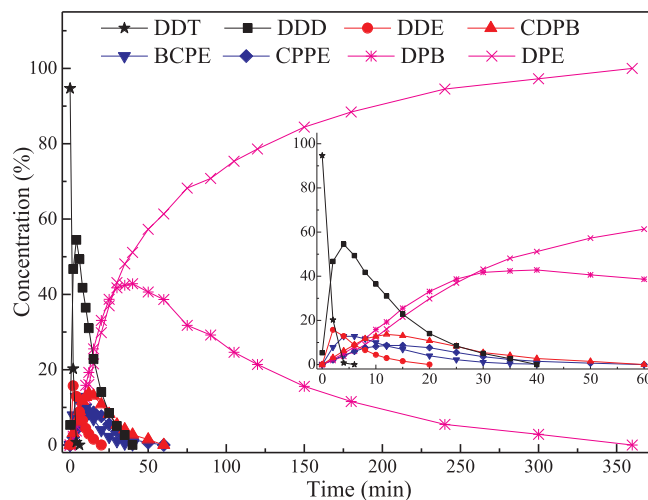
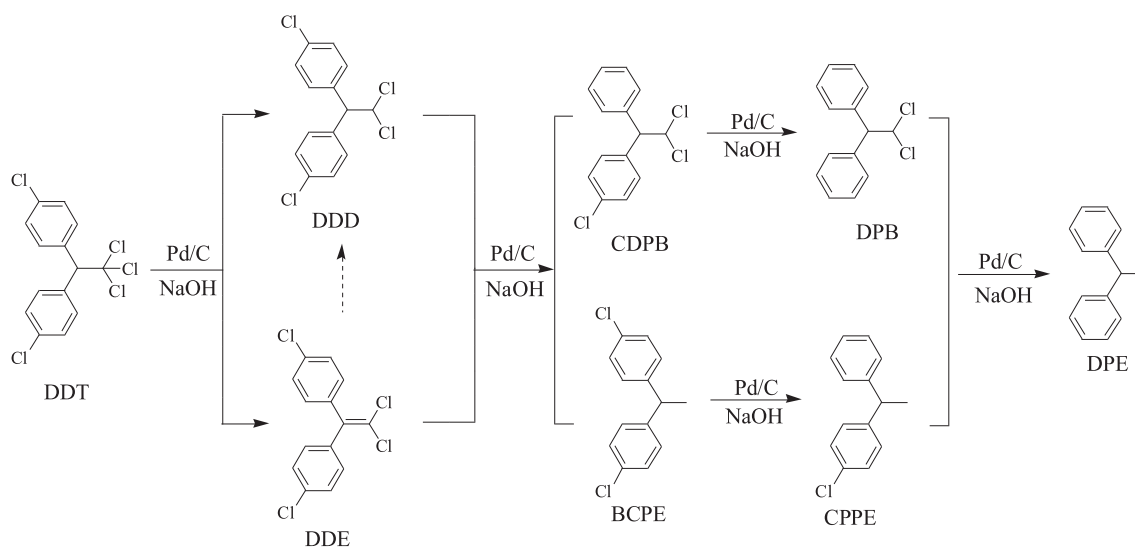


Fig. 1. Reaction profiles of DDT in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst with NaOH. Reaction conditions: DDT (40 mg), 5% Pd/C (25 mg), H_2 : 10 mL min⁻¹.

presented work here.

Firstly, catalytic dechlorination of DDT over Pd/C catalyst in 70% IPA with NaOH was monitored by GC-MS analysis. The reaction profiles of DDT are depicted in Fig. 1. As observed, the chloride atom removal ratio of DDT reaches 100% after 360 min of reaction time. The reaction intermediates were identified as DDD, DDE, 1,1-bis(chlorophenyl)ethane (BCPE), 1-chlorophenyl-1-phenylethane (CPPE), 1-chloro-4-(2,2-dichloro-1-phenylethyl)benzene (CDPB), and (2,2-dichloro-1-phenylethyl)benzene (DPB), and the end-product was 1,1-diphenylethane (DPE) (as listed in the Supporting Information, Table S2). As can be seen in Fig. 1, DDT is completely consumed within 10 min over Pd/C catalyst in reaction medium with NaOH. Meanwhile, the concentrations of DDD, DDE, BCPE, CPPE, and CDPB all increase to maxima within 15 min and then gradually decrease to zero. However, the concentration of DPB reaches its maximum relative rapidly but then decreases sluggishly compared with other intermediates, which suggested that DPB was rather resistant to dechlorination over Pd/C catalyst. During the reaction, DDE was produced from the dehydrochlorination (DHC) of DDT, while DDD was formed via hydrodechlorination (HDC) of one aliphatic chlorine in DDT. These observations were in agreement with the reported results by other researchers [28]. Nevertheless, it was unclear whether DDE could be transformed into DDD. Moreover, there was no effective data for the formation of CDPB, DPB, BCPE, and CPPE. Previous research showed that the chemical dechlorination of hexachlorobenzene and polychlorinated biphenyls progressed with a stepwise dechlorination mechanism [36,37]. Similarly, the debromination of PBDEs with Fe/Ni bimetallic nanoparticles was also achieved through a stepwise reductive debromination process [38]. Although there was not enough evidence obtained to ascertain the precise dechlorination pathway of DDT, the degradation reaction of DDT over Pd/C catalyst with NaOH might also be a stepwise dechlorination process (Scheme 1).

Considering that DDE and DDD were dechlorinated intermediates of DDT, catalytic dechlorination of DDE and DDD over Pd/C catalyst in 70% IPA with NaOH were further investigated to distinguish the dechlorination pathway of DDT (Fig. 2). As illustrated in Fig. 2A, DDE is dechlorinated completely within 30 min, but no DDD is formed via the hydrogenation of DDE. Moreover, the concentrations of intermediates (DDMU (1,1-bis(4-chlorophenyl)-2-chloroethylene), BCPE, and CPPE) increase to maxima and then drop to zero after 30 min. The concentration of final product DPE increases gradually with the reaction time. In the dechlorination of DDE, DDMU was formed after DDE molecules lost one aliphatic chlorine. Meanwhile, DDMU was further



Scheme 1. Proposed dechlorination pathway of DDT in 70% isopropanol-water (70/30, v/v) over Pd/C catalyst with NaOH.

transformed into BCPE, which was then reduced to CPPE and DPE. Based on the detected dechlorination products and reaction profiles, it could be concluded that the dechlorination pathway of DDE was through DDE-DDMU-BCPE-CPPE and produced DPE in the end (Scheme 2). Thus, the dechlorination reaction of DDE over Pd/C catalyst with NaOH was a stepwise dechlorination process.

On the other hand, the dechlorination reaction profiles of DDD over Pd/C catalyst are presented in Fig. 2B. The profiles show that DDD can be dechlorinated and completely transformed into its intermediates (DDMU, CDPB, and DPB) within 50 min. The concentrations of DDMU and CDPB increase to maxima within 25 min and then decrease gradually to zero. Meanwhile, the concentration of DPB increases rapidly but decreases sluggishly with the reaction time, which is similar to the DPB result shown in Fig. 1 (from DPB to DPE). In the dechlorination of DDD, DDMU was produced from the DHC of DDD [29], which could be further transformed into DPE. Meanwhile, CDPB was formed after DDD losing one aromatic chlorine, and was then dechlorinated into DPB. Then, DPB were reduced to DPE in the end. Hence, the dechlorination of DDD over Pd/C catalyst with NaOH followed two general dechlorination pathways, namely DDD-DDMU-DPE and DDD-CDPB-DPB-DPE pathways (Scheme 3).

For the dechlorination of DDT over Pd/C catalyst in 70% IPA with NaOH, DDE and DDD as intermediate products were produced from the DHC and HDC of DDT, respectively. Moreover, the dechlorination pathways of DDE and DDD were also determined based on their

dechlorination profiles (Schemes 2 and 3). Thus, it would be reasonable to conclude that the dechlorination of DDT with NaOH over Pd/C catalyst was a stepwise dechlorination process, and there were three pathways: DDT-DDD-CDPB-DPB-DPE, DDT-DDE-BCPE-CPPE-DPE, and DDT-DDD-BCPE-CPPE-DPE (Scheme 4).

Catalytic dechlorination of DDT, DDE, and DDD over Pd/C catalyst in reaction medium with NaOH was further compared. As illustrated in Fig. 3, the chloride atom removal ratio of DDT, DDE, and DDD within 20 min is in the order of DDE > DDT > DDD. This suggested that complete dechlorination of DDE could be achieved with the least reaction time. Moreover, it was found that the chloride atom removal ratios of DDT and DDD increased quickly in the initial 30 min, which meant that DDT and DDD could be reduced rapidly to dechlorinated intermediates. Yet, as the proceeding of the dechlorination reaction, the chloride atom removal ratio increased very slowly and could not reach 100% until 360 min. In this sense, DDT and DDD were partly transformed into DPB, which was rather resistant to be dechlorinated over Pd/C catalyst. Therefore, the dechlorination rate of DDT and DDD over Pd/C catalyst was rather low. Yet, no DPB was produced in the dechlorination of DDE, thus complete dechlorination of DDE could be achieved within 30 min under mild conditions (Fig. 2).

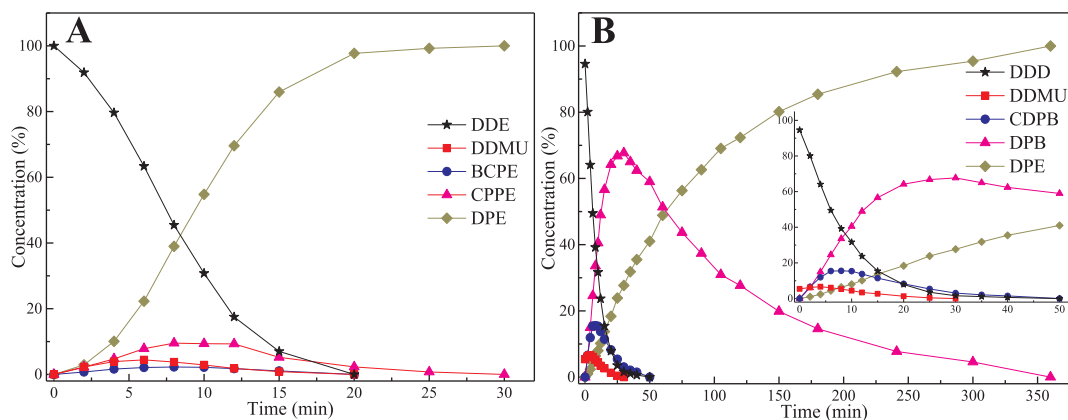
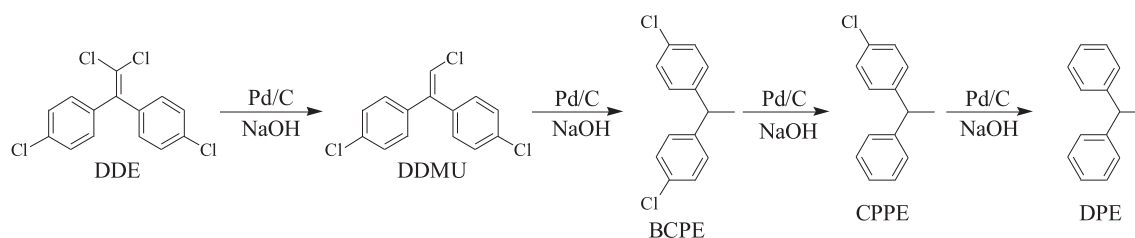


Fig. 2. Reaction profiles of DDE (A) and DDD (B) in 70% isopropanol-water (70/30, v/v) with NaOH over 5% Pd/C catalyst. Reaction conditions: DDE (45.2 mg), DDD (44.8 mg), NaOH (25 mg, 0.625 mmol), 5% Pd/C (25 mg), H₂: 10 mL min⁻¹.



Scheme 2. Proposed HDC pathway of DDE in 70% isopropanol-water (70/30, v/v) with NaOH over Pd/C catalyst.

3.2. Base effects on liquid-phase dechlorination of DDT over Pd/C catalyst

3.2.1. Effect of different bases on liquid-phase dechlorination of DDT over Pd/C catalyst

Generally, base is a considerably important parameter for liquid-phase dechlorination reactions [22,31,32]. In our previous study, it was found that the different existing species and action mechanisms of Et_3N in water and organic solvents possibly affected and determined the dechlorination reactivity or selectivity of chlorophenols over Raney Ni [34]. Yet, it was still unclear that whether different bases would change the dechlorination pathway of DDT, and in turn enabled DDT to be dechlorinated rapidly. Thus, the effect of base on the dechlorination reaction was carried out subsequently.

The effect of different bases on liquid-phase dechlorination reactivity of DDT in 70% IPA over Pd/C catalyst was compared. The results are provided in Table 2. The dechlorination rates of DDT with NaOH, KOH, Na_2CO_3 , NaHCO_3 , NH_4OH , and Et_3N within 360 min are 0.133 min^{-1} , 0.130 min^{-1} , 0.131 min^{-1} , 0.128 min^{-1} , 0.124 min^{-1} , and 0.125 min^{-1} , respectively. It can be seen in Table 2 that the dechlorination reactivity of DDT over Pd/C decreases in the order of $\text{NaOH} > \text{KOH} \approx \text{Na}_2\text{CO}_3 > \text{NaHCO}_3 > \text{Et}_3\text{N} > \text{NH}_4\text{OH}$. This implied that the dechlorination rates of DDT with strong bases were higher than those with weak bases. The results showed that the addition of NaOH, KOH, Na_2CO_3 , NaHCO_3 , NH_4OH , and Et_3N could affect the dechlorination reactivity of DDT over Pd/C catalyst.

Fig. 4 shows the results obtained by examining Pd/C-catalyzed liquid-phase dechlorination profiles of DDT with an assortment of bases, including NaOH, KOH, Na_2CO_3 , NaHCO_3 , Et_3N , and NH_4OH . For the dechlorination of DDT with NaOH and KOH, same intermediates (DDD, DDE, BCPE, CPPE, CDPB, and DPB) and end-product (DPE) were detected according to GC/MS analysis. As displayed in Fig. 4A and B, there is no principal difference between the dechlorination profiles of DDT with strong bases NaOH and KOH. Hence, the dechlorination pathway of DDT with KOH was in agreement with the aforementioned dechlorination pathway of DDT with NaOH (shown in Scheme 4).

On the other hand, the dechlorination profiles of DDT over Pd/C catalyst with weak bases Na_2CO_3 , NaHCO_3 , Et_3N , and NH_4OH are comparable as displayed in Fig. 4C–F. According to GC/MS analysis, the intermediates were DDD, BCPE, CPPE, CDPB, and DPB, and the end-product was DPE. It was noteworthy that no DDE was detected in these

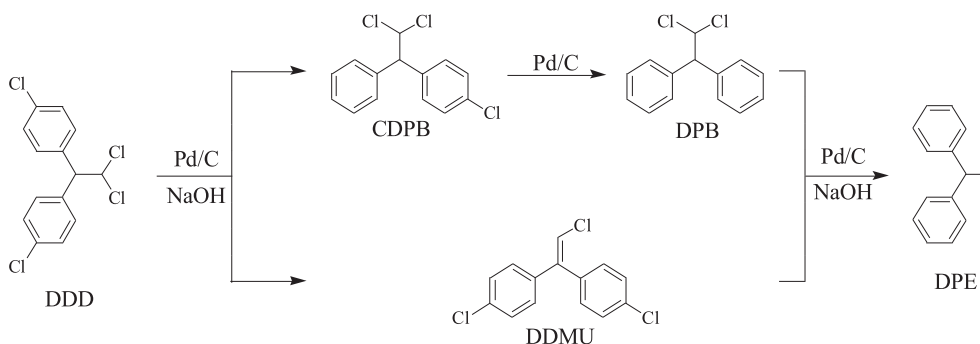
cases (Fig. 4C–F). This indicated that the dechlorination trends of DDT with weak bases were different from those with strong bases. Fig. 4C–F show that DDT concentration drops to baseline within 20 min. The concentrations of DDD, BCPE, CPPE, and CDPB increase to maxima within 25 min and then decrease gradually to zero. However, the concentration of DPB reaches its maximum rapidly and then decreases sluggishly, which is similar to the observation in the presence of strong bases. Based on the reaction profiles, it was concluded that there were two dechlorination pathways of DDT in the presence of weak bases: DDT-DDD-CDPB-DPB-DPE and DDT-DDD-BCPE-CPPE-DPE (Scheme 5). Apparently, there was an extra dechlorination pathway of DDT in the presence of strong bases, as DDE was produced in the dechlorination of DDT in presence of strong bases. These results showed that base would affect the dechlorination pathways of DDT over Pd/C catalyst.

For the dechlorination of DDT over Pd/C catalyst in the presence of different bases, the dechlorination rates of DDT with strong bases were faster than those with weak bases. Moreover, the dechlorination pathway of DDT with strong bases were different from those with weak bases, as DDE was produced in the dechlorination of DDT in presence of strong bases. Besides acting as a proton acceptor, various bases also altered the dechlorination pathways of DDT. Therefore, different bases including NaOH, KOH, Na_2CO_3 , NaHCO_3 , NH_4OH , and Et_3N could affect the dechlorination pathways of DDT, and thus influenced the dechlorination rate of DDT over Pd/C catalyst.

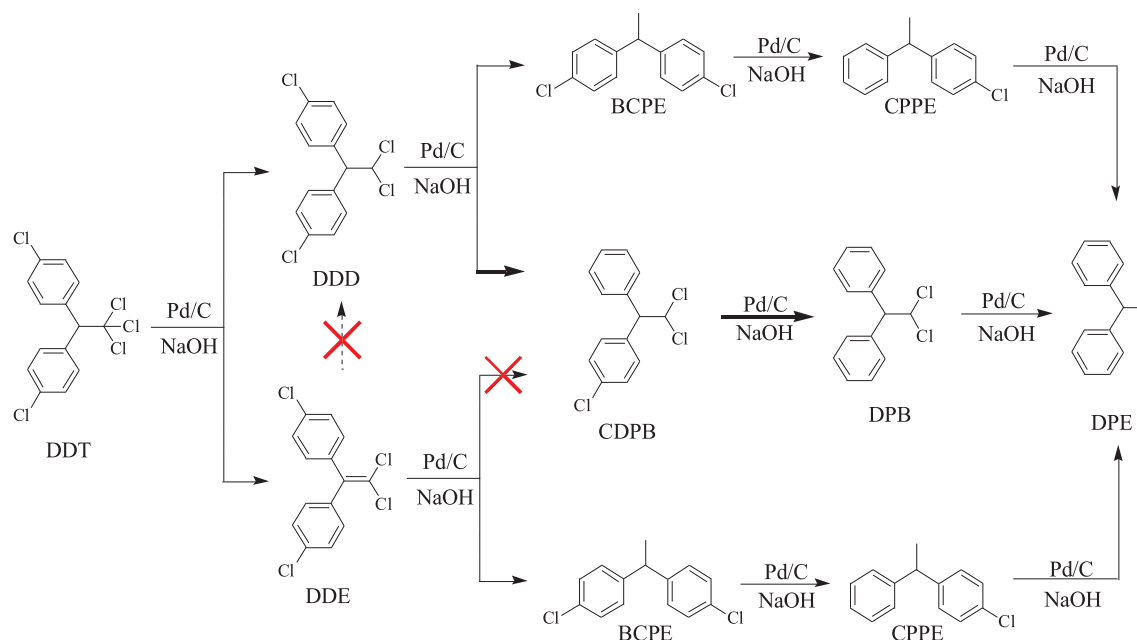
3.2.2. Effect of NaOH addition on liquid-phase dechlorination of DDT over Pd/C catalyst

As mentioned above, the dechlorination rates of DDT with strong bases were faster than that with weak bases and had an extra reaction pathway. Catalytic dechlorination of DDT over Pd/C catalyst with different amount of NaOH addition was further studied to ascertain the effect of the NaOH addition on the dechlorination reactivity and pathway.

The effect of NaOH addition on the dechlorination reactivity of DDT over 5% Pd/C catalyst is analyzed according to the dechlorination rates summarized in Table 3. It can be seen that the dechlorination rates of DDT with 0 mmol, 0.28 mmol, 0.62 mmol, 0.85 mmol, 1.24 mmol, and 2.48 mmol of NaOH within 300 min are 0.125 min^{-1} , 0.134 min^{-1} , 0.158 min^{-1} , 0.160 min^{-1} , 0.159 min^{-1} , and 0.158 min^{-1} , respectively. Increasing NaOH addition to reaction medium from 0.28 to 0.85 mmol showed a positive effect on the dechlorination rate, whereas



Scheme 3. Proposed HDC pathway of DDD in 70% isopropanol-water (70/30, v/v) with NaOH over Pd/C catalyst.



Scheme 4. Proposed precise dechlorination pathway of DDT in 70% isopropanol-water (70/30, v/v) with NaOH.

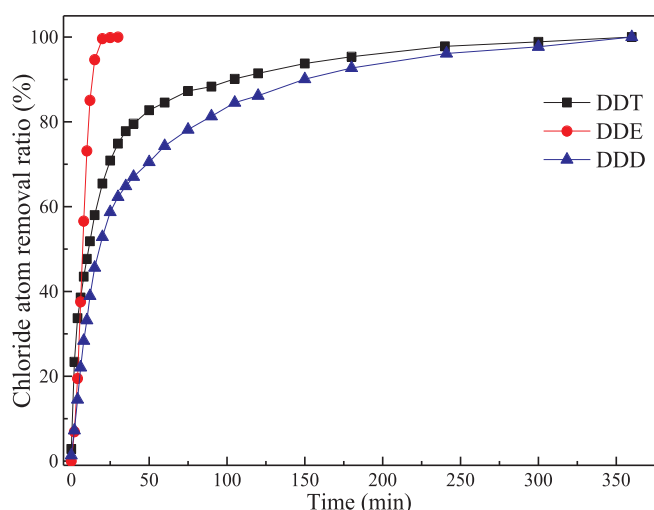


Fig. 3. The dechlorination of DDT, DDE, and DDD in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst. Reaction conditions: organic-Cl (0.564 mmol), NaOH (25 mg, 0.625 mmol), 5% Pd/C (25 mg), H_2 : 10 mL min^{-1} .

no positive effect was observed at higher NaOH addition. The highest dechlorination rate was achieved when NaOH addition was 0.85 mmol. This result further indicated that the presence of water in isopropanol-water solvent advanced the inorganic salts to be dissolved and ionized, which prevented the inorganic salts from accumulating on the surface of catalyst [36]. When NaOH addition was 1.24 mmol or higher, excessive NaOH and NaCl could not be completely dissolved in the reaction medium, and thus would block catalytic active sites and hinder the absorption and activation of hydrogen gas and DDT [39]. In this sense, an appropriate amount of NaOH addition eliminated the HCl poisoning to Pd/C catalyst and enabled the catalyst to keep high activity. In other words, an appropriate addition of NaOH could accelerate the dechlorination reaction.

The dechlorination reaction profiles of DDT over Pd/C catalyst with different amount of NaOH addition are shown in Fig. 5. When no base was added, the reaction intermediates were DDD, BCPE, CPPE, CDPB, and DPB, and the end-product was DPE, with no DDE detected (Fig. 5A). The dechlorination intermediates of DDT showed varied

Table 2

The effect of different bases on liquid-phase dechlorination of DDT in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst.

Entry ^a	Base	Time (min)	Dechlorination rate (min^{-1}) ^b	Yield of product (%) ^c
1	NaOH	360	0.133	DPE (100)
2	KOH	360	0.130	DPE (94.1), DPB (5.9)
3	Na_2CO_3	360	0.131	DPE (95.4), DPB (4.6)
4	$NaHCO_3$	360	0.128	DPE (89.4), DPB (10.6)
5	NH_4OH	360	0.124	DPE (82.8), DPB (17.2)
6	Et_3N	360	0.125	DPE (85.0), DPB (15.0)

^a Reaction conditions: DDT (40 mg), base (0.625 mmol), 5% Pd/C (25 mg), H_2 : 10 mL min^{-1} .

^b $Dechlorination \text{ rate} = \frac{\text{chloride atom removal rate}}{\text{Time}}$, The Dechlorination rate was the average one within 360 min here.

^c Yields of products were determined by GC-MS.

trends with increasing reaction time. As illustrated in Fig. 5A, DDT is consumed completely within 10 min over Pd/C catalyst without base. The concentrations of DDD, BCPE, and CPPE increase initially to maxima and then decrease gradually with the increasing reaction time. In contrast, the concentrations of CDPB and DPB keep on increasing throughout the experiment. After 490 min of the dechlorination reaction, the concentration of DPE reaches 60.2%, and the concentration of CPPE, BCPE, DPB, DDD, and CDPB are 14.1%, 13.0%, 6.3%, 4.7%, and 1.7%, respectively. Thus, DDT disappears completely within 30 min, yet the chloride atom removal ratio of DDT is only 84.7% within 490 min. The dechlorination pathways of DDT without base over Pd/C catalyst were found to be similar to those of DDT pathways with weak base. Yet, the concentrations of CPPE and BCPE were both much higher than those of DPB and CDPB throughout the experiment. This suggested that CPPE and BCPE were the major intermediates in the dechlorination of DDT without base. In other words, the dechlorination pathways of DDT without base were different from those with base. Further, it can be

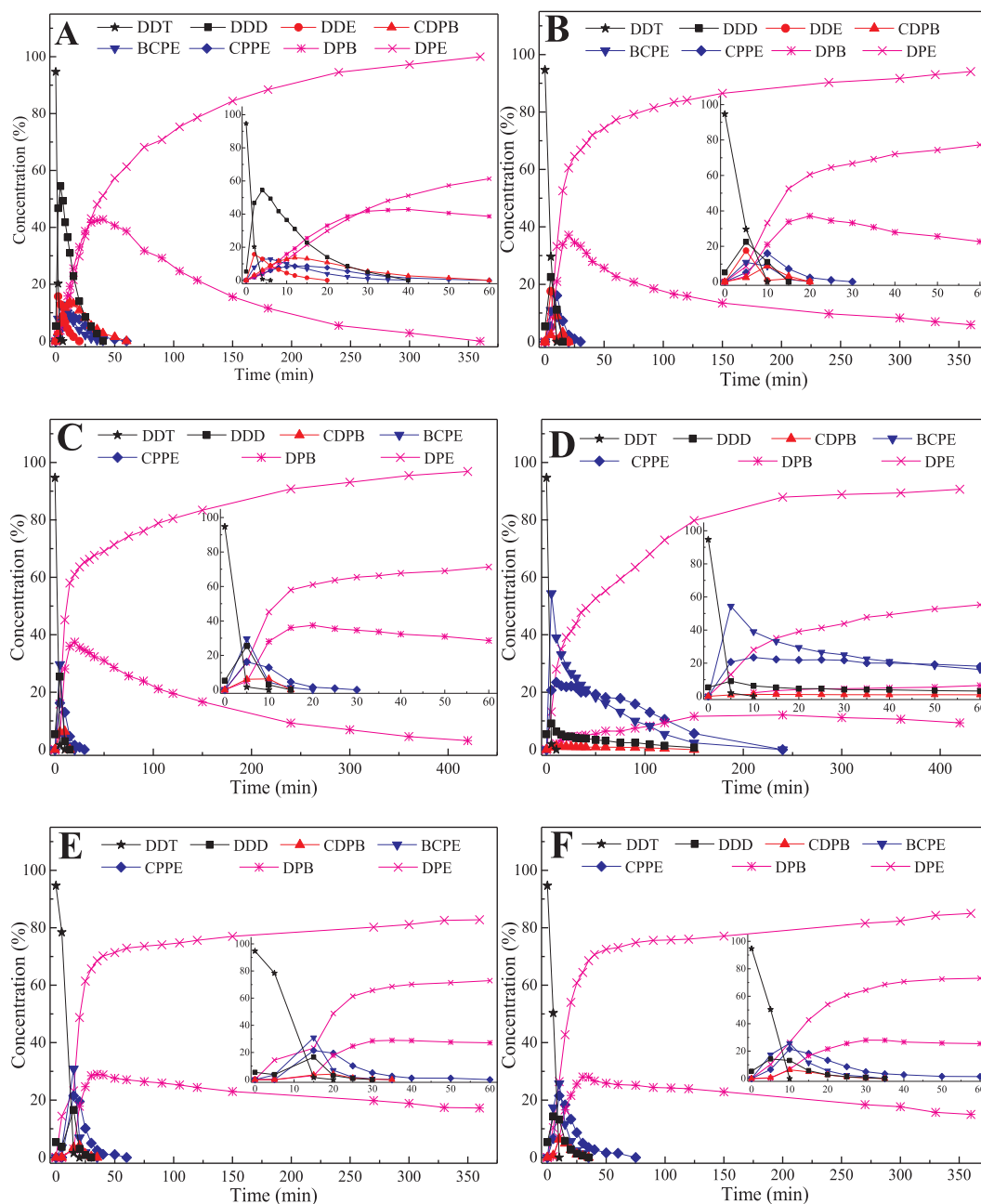
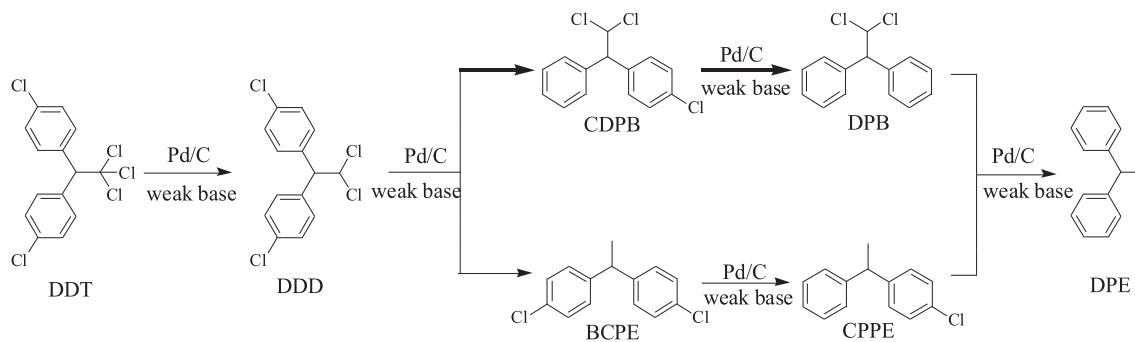


Fig. 4. Reaction profiles of DDT in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst with (A) 0.625 mmol NaOH, (B) 0.625 mmol KOH, (C) 0.313 mmol Na_2CO_3 , (D) 0.625 mmol NaHCO_3 , (E) 0.625 mmol NH_4OH , and (F) 0.625 mmol Et_3N . Reaction conditions: DDT (40 mg), 5% Pd/C (25 mg), H_2 : 10 mL min^{-1} .



Scheme 5. Proposed dechlorination pathway of DDT in 70% isopropanol-water (70/30, v/v) with Na_2CO_3 , NaHCO_3 , Et_3N , and NH_4OH .

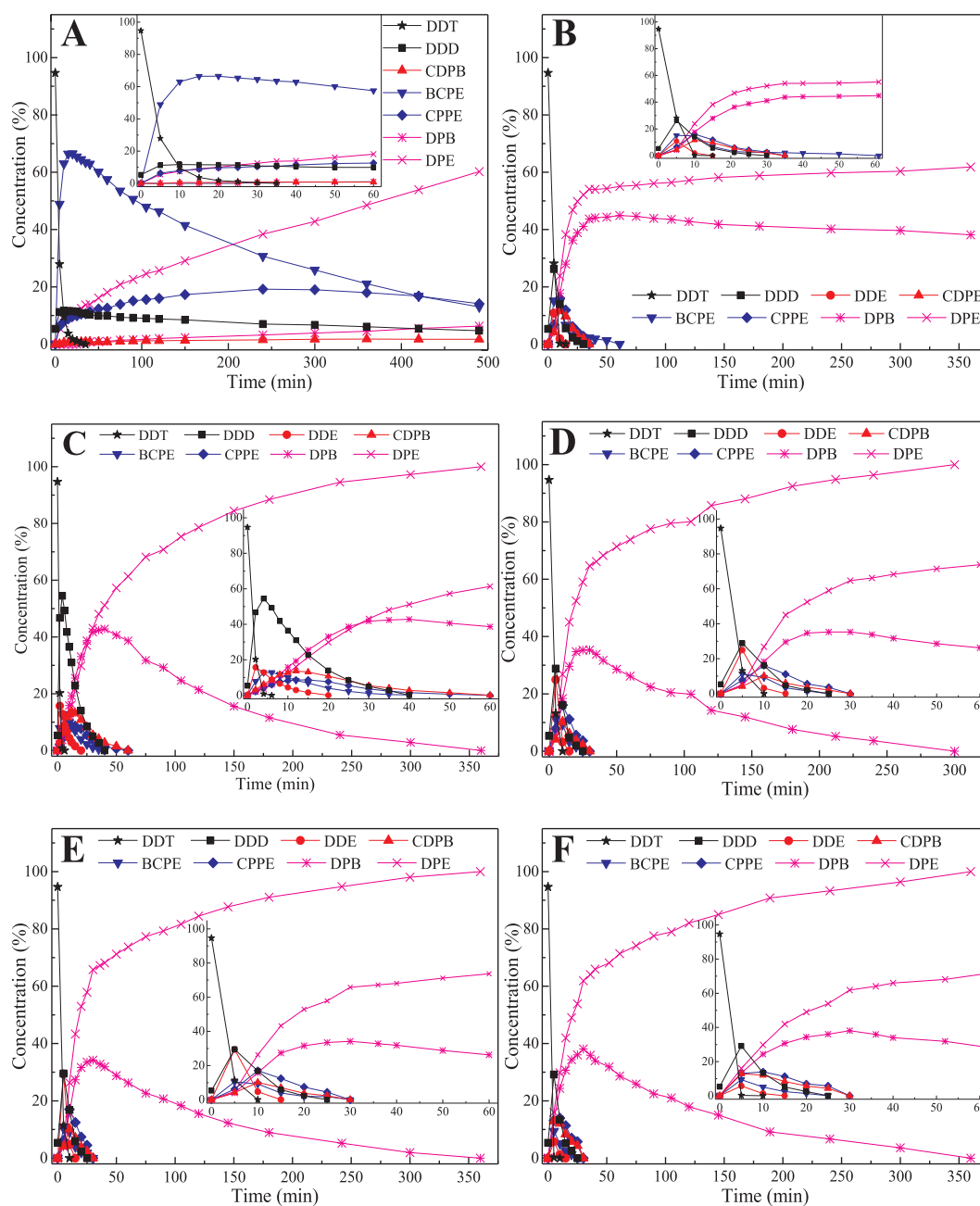
Table 3

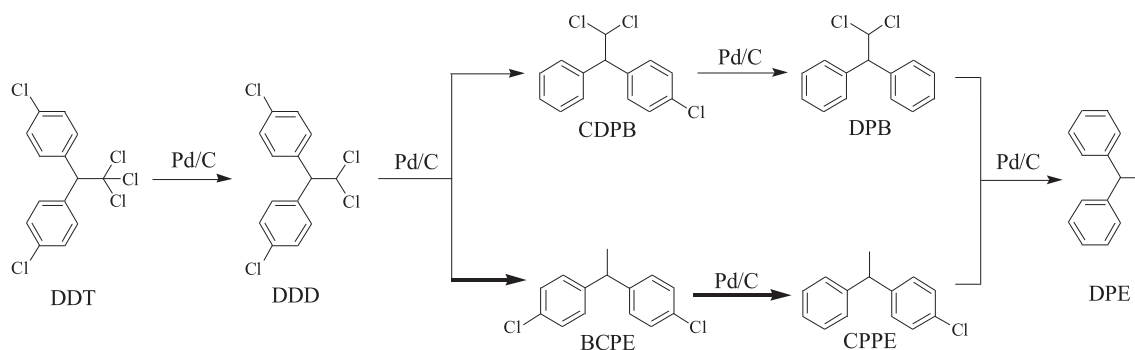
The effect of NaOH addition on liquid-phase HDC of DDT in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst.

Entry ^a	n(NaOH)	n(NaOH)/n(organic-Cl)	Time (min)	Dechlorination rate (min ⁻¹) ^b	Yield of product (%) ^c	C(DDE C _{max})/C(DDD C _{max})
1	0	0	300	0.125	DPE (42.8), CPPE (19.0), BCPE (25.9), DPB (3.9), DDD (6.7), CDPB (1.7)	0
2	0.28 mmol	0.5	300	0.134	DPE (60.3), DPB (39.7)	0.414
3	0.62 mmol	1.1	300	0.158	DPE (97.2), DPB (2.8)	0.781
4	0.85 mmol	1.5	300	0.160	DPE (100)	0.866
5	1.24 mmol	2.2	300	0.158	DPE (98.1), DPB (1.9)	0.995
6	2.48 mmol	4.4	300	0.158	DPE (96.4), DPB (3.6)	0.197

^a Reaction conditions: DDT (40 mg), base (NaOH), 5% Pd/C (25 mg), H₂: 10 mL min⁻¹.^b Dechlorination rate = $\frac{\text{chloride atom removal rate}}{\text{Time}}$, The Dechlorination rate was the average one within 300 min here.

$$= \frac{n_{\text{organic-Cl}} \times \text{chloride atom removal ratio}}{n_{\text{Pd}} \times t}$$

^c Yields of products were determined by GC-MS.**Fig. 5.** Reaction profiles of DDT in 70% isopropanol-water (70/30, v/v) over 5% Pd/C catalyst with different NaOH addition. Reaction conditions: DDT (40 mg), 5% Pd/C (25 mg), H₂: 10 mL min⁻¹, the amount of NaOH addition: (A) 0 mmol, (B) 0.28 mmol, (C) 0.62 mmol, (D) 0.85 mmol, (E) 1.24 mmol, and (F) 2.48 mmol.



Scheme 6. Proposed dechlorination pathway of DDT in 70% isopropanol-water (70/30, v/v) without base.

concluded that the dechlorination of DDT without base over Pd/C catalyst follows two general dechlorination pathways, namely DDT-DDD-BCPE-CPPE-DPE and DDT-DDD-CDPB-DPB-DPE, as shown in Scheme 6. This confirmed that base did affect the dechlorination pathways of DDT over Pd/C catalyst.

As illustrated in Fig. 5B, DDT can be transformed into its dechlorinated intermediates completely within 15 min when 0.28 mmol of NaOH is added. The dechlorination intermediates are DDD, DDE, BCPE, CPPE, CDPB, and DPB, while the end-product is DPE. The concentrations of DDD, DDE, BCPE, CPPE, and CDPB increase to maxima and then decrease gradually to zero. Yet, the concentration of DPB reaches its maximum rapidly and then decreases sluggishly. What is more, DDE and DDD transformed rapidly into their further dechlorination intermediates. Similar patterns were observed for the other runs when the amount of NaOH addition were 0.62 mmol, 0.85 mmol, 1.24 mmol, and 2.48 mmol, respectively (Fig. 5C–F). The same intermediates and end-product were produced for the dechlorination of DDT with different NaOH addition. It could be concluded that the dechlorination of DDT with different amount of NaOH followed the same dechlorination pathways of DDT as presented in Scheme 4.

More interesting results have been obtained from the effect of NaOH addition on the concentration ratio of (DDE C_{max})/(DDD C_{max}), as presented in Table 3. In absence of base, the concentration ratio was zero. When 0.28 mmol NaOH, 0.62 mmol NaOH, 0.85 mmol NaOH, and 1.24 mmol NaOH were added to the reaction medium, the concentration ratios were 0.414, 0.781, 0.866, and 0.995, respectively. Thus, it was clear that the concentration ratio increased with NaOH addition increasing, suggesting that appropriate amount of NaOH addition did advance the formation of DDE. Yet, the concentration ratio of (DDE C_{max})/(DDD C_{max}) was only 0.197 when 2.48 mmol NaOH was added. It was clear that the more DDE was generated, the faster the dechlorination reaction would be. This result further implied appropriate amount of NaOH addition would advance the formation of DDE, and thus accelerated the dechlorination reaction. In this sense, the dechlorination of DDT could be accelerated when more DDE was produced from the DHC of DDT and/or DPB was rapidly dechlorinated within rather short time. Therefore, it would be reasonable to believe that DDT could be dechlorinated rapidly provided that it was treated with an appropriate method. Further investigation on the efficient dechlorination of DDT and application of the reaction system to other POPs are in progress.

4. Conclusions

The present study gave insight into the dechlorination of DDT over Pd/C catalyst. The main conclusions are drawn as follows:

- (1) The dechlorination pathway of DDT with NaOH over Pd/C catalyst were found to be: DDT-DDD-CDPB-DPB-DPE, DDT-DDE-BCPE-CPPE-DPE, and DDT-DDD-BCPE-CPPE-DPE. It was noteworthy that DDT exhibited rather low dechlorination reactivity when DPB

intermediate was formed in the pathway. In the case that no DPB was produced, and thus the dechlorination reactivity of DDE was rather high. Moreover, DDE could not be hydrogenated into DDD using Pd/C catalyst.

- (2) Bases could affect the dechlorination pathways and dechlorination reactivity of DDT over Pd/C catalyst. In the presence of weak bases, only DDD was formed via the dechlorination of one chlorine in DDT molecules. Nevertheless, both DDE and DDD were produced through the dechlorination of one chlorine in DDT molecules when strong bases was added. In general, the dechlorination rates of DDT with strong bases were faster than that with weak bases as no DPB was produced in the dechlorination of DDE.
- (3) It was found that appropriate amount of NaOH addition did advance the formation of DDE during the dechlorination of DDT, and thus affected the dechlorination pathway of DDT over Pd/C catalyst. With the appropriate amount of NaOH addition, the dechlorination reactivity of DDT was obviously enhanced.

On the basis of these studies, we propose that DDT can be dechlorinated rapidly by means of changing the dechlorination pathway. This report provides a practical and efficient strategy to the dechlorination of DDT.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2018.06.148>.

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