

# Dechlorination of hexachlorocyclohexanes with alkaline 2-propanol and a palladium catalyst

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## Abstract

Hexachlorocyclohexane isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH) were dechlorinated in 2-propanol by means of stoichiometric reaction with NaOH and subsequent catalytic dechlorination over a supported palladium catalyst (Pd/C). When the HCH isomers (2–10 mmol/l) were reacted with a molar excess of NaOH ( $[\text{NaOH}]/[\text{HCH}] > 9$ ) in 2-propanol, transformation of  $\alpha$ -,  $\gamma$ - and  $\delta$ -HCH to trichlorobenzenes (TCBs) was complete within 5 min at room temperature, but  $\beta$ -HCH was less reactive. Analysis of TCB isomers produced from individual HCH isomers showed that 1,2,4-TCB was always predominant (70–90% of the product) and 1,2,3-TCB and 1,3,5-TCB were minor products. The produced TCBs were dechlorinated by subsequently adding Pd/C to the alkaline 2-propanol solution and heating at 55 °C for 3 h, resulting in the formation of benzene in high yield (>80%). Technical-grade HCH, which contains these four isomers, was successfully dechlorinated with NaOH and Pd/C at 55 °C. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Dechlorination; Hexachlorocyclohexane; Sodium hydroxide; Supported palladium catalyst; 2-Propanol

## 1. Introduction

Hexachlorocyclohexane (HCH) has been heavily used throughout the world as an insecticide for fruit, grain and vegetable crops, for vector control and for seed treatment [1–3]. Of the eight geometric isomers of HCH, only the  $\gamma$ -isomer is highly insecticidal [4]. HCH isomers are used under the name “lindane” (almost pure  $\gamma$ -HCH) or as a technical-grade product consisting of  $\alpha$ -HCH (60–70%),  $\beta$ -HCH (5–12%),  $\gamma$ -HCH (10–15%),  $\delta$ -HCH (6–10%) and other minor components [1]. Technical-grade HCH has been widely used, particularly in some developing countries, because of its extremely low cost. The total global usage of technical-grade HCH during the half century from 1948 to 1997 was estimated to be around 10 million tonnes [2]. Many countries banned or restricted technical-grade HCH usage in the 1970s because of the environmental and biological persistence of HCH isomers. However, considerable unused stockpiles of

both technical-grade HCH and lindane still exist worldwide. In Japan, about 1800 tonnes of unused HCH products have been stored since 1972 [5].

Once HCH isomers enter the environment, they are distributed broadly and can be found in air, surface water and soil [3].  $\beta$ -HCH is the predominant isomer in soils, animal tissues and human breast milk, because it is resistant to environmental and enzymatic degradation [4]. With the aim of protecting humans and the environment from pollution with HCH isomers, disposal and remediation techniques have been extensively studied. Combustion of HCH isomers is an economical method of disposal, but it is undesirable because toxic polychlorinated dioxins and furans are likely to be produced [6]. Alternatively, processes for chemical transformation of HCH isomers can be environmentally friendly, since these reactions can be performed under relatively mild conditions without producing any toxic compounds. For example, HCH isomers can undergo dechlorination to form trichlorobenzenes (TCBs) by base-assisted processes in ethanol at temperatures below 50 °C [7,8]. Hydrolysis of HCH isomers occurs in aqueous solution at pH 9 and <45 °C, although the reaction

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rate is very slow [9]. Dechlorination of lindane occurs in subcritical water at a temperature range of 125–250 °C to yield phenol as the major product [10]. Photoinduced dechlorination of  $\beta$ -HCH has been performed in alkaline alcohols, yielding benzene as the major product [11]. Lindane can also be reduced electrochemically to benzene [12]. Biodegradation of HCH isomers has also been studied under both aerobic and anaerobic conditions and lower-chlorinated products such as chlorobenzenes and chlorophenols are likely to be obtained [13]. Catalytic dechlorination of lindane over metal catalysts has been examined. Schüth and Reinhard [14] reported that lindane can be transformed to benzene in hydrogen-saturated water at room temperature and ambient pressure with an excess of Pd/Al<sub>2</sub>O<sub>3</sub>. Zinovyev et al. [15] dechlorinated lindane in a multiphase catalytic system composed of isooctane, aqueous KOH, a phase transfer agent (Aliquat 336) and a metal catalyst (Pd/C, Pt/C or Raney-Ni) under atmospheric pressure of H<sub>2</sub> at 50 °C; benzene was obtained as the major product.

We previously reported that catalytic dechlorination of chlorobenzenes [16], chlorotoluenes [17,18], polychlorinated biphenyls [19] and polychlorinated dibenzo-*p*-dioxins and dibenzofurans [20–22] occurs efficiently in a solution of NaOH in 2-propanol in the presence of supported noble-metal catalysts such as Pd/C and Rh/C under mild conditions (<82 °C), and that aliphatic and cycloaliphatic chlorides are dechlorinated at much slower rates than chlorobenzenes [23]. This method does not use molecular hydrogen; instead, 2-propanol serves as a 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 [16,21]. The dechlorination proceeds stepwise to give a chlorine-free product. 2-Propanol releases hydrogen species to give acetone. Dissolved NaOH is indispensable for the catalytic dechlorination because it scavenges released Cl<sup>-</sup> to form NaCl and also enhances the production of hydrogen from 2-propanol [24].

In this paper, we describe a method for complete dechlorination of HCH isomers in 2-propanol under mild conditions (<55 °C). The process consists of transformation to chlorobenzenes with NaOH followed by dechlorination catalyzed by a supported palladium catalyst. 2-Propanol was used as a solvent, because it dissolves relatively large amount of NaOH and functions as a good hydrogen donor. We report the dechlorination properties of various HCH isomers and their dechlorination routes. Finally, we demonstrate dechlorination

of technical-grade HCH (a mixture of HCH isomers) for potential practical use in disposal of HCH stockpiles.

## 2. Experimental

### 2.1. Materials

The catalyst used in this study was palladium supported on activated carbon (Pd/C; N.E. Chemcat Corp., Japan) in powdered form, which contained 5 wt.% of Pd. The BET specific surface and the dispersion of Pd metal 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. HCH isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH), whose purities were all >98%, were purchased from Wako Pure Chemical Industries Ltd., Japan. The molecular structures of HCH isomers are shown in Fig. 1. A technical-grade HCH powder was also used, which had been buried and stored in Japan for about 30 years. After drying at room temperature, the powder was used in the experiments. GC/MS analysis after extraction of the technical-grade powder with toluene revealed that it contained bentonite (ca. 64 wt.%), HCH isomers (34 wt.%) and a small amount of chlorobenzenes (CBs, <2 wt.%) and that the HCH isomers consisted of  $\alpha$ -HCH (65%),  $\beta$ -HCH (9%),  $\gamma$ -HCH (19%) and  $\delta$ -HCH (7%). All other chemicals were high-purity grade and were used without further purification.

### 2.2. Titration of HCH with NaOH

A solution of  $\gamma$ -HCH in 2-propanol (10 mmol/l, 10 ml) was prepared in a flat-bottomed flask. Then a solution of NaOH in 2-propanol (115 mmol/l, 0.4 ml) was added. After the solution was stirred vigorously (ca. 600 rpm) with a magnetic stirrer for 5 min at room temperature, an aliquot of the solution was taken for GC/MS analysis. Addition of NaOH and analysis were repeated until  $\gamma$ -HCH was not detected.

### 2.3. Dechlorination of HCH isomers and of technical-grade HCH powder

Dechlorination of individual HCH isomers was performed as follows. A solution of NaOH in 2-propanol (115 mmol/l, 4 ml) was placed in a Pyrex test tube (14-mm i.d.). A solution of HCH in 2-propanol (9–50 mmol/l, 1 ml) was then added. The mixture was stirred vigorously with a magnetic stirrer

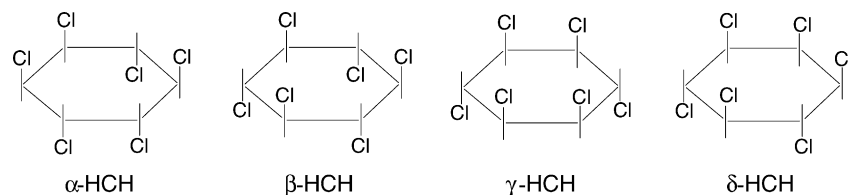


Fig. 1. Molecular structures of HCH isomers.

at room temperature ( $25 \pm 1^\circ\text{C}$ ) for 5 min. Then a catalytic amount of Pd/C (10 mg) was added. After a water-cooled condenser was attached to the top of the test tube, the reaction mixture was maintained at  $55^\circ\text{C}$  by means of a water bath and was stirred vigorously. The reaction was done under an air atmosphere. During the reaction, an aliquot was taken several times for GC/MS analysis.

Dechlorination of technical-grade HCH powder was performed in a similar manner. The powder (45 mg) was added to a solution of NaOH in 2-propanol (115 mmol/l, 5 ml), and the mixture was stirred at  $55^\circ\text{C}$  for 30 min. After the reaction mixture was cooled to room temperature, Pd/C (20 mg) was added. Then the reaction mixture was stirred at  $55^\circ\text{C}$  for 2 h. The yields of products were determined by analyzing an aliquot of the solution by GC/MS.

#### 2.4. GC/MS analysis

A sample taken from a reaction mixture was diluted with *n*-hexane containing *n*-dodecane as an internal standard. The concentrations of HCH isomers and products were determined based on the responses of individual standards relative to the internal standard, using a GC/MS instrument (GC: HP6890; MS: HP5973) equipped with an HP-5MS column (30 m  $\times$  0.25 mm, 0.25- $\mu\text{m}$  film thickness). The GC oven temperature was held at  $40^\circ\text{C}$  for 4 min followed by ramping at  $10^\circ\text{C}/\text{min}$  to  $250^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. Dechlorination of HCH isomers

First, we examined the reactions of HCH isomers with NaOH in 2-propanol, since HCH isomers are known to undergo dehydrochlorination to yield TCBS in a solution of NaOH in an ethanol–water mixture [7,8]. To determine the stoichiometry between an HCH isomer and NaOH,  $\gamma$ -HCH (as a representative HCH isomer) was titrated with NaOH. Fig. 2 shows plots of the molar amounts of  $\gamma$ -HCH consumed and TCBS produced as functions of the molar amount of NaOH added. As more NaOH was added, the amount of  $\gamma$ -HCH in the solution decreased and the solution became cloudy.  $\gamma$ -HCH almost disappeared when more than  $300\ \mu\text{mol}$  NaOH was added, which is three times the initial amount of  $\gamma$ -HCH. The amount of TCBS increased gradu-

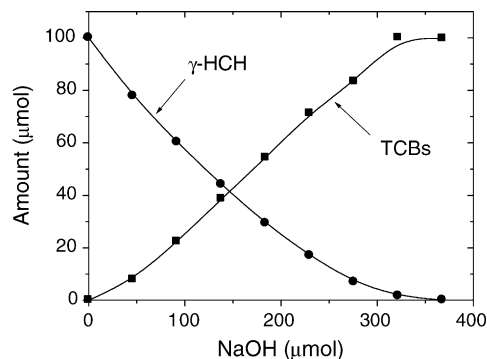


Fig. 2. Molar amounts of  $\gamma$ -HCH and TCBS during titration with NaOH.

ally as the amount of  $\gamma$ -HCH decreased, and the yield of TCBS reached 100% when the remaining  $\gamma$ -HCH reached zero. These results indicate that  $\gamma$ -HCH reacts with NaOH in a molar ratio of ca. 1:3 and is quantitatively transformed into TCBS. However, at NaOH concentrations at which transformation of  $\gamma$ -HCH to TCBS was incomplete, the mass balance between  $\gamma$ -HCH and TCBS was inconsistent; the maximum yield deficit was 18%, implying that an intermediate species is formed. GC/MS analysis revealed the presence of a species assignable to pentachlorocyclohexene, which is produced by removing one HCl from  $\gamma$ -HCH. Although the quantitative analysis of pentachlorocyclohexene was impossible for lack of a standard, the signal intensity correlated with the deficit in mass balance of  $\gamma$ -HCH and TCBS. The same intermediate species has been detected during dehydrochlorination of  $\gamma$ -HCH by the isooctane–aqueous KOH system [15]. In the electrochemical reduction of  $\gamma$ -HCH, tetrachlorocyclohexene (formed by removing two Cl atoms from  $\gamma$ -HCH) has been observed as an intermediate species [12].

Individual HCH isomers were reacted with a molar excess of NaOH ( $[\text{NaOH}]/[\text{HCH}] > 9$ ) in 2-propanol at room temperature for 5 min. The initial concentrations of HCH isomers in the reactions differed somewhat, since the solubility of HCH isomers into 2-propanol decreased in the order  $\delta > \gamma > \alpha > \beta$ . Table 1 summarizes the conversion of HCH isomers and the types of TCB isomers produced. The  $\alpha$ -,  $\gamma$ - and  $\delta$ -HCH isomers were completely converted to TCBS, but the conversion of  $\beta$ -HCH was 79%. Cristol [7,8] suggested that the lower reactivity of  $\beta$ -HCH arises from its molecular configuration; *trans*-elimination resulting in the removal of HCl should be greatly favored over *cis*-elimination, but  $\beta$ -HCH has no hydrogen atoms in a *trans* position relative

Table 1  
Dechlorination of HCH isomers in alkaline 2-propanol at room temperature for 5 min

	Initial concentration (mmol/l)		HCH conversion (%)	TCB selectivity (%)		
	HCH	NaOH		1,3,5-TCB	1,2,4-TCB	1,2,3-TCB
$\alpha$ -HCH	3.6	90	100	6.0	72.0	22.0
$\beta$ -HCH	1.8	90	79	7.2	87.2	5.6
$\gamma$ -HCH	10	90	100	15.6	80.6	3.8
$\delta$ -HCH	10	90	100	10.8	83.6	5.6

Table 2  
Catalytic dechlorination of TCBS in alkaline 2-propanol in the presence of Pd/C at 55 °C<sup>a</sup>

Time (min)	TCBs conversion (%)	Product yields (%)				
		<i>o</i> -DCB	<i>m</i> -DCB	<i>p</i> -DCB	MCB	Benzene
15	74.3	19.2	5.7	2.0	8.1	36.7
60	95.5	15.0	2.2	1.3	7.4	59.8
120	99.9	1.6	0.1	0.1	1.3	76.9
180	100	0	0	0	0	80.3

<sup>a</sup> TCBS were obtained by treatment of  $\gamma$ -HCH with NaOH. The initial composition of TCBS is shown in Table 1.

to a chlorine atom (Fig. 1). The proportions of three TCB isomers produced were slightly affected by the structure of the HCH isomers, but all HCH isomers were preferentially transformed to 1,2,4-TCB (Table 1). Previous papers have also reported preferential formation of 1,2,4-TCB during alkaline treatment of HCH isomers [7,8,15]. Zinovyev et al. [15] suggested that an intermediate species, pentachlorocyclohexene, consists of two conformations in equilibrium and the energetically lower conformer undergoes further dehydrochlorination to give 1,2,4-TCB.

After  $\gamma$ -HCH was treated with NaOH in 2-propanol, Pd/C was added and the solution was heated at 55 °C so that the TCB isomers produced would undergo catalytic dechlorination. We previously reported that catalytic dechlorination of 1,2,4-TCB to benzene proceeds efficiently in a solution of NaOH in 2-propanol in the presence of Pd/C, for which a molar excess of NaOH ( $[\text{NaOH}]/[1,2,4\text{-TCB}] > 3$ ) is required [16]. Even after NaOH (3 mole per mole of  $\gamma$ -HCH) was consumed during the alkaline treatment of  $\gamma$ -HCH, enough NaOH remained in the solution to complete the catalytic dechlorination of TCBS, since a large excess

of NaOH ( $[\text{NaOH}]/[\gamma\text{-HCH}] = 9$ ) was used in the alkaline treatment. Table 2, which summarizes the time dependence of the conversion of TCBS and the yields of dechlorinated products, shows that the dechlorination of TCBS proceeded in a stepwise manner, since dichlorobenzenes (DCBs) and monochlorobenzene (MCB) were observed during intermediate stages of the reaction. *o*-DCB was preferentially produced during the reaction. Benzene was obtained as a final product in high yield (80%). The deficit in material balance was probably due to the high volatility of benzene [15] and to adsorption by the catalyst support (activated carbon) [20].

When 1,2,4-TCB was dechlorinated separately with this Pd/C catalytic system, DCBs were produced as intermediates in the ratio *o*-DCB:*m*-DCB:*p*-DCB = 80:10:10. When 1,2,3-TCB was dechlorinated separately, the intermediate ratio was *o*-DCB:*m*-DCB:*p*-DCB = 99:1:0. Dechlorination of 1,3,5-TCB produced only *m*-DCB. Murena and Schioppa [25] reported that steric and electronic effects affect the dechlorination selectivity of chlorinated aromatic compounds over a sulfidated Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst; the rate of removal of a

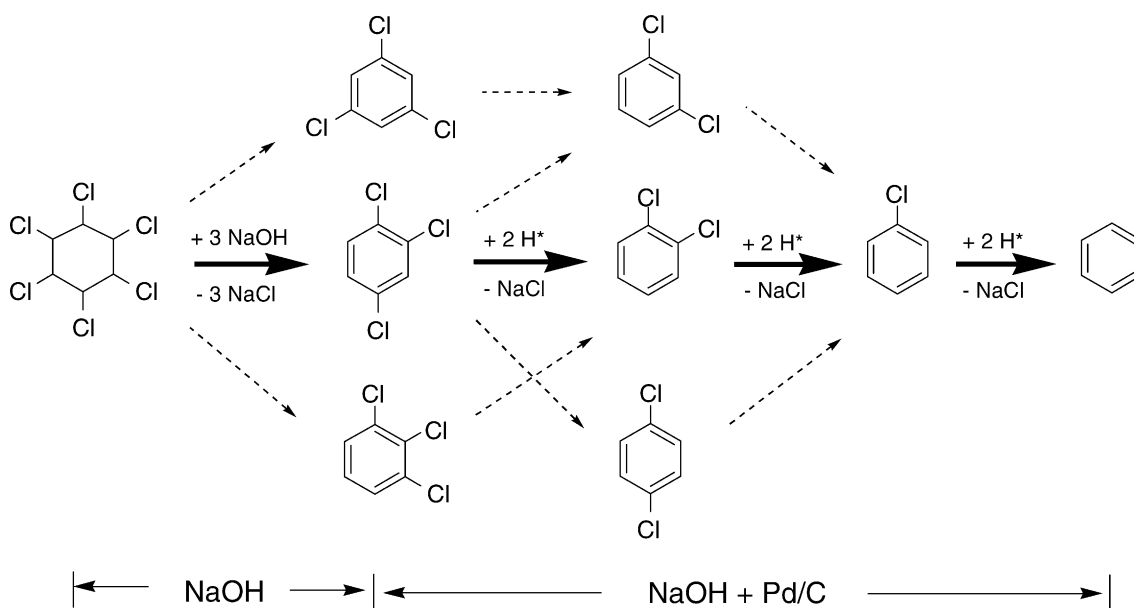


Fig. 3. Dechlorination pathways of HCH in 2-propanol. The bold arrows indicate the main route, and the dotted arrows indicate the minor routes. H\* denotes a hydrogen species generated from 2-propanol.

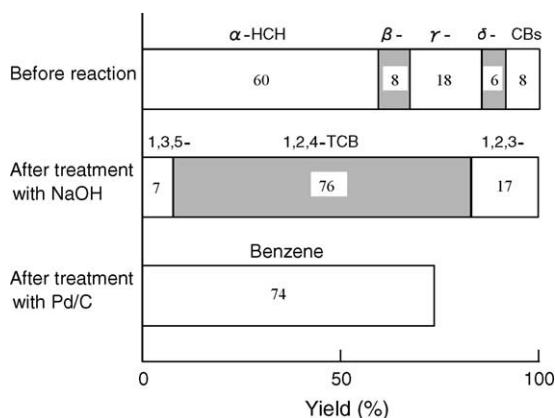


Fig. 4. Dechlorination of technical-grade HCH powder at 55 °C.

chlorine atom located between two hydrogen atoms is higher than that of a chlorine atom between two chlorine atoms, and that of a chlorine atom between a chlorine atom and a hydrogen atom is intermediate.

Fig. 3 shows the dechlorination pathways of HCH isomers occurring upon NaOH treatment and subsequent catalytic reaction with Pd/C. Dechlorination of HCH isomers proceeds preferentially by the highlighted pathway to produce benzene as the final product. A molar amount NaOH ( $[\text{NaOH}]/[\text{HCH}] = 6$ ) is necessary to transform HCH to benzene.

### 3.2. Dechlorination of technical-grade HCH powder

We next examined dechlorination of technical-grade HCH powder, which is a mixture of HCH isomers. Fig. 4 shows the initial composition of the chlorinated substrate and the yields of products after treatment with NaOH and subsequent addition of Pd/C. The initial powder contained relatively large amounts of CBs (mainly TCBs) as impurities, probably because the prolonged storage caused dechlorination of HCH isomers.

The powder was treated with NaOH in 2-propanol for 30 min at 55 °C. The temperature was higher than in the experiment with individual HCH isomers because we wanted to enhance the reaction rate of β-HCH, which is less reactive than the other HCH isomers (Table 1). During this treatment, HCH isomers became dissolved in 2-propanol and were quantitatively transformed to TCBs in an isomer ratio of 1,3,5-TCB:1,2,4-TCB:1,2,3-TCB = 7:76:17 (Fig. 4). Trace amounts of β-HCH, DCBs and MCB were also detected; the total yields were less than 0.5% (not shown in Fig. 4). Then Pd/C was added to the solution and catalytic dechlorination was done at 55 °C for 2 h. Benzene was produced in high yield (74%), and β-HCH, DCBs and MCB were not detected. Thus, dechlorination of technical-grade HCH powder was accomplished. The bentonite in the sample was insoluble in 2-propanol and was recovered as a precipitate after the reaction.

## 4. Conclusions

We demonstrated that HCH isomers (α-, β-, γ- and δ-HCH) could be dechlorinated to benzene in the presence of alkaline 2-propanol and a supported palladium catalyst (Pd/C). All HCH isomers released HCl molecules in a solution of NaOH in 2-propanol at room temperature and were transformed to TCBs (predominantly 1,2,4-TCB), although the reaction rate of β-HCH was lower than that of the other HCH isomers. Catalytic dechlorination of TCBs occurred upon subsequent addition of Pd/C and heating at 55 °C, and benzene was produced in high yield (>80%); 2-propanol was the hydrogen source. Successful dechlorination of technical-grade HCH powder was achieved in a similar manner. This method is facile and operates under mild conditions, which constitute advantages for practical disposal of HCH stockpiles.

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