

DECHLORINATION OF HEXACHLOROCYCLOHEXANE WASTE IN ALKALINE 2-PROPANOL WITH PALLADIUM CATALYSTS

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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 HCH isomers are used under the name "lindane" (almost pure γ -HCH) or as a technical-grade product consisting of α -HCH, β -HCH, γ -HCH, δ -HCH, and other minor components.¹ The total global usage of technical-grade HCH during the half century from 1948 to 1997 was estimated to be around 10 million tons.² Many countries banned or restricted 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 this paper, we report dechlorination of technical-grade HCH powder (a mixture of HCH isomers and bentonite) in a solution of NaOH in 2-propanol with palladium catalysts under mild conditions (1 atm, air atmosphere, 82°C). We also analyzed dioxin impurities (polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (co-PCBs)) contained in the powder before and after the reaction.

Materials and Methods

The catalysts used in this study were palladium supported on activated carbon (Pd/C; 5 wt.% of Pd) and palladium supported on alumina (Pd/Al₂O₃; 5 wt.% of Pd) in powdered forms. They were purchased from N.E. Chemcat Corp., Japan. The BET specific surface area and the metal dispersion were 1035 m²/g and 24 %, respectively, for Pd/C and 205 m²/g and 15 %, respectively, for Pd/Al₂O₃. The technical-grade HCH powder stored in Japan for long time (about 30 years) was used as the substrate after drying at room temperature. The powder sample contained bentonite, HCH isomers (34 wt.%), and a small amount of chlorinated benzenes (< 2 wt.%; mainly trichlorinated species). The HCH isomers consisted of α -HCH (65 %), β -HCH (9 %), γ -HCH (19 %), and δ -HCH (7 %). The molecular structures of HCH isomers are shown in Figure 1.

The dechlorination reaction was done in a flat-bottom glass flask with a water-cooled condenser. The powder sample (1.0 g) was added to a solution of NaOH in 2-propanol (0.11 mol/l, 100 ml), and the mixture was stirred vigorously (ca. 900 rpm) with a magnetic stirrer at room temperature for 5 min. Then the Pd catalyst (0.20 g) was added, and the mixture was stirred vigorously and heated to 82°C (reflux condition). The concentrations of HCH isomers and products were determined by analyzing an aliquot of the solution using a GC/MS instrument (GC: HP6890; MS: HP5973) equipped with an HP-5MS column (30 m × 0.25 mm, 0.25- μ m film thickness). The concentrations of PCDDs, PCDFs, and co-PCBs, including those adsorbed on the catalyst, were determined by the procedure outlined in a previous paper,³ and were indicated based on the weight of powder sample used for the reaction (pg/g or ng/g).

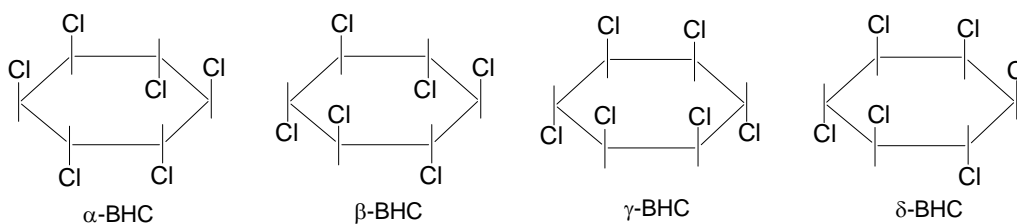
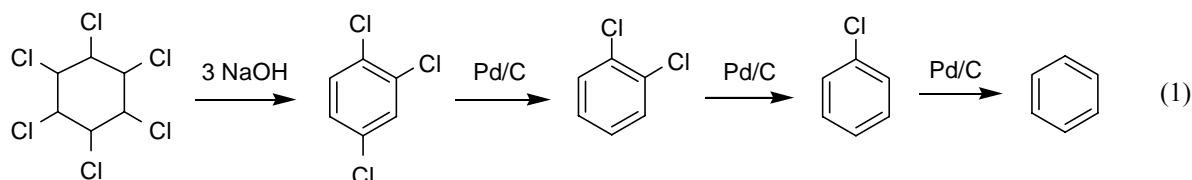


Figure 1: Molecular structures of HCH isomers

Results and Discussion

Dechlorination of HCH isomers contained in the technical-grade HCH powder

We previously reported that HCH isomers were dechlorinated to trichlorobenzenes in 2-propanol by means of stoichiometric reaction with three equivalents of NaOH and then the produced trichlorobenzenes were catalytically dechlorinated stepwise to benzene by subsequently adding Pd/C to the solution of NaOH in 2-propanol; the main dechlorination route is shown in Eq.(1).⁴ In the catalytic dechlorination of trichlorobenzenes with Pd/C, 2-propanol behaved as a hydrogen donor, and NaOH scavenged the released Cl⁻ to form NaCl.⁵



In this study, we carried out dechlorination of the technical-grade HCH powder in a solution of NaOH in 2-propanol in the presence of Pd/C or Pd/Al₂O₃ at 82°C. The HCH isomers were dissolved rapidly into the solution and were dechlorinated stepwise (Eq.(1)). After the reaction for 20 min, no HCH isomers were detected; instead, trichlorobenzenes and lower-chlorinated benzenes were detected. The degree of dechlorination was evaluated by the following equation: Dechlorination (%) = 100 x (Cl₀ - Cl_t) / Cl₀, where Cl₀ is total molar amount of Cl bonding to HCH isomers and chlorinated benzenes at t=0, and Cl_t is total molar amount of Cl bonding to the products at the sampling time. As seen in Table 1, the dechlorination reaction with Pd/C was completed within 3 h, but the reaction with Pd/Al₂O₃ needed longer time (5 h) to complete dechlorination. The difference in catalytic activity may arise from higher metal dispersion of Pd/C than Pd/Al₂O₃.

Table 1: Time dependence of dechlorination of HCH isomers

Catalyst	Dechlorination (%)			
	20 min	1 h	3 h	5 h
Pd/C	87.5	99.8	>99.9	
Pd/Al ₂ O ₃	72.6	82.2	94.4	>99.9

Dechlorination of dioxin impurities contained in the technical-grade HCH powder

We analyzed the concentrations of dioxins before the reaction and after complete dechlorination of HCH isomers (>99.9 %). Before the reaction, the homologues of PCDDs and PCDFs were distributed with a maximum value at OCDD and at TeCDFs, respectively, and the concentration of co-PCBs was relatively high (Figure 2A); the total TEQ value was evaluated to be 864 pg-TEQ/g (Table 2). After the reaction with Pd/C for 3 h, the concentrations of PCDDs and PCDFs decreased, but the concentration of co-PCBs increased considerably (Figure 2B); the total TEQ value was evaluated to be 692 pg-TEQ/g (Table 2). Increase in the concentration of co-PCBs indicates that co-PCBs were not only dechlorinated but also synthesized during the reaction. In the dechlorination of chlorinated benzenes in alkaline 2-propanol with Pd/C, we had observed trace amounts of biphenyl compounds as by-products.⁶ Therefore, we suppose the #77 isomer, whose concentration is much higher than other co-PCB isomers, was produced by dimerization of the intermediate product, 1,2,4-trichlorobenzene (Eq.(1) and (2)). Dioxins and products were left on the Pd/C catalyst, because the activated carbon support has large surface area and strong adsorption ability;³ they were recovered after the dechlorination reaction. As for the reaction with Pd/Al₂O₃ for 5 h, the concentrations of PCDDs, PCDFs, and co-PCBs drastically decreased (Figure 2C); the total TEQ value was evaluated to be 28 pg-TEQ/g (Table 2). Thus, the choice of catalyst support is an important factor for achieving high toxicity reduction.

In conclusion, HCH isomers and dioxins contained in the technical-grade HCH powder were successfully

dechlorinated in a solution of NaOH in 2-propanol in the presence of Pd/Al₂O₃ at 82°C; Pd/C was excellent for dechlorination of HCH isomers, but not efficient for dechlorination of dioxin impurities.

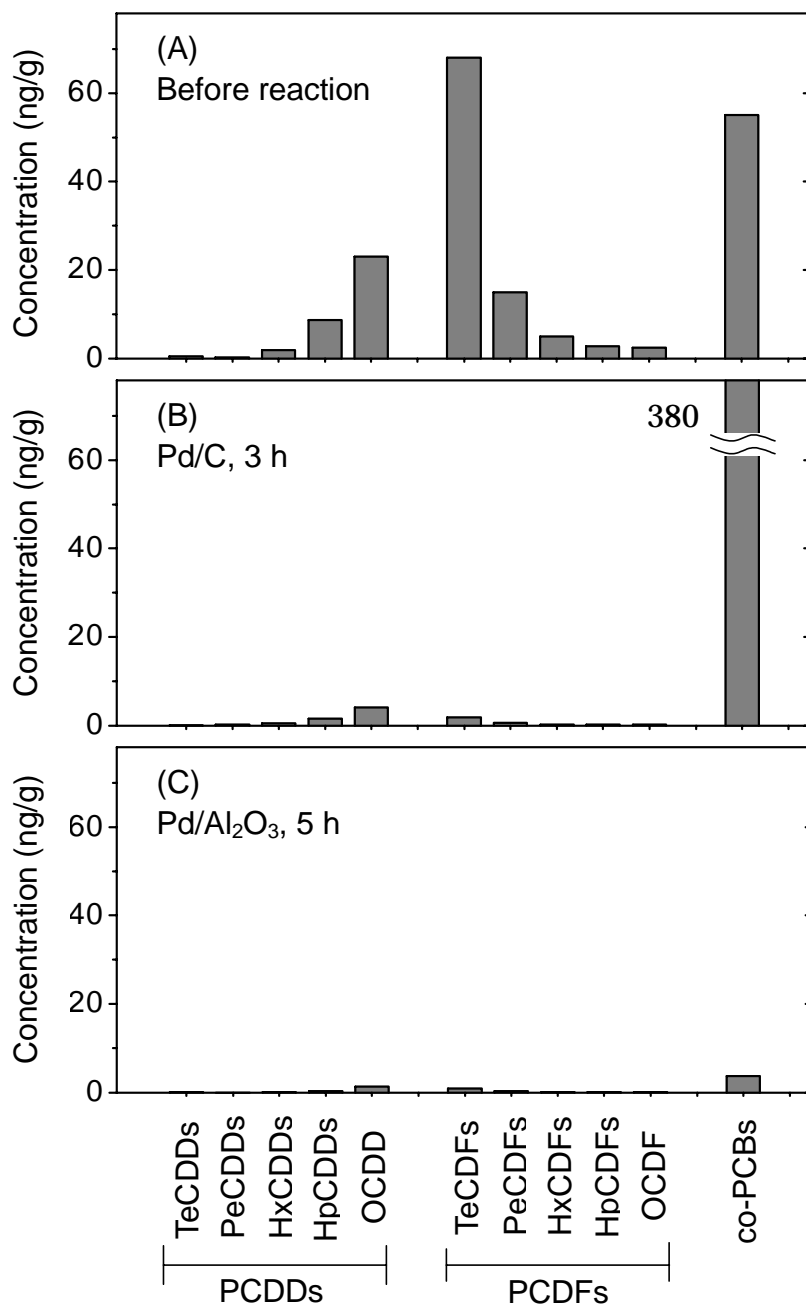
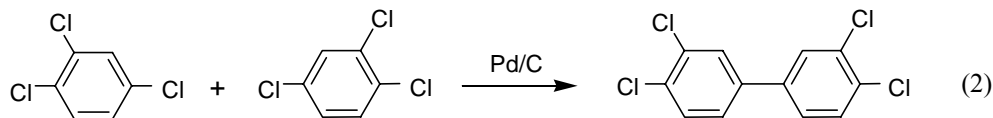


Figure 2: Concentration changes in PCDD/F homologues and co-PCBs

Table 2: Concentration changes in isomers of PCDDs, PCDFs and co-PCBs

PCDDs/PCDFs co-PCBs	WHO-TEF (1998)	Concentration (pg/g)		
		Before reaction	After reaction with Pd/C for 3 h	After reaction with Pd/Al ₂ O ₃ for 5 h
2,3,7,8-TeCDD	1	3.5	2	ND ^a
1,2,3,7,8-PeCDD	1	21	18	ND ^a
1,2,3,4,7,8-HxCDD	0.1	200	20	ND ^b
1,2,3,6,7,8-HxCDD	0.1	55	29	ND ^b
1,2,3,7,8,9-HxCDD	0.1	14	82	ND ^b
1,2,3,4,6,7,8-HpCDD	0.01	2600	510	130
OCDD	0.0001	23000	4100	1300
TEQ (pg/g)		80	39	1.4
2,3,7,8-TeCDF	0.1	51	19	6
1,2,3,7,8-PeCDF	0.05	6000	8	85
2,3,4,7,8-PeCDF	0.5	230	18	9
1,2,3,4,7,8-HxCDF	0.1	490	20	15
1,2,3,6,7,8-HxCDF	0.1	180	11	6
1,2,3,7,8,9-HxCDF	0.1	ND ^a	ND ^b	ND ^b
2,3,4,6,7,8-HxCDF	0.1	47	ND ^b	ND ^b
1,2,3,4,6,7,8-HpCDF	0.01	400	54	35
1,2,3,4,7,8,9-HpCDF	0.01	210	22	11
OCDF	0.0001	2400	250	100
TEQ (pg/g)		498	15	12
3,4,4',5'-TeCB (#81)	0.0001	320	710	25
3,3',4,4'-TeCB (#77)	0.0001	6900	37000	2700
3,3',4,4',5'-PeCB (#126)	0.1	1700	6000	140
3,3',4,4',5,5'-HxCB (#169)	0.01	11000	110	16
2',3,4,4',5'-PeCB (#123)	0.0001	130	78	16
2,3',4,4',5'-PeCB (#118)	0.0001	3600	400	190
2,3,3',4,4'-PeCB (#105)	0.0001	27000	830	520
2,3,4,4',5'-PeCB (#114)	0.0005	290	9	7
2,3',4,4',5,5'-HxCB (#167)	0.00001	400	14	8
2,3,3',4,4',5'-HxCB (#156)	0.0005	780	14	15
2,3,3',4,4',5'-HxCB (#157)	0.0005	2600	100	80
2,3,3',4,4',5,5'-HpCB (#189)	0.0001	650	ND ^b	ND ^b
TEQ (pg/g)		286	638	15
Total TEQ (pg/g)		864	692	28

^a < 2, ^b < 5

References

1. Kutz FW, Wood PH, Bottimore DP. *Rev Environ Contam Toxicol* 1991;120:1.
2. Li YF. *Sci Total Environ* 1999;232:121.
3. Ukisu Y, Miyadera T. *Appl Catal A: Gen* 2004;271:165.
4. Ukisu Y, Miyadera T. *J Hazard Mater* 2005;122:1
5. Ukisu Y, Miyadera T. *J Mol Catal A: Chem* 1997;125:135.
6. Ukisu Y, Miyadera T. *React Kinet Catal Lett* submitted