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Dechlorination of hexachlorobiphenyl by using potassium–sodium alloy

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Abstract

2,2′,4,4′,5,5′-Hexachlorobiphenyl (HCB) was dechlorinated with potassium–sodium (K–Na) alloy under an inert gas atmosphere. Solvent effect was observed in the reaction. Dechlorination yields in benzene and cyclohexane were 99.9998% and 99.99996%, respectively. The reaction was exothermic and proceeded at room temperature. In benzene, trace amounts of polychlorinated biphenyls (PCBs) as products by stepwise dechlorination and polychlorinated quarterphenyls as product of Wurtz–Fittig reaction were detected as reaction intermediate. Reaction products were biphenyl, cyclohexylbenzene, and dicyclohexyl. In cyclohexane, there were no products of Wurtz–Fittig reaction. Dechlorination at para-position preferred to that at ortho-position, judging from analysis of PCBs as intermediates of stepwise dechlorination.

Keywords: Reaction mechanism; By-products; PCBs; Reduction

1. Introduction

The waste polychlorinated biphenyls (PCBs) must be stored under closed condition in Japan until the Minister of Japan Environment Agency directs decomposition methods. At present, about 150 000 t of waste PCBs including PCB-containing insulating oil, as well as 436 000 t of various materials contaminated with PCBs, including electrical equipment, pressure-sensitive paper containing PCBs, PCB-containing sludge and waste, are reported to be in storage awaiting decomposition. The Ministry of Health and Welfare has reported that the amount of waste PCBs lost or missing during storage is increasing, because the storage period has already exceeded more than 20 yr. Therefore, decomposition of PCBs in storage is desired urgently.

Recently, the Japan Environment Agency has decided that waste PCBs should be destroyed by chemical treatments in place of incineration or high-temperature pyrolysis. Lots of investigation has been carried out on chemical decomposition. Representative methods are potassium tert-butoxide method (Ono and Hirata, 1996), degradation method by using alkali–metal hydroxide and polyethylene glycol (DesRosiers, 1989; De Filippis et al., 1997), decomposition method with alkali–metal hydroxide in aprotic solvent such as 1,3-dimethyl-2-imidazolidinone (Toma and Dohmoto, 1997), base catalyzed decomposition (BCD) method (Taniguchi et al., 1996; Taniguchi, 1997) developed by the US Environmental Protection Agency, supercritical water oxidation method (Anjoh et al., 1997), catalytic extraction method (Chanenchuk et al., 1996) developed by Molten Metal Technology in the US, metallic sodium method (Ariizumi et al., 1997; Suzuki, 1997), dehalogenation method with sodium/naphthalene (Oku et al., 1978),

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catalytic hydrogenation (Marques et al., 1994; Liu et al., 1998), dechlorination (Epling et al., 1988; Roth et al., 1994; Liu et al., 1995) with reductants such as $NaBH_4$ and the method (Chaudhary et al., 1984; Hawari et al., 1991, 1992; Zhang et al., 1993; Lin et al., 1995; De Felip et al., 1996; Huang et al., 1996; Lin et al., 1996; Kinbara, 1997; Yao et al., 1997; Schmelling et al., 1998) using ultraviolet irradiation. Two methods have been reported in regard to the metallic sodium method. One is sodium dispersion method, where sodium powder is dispersed in non-reactive oil, and the other sodium naphthalene method, where sodium is dissolved with naphthalene in tetrahydrofuran.

The method developed in this paper is a modification of metallic sodium method. Potassium–sodium (K–Na) alloy in place of sodium powder. The alloy is reactive liquid at room temperature. In this paper, perfect dechlorination of 2,2′,4,4′,5,5′-HCB has been accomplished and toxic by-products have not been detected. Reaction mechanism for dechlorination is discussed.

2. Experimental

2.1. Chemicals

2,2′,4,4′,5,5′-hexachlorobiphenyl (HCB) was synthesized from 2,2′,5,5′-tetrachlorobenzidine according to the literature (Safe and Hutzinger, 1972). Purity of HCB was 99.0% by gas chromatography equipped with fame ionization detector. Hexane, benzene, cyclohexane, methanol, and dichloromethane, which were of special grade, were purchased from Wako Pure Chemical Industries, Osaka, Japan. Solvents for dechlorination reaction were dried with small slices of sodium before use. Sodium and potassium, of practical grade , were purchased from Wako Pure Chemical Industries, Osaka, Japan, and Aldrich Chemical Company, Milwaukee, USA, respectively. Silica gel for column chromatography, whose commercial name was Wakogel C-200, was obtained from Wako Pure Chemical Industries, Osaka, Japan. The silica gel was used without any acitivation procedure. Pure water was generated with the Milli-Q System (Millipore, USA).

2.2. General procedure for dehalogenation with K–Na alloy

Sodium (1.15 g) and potassium (1.95 g) are put into three-necked flask (300 ml) under atmosphere of argon and heated lightly until liquid alloy is produced. All operations are done under atmosphere of argon until methanol is added into the reaction mixture for removal of unreacted K–Na alloy. Thirty-five milliliters of benzene or cyclohexane is poured into the flask as reaction solvent. Then, 0.6347 g of HCB in 35 ml of solvent is added drop by drop into the flask under stirring for 15 min. Ten milliliters of solvent is further added to the reaction mixture after addition of HCB. The reaction mixture is refluxed for 2 h after 30 min keeping at room temperature. After cooling, residual K–Na alloy is destroyed with methanol. The reaction mixture is concentrated to ca. 50 ml with a rotary evaporator and the residual solution is diluted with 20 ml of water. Organic substances in the solution are extracted with hexane (20 ml) and the aqueous layer and the hexane layer are separated. The hexane layer is washed with 20 ml of water. The aqueous layers are combined and are used for measurement of chloride anion. The organic layer is dried with anhydrous sodium sulfate and concentrated to ca. 1 ml. The concentrated solution is cleaned up by column chromatography using silica gel (10 g) and hexane (200 ml). The elute is concentrated to 0.5 ml by using rotary evaporator and successive nitrogen-blowing. Details of reaction conditions are shown in Table 1.

2.3. Measurement of chloride anion

Chloride anion was measured with an instrument, Model IM-40S ion meter purchased from the TOA Electronics, Tokyo, Japan. Analytical principle was a measurement with an electrode for chloride anion.

2.4. Gas chromatography/mass spectrometry

An aliquot of the concentrated solution was injected into a gas chromatograph–mass spectrometer. The

Table 1
Reaction conditions for dechlorination of 2,2′,4,4′,5,5′-HCB

	Run 1	Run 2	Run 3
Amount of HCB (mmol)	1.76	1.76	1.76
Dropping rate of HCB solution (ml/min)	2.5	2.9	2.9
Amount of potassium (mol)	0.05	0.05	0.05
Amount of sodium (mol)	0.05	0.05	0.05
Solvent	Benzene	Cyclohexane	Cyclohexane
Volume of solvent (ml)	80	80	80
Reaction time before heating (min)	30	30	15
Period of heating (min)	120	120	0

operational conditions were as follows: Instrument, Hewlett Packard 5972 mass selective detector equipped with Hewlett Packard 5890 Series II Plus gas chromatograph; column, PTE™-5 fused silica capillary (30 m length, 0.25 mm i.d., 0.25 μm film thickness); oven temperature, 50°C for 1 min, 20°C/min ramp to 220°C, followed by a second ramp of 5°C/min to 300°C for 5-min hold; injector temperature, 280°C; interface temperature, 300°C; carrier gas (He) head pressure, 82 kPa; carrier gas flow rate, 1.4 ml/min; linear velocity of carrier gas, 43.0 cm/s; injection mode, splitless; purge time, 60 s; ion-source temperature, 192°C; ion-source pressure, 6.4×10^{-5} Torr; ionizing energy, 70 eV. Quantitation was carried out by using SIM mode on mass spectrometry. Monitor ions were shown in Table 2.

2.5. Total organic chlorine (TOX) measurement

One hundred microliters of sample solution was combusted at 900°C in a quartz container under oxygen flow after evaporation of solvent. The incineration exhaust gas was passed through an electrolytic solution, made of 85% acetic acid and 0.136% sodium acetate, after removal of water in the gas by passing the gas through conc. H_2SO_4. Concentration of chloride anion in the electrolytic solution was determined by electrolysis titration using silver electrode using a Mitsubishi Kagaku Titration Model TOX-10. The lower quantitation limit was 0.3 μg/ml.

Table 2
Monitor ions on gas chromatography/mass spectrometry

Compound	Ion 1	Ion 2
Monochlorobiphenyl	188	190
Dichlorobiphenyl	222	224
Trichlorobipheny	256	258
Tetrachlorobiphenyl	290	292
Pentachlorobiphenyl	326	328
Hexachlorobiphenyl	360	362
Biphenyl	154	
Dicyclohexyl	166	
Cyclohexylbenzene	160	

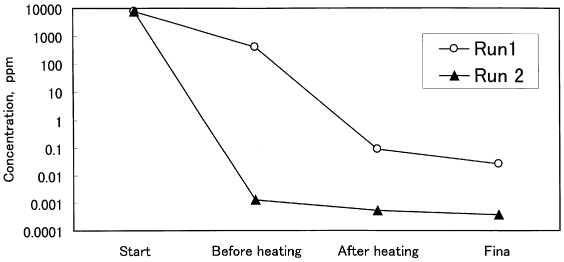


Fig. 1. Decrease of concentration of parent HCB.

3. Results and discussion

Runs 1 and 2 were performed for investigating solvent effect and run 3 was carried out for detecting reaction intermediates in dechlorination. Therefore, heating was not done in run 3 and reaction time was shorter than in run 2.

Reaction between HCB and K–Na alloy was exothermic. Temperature increases in reaction mixture before heating were 8°C for run 1 and 15°C for runs 2 and 3. This difference is due to ability as a hydrogen donor which solvent has in this reaction. Cyclohexane is better than benzene as a solvent.

Insoluble sludge was generated with dechlorination proceeding. The sludge was composed of inorganic salt and adsorbed a small amount of HCB on the surface. The rate of HCB adsorbed on the sludge was around 0.00003% based on starting amount. Dechlorination yields in run 1 were 94.33% before heating and 99.9998 after final treatment. On the other hand, dechlorination yield in run 2 was 99.99996% before heating and this yield was equal to the yield after final treatment. The decrease of parent HCB in the reaction is shown in Fig. 1. This means that the dehalogenation in cyclohexane proceeds rapidly and quantitatively within 30 min at room temperature. Namely, cyclohexane seems to be an excellent solvent in this reaction. The reason is a powerful hydrogen-donating ability of cyclohexane, compared with benzene.

Material balance of chlorine is shown in Table 3. Chlorine in other chlorinated compounds except for parent HCB and polychlorobiphenyls newly formed was calculated by subtracting total chlorine of parent HCB and polychlorobiphenyls newly formed from total organic chlorine determined experimentally. Judging from this result, chlorine atoms in HCB changed almost

Table 3
Material balance of chlorine in dechlorination reaction

	Chloride anion (%)	Parent HCB remaining (%)	Polychlorobiphenyl newly formed (%)	Other chlorinated compounds calculated from TOX (%)	Total (%)
Run 1	97.7	0.6	0.1	0.9	99.3
Run 2	102.0	0.0	0.0	0.0	102.0

completely to chloride anion both in runs 1 and 2. This conclusion is in accordance with the observation that by-products containing chlorine have not been detected or a little detected.

Small amounts of PCBs having 1–5 chlorine atoms were detected. These compounds are thought to be intermediates in dechlorination. Intermediate formations are showed in Figs. 2 and 3. Various kinds of PCBs were observed in run 1, but most of them were almost dehalogenated in final stage. On the other hand, a few PCBs were observed in run 2 and their concentrations were extremely low. Quantity of monochlorobiphenyl was more than other chlorinated biphenyls both in runs 1 and 2.

By-products detected in run 1, which contained chlorine atoms, were polychlorinated terphenyls and quaterphenyls, where the number of chlorine atoms was 3–5, except for PCBs. They were produced by the Wurtz–Fittig reaction. They disappeared after heating reaction mixture. In run 2, they were not detected at all.

Reduction products detected were biphenyl, cyclohexylbenzene, and cyclohexen-1-ylbenzene in run 1 and dicyclohexyl, biphenyl, cyclohexylbenzene, and cyclohexen-1-ylbenzene in run 2. Production situation is shown in Fig. 4. Amounts of reduction products analyzed by gas chromatography were not so much, because most of dechlorinated products or reduction products seemed to polymerize to insoluble amorphous materials which were organic substances not containing any chlorine atoms as demonstrated by TOX measurement. Amounts (ca. 0.3 g) of amorphous materials were nearly equal to the calculated amount (minimum 0.27 g) of perfectly dechlorinated products.

Intermediates in this dechlorination were determined in run 3. The analytical results are shown in Table 4. Dechlorination mechanism is considered in Fig. 5. Chlorine atom located at para-position in PCBs was more reactive than at ortho-position because of steric hindrance. This mechanism is different from the dechlorination mechanism in photolysis where dechlorination at ortho-position is more preferable.

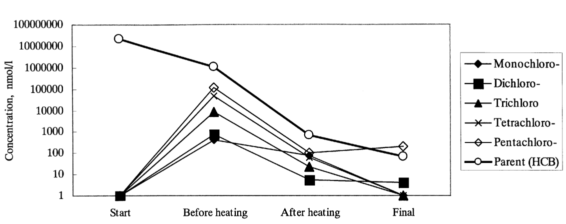


Fig. 2. Concentrations of parent HCB and dechlorinated PCBs in benzene.

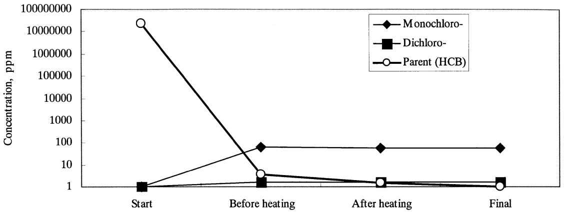
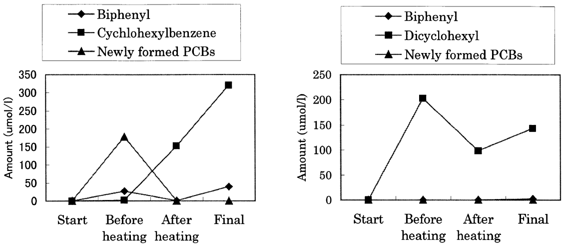


Fig. 3. Concentrations of parent HCB and dechlorinated PCBs in cyclohexane.



(Run 1) (Run 2)

Fig. 4. Formation of reduction products in dechlorination of HCB.

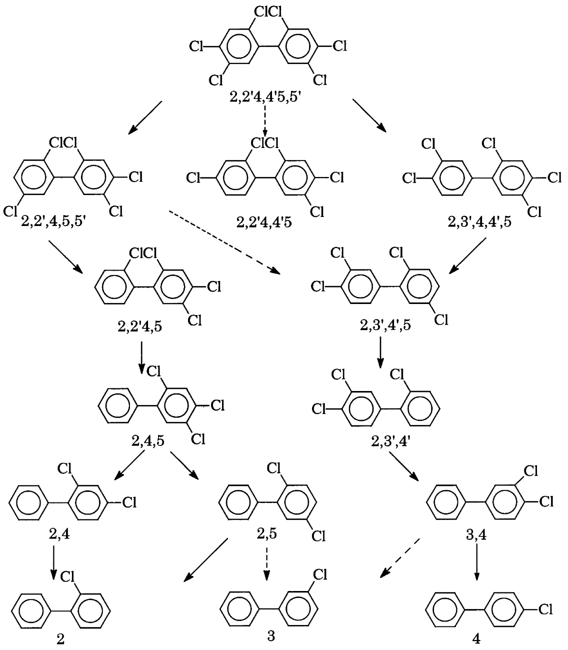


Fig. 5. Estimated dechlorination mechanism of 2,2′,4,4′,5,5′-HCB.

Table 4
PCB isomers detected as intermediates in experiment run 3[a]

Compound	Retention time (min)	Concentration (nmol/ml)
2-Chlorobiphenyl	8.35	0.077
3-Chlorobiphenyl	8.80	0.036
4-Chlorobiphenyl	8.85	0.007
2,2′-Dichlorobiphenyl	9.09	0.095
2,4-/2,5-Dichlorobiphenyl	9.37	0.145
2,3′-Dichlorobiphenyl	9.50	0.066
2,4′-Dichlorobiphenyl	9.56	0.015
3,3′-Dichlorobiphenyl	9.94	0.04
3,4-/3,4′-Dichlorobiphenyl	10.02	0.16
2,2′,5-Trichlorobiphenyl	10.05	0.588
2,4,5-Trichlorobiphenyl	10.45	0.752
2,3′,5-Trichlorobiphenyl	10.50	0.147
2,4′,5-/2,4,4′-Trichlorobiphenyl	10.61	0.028
2,3′,4′-Trichlorobiphenyl	10.76	0.840
3,3′,4-Trichlorobiphenyl	11.34	0.300
3,4,4′-Trichlorobiphenyl	11.46	0.038
2,2′,5,5′-Tetrachlorobiphenyl	11.09	0.901
2,2′,4,5′-Tetrachlorobiphenyl	11.16	0.187
2,2′,4,4′-/2,2′,4,5-Tetrachlorobiphenyl	11.22	8.86
2,3′,4,5-Tetrachlorobiphenyl	11.80	1.11
2,4,4′,5-Tetrachlorobiphenyl	11.95	0.186
2,3′,4′,5-Tetrachlorobiphenyl	12.01	2.59
2,3′,4,4′-Tetrachlorobiphenyl	12.07	0.17
2,2′,4,5,5′-Pentachlorobiphenyl	12.50	38.2
2,2′,4,4′,5-Pentachlorobiphenyl	12.59	6.96
2,3′,4,4′,5-Pentachlorobiphenyl	13.69	14.5

[a] Concentration of 2,2′,4,4′,5,5′-HCB (parent compound) was 770 nmol/ml in this sample.

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