Bull. Chem. Soc. Jpn., ***76***, *567–568 (2003)*

Degradation of Polychlorobiphenyls with Potassium Carbonate in Supercritical Water

Fuminori Akiyama

Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University, Sendai 980-8577

(Received August 7, 2002)

The degradation processes of 2,2′,5,5′-tetrachlorobiphenyl (4Cl-B) and 2,2′,4,4′,5,5′-hexachlorobiphenyl (6Cl-B) with potassium carbonate in supercritical water at 500 °C were studied. Hydrocarbons containing methane as major component were formed in the yield of around 15%. The main reaction product is considered to be inorganic salts, which do not show any NMR spectra and are easily decomposed by dilute acid.

Polychlorobiphenyl (PCB) had long been used as heat exchanger, insulation oil, or dielectric fluid. However, in the 1970's their production and utilization have been prohibited, since their stabilities have brought about serious environmental problems. Many methods have been proposed to degradate PCBs. For chemical degradation methods, hydrogenolysis at high temperature,[1] catalytic hydrogenolysis,[2] base-catalyzed decomposition method,[3] and potassium salt of polyethylene glycol process,[4] have been reported. Degradation using supercritical water has also been investigated.[5,6]

In a previous paper degradation of PCB, 4-chlorobiphenyl (Cl-B) with potassium carbonate in supercritical water has been reported.[7] In the present report, degradation processes of 2,2′,5,5′-tetrachlorobiphenyl (4Cl-B) and 2,2′,4,4′,5,5′-hexachlorobiphenyl (6Cl-B) with potassium carbonate in supercritical water were investigated to elucidate substituent effect of chlorine atoms in degradation of PCB.

When a mixture of PCB, potassium carbonate, and water was heated at 500 °C for an appropriate time, a mixture of hydrocarbons, acetone, and residue was obtained, results being shown in Table 1. In this table, yields of HCO_3^- were determined by the method described in the previous paper and were calculated by Eq. 1, in place of Eq. 5 that was shown in the previous paper,[7]

$$0.5 \times 100 \times ((HCO_3^-)_{obsd} - f \times n \times (\text{mol of PCB}))/ \\ (12 \times \text{moL of PCB used}) \qquad (1)$$

f being the fraction of chlorine atoms released as chloride ions, which was judged from the value of $(\text{Silver salt})_{obsd}/(\text{AgCl})_{calcd}$ shown in Table 2 (vide infra), and n being the number of chlorine atom contained in the PCB.

After analyses of gaseous products, the aqueous reaction solution was filtrated to give a black residue, yields of black residue being shown in Table 1. Although the solid obtained by

Table 1. Yields of Hydrocarbons Formed by the Reaction of PCBs with Potassium Carbonate in Supercritical Water at 500 °C

Entry	Substrate	Time/h	Residue	Yield of product/%[b]										
			(%)[a]	CH_4	C_2	$\geqq C_3$	C_6H_6	C_7H_8	C_8H_{10}	Acetone	Total[c]	HCO_3^-	CO_2	4-Biphenylol
1	4Cl-B	3	12.0	4.31	0.13	0.14	0.33	0.21	t	0.54	5.66	14.2	2.0	—[d]
2	4Cl-B	6	8.7	6.04	0.19	0.12	0.42	0.25	t	0.62	7.64	12.6	2.1	—[d]
3	4Cl-B	24	7.1	11.8	0.43	0.38	1.42	0.61	0.15	0.43	15.2	17.1	2.3	—[d]
4	6Cl-B	3	12.4	5.79	0.33	0.16	0.41	0.04	t	0.89	7.62	2.0	3.2	—[d]
5	6Cl-B	6	8.4	7.60	0.41	0.37	0.57	0.47	t	1.14	10.56	4.9	5.0	—[d]
6	6Cl-B	24	8.3	12.7	0.49	0.41	0.90	0.77	0.16	0.51	15.9	3.0	7.4	—[d]
7[e]	Cl-B	24	—[f]	2.10	0.08	0.04	1.46	5.87	0.3	0.15	10.0	n.d[g]	0.16	14.4

a) wt%. b) carbon basis. c)Summation of the aliphatic and aromatic hydrocarbons and acetone. d)Not determined because of small quantity. e) Ref. 7. f) Black residue was not obtained. g) Not determined.

Table 2. Analyses of Chloride Ion Formed in the Reaction Solution and Residue Formed by the Reaction of PCB with Potassium Carbonate in Supercritical Water at 500 °C

Entry	Substrate	Time/h	$(\text{Silver salt})_{obsd}/(\text{AgCl})_{calcd}$[a]	Elemental analyses of residue(%)[b]		
				C	H	Cl
1	4Cl-B	3	0.68	43.36	2.02	4.76
2	4Cl-B	6	0.81	50.87	3.10	1.55
3	4Cl-B	24	1.0	23.46	1.01	0.81
4	6Cl-B	3	0.85	40.92	1.90	3.78
5	6Cl-B	6	0.87	49.67	2.24	4.88
6	6Cl-B	24	0.98	43.60	1.74	3.16

a) Detemination of chloride ion formed in the reaction solution of PCB (see Text). b) Residue shown in Table 1.

the filtration of the reaction in the previous paper[7] was 4-biphenylol, the residue obtained in the present report was insoluble char in chloroform, the elemental analyses of the residue being shown in Table 2. The residues contain small amounts of chlorine and the remainder of the summation of C, H, and Cl would be oxygen.

After filtration of the black residue, aqueous filtrate was extracted with chloroform several times; then combined extracts were evaporated to give small amounts of the material in the yield of less than 4 wt% based on starting material. Separation of this material by column chromatography indicated that PCB was not observed even in the case of the reaction conducted for 3 h at 500 °C and that biphenyl was not contained in this material. The washed aqueous filtrate was evaporated under reduced pressure to give a light yellow solid. This solid's weight exceeds those of carbonate and hydrogencarbonate, amounts of which were calculated from the titration by 0.1 M HCl. It did not show any ^{1}H NMR peaks except by absorption of OH groups and ^{13}C NMR absorption even in the case of the reaction conducted for 3 h, so it is considered to be a mixture of carbonate, hydrogencarbonate, and other inorganic substances such as $K_xC_yO_z$ described in the previous papers.[7,8] After water was added to this solid, the resultant aqueous solution was acidified with dilute nitric acid and warmed to 70–80 °C to decompose carbonate or hydrogencarbonate, followed by addition of silver nitrate and collection of silver salt, the amounts of silver salts being shown as $(\text{Silver salt})_{\text{obsd}}/(\text{AgCl})_{\text{calcd}}$ in Table 2.

In order to compare the yields of hydrocarbons formed by the reactions of 4Cl-B and 6Cl-B with those of Cl-B, one datum reported in the previous paper[7] is shown in Entry 7 of Table 1. Comparison of these data indicates that yields of hydrocarbons are higher in 4Cl-B or 6Cl-B than in Cl-B and that methane is the major component in 4Cl-B or 6Cl-B, contrary to the reaction of Cl-B, in which aromatic hydrocarbons are the major component. Presumably poly-substitution of biphenyl with chlorine atoms increases the probability of scission of C–C bond adjacent to C–Cl bond and increases yields of aliphatic hydrocarbons. Therefore, the yield of methane is in the order: 6Cl-B > 4Cl-B > Cl-B, as is shown in Table 1. The tendency that yields of hydrocarbons are higher in 4Cl-B or 6Cl-B than in Cl-B agrees with the trend reported in the basic decomposition of PCB.[4] Polychlorination of biphenyl increases the susceptibility to nucleophilic attack by a basic catalyst such as potassium salt of polyethylene glycol[10] or potassium carbonate in our case.

It has been reported that yields of organic products in the basic decomposition of PCB did not exceed 50%.[5] The results reported in the previous papers[7,8] and the result in the present report indicate that summation of the yields of the products does not exceed 50%. The remainder of the products, which do not show any ^{1}H NMR and ^{13}C NMR peaks, are considered to be inorganic salts such as $K_xC_yO_z$, since carbonate or hydrogencarbonate does not give any ^{13}C NMR signal in ordinary measurement time. As described in the previous paper,[8] the inorganic salt obtained from the reaction of char from poly(vinyl chloride) (PVC) contains substances which are not decomposed by dilute nitric acid and which react with silver nitrate to give silver salt, which show FT-IR absorption, $(\text{Silver salt})_{\text{obsd}}/(\text{AgCl})_{\text{calcd}}$ exceeding 1.[8] On the other hand, inorganic salts obtained from the reaction of PCB in the present paper and from the reaction of PVC (not char)[8] reported in the previous paper are easily decomposed by dilute nitric acid and are not able to give silver salt by the reaction with silver nitrate, $(\text{Silver salt})_{\text{obsd}}/(\text{AgCl})_{\text{calcd}}$ not exceeding 1.

In prolonged reaction time, all chlorine atoms of 4Cl-B or 6Cl-B are converted to potassium chloride as is shown in Table 2. However, in short reaction time, values of $(\text{Silver salt})_{\text{obsbd}}/(\text{AgCl})_{\text{calcd}}$ are a little less than 1. In these cases, some of the chlorine atoms presumably exist in the residue, polyhydroxylated PCB, or in water-soluble inorganic salts.

Since the reaction of 4Cl-B or 6Cl-B in the present report gives a volatile reaction product such as methane as a main product, this process has a merit for convenience of separation compared to the complex separation procedure of an unvolatile product such as biphenyl from the solvents in other processes.[2,3] Another merit of the present process is that the reaction does not brings about corrosion of the apparatus contrary to the supercritical water oxidation method.[6]

Experimental

General Procedure. Two sorts of PCB, 4Cl-B and 6Cl-B were synthesized according to the method reported in a literature.[9] Analyses of aliphatic and aromatic hydrocarbons and carbon dioxide were conducted using a Yanagimoto gas chromatograph G 2800 and a Shimadzu GC-14B, respectively. Procedure for analyses were the same as those in the preceding paper.[8]

Reaction of PCBs with Potassium Carbonate in Supercritical Water. A 100 mL autoclave (Nitto Koatsu Co. LTD., Hastelloy X) was charged with 0.7739 g (0.00265 mol) of 4Cl-B or 0.9565 g (0.00265 mol) of 6Cl-B, 4 g of potassium carbonate, and 20 mL of water. The reaction procedures including infomation concerning reaction atmosphere or pressure were described in the preceding paper.[8] Yields of hydrocarbons, hydrogencarbonate, or carbon dioxide are shown on carbon basis; 100 × (mol of product × number of carbon atom)/(12 × mol of PCB).

References

1 J. A. Manion, P. Mulder, and R. Louw, *Environ. Sci. Technol.*, **19**, 280 (1985).

2 P. Forni, L. Prati, and M. Rossi, *Appl. Cat. B, Environ.*, **14**, 49 (1997).

3 S. Taniguchi, M. Hosomi, A. Murakami, S. Imura, and S. Ozawa, *Chemosphere*, **32**, 199 (1996).

4 P. DeFilippis, M. Scasella, and F. Pochetti, *Ind. Eng. Chem. Res.*, **38**, 380 (1999).

5 T. Sako, T. Sugeta, K. Otake, C. Kamizawa, M. Okano, A. Negishi, and C. Tsurumi, J. *Chem. Eng. Jpn.*, **32**, 830 (1999).

6 N. Anjoh, A. Suzuki, S. Kawasaki, and T. Nakamura, *Environ. Management*, **33**, 895 (1997).

7 F. Akiyama, *Nippon Kagaku Kaishi*, **2001**, 595.

8 F. Akiyama, *Bull. Chem. Soc. Jpn.*, **75**, 871 (2002).

9 S. Safe and O. Hutzinger, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 686.