

DIFFERENCES OF DECOMPOSITION MECHANISM AMONG THREE NON-COMBUSTION METHODS FOR PCB

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Abstract

Thirteen single PCB isomers were individually decomposed by catalytic hydro-dechlorination over palladium/carbon catalyst (CHD), photochemical dechlorination (PCD), and sodium dispersion method (SD). The major dechlorination pathways were proposed and the differences of degradation mechanism were compared among the three methods. Although the dechlorinations proceeded via an irreversible stepwise pattern in three cases, the dechlorination pathways were quite different among the three. While the dechlorination pathways were relatively clear by CHD and PCD, the pathways diverged widely by SD. The chlorine at the ortho position was easily dechlorinated by PCD and lost the slowest by CHD and that at the para position was removed slightly easier by SD. As for the total numbers of chlorine atoms, the congeners decomposed more quickly in proportion to the total number by SD. This effect was not clear by CHD and PCD because the presence of ortho chlorine atoms had a large effect on the degradation constants. Furthermore we have checked whether dioxin-like PCBs are to be destructed and/or produced. After total TEQ decreased immediately by CHD and SD, and gradually decreased by PCD, it showed zero finally by the three.

Introduction

In Japan, the effects on humans and environments, such as in the Kanemi-Yusho incident in 1968, became social problems. PCB production and new uses were prohibited in 1972, and PCB makers and users have been under an obligation to store PCB and the associated equipment. Since then, waste containing PCB has remained untreated for a long time. Considerable amounts of waste containing PCB have been stored waiting for decomposition in Japan. This situation has prompted the Japanese government to arrange for and promote reliable and environmentally sound treatment of PCB wastes.¹ The Japan Environment Agency has decided that waste PCB should be destroyed by non-combustion technology (e.g. chemical treatment) instead of incineration or high-temperature pyrolysis. The law concerning special measures for the promotion of proper treatment of PCB waste, which requires waste PCB be treated within 15 years, was enacted on 15 June 2001. The criterion for treating PCB-containing oils by chemical decomposition was set to the strict limit of 0.5 mg/kg. PCB treatment has really been working now according to this national program. In order to confirm the good management of PCB destruction systems, it is important not only to ascertain the disappearance of PCB but also to know the degradation mechanism and to check for the absence of other harmful byproducts.² Thirteen polychlorinated biphenyl (PCB) isomers [2-chlorobiphenyl (#1), 3-chlorobiphenyl (#2), 4-chlorobiphenyl (#3), 2,3,4-trichlorobiphenyl (#21), 2,4,4'-trichlorobiphenyl (#28), 2,2',5,5'-tetrachlorobiphenyl (#52), 2,2',4,5,5'-pentachlorobiphenyl (#101), 2,3',4,4',5-pentachlorobiphenyl (#118), 3,3',4,4',5-pentachlorobiphenyl (#126), 2,2',3,4,4',5'-hexachlorobiphenyl (#138), 2,2',4,4',5,5'-hexachlorobiphenyl (#153), 2,2',3,4,4',5,5'-heptachlorobiphenyl (#180), and decachlorobiphenyl (#209)] were decomposed by three non-combustion methods, catalytic hydro-dechlorination over palladium/carbon catalyst (CHD), photochemical dechlorination (PCD), and sodium dispersion method (SD).³⁻⁵ The reaction solutions were sampled at intervals during the decompositions and analyzed by HRGC/HRMS. On the basis of the identification of the dechlorinated products and the quantitative data obtained during the reactions, the major dechlorination pathways were proposed. The differences in the pathways and the reactivities of the chlorines among the three methods were considered.

Materials and Methods

Thirteen single PCB isomers (IUPAC No., #1, #2, #3, #21, #28, #52, #101, #118, #126, #138, #153, #180 and #209) used as starting materials were purchased from AccuStandard Co. The labeled and native PCBs for quantification, MBP-MXP and BP-MXP, were obtained from Wellington Laboratories. All reactions by CHD were carried out in the 2L glass vessel. 1200g of hexadecane, 0.12g of Pd/C catalyst and PCB isomer were stirred and heated to 260°C in N₂ atmosphere. H₂ gas (1.2L/min) was passed into the vessel for 30 seconds,

followed by H₂, gas was changed to N₂ (0.1L/min) for 4.5 min. This H₂ and N₂ cycle was repeated 10 times or more. All reactions by PCD were carried out in the 50ml glass vessel with a 32W mercury lamp and a stirrer. Each 2mg of PCB isomer and NaOH (100 times moles of chlorine moles in PCB) were added into the vessel with 50 ml of isopropanol. Reactions proceeded at 25°C. All reactions by S.D. were carried out in the 500mL glass flask. 600g of hexadecane and each 60 mg of PCB isomer was added to the flask, stirred and heated to 60°C under N₂ atmosphere. Then 10% dispersed sodium (<10 μm) was added to the flask and the reaction was started when Na/Cl (mol/mol) was 11 in all experiments. The reacted solutions were periodically sampled during the decompositions for these three methods. The samples were analyzed by GC/MS, Auto Spec-Ultima at a resolution of 10,000 with HT-8 capillary column (0.22mm x 50m x 0.25μm).

Results and Discussion

1. Degradation of monochlorobiphenyls (#1, #2, #3)

Degradation of monochlorobiphenyl mainly produced biphenyl, phenylcyclohexadiene, phenylcyclohexane, and phenylcyclohexane. We compared three monochlorobiphenyls (MoCBs) to determine the relative reactivity of the ortho, meta, and para chlorine atoms. Fig. 1 shows the concentrations of the MoCBs at different reaction times. The chlorine at the ortho position was easily dechlorinated by PCD and lost slowest by CHD. Meanwhile, the chlorine at the para position was removed slightly easier than meta or ortho position by SD.

2. Degradation of #21, #28, #52, #101, #118, #126, #138, #153, #180 and #209

The results demonstrated that the dechlorinations proceeded via an irreversible stepwise pattern. However the dechlorination pathways were quite different among the three. While the dechlorination pathways were relatively clear by CHD and PCD, the pathways diverged widely by SD. The pathways and the reactivities of the chlorines were compared among the three methods. Fig. 2 shows the major pathways via three methods.

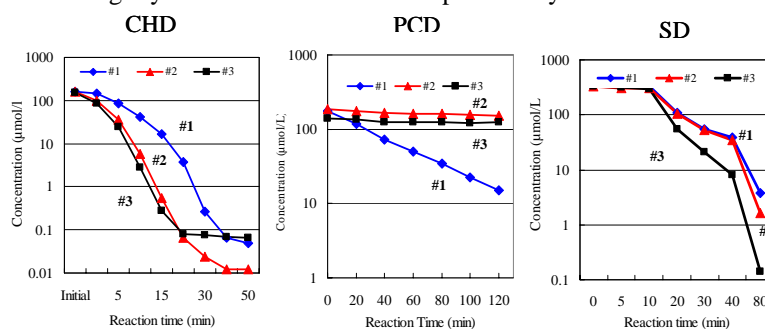


Fig. 1 The concentrations of monochlorobiphenyl at different reaction times

Table 1 Degradation rate constants at the beginning of the reaction

	Total numbers of chlorines	Numbers of para chlorines	Numbers of ortho chlorines	Degradation rate by		
				CHD (min ⁻¹)	PCD (min ⁻¹)	SD (min ⁻¹)
#1	1	0	1	0.253	0.021	0.0107
#2	1	0	0	0.421	0.0015	0.0184
#3	1	1	0	0.445	0.00092	0.0243
#21	3	1	1	0.227	0.066	0.342
#52	4	0	2	0.259	0.0057	0.363
#118	5	2	1	0.442	0.11	0.668
#126	5	2	0	0.586	0.036	0.416
#153	6	2	2	0.273	0.027	0.565
#209	10	2	4	0.125	0.33	0.746

3. Effect of substituents on the degradation rate

The degradation constants of the nine congeners were calculated at the beginning of the reaction, which were experimented in the same conditions by each CHD, PCD, and SD (Table 1). The effects on the degradation rate of the position of the chlorine substituent (ortho, meta, or para), the total number of chlorine atoms, and the nature of the atoms next to the chlorine substituent were discussed in this section.

3-1. Total numbers of chlorine atoms

The total numbers of chlorine atoms influenced the degradation rate because the congeners decomposed more quickly in proportion to the total number of chlorines of the PCB by SD. This effect was not clear by CHD and PCD because the presence of ortho chlorine atoms had a large effect on the degradation constants.

3-2. Position of the chlorine substituents

In the degradation of the MoCBs, the chlorine at the ortho position was easily dechlorinated by PCD and lost the slowest by CHD. Meanwhile, the chlorine at the para position was removed slightly easier than meta or ortho position by SD. In the other six congeners, ortho chlorines were lost at a slower rate than meta and para chlorines by CHD and para chlorine were lost quickly by SD. The low degradation rate is probably due to steric hindrance

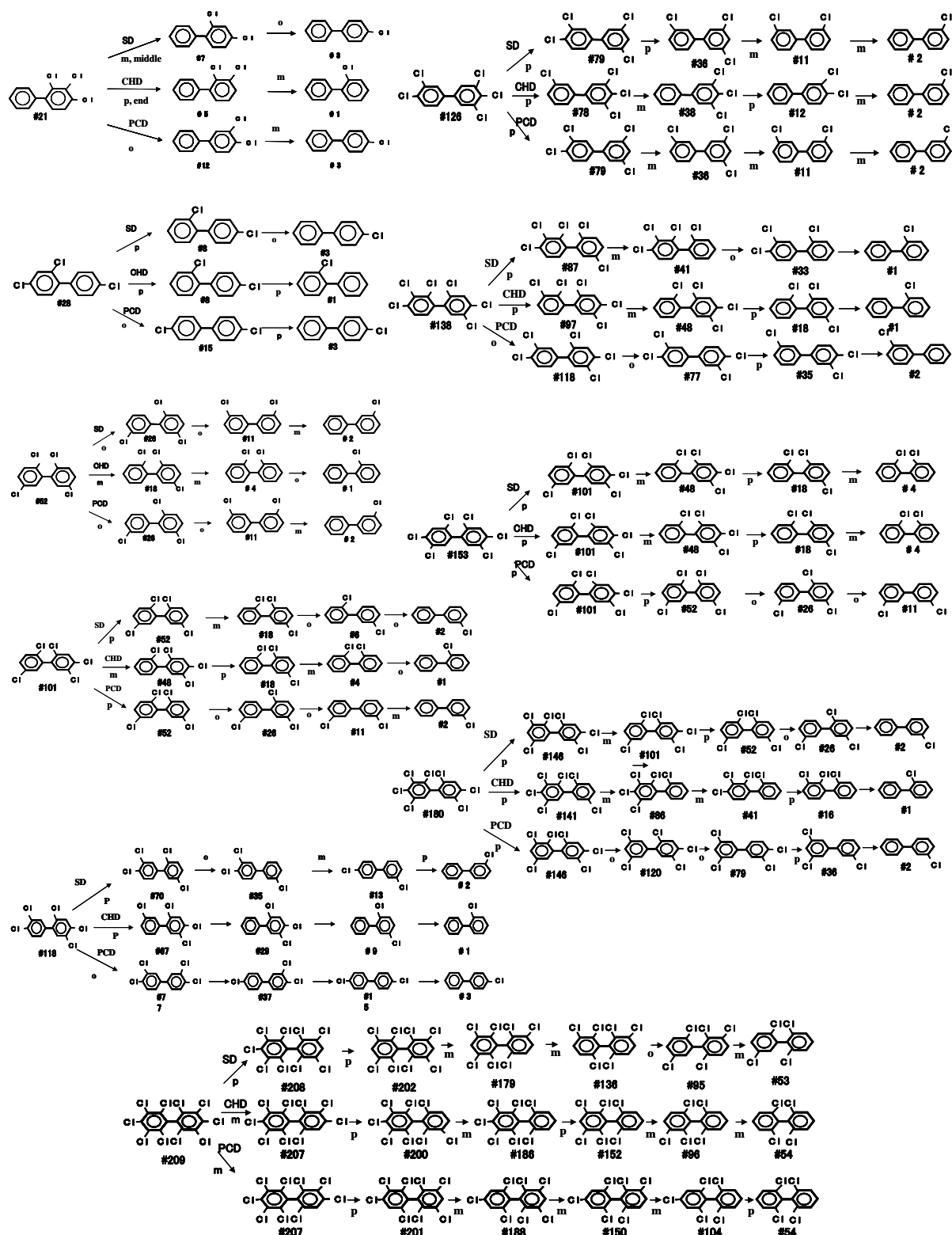


Fig.2 Difference of pathways via the three methods

between the two phenyl rings by CHD. The reactivity of SD was considered to be related to electronic effects. In the case of PCD, the reactivity was different due to the number of ortho chlorine. When the isomer had one ortho-chlorine, it easily released ortho-chlorine to become a plane-structure because of the relief of the twist-structure. When more than two, it did not necessarily release ortho-chlorine at first because the elimination of one ortho-chlorine did not relieve the twist-structure.

3-3. Different numbers of chlorine atoms on each of the phenyl rings

The different numbers of chlorine atoms on each of the phenyl rings seemed to influence the dechlorination. The dechlorination reactions occur on the more-substituted ring and the numbers of chlorine of the dechlorinated products were the same on the two-phenyl rings by PCD and SD. Meanwhile, by CHD, the dechlorination reactions occur on the less-substituted phenyl ring and the numbers of chlorine atoms in the dechlorinated products differed on the two phenyl rings.

3-4. Chlorine atom situated between two other chlorines

The reactivity of 2,3,4-TrCB and 3,4,5-TrCB with three consecutive chlorine atoms was compared. The major product of dechlorination of 2,3,4-TrCB was 3,4-DiCB and that of 3,4,5-TrCB was 3,5-DiCB by PCD. This probably depends on the twist-structure in 2,3,4-TrCB and on the steric congestion of chlorine atoms in 3,4,5-TrCB. The major product of dechlorination of 2,3,4-TrCB was 2,3-DiCB and that of 3,4,5-TrCB was 3,4-DiCB by CHD. This probably depends on the reactivity of atoms adjacent to chlorine. The reactivity was shown to decrease in the order $H-Cl-H > H-Cl-Cl > Cl-Cl-Cl$.⁶ The major product of dechlorination of 2,3,4-TrCB was 2,3-DiCB and that of 3,4,5-TrCB was 3,5-DiCB by SD. The chlorine atom situated between two other chlorines showed high reactivity because of the steric congestion.

4. Dioxin-like PCB

We have checked whether dioxin-like PCBs are to be destroyed and/or produced. When 3,3',4,4',5-PeCB (#126) as non-ortho congener was destroyed by three methods, total TEQ (toxicity equivalent quantity) immediately decreased (Fig. 3). When 2,3',4,4',5-PeCB (#118) as mono-ortho congener was destroyed by CHD and SD, total TEQ also decreased immediately. In the case of the destruction of #118 by PCD, TEQ originated from 3,3',4,4'-TeCB (#77) increased in the beginning of the experiment because #77 was mainly produced by ortho-dechlorination of #126. The TEQ, however, gradually decreased with the degradation of #77 and finally showed zero.

In this way, we could explain the safety of three typical methods. These results are expected to be very useful for the promotion of real waste PCB treatments.

Acknowledgements

This study was financially supported by a grant-in-aid for the Development of Innovative Technologies from the Ministry of Education, Culture, Sports, Science and Technology of Japan and Waste Management Research Grants from the Ministry of the Environment of Japan.

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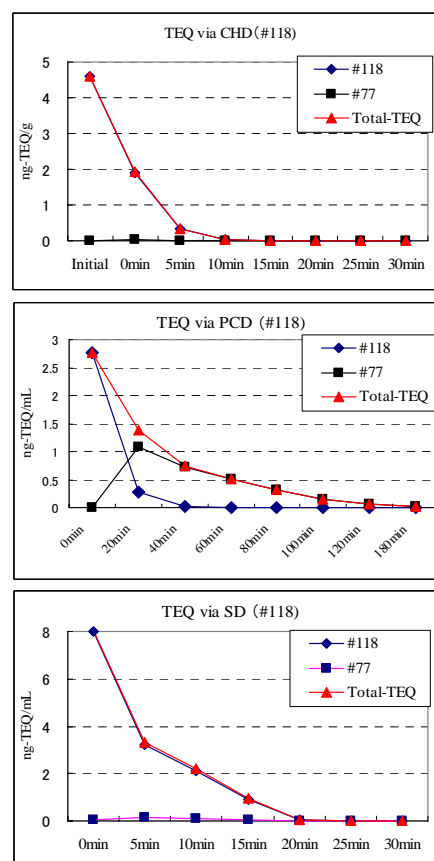


Fig. 3 The change of TEQ during degradation