DECHLORINATION PATHWAYS AND KINETICS IN PHOTO-CHEMICAL REACTION AND CATALYTIC HYDRO-DECHLORINATION
-EFFECT OF THE COEXISTENCE OF TWO PCB CONGENERS-

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Introduction

Photo-chemical dechlorination (P.C.D.) [1)] and catalytic hydro-dechlorination (C.H.D.) [2)] have potential to be the actual commercial processes to degrade PCBs because of their closed systems, mild conditions and clearness of the final products (biphenyl). In the previous work, dechlorination pathways of nine individual PCB in the reactions of C.H.D. and P.C.D. were reported [3,4)]. In this work, 2,3,4-trichlorobiphenyl (#21), 2,4,4'-trichlorobiphenyl (#28), 3,3',4,4',5-penthachlorobiphenyl (#126), 2,2',4,4',5,5'-hexachlorobiphenyl (#153), the mixture of #21 and #28, and those of #153 and #126 have been used for the starting materials in the P.C.D. and C.H.D. We analyzed PCB congeners produced in the different reaction times by each dechlorination method, and then the effect of the coexistence of two congeners to the dechlorination pathways and the degradation kinetics has been discussed.

Materials and Methods

Four individual congeners (IUPAC No., #21, #28, #126, and #153) were purchased from AccuStandard Co. They were used for the starting materials of each single reaction of C.H.D and P.C.D to examine the dechlorination pathways and the kinetics. And next, the same concentration mixture of #21/#28 and those of #153/#126 were used for the starting mixture in order to compare the differences by the effect of the coexistence. The reaction equipments, conditions and the analytical methods were mentioned in the previous report[3)].

Results and Discussion

1. Dechlorination pathways

Table1 and 2 show the concentrations of the starting materials and the products at each reaction time in the single reaction by the C.H.D using #21 and #28, and Table3 shows the mixing reaction of them. Table4, 5 and 6 show them by the P.C.D. Figure 1 and 2 show them using #126 and #153 by the C.H.D and P.C.D. Dechlorination did not changed when they were mixed in the each reactions. Differences of the dechlorination pathways between at the single reaction and at the coexistence reaction were not found in the C.H.D. and P.C.D. reactions. Similar to the previous report[3,4)], ortho chlorines were lost at a slower rate than meta and para chlorines, and the dechlorination reactions mainly produced ortho-chlorinated congeners in the C.H.D. In the case of only ortho chlorine, ortho chlorine is easily released and in the case of two ortho chlorines, para chlorine is easily released in the P.C.D. In the case of the congener that has three adjacent chlorine substituents, middle chlorine atom situated between two other chlorines showed low reactivity in the C.H.D., but showed high reactivity in the P.C.D. The dechlorination pathways of #21, #28 and #126, #153 in the mixing reaction are shown in the Figure 3 and 4.

Table1 The concentration of #21 and their products at different times in the C.H.D. reaction

	Congeners	Concentration (μmol/L)				
		Initial	0min	5min	10min	20min
T3CBs	2,3,4 (#21)	127	79	45	19	11
D2CBs	2,3 (#5)		55	58	49	23
	2,4 (#7)		33	29	16	2.5
	3,4 (#12)		0.88	2.5	3.6	1.5
M1CBs	2 (#1)		22	43	51	33
	3(#2)		0.34	1.1	1.9	1.3
	4(#3)		3.3	5.5	4.9	0.73

Table2 The concentration of #28 and their products at different times in the C.H.D. reaction

	Congeners	Concentration (μmol/L)						
		Initial	0min	5min	10min	15min	20min	30min
T3CBs	2,4,4'(#28)	133	41	11	1.6	0.1		
	2,4',5(#31)	13	4	1.5	0.3	0.026		
D2CBs	2,4(#7)		29	23	10	2.2	0.25	
	2,4'(#8)	0.46	35	24	8.1	1.2	0.1	
	2,5(#9)		2.8	2.6	1.1	0.43	0.06	
M1CBs	2(#1)		16	34	34	17	5.6	0.13
	4(#3)		3.2	5.2	2.3	0.55	0.091	

Table3 The concentration of #21/#28 and their products at different times in the C.H.D. reaction

	Congeners	Concentration (μmol/L)						
		Initial	0min	5min	10min	15min	20min	30min
T3CBs	2,3,4(#21)	139	99	73	47	24	11	11
	2,4,4'(#28)	133	39	15	3.2	0.45		
	2,4',5(#31)	10	3.5	1.6	0.36			
D2CBs	2,3(#5),2,4'(#8)		55	58	49	35	23	5.7
	2,4(#7)		33	29	16	6.9	2.5	0.15
	2,5(#9)		2.4	2.2	1.3	0.65	0.22	
	3,4(#12)		0.88	2.5	3.6	2.7	1.5	0.14
	4,4'(#15)		0.63					
M1CBs	2(#1)		22	43	51	43	33	9.3
	3(#2)		0.34	1.1	1.9	2	1.3	0.22
	4(#3)		3.3	5.5	4.9	2.1	0.73	0.062

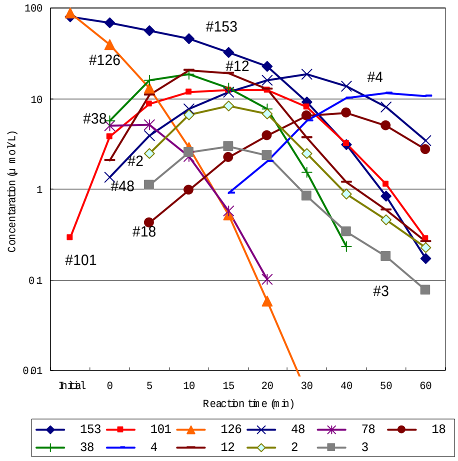

Figure 1 The concentration in the mixing reaction of #126/#153 by CHD

Table4 The concentration of #21 and their products at different times in the P.C.D. reaction

	Congeners	Concentration (μmol/L)						
		Initial	10min	20min	30min	40min	50min	60min
T3CBs	2,3,4(#21)	200	22	4.4	1.1	0.41	0.17	
	2,4,5(#29)		0.82	0.35	0.2			
	2',3,4(#33)		18	5.6	1.8	0.96	0.51	0.14
D2CBs	2,3'(#6)		0.27	0.25	0.12	0.091	0.056	
	2,4(#7)	0.45	1.1	0.49	0.21	0.13	0.093	
	2,4'(#8)		1.4	0.74	0.4	0.22	0.13	
	3,4(#12)/3,4'(#13)		70	39	22	14	12	11
M1CBs	3(#2)		0.92	1.4	1.6	2	2.5	2.6
	4(#3)		13	17	20	23	31	34

Table5 The concentration of #28 and their products at different times in the P.C.D. reaction

	Congeners	Concentration (μmol/L)						
		Initial	10min	20min	30min	40min	50min	60min
T3CBs	2,4,4'(#28)	150	12	1.9	0.43			
	2,4',5(#31)	3.8	1.9	1.2	0.76	0.34	0.21	0.17
D2CBs	3,4'(#13)		0.69	1.7	1.4	1.8	1.9	2
	4,4'(#15)		100	140	120	130	110	140
M1CBs	3(#2)			0.068	0.036	0.12	0.15	0.23
	4(#3)		1	2.4	3.6	5.5	6.3	9

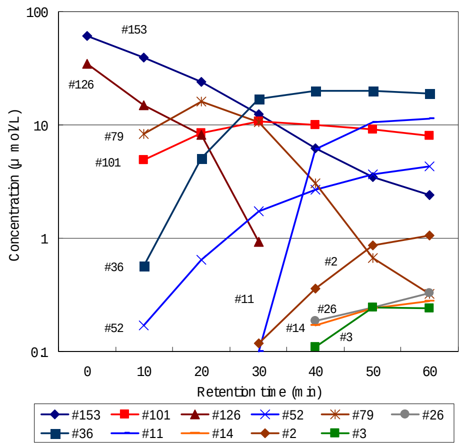

Figure 2 The concentration in the mixing reaction of #126/#153 by PCD

Table6 The concentration of #21/#28 and their products at different times in the P.C.D. reaction

	Congeners	Concentration (μmol/L)						
		Initial	10min	20min	30min	40min	50min	60min
T3CBs	2,3,4(#21)	69	6.9	1.3	0.33			
	2,4,4'(#28)	46	2.3	0.3				
	2,4,5(#29)		0.28	0.12				
	2,4',5(#31)	3.4	1.6	0.89	0.5	0.3	0.13	
	2',3,4(#33)		5.4	1.8	0.49	0.19		
D2CBs	2,3'(#6)			0.13				
	2,4(#7)		0.33	0.15	0.052			
	2,4'(#8)		0.48	0.29	0.14			
	3,4(#12)/3,4'(#13)		22	21	14	12	6.4	4.9
	4,4'(#15)		33	40	39	44	33	37
M1CBs	3(#2)		0.69	1.6	2.1	2.7	2.6	2.6
	4(#3)		8.2	20	28	38	35	35

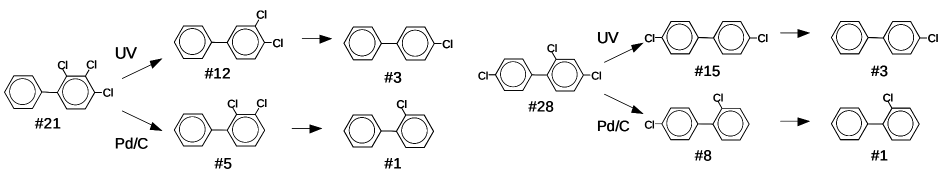

Figure 3 Major pathways of #21 and #28

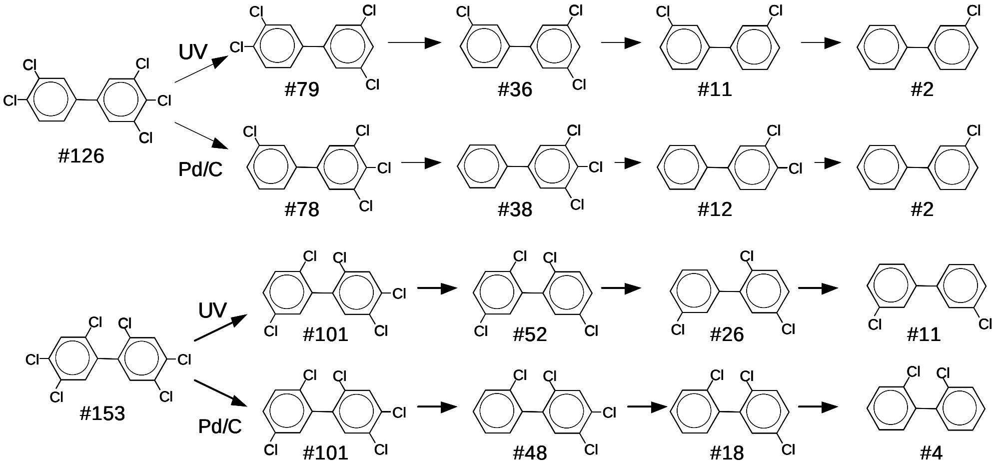

Figure 4 Major pathways of #126 and #153

2. Dechlorination kinetics

Figure 5 and 6 shows the decreases of the each congener in the reaction of C.H.D using #21, #28 and #126, #153 in the cases of single reaction and the mixing reaction. Figure 7 and 8 shows them in the case of P.C.D. Table 7 and 8 show the degradation rate constant and the half-lives of each congener in the single or mixing reaction by C.H.D and P.C.D. respectively. The degradation rate in the mixing reaction (Km) was smaller than that in the single reaction (Ks) by C.H.D. It was considered that the chance of the chlorine contact against the catalyst was about half, because the total concentrations of the starting congeners in the solution of the mixing reaction were twice as those of the single reaction. Meanwhile, Km was larger than Ks by P.C.D. That might be influenced by total initial concentrations. Because concentrations in the mixing reaction were lower than those in the single reaction by P.C.D.

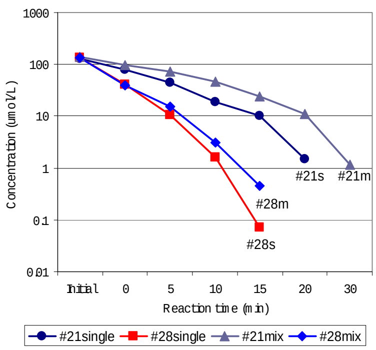

Figure 5 The Concentration of #21 and #28 by CHD

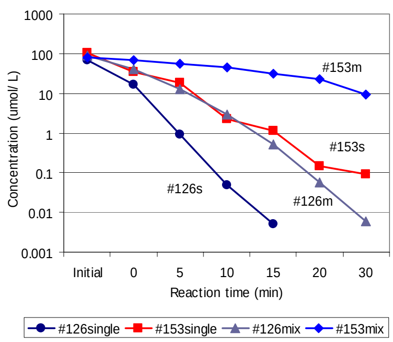

Figure 6 The Concentration of #126 and #153 by CHD

The ratio of the kinetic constant in the single reaction of #28 and #21 by the C.H.D, Ks (#28/#21) was 2.1, and that in the mixing reaction, Km (#28/#21) was 3.2. The ratio of Ks (#126/#153) was 2.2, and Km (#126/#153) was 4.6. Ratio of the degradation rates became progressively greater when the two congeners were mixed in the C.H.D reaction. In the case of C.H.D, two congeners compete with each other to react on the catalyst surface, and then the congener that has a bigger degradation rate would more preferentially adsorbed on the catalyst surface than that has smaller degradation rate. After all, in the case of mixing reaction, #28 and #126 were decomposed more preferentially than #21 and #153 respectively, and then the ratio of the degradation rates became bigger than those of the single reaction. On the other hand, the ratio of Ks (#28/#21) was 1.4, and Km (#28/#21) was 1.4. The ratio of Ks (#126/#153) was 2.6, and Km (#126/#153) was 2, in the case of P.C.D. The ratio of them was little changed. The degradation rate might be determined by the first step of chlorine releasing from the PCB molecule by getting the ultra-violet energy in the P.C.D.

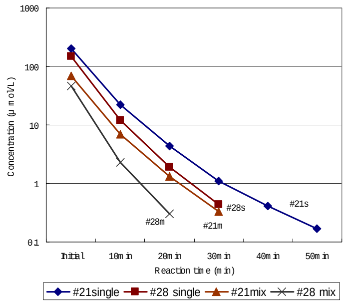

Figure 7 The Concentration of #21 and #28 by PCD

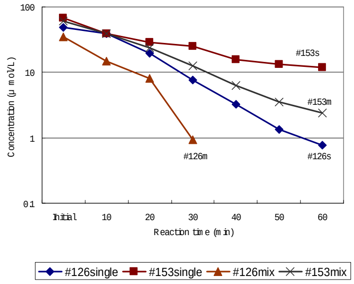

Figure 8 The Concentration of #126 and #153 by PCD

Table7 Kinetic constants and half-lives in the single or mixing reaction by C.H.D.

Congeners	Single reaction		Mixing reaction	
	Kinetic constants (Ks) (min)	Half-life (min)	Kinetic constants (Km) (min)	Half-life (min)
#21	0.203	3.41	0.093	7.42
#28	0.418	1.66	0.299	2.32
#28 /#21	2.1		3.2	
#126	0.591	1.17	0.309	2.24
#153	0.274	2.53	0.067	10.3
#126 /#153	2.2		4.6	

Table8 Kinetic constants and half-lives in the single or mixing reaction by P.C.D.

Congeners	Single reaction		Mixing reaction	
	Kinetic constants (Ks) (min)	Half-life (min)	Kinetic constants (Km) (min)	Half-life (min)
#21	0.139	4.87	0.176	3.94
#28	0.194	3.57	0.251	2.76
#28 /#21	1.4		1.4	
#126	0.0748	9.26	0.115	6.03
#153	0.0285	24.3	0.0569	12.2
#126 /#153	2.6		2	

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