

A STUDY ON THE PHOTOCATALYTIC DECOMPOSITION OF POLYCHLORINATED BIPHENYLS IN INSULATING OIL

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Introduction

Poly-Chlorinated Biphenyls (PCBs) are a group of organic compounds that consist of chlorine atoms attached to a biphenyl, with 209 different PCB congeners possible. PCBs were widely used for many applications, especially as dielectric fluids in transformers, because of their thermal stability, high heat capacity and dielectric properties. However, PCBs are known to harm human health and the ecosystem and the production and use of PCBs were banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001, classifying PCBs as one of the POPs. Therefore, Korea and many other countries are in the process of eliminating PCBs through overall management and environmentally friendly treatment. At present, there are several technologies for PCB treatment, such as incineration, chemical dechlorination, thermochemical decomposition, photodegradation, biological transformation and others. Among these, chemical dechlorination and photodegradation have advantages of high reliability and economic feasibility since the processes are very simple and do not require high temperature and pressure conditions. In this study, we investigated photocatalytic decomposition of PCBs using TiO₂, and the pathway of photodecomposition of PCBs was investigated by measuring concentrations of 209 PCBs as a function of time under an optimum decomposition condition.

Materials and methods

1) Photocatalytic decomposition : Approximately 10 g of insulating oil containing 186.2 ppm of PCBs and 200 ppm of TiO₂ were added to 200 ml of 0.5 mol KOH in a deionized water and ethyl alcohol (1:9) solution. This mixture was fully stirred throughout the reaction and the photocatalytic decomposition was carried out under UV light (235 nm) at 75 °C. Six 1 g samples were taken from the reactor at various reaction stages. The initial sample concentration sample (C₀) was taken after 30 minutes of stirring without UV light. Subsequently, UV light was applied and decomposed samples (C_i) were taken 0.5, 1, 2, 4, and 6 hours after the initial sample.

2) Pre-treatment and analyses: All samples were passed through several pre-treatments, such as alkaline digestion, acid treatment, liquid-liquid extraction, silica gel and florisil column cleanup to remove interfering substances. A total of 209 PCBs in each sample were analyzed with HRGC/HRMS (Autospec Micromass, UK) following the procedures for unintentionally produced persistent organic pollutants in liquid waste-HRGC/HRMS by the National Institute of Environmental Research in Korea and EPA method 1668B.

Results and discussion

1) Changes in concentrations of PCBs with various numbers of Cl : As the photocatalytic decomposition reaction progressed, the concentrations of PCBs with Cl₅~Cl₉ rapidly decreased at the initial stage, while the concentration of PCBs with Cl₃~Cl₄ initially increased and then decreased. The concentration of PCBs with Cl₁~Cl₂ steadily increased, as shown in Figure 1a. The data suggested that the photocatalytic decomposition of PCBs proceeded by selective elimination of chlorines, resulting in accumulation of PCBs with a smaller number of Cl, as shown in Figure 1b.

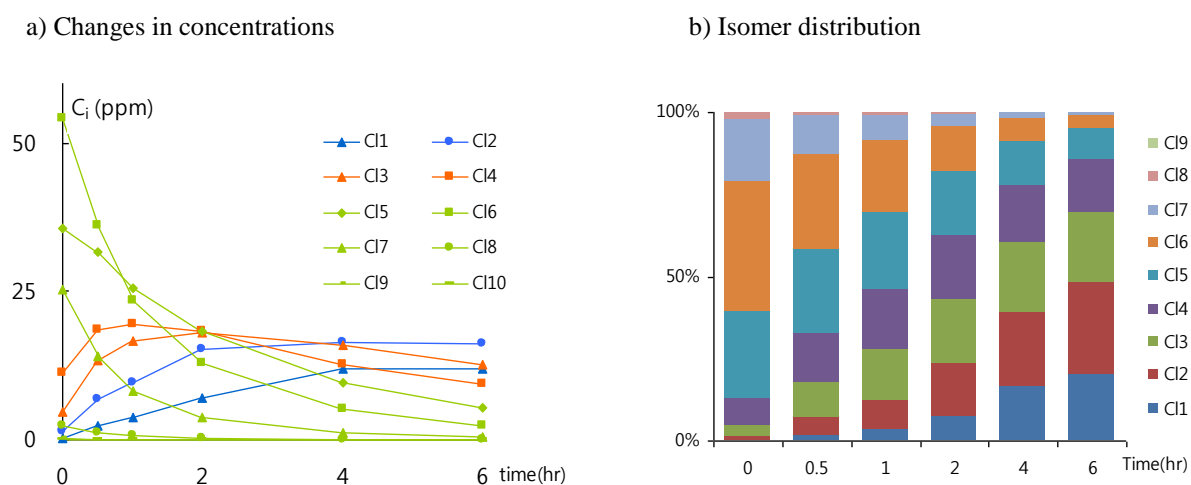




































Figure 1. Changes in concentration of PCBs with various numbers of Cl (a) and isomer distribution (b)

2) Effect of molecular structure on the changes in concentration of PCBs: The changes in concentration (C_i/C_0) of each isomer are shown in Tables 1 to 3 in order of rapid decomposition, along with the molecular structure. Inseparable peaks of isomers and immaterial changes in concentration in HRGC/HRMS analyses were excluded from the table.


















PCBs with a large number of Cl (Cl₉-Cl₆) are listed in Table 1 in the order of rapidly decreasing C_i/C_0 . It was noted that asymmetric PCBs, in which one of the biphenyl rings has more Cl than the other, decomposed more rapidly than symmetric PCBs. This is caused by a large number of Cl on one side, which gives a greater electronegativity than the side with a small number of Cl, so that they strongly attract hydrogen ions. This tendency was more apparent as the number of Cl substituents in PCBs decreased. In addition, the molecular structure affects the decomposition rate: the vacant *ortho*-substituted PCBs decomposed more rapidly than vacant *meta* and *para*-substituted PCBs. This implies that vacant *ortho*-phenyl may offer less steric hinderance to the opposite phenyl ring having a smaller number of Cl and, therefore, makes H-Cl substitution occur more readily.

Table 1. Changes in concentration of PCBs with Cl₉-Cl₆

isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀	isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀	isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀
206 	0.372	0.077	0.000	185 	0.483	0.096	0.000	156 	0.482	0.095	0.000
207 	0.419	0.114	0.000	173 	0.495	0.103	0.000	137 	0.575	0.000	0.000
208 	0.469	0.160	0.000	189 	0.510	0.089	0.000	141 	0.577	0.162	0.019
198 	0.415	0.068	0.000	191 	0.546	0.119	0.000	162 	0.584	0.143	0.014
205 	0.420	0.054	0.000	171 	0.591	0.161	0.017	144 	0.712	0.216	0.040
195 	0.454	0.066	0.000	183 	0.583	0.164	0.018	168 	0.730	0.312	0.072
200 	0.475	0.090	0.000	177 	0.601	0.175	0.023	167 	0.818	0.301	0.029
194 	0.483	0.086	0.005	176 	0.637	0.231	0.038	135 	1.064	0.267	0.113
199 	0.519	0.117	0.013	179 	0.658	0.234	0.043	130 	1.243	0.720	0.134
201 	0.554	0.151	0.019	175 	0.709	0.247	0.040	132 	-	-	-
197 	0.567	0.148	0.000	178 	0.669	0.227	0.035	128 	-	-	-
202 	0.629	0.160	0.000								



















PCBs with a medium number of Cl (Cl₅-Cl₄) are listed in Table 2 in the order of rapidly decreasing C_i/C₀. As in the larger molecules of PCB, asymmetric PCBs decomposed more rapidly than symmetric PCBs. The smaller the number of Cl substituents on the biphenyl, the greater this tendency was. In this group of PCBs, the position of Cl substituents did not affect the decomposition rate significantly.

Table 2. Changes in concentration of PCBs with Cl₅-Cl₄

isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀	isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀	isomers	C _{0.5} /C ₀	C ₂ /C ₀	C ₆ /C ₀
106 	0.000	0.000	0.000	91 	1.200	0.937	0.410	44 	1.326	1.317	0.8
105 	0.593	0.167	0.018	92 	1.588	1.460	0.560	59 	1.453	1.453	1.057
99 	0.727	0.290	0.050	126 	-	-	-	52 	1.811	2.474	1.824
110 	0.742	0.300	0.065	60 	0.198	0.144	0.000	53 	2.247	4.05	4.791
84 	0.981	0.706	0.317	74 	0.627	0.211	0.000	77 	17.96	14.97	3.681
101 	1.022	0.670	0.201	56 	1.184	0.551	0.14				

PCBs with a small number of Cl (Cl_3 - Cl_1) are listed in Table 3 in the order of rapidly decreasing C_i/C_0 . As for the larger molecules, asymmetric PCBs decomposed more rapidly than symmetric PCBs. The smaller the number of Cl substituents, the greater this tendency was. In this group of PCBs, the decomposition rate depended on the specific molecular structure, and the order was as follows: *ortho*-substituted PCBs > *para*-substituted PCBs \gg *meta*-substituted PCBs.

Table 3. Changes in concentration of PCBs with Cl_1 - Cl_3

isomers	$C_{0.5}/C_0$	C_2/C_0	C_6/C_0	isomers	$C_{0.5}/C_0$	C_2/C_0	C_6/C_0	isomers	$C_{0.5}/C_0$	C_2/C_0	C_6/C_0
22 	0.621	0.187	0.060	37 	3.757	3.622	1.243	13 	19.03	34.06	27.81
17 	0.797	0.414	0.121	26 	15.46	28.34	25.190	11 	28.41	79.98	95.07
19 	0.952	0.628	0.900	35 	21.23	27.65	13.09	14 	-	-	-
27 	1.050	1.444	1.448	6 	1.271	1.418	1.070	2 	1.069	0.754	0.638
18 	1.101	1.288	1.468	15 	2.460	3.022	1.772	3 	34.36	117.8	201.0
39 	2.840	3.616	2.756	12 	18.90	44.43	32.32	4 	12.03	23.72	23.86

In conclusion, this study confirms that photocatalytic decomposition of PCBs proceeds by the substitution of chlorine by hydrogen in the C-Cl bond. A different decomposition rate was observed between symmetric and asymmetric PCBs because of the differing electronegativity on each phenyl ring. The decomposition of the Cl_{6-9} substituted PCBs occurred in the following order: vacant *ortho* > *meta* > *para*-phenyl, which has a small number of Cl, which means vacant *ortho*-phenyl offers an open-door structure for the opposite phenyl and makes H-Cl substitution readily happen. In case of a small number of Cl_{1-3} substituted PCBs, the decomposition reaction happened in the following order: *ortho* > *para* \gg *meta*-phenyl, which has a large number of Cl. This can be explained in that vacant *meta*-phenyl has a much more unstable charge distribution than *para* and *ortho*-PCBs, and opposite *ortho* substituents act as obstacles for each other for replacement with hydrogen ions.

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