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RADIOLYTIC DECHLORINATION OF POLYCHLORINATED BIPHENYLS (PCB) IN ORGANIC SOLUTIONS

Takeshi SAWAI and Yoshiharu SHINOZAKI
Tokyo Metropolitan Isotope Research Center
Fukazawa, Setagaya-ku, Tokyo, Japan

The radiolytic dechlorination from PCB in organic solutions has been studied. The chain reaction does not occur in neutral alcoholic solutions and alkaline methanol solution but occurs in alkaline 2-propanol solutions, and $G(Cl^-)$ reaches about 450 at 5×10^{-2} M potassium hydroxide concentration.

The environmental pollution caused by polychlorinated biphenyls (PCB) has recently become one of the serious social problems. PCB is almost insoluble in pure water (soluble in ppm order) but soluble in organic materials. In rivers and seas, it is probably dissolved in organic materials or detergents in water. It has been known that PCB is stable towards oxidation, hydrolysis, and other chemical reactions which conceivably occur in the environment and also that it is concentrated in living lives. Therefore, we undertook to study the decomposition of PCB organic solutions by irradiation of ionizing radiations. The efficiency of the energy absorbed by materials for the chemical change is generally low, thus it is very important to introduce a chemical chain reaction in the decomposition process, for the economical use of the ionizing radiation.

Sherman et al. have found that DDT[1] and carbon tetrachloride[2] in neutral alcoholic solutions undergo the radiolytic dechlorination to form hydrogen chloride with high G values, indicating a chemical chain reaction. It is interesting to study if the chain dechlorination reaction can be found in alcoholic solutions of PCB as in DDT or CCl_4.

Therefore, it is the purpose of the study to examine the possibility of the similar chain reactions in PCB systems.

PCB solution of 7 ml in a glass tube of 22 mm o.d. with a stopper was aerated or purged with nitrogen and then was irradiated with 4K Ci ^{60}Co γ-rays at room temperature. After irradiation, hydrogen ion and chloride ion were determined by acid-base ti-

tration and the Mohr method[3], respectively. In the case of n-hexane solution, these ions were estimated by the same methods for the aqueous layer after shaking the irradiated samples with the same volume of water. The dose rate was determined by the ferrous-sulfate dosimetry, taking 15.6 as $G(Fe^{+++})$ and the dose absorbed by the sample is corrected for the electron density of PCB solutions. Methanol, 2-propanol and n-hexane (special grade from Wako Pure Chemical Co.) were used as solvents without further purifications. PCB samples used were Kanechlor-300 and 400(Kanegafuchi Chemical Industry Co.), and pentachloro and dichloro biphenyl (Wako Pure Chemical Co.).

The concentration of chloride and hydrogen ions in the solutions of methanol, 2-propanol and n-hexane increased linearly with the radiation dose and the chloride ion concentration was almost equal to that of hydrogen ion. Table 1 shows the chloride ion yield in various solutions of 0.3 volume % Kanechlor-400. These yields were 1.0 ~ 1.3, except for the PCB suspended aqueous solution. The fact that the chloride ion yields are not affected in the presence of oxygen or 10^{-2} M hydrogen peroxide which are known to be good electron scavengers, suggests that the electron (free or solvated) formed by γ-irradiation may not play an important role in the formation of chloride ion.

Table 1. The yield of chloride ion in various solutions of 0.3% PCB.

solution		$G(Cl^-)$
methanol	+air	1.07
	$+N_2$	1.12
2-propanol	+air	0.90
	$+N_2$	1.30
	$+N_2$ $+10^{-2}$M H_2O_2	1.25
	-air	1.27
n-hexane	+air	1.01
	$+N_2$	1.01

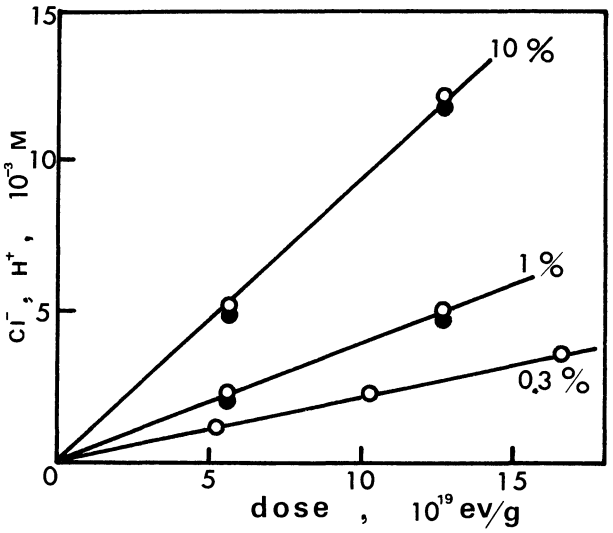

Fig.1 Yields of chloride ion and hydrogen ion for various concentrations of PCB-400 in N_2 purged 2-propanol solution
dose rate : 5.2×10^{19} eV/g hr
○ : Cl^- , ● : H^+

Fig.1 shows the effect of the concentration of PCB in 2-propanol solutions on the $G(Cl^-)$. The yield increases with increasing the concentration, for example, $G(Cl^-)=1.3$ in 0.3% PCB and $G(Cl^-)=5.8$ in 10% PCB. The yield is also larger in higher chlorinated biphenyls (Table 2). From the fact that $G(Cl^-)$ shows considerably

low yield as shown in Table 1, 2 and Fig.1, the chain reaction of radiolytic dechlorination as shown previously in the alcohol solutions of DDT[1] and carbon tetrachloride[2] does not occur in neutral alcohol solutions of PCB.

Table 2. The yield of chloride ion in 0.3% various chlorinated biphenyls in N_2 purged 2-propanol solution.

P C B	$G(Cl^-)$
dichloro biphenyl	1.10
Kanechlor-300	1.23
Kanechlor-400	1.30
pentachloro biphenyl	1.38

In alkaline 2-propanol solutions the radiolytic dechlorination from PCB undergoes with high G values until almost all hydroxide ions are consumed and the yield is almost equal to the yield of the decrease of hydroxide ions. These results are shown in Fig.2. The concentration of chloride ion increases slowly with dose below ~2 x 10^{18} and above

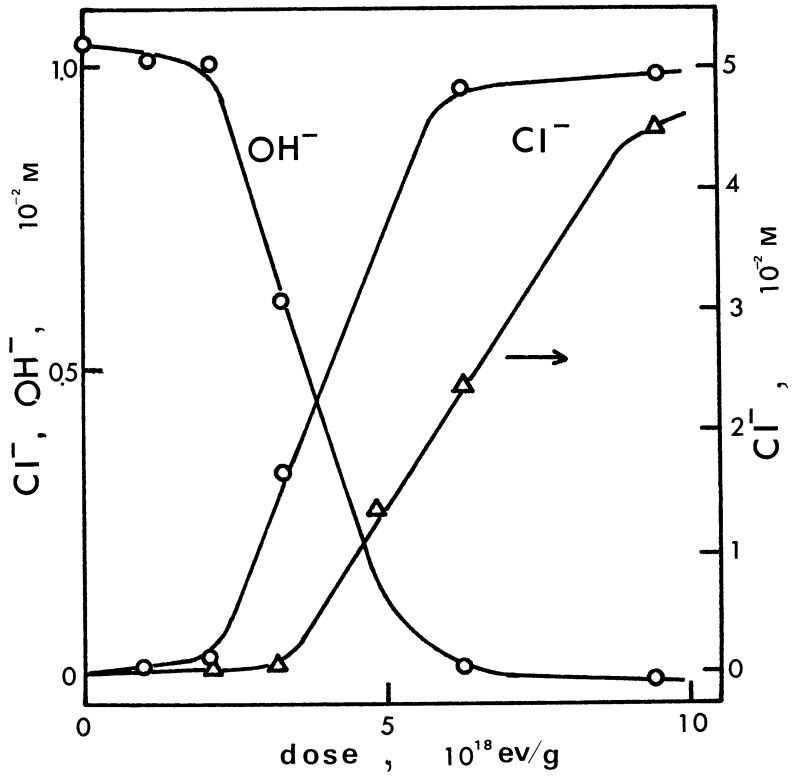

Fig.2 Relationship between chloride ion and hydroxide ion concentrations and dose in N_2 purged alkaline 2-propanol solution of PCB-400

dose rate : 4.0×10^{18} eV/g hr

o : 1×10^{-2}M NaOH, Δ : 5×10^{-2}M KOH

$\sim 6 \times 10^{18}$eV/g ($G(Cl^-)=2\sim3$) and increases remarkably with dose between ~ 2 and $\sim 6 \times 10^{18}$eV/g, and the yield reaches about 170. On the other hand, $G(-OH^-)$ shows the same tendency with $G(Cl^-)$ and $G(-OH^-)$ is about 180 at maximum. Upon irradiating the solution over $\sim 3 \times 10^{18}$eV/g, it is observed that some white small particles deposit on the wall of the irradiation vessel. The deposit can be dissolved easily by the addition of small amount of water, and is presumed to be sodium chloride.

In 5×10^{-2} M pottassium hydroxide solution, the increase of chloride ion and decrease of hydroxide ion with dose gave a similar tendency. $G(Cl^-)$ and $G(-OH^-)$ were caluculated to be about 450 and 410 respectively, and the concentration of Cl^- reached to 4.5×10^{-2} M at 1×10^{19}eV/g. This result shows that about 80% of chlorine was detached from PCB, because 0.3% PCB-400 corresponds to about 6×10^{-2}M as the chloride ion. In the methanol solutions containing 10^{-2}M sodium hydroxide, on the other hand, the concentration of chloride ion formed was linear with dose up to 10^{19}eV/g, and $G(Cl^-)$ was only 2.5. The hydroxide concentration changed a little with dose. These high G values in alkaline 2-propanol solutions suggest the chain reaction mechanism because the radical yield formed by the radiolysis of 2-propanol is 6.7 radicals/100 eV[4]. The chain decomposition of methyl iodide and methyl bromide to methane in irradiated alkaline 2-propanol has been observed previously by Sherman[5]. The similar chain reaction seems to occur in alkaline 2-propanol solution of PCB. Work along this line is in progress and details will be published later.

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