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The Radiolytic-chain Dechlorination of Polychlorinated Biphenyls in Alkaline 2-Propanol Solutions

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The radiolysis of solutions of polychlorinated biphenyls(PCB's) and potassium hydroxide in simple aliphatic alcohols was studied. The major products in alkaline 2-propanol solutions were potassium chloride, acetone, lower chlorinated biphenyls, and biphenyl. Their yields increased and the concentration of the hydroxide ions decreased with the dose. Acetone and potassium chloride were formed in high yields, and their concentrations were almost equal to the diminution in the hydroxide ions. The dechlorination yield was determined as a function of the dose, the dose rate, and the concentrations of PCB's, potassium hydroxide, and organic solutes. The chain-dechlorination reaction proceeded in the alkaline 2-propanol solution, but not in alkaline methanol, ethanol, 1-propanol, and butanols. The 2-propoxide radical anion, which is formed by the electron transfer from the hydroxide ion to the 2-propanol radical, is the chain carrier for the dechlorination reaction of PCB's in alkaline 2-propanol solutions. The mechanism is discussed in detail.

In neutral or alkaline aliphatic alcohol solutions, carbon tetrachloride,1) 1,1,1-trichloro-2,2-*bis*(*p*-chlorophenyl)ethane,2) nitrous oxide, 3) and methyl halide4) undergo radiolytic decomposition with high yields. For example, in alkaline alcoholic solutions of methyl halide, methane is produced in a high yield on exposure to ^{60}Co γ-rays, but the yields can be changed by varying the kinds of alcohol and solutes; *e.g.*, the dehalogenation yields of CH_3Cl, CH_3Br, and CH_3I in alkaline 2-propanol were 2.2, 130, and 179, respectively. Sherman has proposed the following reactions for the most important propagation steps in the chain decomposition in alkaline alcoholic solutions:4)

$$\mathrm{R\cdot} + \overset{|}{\underset{|}{\mathrm{C}}}\mathrm{HOH} \longrightarrow \mathrm{RH} + \text{-}\overset{\cdot}{\underset{|}{\mathrm{C}}}\mathrm{OH}\ (\mathrm{I}) \tag{1}$$

$$\mathrm{I} + \mathrm{B}^- \rightleftharpoons \text{-}\underset{|}{\mathrm{C}}\mathrm{O}^-\ (\mathrm{II}) + \mathrm{BH} \tag{2}$$

$$\mathrm{MX} + \mathrm{II} \longrightarrow \mathrm{M\cdot} + \mathrm{X}^- + \text{-}\underset{|}{\mathrm{C}}\mathrm{O} \tag{3}$$

$$\mathrm{N_2O} + \mathrm{II} \longrightarrow \mathrm{O}^- + \mathrm{N_2} + \text{-}\underset{|}{\mathrm{C}}\mathrm{O} \tag{3'}$$

$$\mathrm{M\cdot(or\ O^-)} + \overset{|}{\underset{|}{\mathrm{C}}}\mathrm{HOH} \longrightarrow \mathrm{MH(or\ OH^-)} + \mathrm{I} \tag{4}$$

where R·, B$^-$, and MX are the radical, the base, and alkyl halide, respectively. Moreover, it has been suggested that the radical-induced chain decomposition of some compounds in the alkaline alcohol solution can be observed under the following conditions: 1. MX should have a sufficiently high electron affinity, so that electron transfer from the alcohol radical anion-(II) is an efficient process, and 2. the compound produced by the electron-transfer reaction (3) is able to abstract a carbinol hydrogen from alcohol, thus giving the alcohol radical (I).

In general, it is well known that organic halides have a very high reactivity toward hydrated electrons and form halide ions by dissociative electron attachment. The rate constants of hydrated electrons for monofluoro- or monochlorobenzene and polyfluorobenzenes are $5\times10^8\ \mathrm{M^{-1}\,s^{-1}}$ and $10^9\sim10^{10}\ \mathrm{M^{-1}\,s^{-1}}$.5,6) Therefore, it may be expected that the reactivity for polychlorinated biphenyls (PCB's) is relatively high. The study of the dechlorination reactions of aromatic polychlorides in organic solutions, especially in alkaline alcoholic solutions, is very interesting. In a preliminary experiment,7) it was found that the chain dechlorination of PCB's proceeded and yielded potassium or sodium chloride and biphenyl with high *G*-values in the alkaline 2-propanol solutions, but not in the neutral 2-propanol and the alkaline methanol. The authors suggested that the chain-propagation steps in the dechlorination of PCB's must be similar to that proposed by Sherman.3,4) This radiolytic-chain dechlorination of PCB's in 2-propanol-alcoholate solutions has also been found independently by Arai *et al.*8)

The present paper is concerned with a more detailed study of the chain-dechlorination reaction of PCB's.

Experimental

Sample. PCB's dissolved in alkaline alcohol solutions were placed in a Pyrex irradiation vessel 12 mm in o.d. The solutions were irradiated with 3K Ci ^{60}Co γ-rays at room temperature after having been purged with pure nitrogen gas for about 30 min or after having been degassed by freeze-pump-thaw cycles. The dose rate was determined by means of a ferrous sulfate solution, and the energy absorbed in the samples was corrected with the electron density of the solutions.

The PCB's (Kanechlor-300, 400, 500*), alcohols, and potassium hydroxide (special grade, from Wako Pure Chemical Co.) were used without further purification. As the PCB's used in our experiments consist of mixtures of various chlorinated biphenyls, the contents of chlorine were analyzed by means of elemental analysis with a Shimadzu UM-2 element analyzer.

Analysis. The potassium chloride produced by irradiation was dissolved in water and was determined by Mohr's method.9) The hydroxide-ion concentration was measured by means of acid-base titration, with phenolphthalein as an indicator. The PCB's remaining in the solutions after irradiation were analysed with a Shimadzu 4B gas chromatograph with an electron-capture-type detector and using a 2 m glass column of SE-30 at 190—210 °C. The acetone and biphenyl were determined by means of a Shimadzu 4A gas chromatograph with a hydrogen flame detector at 60

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* Kanechlor (identified as KC for short) is a commercial name of the PCB's manufactured by the Kanegafuchi Chemical Industrial Co., Ltd. The numeral indicates the average number of substituted chlorine; *e.g.*, 400 shows a PCB containing 4 chlorines as the average.

and 220 °C respectively; for these analyses, a 2 m stainless steel column of 20% polyethylene glycol 20 M on chromosorb was used. A gas chromatograph-mass spectrometer (Shimadzu LKB-9000) was also used for the confirmation of the PCB's, acetone, and biphenyl.

Results and Discussion

Yield of Chloride Ion, Acetone, and Biphenyl. As has been shown in the previous paper,[7] the chloride ion was effectively liberated from the PCB's in the alkaline 2-propanol solutions purged with nitrogen gas, and a complementary amount of the hydroxide ion was consumed on exposure to ^{60}Co γ-rays at room temperature; the dechlorination was completely suppressed when the OH^- was almost consumed. In the case of 2-propanol solution containing 0.05 M potassium hydroxide and 1% KC-400, the initial yield of the chloride ion ($G(Cl^-)$) was ~450; meanwhile, the decreasing yield of the hydroxide ion was equal to that of the dechlorination. These high yields suggest that the radiolytic-chain dechlorination reaction apparently occurred, because the radical yield in the radiolysis of 2-propanol was only ~7.[10] The chain dechlorination, on the other hand, did not occur in the presence of dissolved oxygen. In the presence of an excess of potassium hydroxide in relation to the PCB's, the formation of chloride ions and the decrease in the quantity of hydroxide ions with the dose are shown in Fig. 1. The formation and the consumption were almost equal in each dose, and these rates decreased with the dose. The acetone and biphenyl also increased with an increase in the dose in a 0.2 M alkaline 2-propanol solution of 0.5% KC-300, as is shown in Fig. 2. The yield of acetone was almost the same as that of the chloride ion, and the rate was also suppressed with the dose. The formation of biphenyl increased sharply at a dose between 6×10^{18} and 2×10^{19} eV/g. At a dose of 3.2×10^{19} eV/g, the dechlorination of PCB's was found to reach about 100%, as calculated from the chlorine content. The amount of biphenyl multiplied by a factor of 3.2** was almost equal to the chloride-ion concentration at a dose of 3.2×10^{19} eV/g. This fact suggests that the dechlorination reaction of PCB's is predominant and that other reactions, such as C–C bond dissociation, the dimerization of PCB's, or the addition of radicals to a benzene ring, scarcely proceed. Pinacol was not detected.

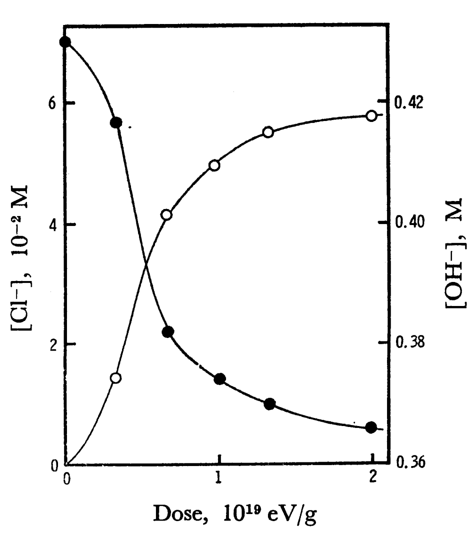

Fig. 1. Increase of chloride ion and decrease of hydroxide ion at various dose in 0.42 M KOH-2-propanol solutions of 0.3% KC-400.
○: chloride ion, ●: hydroxide ion
dose rate: 6.6×10^{18} eV/g hr

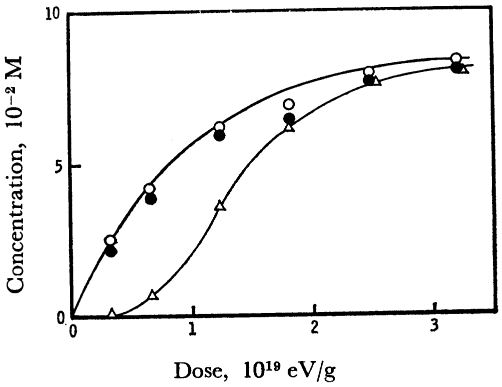

Fig. 2. Yields of products in 0.2 M KOH-2-propanol solutions of 0.5% KC-300.
○: chloride ion, ●: acetone, △: biphenyl
dose rate: 1.1×10^{19} eV/g hr

The initial yields of the dechlorination and of the decrease in the quantity of hydroxide ions were affected by the alkaline concentration. These results are summarized in Table 1. As can be seen from Table 1, the yield obviously increased with the hydroxide-ion concentration; however, the effect of the PCB concentrations from 1% to 10% on the $G(Cl^-)$ value was small: we found no remarkable difference between KC-300, -400, and -500.

On irradiating 0.2 M alkaline 2-propanol solutions containing 0.5% KC-300 at a dose rate of $6.94\sim244\times10^{17}$ eV/g hr, the initial yields of Cl^- were found to be as given in Table 2. As is shown in Table 2, the yield

Table 1. Initial yields in alkaline 2-propanol solutions

PCB's	OH^-/M	$G(Cl^-)$	$G(-OH^-)$	Dose rate eV/g hr
1% KC-400	1×10^{-2} a)	170	180	4.0×10^{18}
	5×10^{-2}	450	420	
	8×10^{-2}	670		
0.5% KC-400	0.25	600	600	2.4×10^{19}
1% KC-300	0.1	650		6.6×10^{18}
	0.25	680		
	0.5	730		
0.5% KC-300	0.2	630		2.4×10^{19}
0.3% KC-300	0.2	400		

a) NaOH was used.

** The average number of substituted chlorine in KC-300 was 3.2.

Table 2. Initial dechlorination yields in 0.2 M KOH-2-propanol solutions of 0.5% KC-300 at various dose rates

Dose rate (10^{17} eV/g hr)	$G(Cl^-)$
244	630
126	700
67.7	730
31.2	830
14.6	1200
6.94	1500

Table 3. Dechlorination of PCB's in 0.2 M KOH-2-propanol solutions as a function of concentration of additives

(1)	Biphenyl (M)	0	0.005	0.025	0.1
	Cl^- (M)	0.061	0.055	0.048	0.024
(2)	Acetone (M)	0	0.1	0.3	1.0
	Cl^- (M)	0.059	0.045	0.005	0.002
(3)	Nitrobenzene (M)	0	0.002		
	Cl^- (M)	0.060	0.001		
(4)	*n*-Hexane (M)	0	0.38	0.77	1.5
	Cl^- (M)	0.060	0.052	0.023	0.012

(1): 0.5% KC-300, dose rate 1.6×10^{19} eV/g hr, 1 hr
(2): 0.5% KC-400, dose rate 6.7×10^{18} eV/g hr, 1.5 hr
(3, 4): 0.5% KC-300, dose rate 8.4×10^{17} eV/g hr, 17 hr

increased with a decrease in the dose rate.

The dechlorination has to depend on additives such as electron acceptors or radical scavengers if the initiation step is Reaction (1) and if the chain-propagation steps are Reactions (3) and (4). Table 3 shows the effects of various additives on the chloride-ion concentration. The presence of a small amount of these electron acceptors inhibited the formation of chloride ions, this effect was especially notable in nitrobenzene. The addition of *n*-hexane had no particular effect, though. The reactivity of PCB's towards the solvated electrons has not been established, but it may be at least of the order of $10^9\sim10^{10}$ $M^{-1}s^{-1}$ in view of the facts that the rate constants of hydrated electrons for halogenated benzenes in aqueous solutions were 5×10^8 in monochlorobenzene,5) $6\sim7\times10^7$ in monofluorobenzene,5,6) $1\sim2\times10^9$ in difluorobenzene,6) and $\sim2\times10^{10}$ $M^{-1}s^{-1}$ in tetra and hexafluorobenzene.6) On the other hand, the rate constants were 5×10^9 for acetone or biphenyl and 3×10^{10} $M^{-1}s^{-1}$ for nitrobenzene.5) The almost complete suppression of the dechlorination by the presence of these electron acceptors, in the case of nitrobenzene particularly, cannot be explained only by the competition reaction of electrons with the dissociative electron attachment for PCB's, because $G(e^-_{solv})$ was only $0.9\sim1.0$, while $G(H)$, $G(H_2)$, and $G(CH_3)$ were 2.6, 1.27, and 1.06, respectively.10–12) A simple explanation of the suppression of the dechlorination is to inhibit the charge-transfer reaction in the propagation steps. The inhibition may involve the competition for an intermediate in one of the propagation steps, as has been mentioned by Sherman:3)

$$-\underset{|}{C}O^- + S \longrightarrow -\underset{|}{C}O + S^- \qquad (9)$$

The effect of the irradiation temperature on the dechlorination was studied at ~20 °C, 60 °C, and 90 °C. The samples were irradiated in an oil bath with a regulator, and the temperature was monitored by means of a thermocouple on a recorder. The dechlorination yield at 60 °C showed an increase of ~30%, but there was a small decrease at 90 °C in comparison with the value at ~20 °C. Arai *et al.*8) has shown that the yield decreased at higher temperatures in alcoholate solutions and that phenylcyclohexadiene instead of biphenyl was the main product at 200 °C. They presumed that a different reaction might occur at higher temperatures, *e.g.*, the decomposition of radicals or addition to a benzene ring.

Dechlorination of PCB's. In irradiating the PCB's in alkaline 2-propanol solutions, each peak height on the gas chromatogram varied with the dose. The gas chromatograms of the KC-300 solutions, irradiated and unirradiated, are shown in Fig. 3. From the analysis with the gas chromatograph-mass spectrometer, it was deduced that the peak numbers of 1, 2-3, 4-6, and 7 in Fig. 3 were identified with mono-, di-, tri-, and tetrachlorobiphenyl respectively. However, no special attention was paid to the concentration of each PCB and isomer. Figure 4 shows the effect of the dose on these peak heights. The yields of chloride ion are also plotted in Fig. 4. As the chloride ion was formed, the tetra- and trichlorobiphenyl decreased quickly, while the di- and monochlorobiphenyl decreased after having

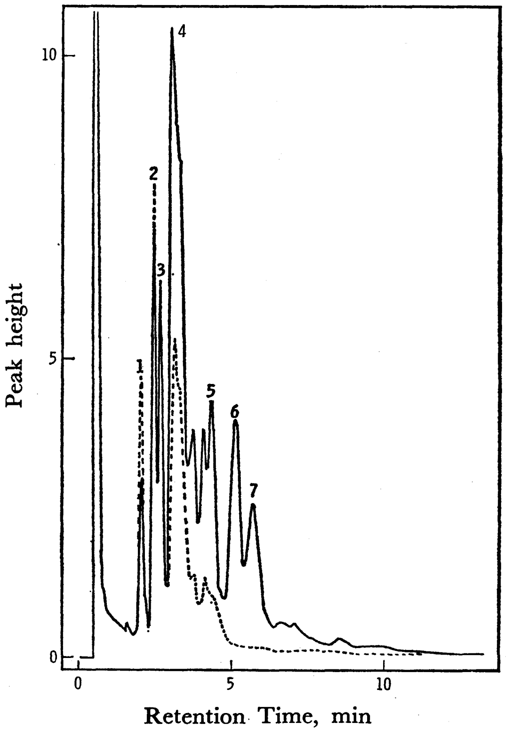

Fig. 3. Gas chromatogram of unirradiated and irradiated 0.2 M KOH-2-propanol solutions of 0.5% KC-300.
solid line: unirradiated solution
dashed line: irradiated solution

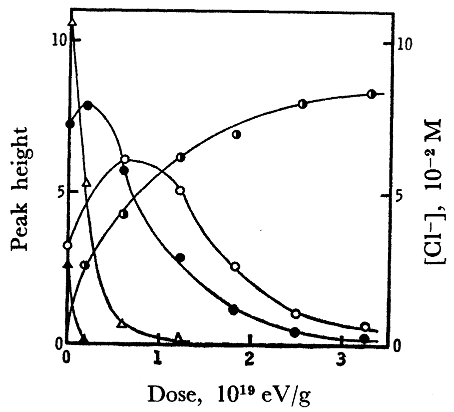

Fig. 4. Effect of irradiation dose on peak heights of chlorinated biphenyls in 0.2 M KOH-2-propanol solutions of 0.5% KC-300.

▲: tetrachlorobiphenyl, △: trichlorobiphenyl

●: dichlorobiphenyl, ○: monochlorobiphenyl

◑: chloride ion

dose rate: 1.1×10^{19} eV/g hr

increased temporarily. The facts indicate that the PCB's were dechlorinated by irradiation to form the less chlorinated biphenyls and were then finally converted to biphenyl *via* monochlorobiphenyl. It is well known that biphenyl is very stable to ionizing radiations. The variation in each peak height of the KC-400 and KC-500 solutions with the dose was similar to that of KC-300, but was a little more complicated.

Reaction of Chain Dechlorination. The radiolytic chain dechlorination of PCB's in the alkaline 2-propanol solution must be similar to the mechanism suggested by Sherman[3,4] for the decomposition of N_2O or of bromo- and iodobenzene in alkaline aliphatic alcohols.

In the dechlorination of PCB's: 1) Chain dechlorination did not occur in neutral alcohols but occurred in alkaline 2-propanol solutions and the $G(Cl^-)$ value depended on the concentration of the hydroxide ion. 2) The amounts of chloride ion and acetone formed, and the decrease in the hydroxide-ion concentration upon irradiation, were almost equal at each radiation dose. 3) The formation of the radical ion ($(CH_3)_2CO^-$) is known in alkaline aqueous solutions of 2-propanol,[13,14] and the rate of Reaction (2) was relatively fast and the pK-value was 12.2.[13] 4) The charge-transfer process was very important in the propagation steps of the chain-dechlorination reactions, because the dechlorination was effectively suppressed in the presence of a small amount of an electron acceptor such as nitrobenzene. 5) The dechlorination from highly chlorinated biphenyls was a predominant reaction in the first stage, and then the lowly chlorinated biphenyls were converted to biphenyl *via* monochlorobiphenyl.

On the basis of the above facts, the radiolytic-chain dechlorination of PCB's in deoxygenated alkaline 2-propanol solutions can be represented as follows:

$$(CH_3)_2CHOH \rightsquigarrow R\cdot,\ e^-_{solv},\ \text{other products} \tag{5}$$

$$C_{12}H_{10-n}Cl_n + e^-_{solv} \longrightarrow \cdot C_{12}H_{10-n}Cl_{n-1} + Cl^- \tag{6}$$

$$R\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + RH \tag{7}$$

$$\cdot C_{12}H_{10-n}Cl_{n-1} + (CH_3)_2CHOH \longrightarrow C_{12}H_{10-n+1}Cl_{n-1} + (CH_3)_2\dot{C}OH \tag{8}$$

$$(CH_3)_2\dot{C}OH + OH^- \rightleftharpoons (CH_3)_2CO^- + H_2O^{13)} \tag{9}$$

$$(CH_3)_2CO^- + C_{12}H_{10-n}Cl_n \longrightarrow (CH_3)_2CO + \cdot C_{12}H_{10-n}Cl_{n-1} + Cl^- \tag{10}$$

As Reactions (8), (9), and (10) proceed, n decreases to $n-1$, $n-2$, ⋯, and finally biphenyl is produced:

$$(CH_3)_2CO^- + C_{12}H_9Cl \longrightarrow (CH_3)_2CO + \cdot C_{12}H_9 + Cl^- \tag{11}$$

$$\cdot C_{12}H_9 + (CH_3)_2CHOH \longrightarrow C_{12}H_{10} + (CH_3)_2\dot{C}OH \tag{12}$$

The rate of the dechlorination, on the other hand, decreased with the dose, as is shown in Figs. 1, 2, and 4. This can be accounted for by the following reactions: 1. An electron acceptor such as biphenyl was formed. Indeed, the presence of a small amount of biphenyl decreased the $G(Cl^-)$. 2. The concentration of the hydroxide ion decreased with the dose. 3. Highly chlorinated PCB's changed into lowly chlorinated PCB's. The rate constant of Reaction (10) in the lowly chlorinated compounds may be lower than that in the highly chlorinated compounds, because the dechlorination yield of trichlorobenzene in the alkaline 2-propanol was higher than those of di- and monochlorobenzene.[15]

Assuming the initiation by Reactions (5)—(9), the propagation by (8)—(10), and a biomlecular termination by Reaction (13)[3];

$$2(CH_3)_2CO^- \xrightarrow[(CH_3)_2CHOH]{} (CH_3)_2CO + 2(CH_3)_2CHO^- \tag{13}$$

the initial yield of the dechlorination is given by Expression (I):

$$G(Cl^-) = G_e + k_{10}[\text{PCB's}]\{(G_e+G_R)/k_{13}\times D\}^{1/2} \tag{I}$$

where G_e: yield of scavengable electrons by PCB's
G_R: yield of the radical R
D: dose rate

A straight line is obtained in a plot of $G(Cl^-)$ *vs.* $(1/D)^{1/2}$ as is shown in Fig. 5. The bimolecular reaction (13) should be very important in the chain dechlorination; however, the positive intercept at $(1/D)^{1/2}=0$ may

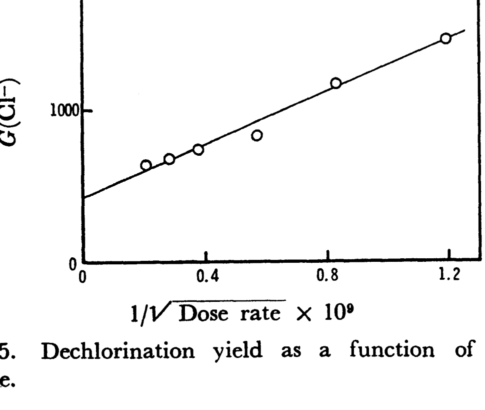

Fig. 5. Dechlorination yield as a function of dose rate.

TABLE 4. DECHLORINATION YIELDS OF PCB'S IN VARIOUS ALCOHOL SOLUTIONS OF 0.2 M KOH-0.5% KC-300

Solvent	G(Cl$^-$)	pK[13]
Methanol	4.2	10.7
Ethanol	4.9	11.6
1-Propanol	3.2	11.5
2-Propanol	700	12.2
n-Butanol	6.5	11.5
i-Butanol	9.0[a]	11.6
sec-Butyl alcohol	40	
t-Butyl alcohol	4.9	b)

Dose rate: 1.2×10^{19} eV/g hr. a) Dose rate 1.4×10^{18} eV/g hr. b) No observable dissociations up to pH 13.5.[14]

indicate an additional termination process.

Dechlorination of PCB's in Other Alcohols. It was found that the radiolytic dechlorination of PCB's in the alkaline 2-propanol solutions occurred efficiently. We studied whether a similar reaction proceeded in other simple aliphatic alcohols. The G(Cl$^-$) values in various alcohols containing 0.5% KC-300 and 0.2 M KOH are shown in Table 4. The G(Cl$^-$) in the solution of *sec*-butanol was relatively high, but it was only 4∼9 in the other alcohols.

In alkaline alcohol solutions, the G(dechlorination) value of carbon tetrachloride were 270, 62, and 7.7 in 2-propanol, 1-propanol, and *tert*-butyl alcohol respectively.[1] The magnitude in 1-propanol was indicative of a chain reaction. Moreover, the G(Cl$^-$) of DDT in neutral alcohols showed the same tendency.[2] The order of decreasing yield paralleled the order of increased C–H bond strength of the alcohols.

In our experiments, the chain-dechlorination reaction did not involve any alcohols other than 2-propanol and *sec*-butyl alcohol. It is known that in the pulsed radiolysis of alkaline aqueous solutions of aliphatic alcohol, the α-hydroxyl radicals dissociate to the transient RO$^-$ and that the pK-value of the reversible reaction (9) in 2-propanol is 12.2, while the others are lower, as is shown in Table 4.[13,14] Therefore, the equilibrium in Reaction (9) apparently shifts to the right-hand side except for the case of *sec*- and *tert*-butyl alcohol. The fact that PCB's in alcoholic solutions other than 2-propanol did not undergo the radiolytic chain dechlorination may be attributed to either the fact that the electron-transfer process to PCB's from RO$^-$ is inefficient or to the fact that the PCB radical cannot abstract the α-hydrogen of alcohols. We cannot decide which is the case. The 2-propoxide radical ion may release an electron more easily than the ions of other alcohols: also, the bond strength of α-hydrogen in 2-propanol is smaller than that of methanol, ethanol, 1-propanol, *n*-butanol, and isobutyl alcohol.

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