March, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 821—825 (1979) 821

Dechlorination of Polychlorinated Biphenyls by UV-irradiation. V. Reaction of 2,4,6-Trichlorobiphenyl in Neutral and Alkaline Alcoholic Solution

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(Received July 11, 1978)

2,4,6-Trichlorobiphenyl and seven other chlorobiphenyls have been photolyzed in both alkaline and neutral 2-propanol in order to investigate the reactivity and selectivity towards dechlorination. Predominant dechlorination at the 2-position has been confirmed for all PCBs in neutral solution and interpreted in terms of the steric and electronic effects of the phenyl group. In the presence of alkali, however, competitive elimination between the ortho and para chlorine atoms of 2,4-dichlorobiphenyl and 2,4,6-trichlorobiphenyl occurred. The photo-dechlorination of 2,3- and 2,5-dichlorobiphenyls took place however only at the ortho position. The dechlorination ratios (ortho/para) were 7.5 and 0.8 for 2,4-dichlorobiphenyl and 2,4,6-trichlorobiphenyl, respectively. This characteristic of the ortho chlorine atom has been elucidated assuming the steric and electronic effects of the phenyl group in the radical anion. A correlation has been found between the reduction potential and the reactivity of PCB in alkaline solution. The differences in reactivity among the chlorobiphenyls has been attributed to the electron acceptabilities in the ground states.

The authors have reported that a commertial PCB mixture (KC-300) dissolved in 2-propanol was successfully decomposed by ultraviolet radiation to biphenyl in the presence of sodium hydroxide,[1] the reaction proceeding rapidly by the chain degradative mechanism.[2–4] Some chlorobiphenyls, however, *e.g.* 2-chlorobiphenyl and 2,6-dichlorobiphenyl (2-CB and 2,6-DCB),[5] decomposed only slightly by the photolysis in alkaline solution and were detected in solution after other chlorobiphenyls had been completely decomposed to biphenyl.[4] In neutral alcoholic solutions the chlorine atom at the ortho position of tetrachlorobiphenyls was much more readily eliminated than at other positions.[6,7] No investigation has been undertaken on the difference in reactivities found among chlorobiphenyl homologues.

In the present study eight chlorobiphenyls (2-CB, 3-CB, 4-CB, 2,3-DCB, 2,4-DCB, 2,5-DCB, 2,6-DCB, and 2,4,6-TCB) have been photolyzed in both alkaline and neutral 2-propanol solutions in order to investigate the behavior of the ortho chlorine atom in detail.

Experimental

GLC analysis was conducted on a JEOL 20-K gas chromatograph with a flame ionization detector employing a 2 m× 3 mmϕ stainless steel column packed with 10% SE30 on 80—100 mesh chromosorb A (HMDS) or 15 m×1 mmϕ glass capillary column with OV-101 (Chromato Research Co.). Preparative liquid chromatography was performed with a JAI LC-08 employing a 600 mm×20 mmϕ stainless steel column packed with JAIGEL-1H; chloroform was used as the eluting solvent. Infrared spectra were obtained on a JASCO DS-701G spectrometer and mass spectra recorded at 24 eV on a JEOL Model D-100 mass spectrometer equipped with a gas chromatograph. UV spectra were taken with a Union Giken SM-401 spectrophotometer and melting points determined on a Yanagimoto micro melting apparatus.

Materials. The following reagents of special and guaranteed grade were used without further purification: 2,6-DCB (Nihon Chromato Co.), chloroanilines, 2-propanol and benzene (Wako Junyaku Co.). Isopentyl nitrite (Tokyo Kasei Co.) was distilled under a nitrogen atmosphere. 2-CB, 3-CB, 4-CB, 2,3-DCB, 2,4-DCB, 2,5-DCB, and 2,4,6-TCB were prepared by a modification of Cadogan's method,[8] the crude CBs being chromatographed over a silica-gel column using hexane as an eluent, and recrystallized from ethanol, ethanol–water, or petroleum ether. The melting points and UV spectra showed good agreement with the literature.[9] The purity was further checked by gas chromatography (>98%).

Irradiation Experiments. A solution of chlorobiphenyl (15 mmol/dm^3) and sodium hydroxide (30 mmol/dm^3) if necessary, in 2-propanol was photolyzed under the following conditions:

Procedure 1: After the solution (4.5 ml) in a quartz reaction cell was bubbled with purified nitrogen for 5 min, the cell was sealed and placed in a water bath kept at 30 °C. The solution was then irradiated through an interference filter (Nihon Shinku S50ϕ, 298 nm) with a 250 W high pressure mercury lamp (Ushio USH-250).

Procedure 2: A solution (400 ml) was photolyzed in a photochemical reaction vessel with an immersed 100 W high pressure mercury lamp (Ushio UM-102) without a filter under a stream of nitrogen at 30 °C.

Dechlorination Products. Irradiation of chlorobiphenyls gave low chlorinated biphenyls and biphenyl in both neutral and alkaline 2-propanol. 2,4,6-TCB gave, however, a biphenyl derivative having an alcoholic hydroxyl group together with the ordinary dechlorinated products in the alkaline solution. After evaporation of the solvent the residue was dissolved in chloroform. Preparative column chromatography and subsequent recrystallization from ethanol gave white needle crystals (mp 160—161 °C). NMR ($CDCl_3$), phenyl protons (δ 7.5—7.2, 7H, m), hydroxyl proton (δ 1.80, 1H, s), methyl protons (δ 1.60, 6H, s); IR (KBr), hydroxyl group (ν_{OH}, 3300 cm^{-1}, polymeric; ν_{C-O}, 1157 cm^{-1}, tertiary), methyl group (δ_{CH_3}, 1380, 1365 cm^{-1}; $\nu_{(CH_3)_2C}$, 1195 cm^{-1}, skeletal); MS (*m/e*), 282 ($M^+ + 2$), 280 (M^+), 267 ($M^+ - CH_3$), 262 ($M^+ - H_2O$). On the basis of this data the compound has been identified as *xx′*-dichloro-*y*-(1-hydroxy-1-methylethyl)biphenyl. The substituted position in

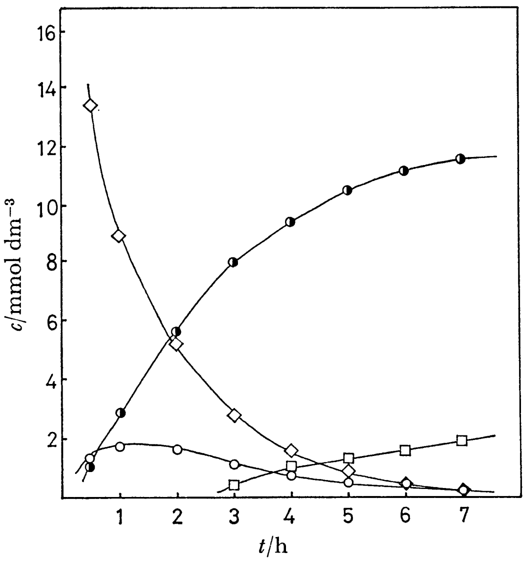

Fig. 1. Decomposition of 2,4,6-TCB in neutral 2-propanol ◇: 2,4,6-TCB, ○: 2,4-DCB, ◑: 4-CB □: biphenyl.
Initial concentration of 2,4,6-TCB: 16.2 mmol/dm^3.
Photolysis was carried out by Procedure 2 (no filter).

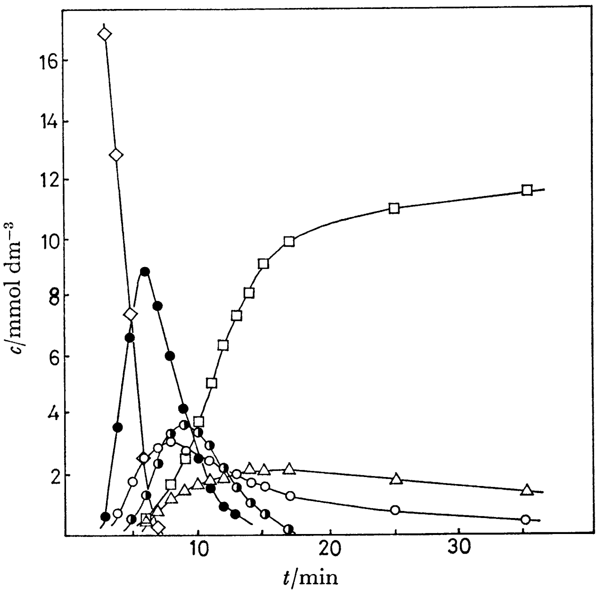

Fig. 2. Decomposition of 2,4,6-TCB in alkaline alcoholic solution
◇: 2,4,6-TCB, ●: 2,4-DCB, ◑: 4-CB, ○: 2,6-DCB, △: 2-CB, □: biphenyl.
Initial concentration of 2,4,6-TCB: 17.9 mmol/dm^3.
Photolysis was carried out by Procedure 2 (no filter).

Table 1. Dechlorination of CBs[a)]

Compound	Positional selectivity (%)		
	Neutral	Alkaline	
2,3-DCB	100 (ortho)	100 (ortho)	
2,4-DCB	100 (ortho)	88 (ortho)	12 (para)
2,5-DCB	100 (ortho)	100 (ortho)	
3,4-DCB	100 (meta)	100 (para)	
2,4,6-TCB	100 (ortho)	44 (ortho)	56 (para)

a) Photolysis was carried out by Procedure 1.

the phenyl ring cannot be clarified from this data. When the alkaline solutions of 2,6- and 2,4-DCB were photolyzed, however, 2,4-DCB afforded an alcohol in a small amount while 2,6-DCB did not and from this, 2,6-dichloro-4-(1-hydroxy-1-methylethyl)biphenyl (**1**) was considered to be formed in the photolysis of 2,4,6-TCB. On irradiation in alkaline solution **1** was both dechlorinated and dehydrated and gave the following compounds; 2-chloro-4-isopropenylbiphenyl (**2**), MS (*m/e*), 230 ($M^+ + 2$), 228 (M^+), 193 ($M^+ - Cl$); 4-isopropenylbiphenyl (**3**), MS (*m/e*), 194 (M^+), 179 ($M^+ - CH_3$), 153 ($M^+ - C(CH_3){=}CH_2$).

Results and Discussion

Dechlorination of CBs in Neutral Solution. The photolysis of 2,4,6-TCB in 2-propanol gave 2,4-DCB, 4-CB, and biphenyl as shown in Fig. 1. Elimination occurred predominantly at the ortho position, and indeed no para dechlorinated products, *e.g.* 2,6-DCB or 2-CB, were found in the photolyzed solution. This prominent feature of the ortho chlorine atom was also observed in the photolysis of other chlorobiphenyls as follows. The photo-products of 2,3-DCB, 2,4-DCB, and 2,5-DCB were 3-CB, 4-CB, and 3-CB, respectively. 2-CB showed an outstanding reactivity among the monochlorobiphenyls and all results indicate a preference for elimination at the ortho chlorine atom in the neutral solution. The selectivities of the dechlorination are summarized in Table 1. The results in neutral solution are understandable bearing in mind the steric and the electronic effects of the phenyl group. Since biphenyl is known to have a planar structures in the excited state,[10] involving a high degree of conjugation between the two phenyl rings, the ortho chlorinated biphenyl would be largely unstable in the excited state. Therefore, the departure of the chlorine atom from the ortho position stabilizes the conjugation system. Ruzo *et al.*,[6,7] on the basis of the photolysis of tetrachlorobiphenyls in neutral solution, concluded that the marked elimination of the ortho chlorine atom was caused by both electronic and steric effects of the phenyl group, especially the latter.

Dechlorination of CBs in the Presence of Alkali. In the presence of alkali the competitive elimination of the ortho and para chlorine atoms of 2,4,6-TCB occurred as indicated in Fig. 2. The primary products were 2,4-DCB and 2,6-DCB, and further irradiation resulted in the formation of 4-CB and 2-CB from 2,4-DCB. The photo-dechlorination of 2,3- and 2,5-DCBs took place only at the ortho position, even in the presence of alkali. The reactivities of 2,6-DCB and 2-CB were, however, much lower than that of 2,4-DCB and 4-CB. The selectivities of the dechlorination reaction in the presence of alkali are compared in Table 1. Thus the ortho chlorine atom was not predominantly eliminated, in contrast to the prominent feature in the neutral solution.

The following chain mechanism, proposed for the photoreaction of PCBs,[2–4] appears to help the understanding of the reactivity of ortho chlorinated biphenyls.

$$\mathrm{PCB}(n) \xrightarrow{h\nu} \mathrm{PCB}(n-1,\mathrm{j})\cdot + \mathrm{Cl}\cdot \quad (1)$$

$$\mathrm{Cl}\cdot + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \mathrm{HCl} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \quad (2)$$

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + (\mathrm{CH_3})_2\mathrm{CHO}^- \longrightarrow (\mathrm{CH_3})_2\mathrm{CO}^{\dot{-}} + (\mathrm{CH_3})_2\mathrm{CHOH} \quad (3)$$

$$(\mathrm{CH_3})_2\mathrm{CO}^{\dot{-}} + \mathrm{PCB}(n) \xrightarrow{k_{\mathrm{red}}} (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{PCB}(n)^{\dot{-}} \quad (4)$$

$$\mathrm{PCB}(n)^{\dot{-}} \xrightarrow{k_{\mathrm{el}}(\mathrm{i})} \mathrm{PCB}(n-1,\mathrm{i})\cdot + \mathrm{Cl}^- \quad (5)$$

$$\mathrm{PCB}(n-1,\mathrm{i})\cdot + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \mathrm{PCB}(n-1,\mathrm{i}) + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \quad (6)$$

$$2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \longrightarrow \text{Termination} \quad (7)$$

PCB(n); n is the number of chlorine atoms substituted in the phenyl ring.
PCB($n-1$,i)$\cdot$; CB radical formed by the chlorine elimination at the i-position.
k_{el}(i); the rate constant of the chlorine elimination at the i-position of PCB(n)$^{\dot{-}}$.

The radical anion of PCB would afford PCB($n-1$,i)$\cdot$ by elimination of the chloride ion. Assuming steady state conditions for the CB radical PCB($n-1$, i)$\cdot$, the rate of dechlorination may be written:

$$\mathrm{d}[\mathrm{PCB}(n-1,\mathrm{i})]/\mathrm{d}t = k_{\mathrm{el}}(\mathrm{i})[\mathrm{PCB}(n)^{\dot{-}}], \quad (8)$$

where, Reaction 1[11] is assumed negligible compared with Reaction 5, since the chain length is expected to be large in alkaline solution : the quantum yield at 298 nm for KC-300 has been determined to be 36 in alkaline solution and 0.09 in neutral solution.[12] Then the relative rate constant for dechlorination at the i-position to that at the j-position is given by

$$[\mathrm{PCB}(n-1,\mathrm{i})]/[\mathrm{PCB}(n-1,\mathrm{j})] = k_{\mathrm{el}}(\mathrm{i})/k_{\mathrm{el}}(\mathrm{j}). \quad (9)$$

The value $k_{\mathrm{el}}(\mathrm{i})/k_{\mathrm{el}}(\mathrm{j})$ can be evaluated by the amount of two daughter CBs derived from the parent PCB. As considered above the chlorine atom at the ortho position was selectively eliminated in the photolysis. Therefore similar acceleration due to the steric effect of the phenyl group as observed in the neutral solution can be expected in the dechlorination of PCB(n)$^{\dot{-}}$ to yield PCB($n-1$, i)$\cdot$.

Photolysis of 2,4-DCB in Alkaline Solution: 2,4-DCB produced 2-CB and 4-CB by photolysis followed by degradation to biphenyl as shown in Table 2. These reactions proceeded simultaneously so that the concentration ratio [2-CB]/[4-CB] in the photolyzed solution did not give the true ratio of daughter CBs derived from 2,4-DCB. Therefore, in order to obtain the true value of $k_{\mathrm{el}}(\mathrm{i})/k_{\mathrm{el}}$ (j) it is necessary to find the respective rates of 4-CB and 2-CB to yield biphenyl. Assuming steady state conditions for [2-CB$^{\dot{-}}$], [4-CB$^{\dot{-}}$], [Biph-(2-CB)$\cdot$], and [Biph(4-CB)$\cdot$], the rate of biphenyl formation attributed to 4-CB is given by

$$\frac{\mathrm{d}[\mathrm{Biph(4\text{-}CB)}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{4\text{-}CB}]}{\mathrm{d}t}, \quad (10)$$

$$\frac{\mathrm{d}[\mathrm{Biph(4\text{-}CB)}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Biph}]}{\mathrm{d}t}\cdot\frac{(k_{\mathrm{red}}(4)/k_{\mathrm{red}}(2))[\mathrm{4\text{-}CB}]}{(k_{\mathrm{red}}(4)/k_{\mathrm{red}}(2))[\mathrm{4\text{-}CB}]+[\mathrm{2\text{-}CB}]}, \quad (11)$$

where, [Biph(4-CB)] and [Biph] represent the concentration of biphenyl derived from 4-CB and the biphenyl concentration in the photolyzed solution, respectively. The formation rate of Biph(2-CB) can also be written by similar equations. Combination of these four equations results in Eq. 12, by which the $k_{\mathrm{red}}(4)/k_{\mathrm{red}}(2)$ can be determined.

$$\frac{\ln([\mathrm{4\text{-}CB}]_0/[\mathrm{4\text{-}CB}])}{\ln([\mathrm{2\text{-}CB}]_0/[\mathrm{2\text{-}CB}])} = k_{\mathrm{red}}(4)/k_{\mathrm{red}}(2) \quad (12)$$

TABLE 2. DECOMPOSITION OF 2,4-DCB IN ALKALINE ALCOHOLIC SOLUTION[a,b)]

Conversion of 2,4-DCB %	Biph	2-CB	4-CB	Biph+ 4-CB	(Biph+4-CB)/ 2-CB[c)]
	c/mmol dm^{-3}				
6.4	0.14	0.13	0.70	0.84	6.5
7.0	0.17	0.17	0.76	0.93	6.1
16.5	0.94	0.25	1.32	2.25	9.0
39.3	1.97	0.77	3.23	5.20	6.8
49.3	3.70	0.93	2.87	6.57	7.1
61.4	5.23	1.13	2.98	8.21	7.3
72.0	8.02	1.17	1.75	9.78	8.4
72.2	8.40	1.16	1.42	9.82	8.5

a) Initial concentration of 2,4-DCB; 15.2 mmol/dm^3. b) Photolysis was carried out by Procedure 1. c) ((Biph+4-CB)/2-CB)$_{\mathrm{av}}$=7.5±1.0.

4-CB and 2-CB were consequently decomposed competitively in alkaline solution in order to evaluate the left hand side of Eq. 12, the results of which are summarized in Table 3. The average value of 17.2±4.5 suggests that 4-CB is far more reactive than 2-CB. Table 2 indicates that the concentration of 4-CB is always higher than that of 2-CB by a factor of 1.2 to 5.1. Consequently the following inequality can be assumed:

$$(k_{\mathrm{red}}(4)/k_{\mathrm{red}}(2))[\mathrm{4\text{-}CB}] \gg [\mathrm{2\text{-}CB}].$$

Resolving Eq. 11 under these conditions gives the simple relation ; [Biph(4-CB)]=[Biph]. This indicates that all biphenyl can be assumed to be derived from 4-CB, and that 2-CB makes a negligible contribution to the biphenyl formation. Thus the true amounts of 4-CB and 2-CB produced by the dechlorination of the radical anion 2,4-DCB$^{\dot{-}}$ are [Biph]+[4-CB] and [2-CB], respectively. These concentrations were then utillized to calculate the value of $k_{\mathrm{el}}(2)/k_{\mathrm{el}}(4)$ using Eq. 9. As Table 2 shows, in the dechlorination of 2,4-DCB$^{\dot{-}}$ the chlorine at the ortho position is more easily eliminated by a factor of 7.5±1.0 than that at the para position, a result explainable on the assumption of the steric acceleration effect of the phenyl group.

Photolysis of 2,4,6-TCB in Alakline Solution: 2,4,6-TCB gave 2,4-DCB, 2,6-DCB, and compound **1**. These compounds were negligibly dechlorinated during the photolysis so that any further reduction of the compounds was neglected in the calculation of Eq. 9. As compound **1** has a 1-hydroxy-1-methylethyl group at position 4, the true ratio of daughter compounds derived from 2,4,6-TCB will be given by [2,4-DCB]/([2,6-

TABLE 3. COMPETITIVE DECHLORINATION OF 2-CB AND 4-CB IN ALKALINE ALCOHOLIC SOLUTION[e)]

Conversion %	2-CB c/mmol dm^{-3}	4-CB	$k_{red}(4)/k_{red}(2)$[d)]
2.4[a)]	3.74	3.55	17.5
6.9[b)]	3.52	3.23	24.9
8.4[c)]	3.47	2.84	15.0
22.8[a)]	3.59	2.18	12.3
35.1[a)]	3.58	1.27	23.2
55.7[c)]	2.83	0.22	12.7
58.2[a)]	2.99	0.14	14.5

Initial concentration of 2-CB and 4-CB: a) 3.75, 3.72; b) 3.54, 3.37; c) 3.51, 3.37 mmol/dm^3, respectively. d) $(k_{red}(4)/k_{red}(2))_{av}=17.2\pm4.5$. e) Photolysis was carried out by Procedure 1.

TABLE 4. DECOMPOSITION OF 2,4,6-TCB IN ALKALINE ALCOHOLIC SOLUTION[a),b)]

Conversion %	2,6-DCB c/mmol dm^{-3}	2,4-DCB	**1**	2,4-DCB/(2,6-DCB+**1**)[c)]
5.5	0.13	0.50	0.20	1.52
7.5	0.18	0.58	0.27	1.29
9.3	0.23	0.87	0.31	1.61
9.8	0.28	0.91	0.35	1.44
20.1	0.48	1.62	0.48	1.69
27.2	0.84	2.66	0.72	1.70
43.7	1.13	4.14	1.10	1.86
44.1	1.03	4.14	1.10	1.94

a) Initial concentration of 2,4,6-TCB were 15.7—13.7 mmol/dm^3. b) Photolysis was carried out by Procedure 1. c) $(2,4\text{-DCB}/(2,6\text{-DCB}+\mathbf{1}))_{av}=1.6\pm0.1$.

DCB]+[**1**]), the experimental results of which are shown in Table 4. The value of 1.6±0.1 was obtained as the average ratio from eight measurements. The $k_{el}(2)/k_{el}(4)$ is thus 0.8 since the elimination at the 2-, and 6-position of 2,4,6-TCB are equivalent. Contrary to expectations this indicates that the para chlorine atom is more active than the ortho chlorine atom. The explanation for this result is as follows. Since the presence of the chlorine atom at position 6 disturbs the release of the dihedral angle between the two phenyl rings by the dechlorination at position 2, the steric acceleration effect by the phenyl group cannot markedly affect the dechlorination.

Photolysis of 3,4-DCB. 3,4-DCB was dechlorinated exclusively at position 4 in the presence of alkali. Since this elimination cannot be explained only by the steric effect of the phenyl group, the electronic effect must be considered. As shown in Table 1 the elimination of para chlorine atom was also observed in the alkaline solution of 2,4-DCB and 2,4,6-TCB. From these results it has been assumed that the para position of $PCB^{\dot{-}}$ is activated by the electronic effect.

In neutral solution 3,4-DCB did not eliminate the para chlorine atom and similar inactivity in the para position has been observed in 2,4-DCB and 2,4,6-TCB. This shows a remarkable contrast to the alkaline reaction. In the photolysis of 3,4-DCB only the meta chlorine atom was eliminated but 2,3-DCB and 2,5-DCB did not eliminate the meta chlorine. This suggests that the para chlorine atom may be stabilized by the electronic effect of the phenyl group in the photo-excited state, but that the steric acceleration effect is far more important than the electronic effect in the dechlorination at the ortho position from the photo-excited CB.

Relative Reactivities of PCBs in the Presence of Alkali. Successive dechlorination of 2,4,6-TCB produced 2,4-DCB, 2,6-DCB, 4-CB, and finally biphenyl in the presence of alkali as shown Fig. 2. Consequently the ease of dechlorination is expected to increase in the order : 2,4,6-TCB > 2,4-DCB > 4-CB > 2,6-DCB ≈ 2-CB. This reaction scheme suggests that the relative reactivities of PCBs in the presence of alkali will be determined by the k_{red} value. As described above the value of $(k_{red})_{4-CB}/(k_{red})_{2-CB}$ has been evaluated as 17.2±4.5 from Eq. 12. This shows 4-CB is more readily dechlorinated than 2-CB by a factor of 17.2. For di-, and poly-CBs, however, k_{red} is not easy to estimate experimentally due to further reaction of the daughter CBs. Since Reaction 4 is an electron transfer step from the radical anion $(CH_3)_2CO^{\dot{-}}$ to PCB(n), the reactivity k_{red} will depend on the reduction potential of PCB(n). The reduction potentials of 2-CB, 4-CB, 2,6-DCB, 2,4-DCB, 2,4,6-TCB, and biphenyl have been reported[13)] as −2.097, −2.056, −2.107, −1.983, −1.966, and −2.411 E/V *vs.* SCE, respectively. These reduction potentials are reasonably correlated with the ease of dechlorination of CBs. It was thus considered that the reactivities of the CB homologues largely depend on the electron acceptabilities in the ground state.

The authors wish to express their thanks to Mr. Haruo Inoue of Tokyo Metropolitan University for his valuable suggestions, and to Mr. Tsutomu Shinoda for his help in the preparation of this paper.

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5) CB denotes chlorobiphenyl; *e.g.*, dichlorobiphenyl and 2,4,6-trichlorobiphenyl are abbreviated to DCB and 2,4,6-TCB, respectively.

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triethylamine (M. Ohashi, K. Tsujimoto, and K. Seki, *J. Chem. Soc., Chem. Commun.*, **1973**, 384.) the following electron transfer reaction, besides the direct photo-dissociation shown in the Reaction 1, may be considered in alkaline solution.

$\mathrm{PCB}(n)^* + (\mathrm{CH_3})_2\mathrm{CHO}^-$ or $\mathrm{OH}^- \rightarrow \mathrm{PCB}(n)^- + (\mathrm{CH_3})_2\mathrm{CHO}\cdot$ or $\mathrm{OH}\cdot$

Even if this reaction takes place in the dechlorination reaction, this will be disregarded for similar reasons that Reaction 1 was neglected.

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