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The Kinetics of the Radiation-induced Chain Dechlorination of Hexachloroethane in Alcohols

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The kinetics of the radiation-induced dechlorination of hexachloroethane was investigated in deoxygenated alcohol solutions. The major products were hydrogen chloride, pentachloroethane, 1,1,2,2-tetrachloroethane, tetrachloroethylene, and aldehydes or acetone. No 1,1,1,2-tetrachloroethane was observed. The radiation-chemical yields of these products and the disappearance of hexachloroethane were quite high; these facts indicate that a chain reaction is involved in these processes. After the hexachloroethane had effectively dechlorinated down to tetrachloro compounds, there were no marked changes in the lower chlorinated compound upon continuous irradiation. Tetrachloroethane was formed *via* pentachloroethane, but tetrachloroethylene was produced by means of $C_2Cl_5 \rightarrow C_2Cl_4 + Cl$ reaction and the yield was paticularly high in methanol compared with the other alcohols. The chain length of the dechlorination from hexachloroethane to pentachloroethane and from pentachloroethane to tetrachloroethane increased in the order of 2-propanol>ethanol>methanol. The $G(-C_2Cl_6)$ and G(products) were proportional to (dose rate)$^{-1/2}$, and the ratio of $G(C_2HCl_5)$ to $G(C_2Cl_4)$ was a constant in each alcohol solution, regardless of the dose rate. The α-hydroxy alkyl radical is the chain carrier for the dechlorination reaction of hexachloroethane in alcohol solutions. The relative rates of the dechlorination were found to be 1, 3, and 14 for $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$, respectively. The order in the rate is in agreement with that of the redox potential of these radicals. The effect of the irradiation temperature on the products yields was also examined.

Halocarbons are important for examining the fundamental processes in radiation chemistry because of their high electron affinity, and the main reaction of the radiolysis is dehalogenation.[1] It is known that the radiation-induced chain dehalogenation of some organic halocompounds proceeds in aqueous solutions containing a small amount of alcohol[2,3] and in the solutions of alcohols[4–6] or cyclohexane.[7–11] Sherman *et al.* showed that tetrachloromethane[4] and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT)[5] were dechlorinated to trichloromethane and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDE) by a relatively short chain reaction in γ-irradiated 1- and 2-propanol solutions at room temperature. Rajbenbach *et al.* indicated that the chain-dechlorination process was induced by the γ-irradiation of dilute cyclohexane solutions of chloroethanes at temperatures of 25—250 °C.[7–11] The dechlorination yield was not so high at room temperature (for example, $G(HCl) \approx 100$ in 0.1 M hexachloroethane), and a relatively high temperature was required for a high G-value.

On the other hand, it is known that a chain dechlorination reaction took place upon the γ-irradiation of dilute alkaline 2-propanol solutions of alkyl halides,[12] polychlorinated biphenyls[13,14] and of penta and trichlorobenzene[15] at room temperature (for instance, $G(Cl^-) \approx 6500$ in a 0.2 M KOH-2-propanol solution of 0.07 M pentachlorobenzene). These substances were changed to the lower chlorinated compounds, producing potassium chloride and acetone. The chain reaction is probably caused by the $(CH_3)_2\dot{C}O^-$ formed by the reaction of the hydroxide ion with the $(CH_3)_2\dot{C}OH$ radical. On the other hand, no marked chain dechlorination occurred in alkaline methanol and ethanol solutions or in neutral simple aliphatic alcohols.

The purpose of this study is to investigate the kinetics of the radiation-induced chain dechlorination in simple, neutral aliphatic alcohol solutions of hexachloroethane with a half-wave potential lower than tetrachloromethane, DDT, and pentachlorobenzene.

Experimental

Materials. The methanol, ethanol, and 2-propanol (Dojin Chemical's spectrophotometric reagent or super special grade) were used as received. The chloroethanes and tetrachloroethylene used were special reagent grade from the Tokyo Kasei Co., Ltd.

Procedure. Aliquots(4 ml) of freshly prepared alcohol solutions of $1—2 \times 10^{-2}$ M hexachloroethane in a 12-mm OD Pyrex tube equipped with a stopper were irradiated with ^{60}Co γ-rays at room temperature after having been deoxygenated by flushing the solutions for about 30 min with pure nitrogen gas. The dose rate was determined by means of a ferrous sulfate dosimeter, and the absorbed dose in the samples was calculated by correcting for the electron density of the solutions. Irradiation was performed at the dose rate of $5.25 \times 10^{17}—2.80 \times 10^{19}$ eV/g h. The irradiation under a constant temperature was carried out in a water bath with a regulator.

Analysis. The hydrochloric acid was analysed by titration with a 0.02 M sodium hydroxide solution and with a 0.01 M silver nitrate solution. The determination of the other substances was carried out by means of a Shimadzu 4B gas chromatograph equipped with a flame-ionization detector. Chloroethanes (hexa-, penta-, and tetra chloroethane) were determined at 80 °C by the use of a 3-m glass column filled with silicon OV-17 on chromosorb. For tetrachloroethylene and aldehydes, a 2-m glass column packed with polyethylene glycol-200 was used. The acetone was measured at 50 °C by using a 2-m glass column of polyethylene glycol-20M. These substances were quantitatively determined by a comparison of their peak heights with those of authentic samples. A formalin solution(about 37%) was used as a standard for formaldehyde, and the concentration was measured in advance by iodometry. All the products except hydrochloric acid were identified by the use of a gas chromatograph-mass spectrometer(Nihondenshi Model JMS-D100).

Results and Discussion

Yield-dose Curve in Alcohol Solutions of Hexachloroethane. The products identified in the radiolysis of deoxygenated alcohol solutions of hexachloroethane were hydrogen chloride, pentachloroethane(C_2HCl_5), 1,1,2,2-tetrachloroethane($C_2H_2Cl_4$), tetrachloroethylene(C_2Cl_4), and some carbonyl compounds. No 1,1,1,2-tetrachloroethane was observed.

2-Propanol Solution: Figure 1 shows the concentrations of C_2Cl_6, HCl, C_2HCl_5, $C_2H_2Cl_4$, and C_2Cl_4 as functions of the dose. The chloride ion increased with a very high yield up to about 7×10^{17} eV/g, and then showed an almost constant value above 1.5×10^{18} eV/g. The hexachloroethane decreased rapidly with the dose until most of it disappeared at about 3×10^{17} eV/g. On the other hand, the C_2HCl_5 increased with the decrease in C_2Cl_6, and the concentration of C_2HCl_5 was practically comparable to that of the C_2Cl_6 consumption. Further irradiation caused a rapid decrease in C_2HCl_5 and a concomitant increase in $C_2H_2Cl_4$. The concentrations of $C_2H_2Cl_4$ formation and C_2HCl_5 consumption were almost equal in the dose range from 0.58 to 1.8×10^{18} eV/g, and above 2×10^{18} eV/g there were also no marked change in the concentration of $C_2H_2Cl_4$, which was a half of that of the chloride ion and was equal to the initial concentration of C_2Cl_6. Only a tetrachloroethylene was observed in the whole dose region. The radiation-chemical yields(*G*-values) at the dose of 3.42×10^{17} eV/g are calculated to be 2300, 1700, 60, and 2000 for the chloride ion, C_2HCl_5, C_2Cl_4, and, $-C_2Cl_6$ respectively. It was confirmed in other experimental series that the yield of acetone was almost equivalent to that of the chloride ion. These results suggest that C_2Cl_6 in the deoxygenated 2-propanol solution is effectively dechlorinated by a chain reaction to $C_2H_2Cl_4$ via C_2HCl_5, thus forming hydrochloric acid and acetone.

Methanol Solution: The yield-dose plots in methanol solution of C_2Cl_6 are shown in Fig. 2. The concentrations of HCl, $C_2H_2Cl_4$, C_2Cl_4, and formaldehyde increased monotonously with the decrease in C_2Cl_6 up to about 1.3×10^{19} eV/g; on the other hand, C_2HCl_5 decreased very slowly with the dose above $\approx6\times10^{18}$ eV/g. These *G*-values, which were calculated from the linear portions of these curves in Fig. 2, were 540, 110, 200, 290, and 320 for HCl, C_2HCl_5, C_2Cl_4, $-C_2Cl_6$, and formaldehyde.

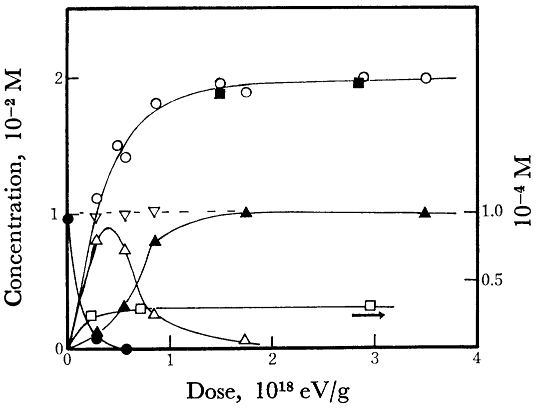

Fig. 1. Product yields as a function of dose from 9.6×10^{-3} M C_2Cl_6 in 2-propanol.
Dose rate, 1.71×10^{18} eV/g h.
○: Cl^-, ■: H^+, ●: C_2Cl_6, △: C_2HCl_5, ▲: $C_2H_2Cl_4$, □: C_2Cl_4, ▽: sum of C_2Cl_6, C_2HCl_5, $C_2H_2Cl_4$, and C_2Cl_4.

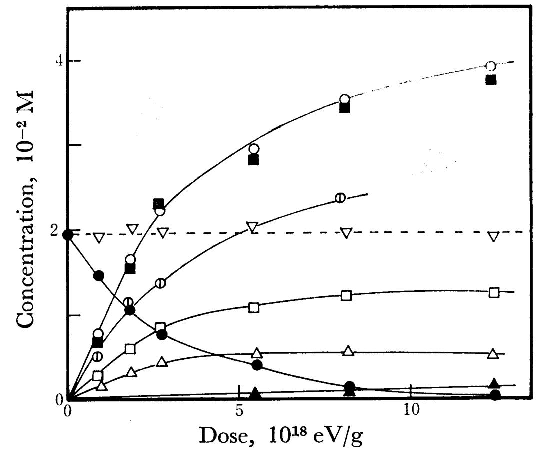

Fig. 2. Product yields as a function of dose from 1.96×10^{-2} M C_2Cl_6 in methanol.
Dose rate, 5.43×10^{18} eV/g h.
○: Cl^-, ■: H^+, ●: C_2Cl_6, △: C_2HCl_5, ▲: $C_2H_2Cl_4$, □: C_2Cl_4, ⦶: HCHO, ▽: sum of C_2Cl_6, C_2HCl_5, $C_2H_2Cl_4$, and C_2Cl_4.

The largest differences in comparison with the results for 2-propanol solutions are found to be as follows:

a. All the *G*-values in the methanol except $G(C_2Cl_4)$ are much lower than those of 2-propanol.

b. $G(-C_2Cl_6)$ is considerably lower than $G(Cl^-)$ and, on the contrary, is about three times as high as $G(C_2HCl_5)$.

c. $G(C_2Cl_4)$ is two times as high as $G(C_2HCl_5)$.

d. A considerable amount of formaldehyde is produced instead of acetone in the 2-propanol, and the concentration of formaldehyde is remarkably lower than that of the chloride ion.

e. After almost all of the C_2Cl_6 has disappeared (above 8×10^{18} eV/g), the decrease of C_2HCl_5 with the dose is only a little.

The effect of the initial concentration of C_2Cl_6 on the *G*-values is given in Table 1. These values increased with the initial concentration.

Ethanol Solution: The relationship between the concentrations of products and the dose was relatively similar to the result for 2-propanol, as is shown in Fig.

TABLE 1. EFFECTS OF THE CONCENTRATION OF C_2Cl_6 IN METHANOL ON THE *G*-VALUES

C_2Cl_6 10^{-2} M	*G*-value				
	Cl^-	$-C_2Cl_6$	C_2HCl_5	C_2Cl_4	HCHO
0.54	161	90	29	58	93
1.96	542	288	109	218	320
4.91	730	445	147	277	490

Dose rate : 5.43×10^{18} eV/g h.

3. Further irradiation suppressed the C_2HCl_5 completely, and the concentrations of the chloride ion and $C_2H_2Cl_4$ reached an almost constant value. At that time, the concentration of $C_2H_2Cl_4$ was equivalent to the initial C_2Cl_6 concentration and was one half of the chloride ion.

As can be seen in Figs. 1, 2, and 3, the fact that the sums of the concentrations of C_2Cl_6, C_2HCl_5, C_2Cl_4, and $C_2H_2Cl_4$ observed in the irradiated solutions were always correspondent to the initial concentration of C_2Cl_6 indicates that the production of other chlorinated compounds can be ignored.

Dechlorination of C_2HCl_5, $C_2H_2Cl_4$, and C_2Cl_4 in Alcohol Solutions. The results in the methanol and 2-propanol solutions of 1×10^{-2} M C_2HCl_5 are given in Fig. 4. In the 2-propanol, the concentrations of the chloride ion, $-C_2HCl_5$, and acetone were almost equal to $G\approx700$. This fact shows that C_2HCl_5 is also dechlorinated by the chain reaction to form $C_2H_2Cl_4$, the chloride ion, and acetone. On the other hand, the $G(Cl^-)$ in the methanol was merely 24, and no C_2Cl_4 was observed in either solution.

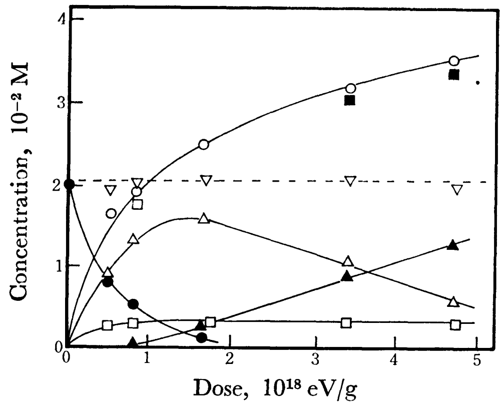

Fig. 3. Product yields as a function of dose from 2.01 $\times10^{-2}$ M C_2Cl_6 in ethanol.
Dose rate, 1.68×10^{18} eV/g h.
○: Cl^-, ■: H^+, ●: C_2Cl_6, △: C_2HCl_5, ▲: $C_2H_2Cl_4$, □: C_2Cl_4, ▽: sum of C_2Cl_6, C_2HCl_5, $C_2H_2Cl_4$, and C_2Cl_4.

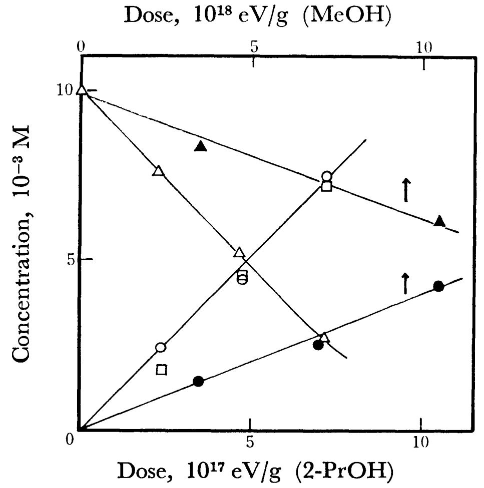

Fig. 4. Product yields as a function of dose from 1.0 $\times10^{-2}$ M C_2HCl_5 in methanol and in 2-propanol.
Dose rate, 5.22×10^{18} eV/g h in methanol (closed symbol), 1.43×10^{18} eV/g h in 2-propanol (open symbol).
○, ●: Cl^-, △, ▲: C_2HCl_5, □: $C_2H_2Cl_4$.

Upon irradiating the solutions of 1×10^{-2} M $C_2H_2Cl_4$ and C_2Cl_4, the hydrochloric acid increased linearly with the dose. The G-values in the $C_2H_2Cl_4$ solutions were 4.3, 4.2 (dose rate, 1.1×10^{19} eV/g h), and 3.5 (dose rate, 7.6×10^{18} eV/g h) for 2-propanol, ethanol, and methanol. For C_2Cl_4, these values were 6 in 2-propanol (dose rate, 2.1×10^{19} eV/g h) and 2.2 in methanol (dose rate, 1.1×10^{19} eV/g h). Therefore, it is found that $C_2H_2Cl_4$ and C_2Cl_4 are not dechlorinated by the chain reaction any longer. These findings are in good agreement with the results for C_2Cl_6 solutions presented in Figs. 1, 2, and 3.

Effect of the Dose Rate on the G-values in 2×10^{-2} M C_2Cl_6 Solutions. The effects of the dose rate on

TABLE 2. EFFECTS OF THE DOSE RATE ON THE G-VALUES

Solution	Dose rate 10^{18} eV/g h	G-value							
		Cl^-	$-C_2Cl_6(a)$	$C_2HCl_5(b)$	$C_2Cl_4(c)$	R_1R_2CO	$a+c$	$b+c$	b/c
2-Propanol	0.525	8000	7700	7000	140	7500	7840	7140	50
	0.855	6800	6000	5900		5100			
	1.70	5100	4900	4600	100	5100	5000	4700	46
	2.76	4900	4400	4600		4600			
	5.32	3500	3000	3000		3300			
	6.71	3100	2900	3000	65	3000	2965	3065	46
	11.9	2500			55				
Ethanol	0.855	2600	2200	2000	220		2420	2220	9.1
	1.70	2200	1800	1700	180		1980	1880	9.4
	5.21	1800	1400	1200	150		1550	1350	8.0
Methanol	0.585	1200	700	210	400	660	1100	610	0.52
	1.71	750	410	150	290		700	440	0.52
	5.48	540	290	110	220	320	510	330	0.50
	11.2	340	220	58	140	260	360	198	0.42
	28.0	250	150	45	98	190	248	143	0.46

$C_2Cl_6=2.0\times10^{-2}$ M, R_1,R_2 : CH_3 or H.

the G-values are summarized in Table 2. All the G-values, except $G(C_2Cl_4)$, decreased with an increase in the dose rate and, at the same dose rate, became lower in the order of 2-propanol, ethanol, and methanol. On the G-values shown in Table 2, the following relations can be seen, within the limits of experimental error;

a. $G(Cl^-)$ equals the sum of $G(-C_2Cl_6)$ and $G(C_2Cl_4)$.

b. $G(-C_2Cl_6)$ is approximately correspondent to $G(R_1R_2CO)$, and also to $G(C_2HCl_5)$ plus $G(C_2Cl_4)$.

c. The ratio of $G(C_2HCl_5)/G(C_2Cl_4)$ is a constant for each solution and decreases in the order of 2-propanol, ethanol, and methanol.

Dechlorination of C_2Cl_6 in Alkaline Solutions of 2-Propanol and Methanol. In the irradiation of deoxygenated alkaline(KOH) alcohol solutions of C_2Cl_6, potassium chloride precipitated much as in the alkaline 2-propanol solutions of polychlorinated biphenyls[13,14] and chlorobenzenes.[15] The yield of the chloride ion increased with the dose, as is shown in Table 3. The initial $G(Cl^-)$s were $\gtrsim 13000$ and $\gtrsim 1900$ for the 2-propanol and methanol respectively. These values are found to be considerably higher than those of the neutral solutions at the same dose rate in Table 2. Moreover, in the neutral solutions, the percentage of the dechlorination did not exceed 33% within this dose range, but in the alkaline solutions it did so at a relatively low dose and the chloride ion was still produced with a fairly high yield. Thus, the $G(Cl^-)$s were calculated to be 230 and 50 at the doses between 0.90 and 4.5×10^{18} eV/g in the 2-propanol, and between 2.6 and 19.2×10^{18} eV/g in the methanol respectively. The product analysis by gas chromatography was not carried out, but these high G-values indicate that C_2Cl_6 may be more dechlorinated by the chain reaction to the lower chlorinated compound than to tetrachloro compound in the alkaline solutions.

Dechlorination Reaction of Chloroethanes in Alcohols. The hexachloroethane in the solutions of methanol, ethanol, and 2-propanol was dechlorinated to form hydrochloric acid, C_2HCl_5, C_2Cl_4, and aldehydes or acetone. These high G-values (see Table 2) show that all the products are produced by a chain-reaction mechanism. Sherman *et al.* proposed the following radical chain reaction for the dechlorinations of tetrachloromethane[4] and DDT[5] to trichloromethane and DDE in the 2-propanol solutions:

Initiation

$$(CH_3)_2CHOH \rightsquigarrow X \text{ (radicals, } e^-_{\text{solv.}}) \tag{1}$$

$$X + RCl_n \longrightarrow XCl + \dot{R}Cl_{n-1} \tag{2}$$

(where RCl_n is CCl_4 or DDT)

Propagation

$$\dot{R}Cl_{n-1} + (CH_3)_2CHOH \longrightarrow RCl_{n-1}H + (CH_3)_2\dot{C}OH \tag{3}$$

$$(CH_3)_2\dot{C}OH + RCl_n \longrightarrow (CH_3)_2CO + HCl + \dot{R}Cl_{n-1} \tag{4}$$

If the chain dechlorination of C_2Cl_6 in the alcohol solutions follows the above mechanisms, the $G(HCl)$ should be in agreement with $G(-C_2Cl_6)$, $G(C_2HCl_5)$, and $G(R_1R_2CO)$; moreover, C_2Cl_4 should not be found as a product. On the other hand, the results in Table 2 do not apparently support the above findings because of the large discrepancy among G-values, especially in the methanol, and also the formation of a considerable amonut of C_2Cl_4. Therefore, some additional reaction may be required for the direct formation of C_2Cl_4 from C_2Cl_6, since C_2Cl_4 was observed immediately after irradiation (Figs. 1, 2, and 3) and was not formed from C_2HCl_5 (Fig. 4).

Horowitz *et al.* showed that HCl, C_2HCl_5, monochlorocyclohexane, and C_2Cl_4 were produced in high yields by the γ-radiolysis of C_2Cl_6 in cyclohexane at 24—100 °C; for example, $G(HCl)$ and $G(C_2Cl_4)$ reached to ≈ 4000 in a 0.1 M C_2Cl_6 solution at 100 °C. They suggested that these high G-values arose from sequence of reactions:[7]

$$2\,\text{c-}C_6H_{12} \rightsquigarrow 2\,\text{c-}C_6\dot{H}_{11} + H_2 \tag{5}$$

$$\text{c-}\dot{C}_6H_{11} + C_2Cl_6 \longrightarrow \text{c-}C_6H_{11}Cl + \dot{C}_2Cl_5 \tag{6}$$

$$\dot{C}_2Cl_5 + \text{c-}C_6H_{12} \longrightarrow C_2HCl_5 + \text{c-}\dot{C}_6H_{11} \tag{7}$$

$$\dot{C}_2Cl_5 \longrightarrow C_2Cl_4 + Cl \tag{8}$$

$$Cl + \text{c-}C_6H_{12} \longrightarrow HCl + \text{c-}\dot{C}_6H_{11} \tag{9}$$

Assuming that C_2Cl_4 is formed by Reaction 8 in the alcohol solutions, the following correlation can be expected to hold for the G-values in Table 2 on the bases of Reactions 1, 2, 3, 4, 8, and 9′:

$$Cl + R_1R_2CHOH \longrightarrow HCl + R_1R_2\dot{C}OH \tag{9′}$$

a. $G(HCl)$ equals the sum of $G(-C_2Cl_6)$ and $G(C_2Cl_4)$.

b. $G(-C_2Cl_6)$ is equal to the sum of $G(C_2HCl_5)$ and $G(C_2Cl_4)$, and also to $G((CH_3)_2CO)$ or $G(HCHO)$. As can be seen in Tables 1 and 2, the above correlations

TABLE 3. THE CHLORIDE-ION YIELD AS A FUNCTION OF THE DOSE IN 0.2 M KOH ALKALINE SOLUTIONS OF 2.0×10^{-2} M C_2Cl_6

Solution	Dose 10^{18} eV/g						
	0.10	0.90	1.75	2.60	4.25	7.70	19.2
2-Propanol	3.1	4.1			5.4		
Methanol		2.7	3.8	4.1		4.5	5.4

Cl^- yield : $\times10^{-2}$ M,
Dose rate : 8.35×10^{17} eV/g h in 2-propanol
5.22×10^{18} eV/g h in methanol.

hold within the limits of experimental error. Therefore, the chain-dechlorination reaction of C_2Cl_6 in alcohol solutions can be described as follows:

Initiation

$$R_1R_2CHOH \rightsquigarrow X,\ e^-_{solv.} \tag{10}$$

(where R_1 and R_2 are CH_3 or H)

$$X + R_1R_2CHOH \longrightarrow XH + R_1R_2\dot{C}OH \tag{11}$$

$$e^-_{solv.} + C_2Cl_6 \longrightarrow \dot{C}_2Cl_5 + Cl^- \tag{12}$$

Propagation

$$R_1R_2\dot{C}OH + C_2Cl_6 \longrightarrow R_1R_2CO + \dot{C}_2Cl_5 + HCl \tag{13}$$

$$\dot{C}_2Cl_5 + R_1R_2CHOH \longrightarrow C_2HCl_5 + R_1R_2\dot{C}OH \tag{14}$$

$$\dot{C}_2Cl_5 \longrightarrow C_2Cl_4 + Cl \tag{15}$$

$$Cl + R_1R_2CHOH \longrightarrow HCl + R_1R_2\dot{C}OH \tag{16}$$

The steady-state treatment for Reactions 14 and 15 leads to the following expression:

$$G(C_2HCl_5) = k_{14}[R_1R_2CHOH]/k_{15} \times G(C_2Cl_4) \tag{I}$$

Thus, $G(C_2HCl_5)$ should be proportional to $G(C_2Cl_4)$. The relationship between the two G-values is given in Fig. 5 for the methanol, ethanol, and 2-propanol solutions. From the slopes in Fig. 5, k_{14}/k_{15} is obtained as 0.02, 0.59, and 3.1 for methanol, ethanol, and 2-propanol respectively. These results show that Reaction 14 is more predominant in the 2-propanol than in the methanol. Thus, the ratio of $G(C_2Cl_4)$ to $G(C_2HCl_5)$ was very low in the former solution, but, on the contrary, was quite high in the latter solution. The values of k_{14}/k_{15} show that hydrogen abstraction from 2-propanol by the C_2Cl_5 radical is much faster than that from methanol and ethanol. The order of the hydrogen abstraction from alcohols is in agreement with that by the CF_3,$^{3)}$ OH,$^{16)}$ and H$^{17)}$ radicals.

If the termination of the chain involves a reaction between two alcohol radicals ($2k_{17} = 1-3 \times 10^9$ M^{-1} s^{-1}):$^{18-23)}$

$$2\,R_1R_2\dot{C}OH \begin{cases} \nearrow R_1R_2CHOH + R_1R_2CO & (17a) \\ \searrow \begin{matrix} R_1R_2COH \\ | \\ R_1R_2COH \end{matrix} & (17b) \end{cases}$$

the G-values shown in Table 2 are given by following expressions under steady irradiation:

$$G(-C_2Cl_6) = G(\dot{C}_2Cl_5) = G(X) + 10k_{13}[C_2Cl_6](G(X)/k_{17}I)^{1/2} \tag{II}$$

$$G(C_2HCl_5) = G(\dot{C}_2Cl_5)k_{14}[R_1R_2CHOH]/k_{15} \tag{III}$$

$$G(C_2Cl_4) = G(\dot{C}_2Cl_5)k_{15}/k_{14}[R_1R_2CHOH] \tag{IV}$$

$$G(HCl) = G(-C_2Cl_6) + G(C_2Cl_4) = G(\dot{C}_2Cl_5)(1+k_{15}/k_{14}[R_1R_2CHOH]) \tag{V}$$

where I is the dose rate.

It is known that the ratio of the combination reaction 17b to the disproportionation 17a depends on the nature of the R_1R_2COH radical. For the CH_2OH radical, the ratio of 17b to 17a is 10; in contrast, $(CH_3)_2\dot{C}OH$ more probable results in acetone.$^{24)}$ Assuming that the production of acetone by Reaction 17a can be neglected in comparison with that by Reaction 13, $G((CH_3)_2CO)$ can be also expressed by Equation II. The predicated linear dependence of the G-values on $I^{-1/2}$ is in agreement with the experimental data (Figs. 6 and 7). From the slopes of $G(-C_2Cl_6)$ *vs.* $I^{-1/2}$, the ratio of k_{13} for methanol, ethanol, and 2-propanol is obtained to be 1 : 3 : 14 by using $2k_{17} = 2.7 \times 10^9$,$^{22)}$ 2.0×10^9,$^{19)}$ and 1.4×10^9 M^{-1} s^{-1} $^{20)}$ for $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$, respectively.

It is very interesting that the dechlorination yield is dependent on the kinds of chloroethanes and solvents. Sherman showed that the following charge-transfer process seems most likely to be involved in the dechlorination of CCl_4:$^{4)}$

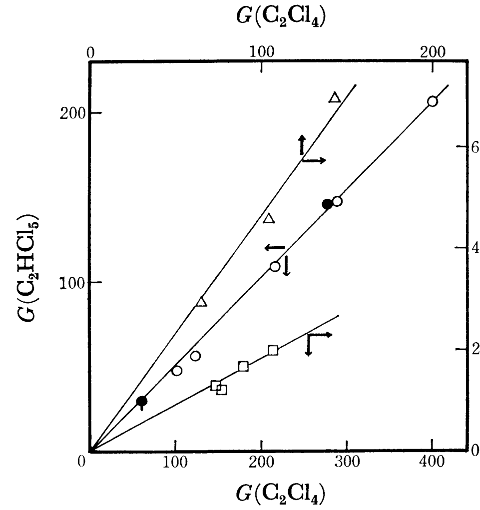

Fig. 5. $G(C_2HCl_5)$ as a function of $G(C_2Cl_4)$ in the solutions of 2.0×10^{-2} M C_2Cl_6.
△: 2-Propanol, □: ethanol, ○, ●: methanol, ●: 4.9×10^{-2} M C_2Cl_6, ●: 0.54×10^{-2} M C_2Cl_6.

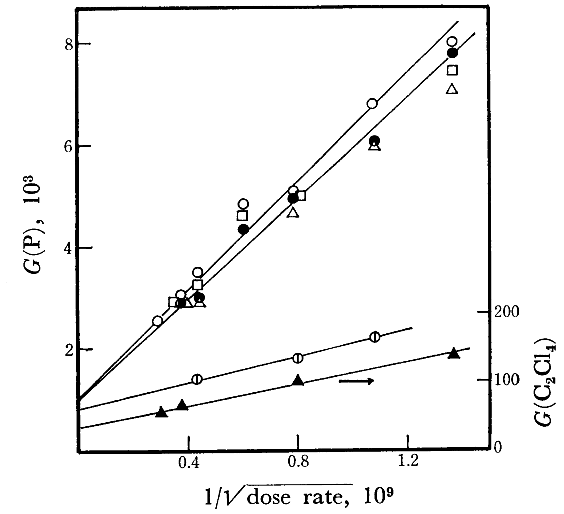

Fig. 6. G-values as a function of (dose rate)$^{-1/2}$ from 2×10^{-2} M C_2Cl_6 in 2-propanol and in ethanol.
○: Cl^-, ●: $-C_2Cl_6$, △: C_2HCl_5, ▲: C_2Cl_4, □: $(CH_3)_2CO$, ⦶: $-C_2Cl_6$ in ethanol.

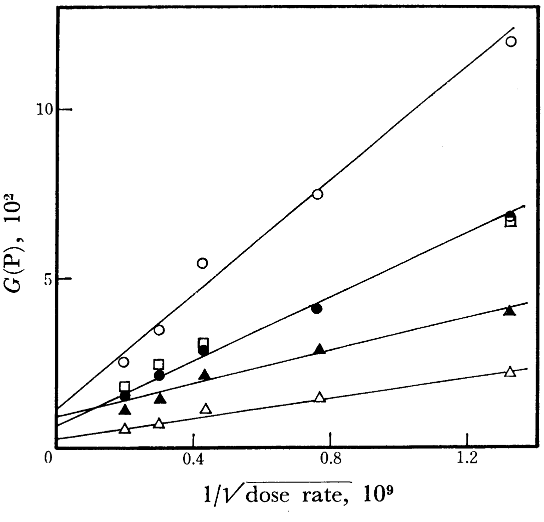

Fig. 7. G-values as a function of (dose rate)$^{-1/2}$ from 2×10^{-2} M C_2Cl_6 in methanol.
○: Cl^-, ●: $-C_2Cl_6$, △: C_2HCl_5, ▲: C_2Cl_4, □: HCHO.

$$(CH_3)_2\dot{C}OH + CCl_4 \longrightarrow (CH_3)_2C{=}OH^+ + \dot{C}Cl_3 + Cl$$

$$(CH_3)_2C{=}OH^+ + \text{solvent} \longrightarrow (CH_3)_2CO + H^+$$

In the investigation of the dehalogenation of aliphatic halogen compounds, such as bromoacetic acid, by an aliphatic free radical in aqueous solutions, Andar *et al.* also indicated that the dehalogenation was due to a charge-transfer mechanism rather than halogen abstraction and that the reactivity of charge-transfer followed the sequence of $(CH_3)_2\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH$ for simple aliphatic alcohol radicals. For instance, the $G(Br^-)$s were 9.5, 61, and >350 for methanol, ethanol, and 2-propanol in the aqueous solutions of 1×10^{-3} M bromoacetic acid containing 5M alcohol. The reactivity of halogen compounds toward the radical, on the other hand, increased in this order: $ClCH_2COOH < BrCH_2COOH < CBr_3COOH$.[2]

It is also known that the α-hydroxy alkyl radical acts as a reducing agent.[25] The $RH + A \rightarrow R + A^- + H^+$ reaction occurs at an appreciable rate whenever the redox potential (E) of A(acceptor molecule) is lower than that of RH(donor radical), and the electron-transfer reaction is dependent on the difference of the E between RH and A.[26] In our case, A and RH correspond to C_2Cl_6 and $R_1R_2\dot{C}OH$. The redox potential is generally proportional to the half-wave potential ($E_{1/2}$) of polarography($E = E_{1/2} + 0.244$).[26] The values for C_2Cl_6, $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$ are known to be −0.66,[27] −0.98, −1.18, and −1.30 V.[28] Therefore, the dechlorination of C_2Cl_6 occurs significantly in all solutions; therefore, the finding that $G(-C_2Cl_6)$ was highest in the 2-propanol is reasonable.

It is clear that $C_2H_2Cl_4$ is formed by the dechlorination of C_2HCl_5 from the change in the concentrations of the chloride ion, C_2HCl_5, and $C_2H_2Cl_4$ after consuming C_2Cl_6 (Figs. 1 and 3), and from the correlation of $G(Cl^-) = G(-C_2HCl_5) = G(C_2H_2Cl_4)$ (Fig. 4). The G-value of $-C_2HCl_5$ was about 600 in the 2-propanol and 24 in the methanol(Fig. 4). For the ethanol, a mean G-value between the 2-propanol and methanol should be obtainable by judging from the decrease in C_2HCl_5 shown in Fig. 3. The chain dechlorination of C_2HCl_5 in alcohol solutions seems to proceed in the same way as the reaction of C_2Cl_6. The large difference in $G(-C_2HCl_5)$ for the 2-propanol and the methanol may be due to the difference in their redox potentials between C_2HCl_5 and $R_1R_2\dot{C}OH$. On the other hand, C_2Cl_4 and $C_2H_2Cl_4$ were not dechlorinated by the chain reaction any longer. This is because their half-wave potentials are apparently higher than those of $R_1R_2\dot{C}OH$ ($C_2Cl_4 \approx -1.8$ V, $C_2H_2Cl_4 \approx -2$ V).[27]

On the other hand, it is known that the α-hydroxy alkyl radical behaves as either an acid or a base[28] and that the half-wave potentials in the basic form are ≈ −1.8 and −2.2 V for $\dot{C}H_2O^-$ and $(CH_3)_2\dot{C}O^-$.[25,29]

$$R_1R_2\dot{C}OH \rightleftharpoons R_1R_2\dot{C}O^- + H^+ \qquad (pK \approx 12)$$

In this case, the potentials in the basic form are apparently higher than those in the basic form; moreover, the potentials of $(CH_3)_2\dot{C}O^-$ and $\dot{C}H_2OH$ are higher than, or almost equal to, those of $C_2H_2Cl_4$ and C_2Cl_4. Therefore, in the alkaline alcohols, the initial $G(Cl^-)$ was higher than that in the neutral solutions; C_2Cl_6 might thus be more easily dechlorinated to the lower chlorinated compound than the tetrachloro compound.

Effect of Temperature on the Product Yields. The yields of products are shown in Table 4 upon irradiating 1.6−1.7×10^{-2} M C_2Cl_6 in solutions of methanol and

TABLE 4. EFFECT OF THE TEMPERATURE ON THE PRODUCT YIELDS

Solution	Temp (°C)	Concentration, 10^{-2} M								
		Cl^-	$-C_2Cl_6(a)$	$C_2HCl_5(b)$	$C_2Cl_4(c)$	$C_2H_2Cl_4(d)$	Σ	b/c	$a+c$	$b+c$
Methanol	0	0.70	0.45	0.21	0.18	0	1.54	1.2	0.63	0.39
	25	1.84	1.01	0.34	0.66	0.01	1.60	0.52	1.67	1.0
	50	2.87	1.51	0.25	1.15	0.03	1.52	0.22	2.67	1.4
2-Propanol	0	2.29	1.69	1.38	0.05	0.31	1.75		2.05[a)]	1.74[b)]
	25	2.86	1.70	0.66	0.09	1.03	1.78		2.82[a)]	1.75[b)]
	50	3.40	1.70	0.04	0.18	1.59	1.81		3.47[a)]	1.81[b)]

Methanol : 1.6×10^{-2} M C_2Cl_6, 1.6×10^{18} eV/g,
2-propanol : 1.7×10^{-2} M C_2Cl_6, 0.8×10^{18} eV/g,
Σ, a) $a+c+d$, b) $b+c+d$.

2-propanol at 0, 25, and 50° C. The chloride ion increased with the temperature, and the total concentration of chlorocompounds observed in the irradiated solutions was a constant(=the initial concentration of C_2Cl_6) in both the solutions.

In the methanol, the concentrations of the chloride ion and $-C_2Cl_6$ were correspondent to those of $-C_2Cl_6$ plus C_2Cl_4, and C_2HCl_5 plus C_2Cl_4, respectively at each temperature. On the other hand, in the 2-propanol, the above correlations were not found because almost all of the C_2Cl_6 disappeared, to be followed by the formation of a considerable amount of $C_2H_2Cl_4$. However, taking into consideration the fact that all the $C_2H_2Cl_4$ was produced from C_2HCl_5, the sum of $-C_2Cl_6$ C_2Cl_4, and $C_2H_2Cl_4$ equals the concentration of the chloride ion(last column in Table 4). Therefore, the dechlorination reaction is likely to be the same at temperatures of 0—50 °C. The decrease in the ratio of C_2HCl_5 to C_2Cl_4 in the methanol with the temperature may be caused by the fact that Reaction 14 was much more promoted than Reaction 15 at high temperatures.

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