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The Radiation-Induced Addition of Hydrogen Chloride to Ethylene

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In a stainless steel autoclave, ethylene and hydrochloric acid or dried hydrogen chloride were irradiated with cobalt-60 gamma-rays. *n*-Butyl chloride and ethyl chloride were thus produced efficiently, unlike as when an ultraviolet light or catalyst was used. The products were quantitatively analyzed by gas chromatography. This reaction was supposed to be a vapor-phase radical chain reaction; the proposed reaction mechanism agreed well with our results. The selectivity of ethylene to the products was considered to be practically 100%. The *G* values of ethyl chloride, *n*-butyl chloride and the ethylene consumed, using the ratio of the total absorbed dose to ethylene, were calculated to be 16000, 10000 and 35000 respectively at 50°C and at a dose rate of 1.10×10^4 r./hr. The ratios of the rate constants for ethyl chloride and *n*-butyl chloride were 366, 499 and 580 at 50, 40 and 15°C respectively, and the apparent activation energies for ethyl chloride and *n*-butyl chloride were calculated from the reaction rates to be 6.94 and 8.95 kcal./mol. respectively.

Although the chain addition of hydrogen bromide to olefins is readily brought about by peroxide[1] or by radiation,[2] it has been generally recognized that the analogous reaction of hydrogen chloride is much less likely. There are only a few articles which are concerned with this reaction. One of them is by Ford and Hanford,[3,4] who reported the formation of mixtures of straight-chain primary alkyl chlorides, ranging from ethyl chloride to greases and waxes, by the reaction between ethylene and hydrogen chloride in the presence of catalysts and water at a high temperature and a high pressure.

Another article is that by Raley, Rust and Vaughan,[5] who recognized that the vapor-phase addition of hydrogen chloride to ethylene, as initiated by ultraviolet light or di-*t*-butyl peroxide, yielded ethyl chloride and small amounts of hydrogen and ethane (both 0.1% or less).

The general methods of preparing alkyl chlorides include one working from corresponding *n*-alcohol using zinc chloride and concentrated hydrochloric acid,[6] and one working from the chlorination of the corresponding alkyl hydrocarbons with hydrogen chloride.[7] However, it is generally considered that the selective preparation of *n*-alkyl chlorides from the chlorination of olefins is rather difficult; besides, there is no report on such a reaction using actinic radiation. The authors found that both *n*-butyl chloride and ethyl chloride were efficiently formed from a gamma-ray-induced reaction between ethylene and hydrogen chloride; the results of this process will be given in the present paper.

Experimental

Materials.—Ethylene and dried hydrogen chloride were obtained from the Nihon Sekiyu Kagaku Co., Ltd. (Kawasaki), and the Dow Chemical Co. (Matheson Co., Inc., U. S. A.) respectively, and were used without further purification. Reagent-grade concentrated hydrochloric acid (sp. gr. 1.184, 20°C) was obtained from the Kanto Kagaku Co., Ltd. (Tokyo), or the Wako Junyaku Co., Ltd. (Osaka), and all chemicals and materials used for analysis and identification were guaranteed reagents.

Apparatus and Procedures.—Dried hydrogen chloride or 15 ml. of concentrated hydrochloric acid in a glass vessel was introduced into a stainless steel autoclave with a capacity of 50 ml. After that, ethylene was compressed at pressures ranging from 25 to 65 kg./cm^2 and irradiated with cobalt-60 gamma-rays at a does rate of 1.10×10^4 r./hr. or 3.82×10^4 r./hr. After irradiation for 0—160 hr., the gaseous components in the autoclave were absorbed in toluene. The absorbants, as well as the liquid components, were then stored in a refrigerator for analysis. The autoclave was washed and cleaned with ethyl alcohol and ethyl ether after each reaction in order to avoid the effects of any impurities.

Dosimetry.—The intensity of the cobalt-60 source used was about 230 curies. The dose rates were determined with a Fricke dosimeter, using $G(\mathrm{Fe}^{3+}) = 15.6$. The does absorbed by ethylene was calculated by the following equation[8]:

$$D_{\mathrm{C_2H_4}} = D_{\mathrm{H_2O}} \times \frac{(a/\rho)_{\mathrm{C_2H_4}}}{(a/\rho)_{\mathrm{H_2O}}} = D_{\mathrm{H_2O}} \times \frac{(Z/A)_{\mathrm{C_2H_4}}}{(Z/A)_{\mathrm{H_2O}}}$$

where $D_{\mathrm{C_2H_4}}$ and $D_{\mathrm{H_2O}}$ represent the doses absorbed by ethylene and by water in the system. (a/ρ) denotes the mass energy absorption coefficient, and Z and A represent the atomic number and the molecular weight of the substances in the system respectively.

Analytical.—The products, ethyl chloride and *n*-butyl chloride, were identified by comparing them with pure materials, by flame tests, by boiling point and refractive index measurements, by examining the infrared spectrum, and by gas chromatography. Hydrogen and chlorine were identified by gas chromatography. The products were quantitatively analyzed by gas chromatography using Kotaki Gu-12 model equipment. A 5-m. column of tri-*m*-cresyl phosphate on cerite was used at an operating temperature of 65°C and at a flow rate of 80 ml./min. of helium (Southern Oxygen Co.).

A known volume of the toluene absorbant of the gaseous products was taken for gas chromatography. As to the liquid products, known volumes of the toluene phase from the product of the extraction and of the aqueous hydrochloric acid phase were analyzed by gas chromatography.

Results

Products and *G* Values.—Table I shows the results obtained without irradiation and with and without the addition of the $\mathrm{AlCl_3}$ catalyst, which is commonly employed in the production of ethyl chloride. No ethyl chloride, or only a small amount of it, was produced, and no *n*-butyl chloride was detected in any case. The pressure of hydrochloric acid in Table I represents the partial pressure of

TABLE I. YIELDS OF ETHYL CHLORIDE AND *n*-BUTYL CHLORIDE IN THE CASE OF NON-IRRADIATION

Temp. °C	Reaction time hr.	Initial pressure		Yield	
		HCl mmHg	$\mathrm{C_2H_4}$ mmHg $\times 10^{-2}$	$\mathrm{C_2H_5Cl}$ mol. $\times 10^3$	n-$\mathrm{C_4H_9Cl}$ mol.
28.5	66.0	207.0	441.3	0	0
50.0	66.0	573.0	470.7	1.48	0
50.0*	111.0	573.0	470.7	2.61	0

* 0.276 wt.% of $\mathrm{AlCl_3}$ added to aqueous hydrochloric acid.

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[1] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] W. E. Vaughan, F. F. Rust and T. W. Evans, *J. Org. Chem.*, **7**, 477 (1942)

[3] U. S. Pat. 2418832, April 15 (1947).

[4] T. A. Ford, W. E. Hanford and J. H. Harman, *J. Am. Chem. Soc.*, **74**, 4323 (1952).

[5] J. H. Raley, F. F. Rust and W. E. Vaughan, ibid., **70**, 2767 (1948).

[6] A. M. Whaley and J. E. Copenhaver, ibid., **60**, 2497 (1938).

[7] G. Egloff and M. Alexander, *Oil Gas J.*, **41**, No. 15—18 (1942).

[8] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, New York (1964), p. 88.

hydrogen chloride over the aqueous hydrochloric acid.

A comparison of the reactions of ethylene with dried hydrogen chloride gas and with the aqueous hydrochloric acid are given in Table II. The products, yields and quantities expected from our postulated reaction mechanism agreed with each other in these two cases. Furthermore, Raley and

TABLE II. COMPARISON OF REACTION OF ETHYLENE WITH HYDROGEN CHLORIDE GAS AND AQUEOUS HYDROCHLORIC ACID

Reaction temp., 15°C Dose rate: 3.82×10^4 r./hr.

	Time hr.	Initial pressure		Yield		Selectivity of C_2H_4 %
		C_2H_4 mmHg$\times 10^{-3}$	HCl mmHg	C_2H_5Cl mol.$\times 10^3$	n-C_4H_9Cl mol.$\times 10^3$	
Hydrogen chloride	15.5	368	760	3.98	0.10	92.9
Hydrogen chloride	16.0	368	83	1.23	0.61	98.9
Aqueous hydrochloric acid	15.0	368	83	1.14	0.61	95.1

TABLE III. RELATION BETWEEN YIELDS AND INITIAL PRESSURE OF ETHYLENE

Temp. °C	Initial pressure of C_2H_4 kg./cm²	Pressure ratio $\frac{HCl}{C_2H_4} \times 10^2$	Yield		Conversion of C_2H_4 %	Selectivity of C_2H_4 %	Mole ratio $\frac{C_2H_5Cl}{n\text{-}C_4H_9Cl}$	G value of C_2H_4 consumed
			C_2H_5Cl mol.$\times 10^3$	n-C_4H_9Cl mol.$\times 10^3$				
50	157.0	1.7						
50	64.0	1.21	31.30	19.32	60.8	89.4	1.11	25500
50	60.0	1.29	34.74	12.40	40.3	100.0	2.80	23900
50	49.6	1.56	18.67	3.41	24.4	95.4	5.42	11200
50	33.1	2.34	13.83	1.49	25.1	100.0	9.28	7800
20	55.0	0.30	7.12	7.27	8.2	98.0	0.98	7300
20	45.0	0.36	3.96	2.08	12.0	68.5	1.90	3100
20	35.0	0.47	3.33	1.19	9.4	78.2	2.80	2300
20	25.0	0.65	1.94	0.56	6.0	92.2	3.46	1300

TABLE IV. DEPENDENCY OF YIELDS ON TIME AND G VALUES

Initial pressure of C_2H_4: 471×10^2 mmHg (64 kg./cm²)
Initial pressure of HCl: 573 mmHg
Reaction temperature: 50°C
Dose rate: 1.10×10^4 r.hr.

Time hr.	Conversion of C_2H_4 %	Selectivity of C_2H_4 %	Yield		G Values			$\frac{C_2H_5Cl}{n\text{-}C_4H_9Cl}$
			C_2H_5Cl mol.$\times 10^3$	n-C_4H_9Cl mol.$\times 10^3$	C_2H_5Cl	n-C_4H_9Cl	$-C_2H_4$	
14.0	9.7	82.6	7.55	1.37	13400	2440	18280	5.53
16.0	11.7	85.3	8.89	1.98	14100	3140	20380	4.49
40.5	24.2	83.2	19.10	5.90	13400	4130	21660	3.24
67.0	54.4	89.4	31.30	19.32	15500	9540	34580	1.62
73.0	58.2	92.9	33.08	20.81	15600	9800	35200	1.59
90.0	67.5	94.1	34.96	23.39	14700	9870	34440	1.49
161.5	80.8	91.2	40.45	26.82	13100	8680	30460	1.51

TABLE V. DEPENDENCY OF YIELDS ON TIME AND G VALUES

Initial pressure of C_2H_4: 435×10^2 mmHg (59.2 kg./cm²)
Initial pressure of HCl: 351 mmHg
Reaction temperature: 40°C
Dose rate: 1.10×10^4 r./hr.

Time hr.	Conversion of C_2H_4 %	Selectivity of C_2H_4 %	Yield		G Values			$\frac{C_2H_5Cl}{n\text{-}C_4H_9Cl}$
			C_2H_5Cl mol.$\times 10^3$	n-C_4H_9Cl mol.$\times 10^3$	C_2H_5Cl	n-C_4H_9Cl	$-C_2H_4$	
15.5	6.3	81.9	4.01	1.14	6530	1850	10230	3.52
37.0	16.4	84.2	10.43	3.26	7660	2390	12440	3.20
65.0	31.7	98.3	20.70	9.22	9600	4270	18140	2.24
87.0	40.8	99.5	23.13	13.16	8500	4830	18160	1.76
114.0	41.9	99.0	23.83	15.48	7100	4610	16320	1.54

TABLE VI. DEPENDENCY OF YIELDS ON TIME AND *G* VALUES

Initial pressure of C_2H_4: 383×10^2 mmHg (52 kg./cm²)
Initial pressure of HCl: 83 mmHg
Reaction temperature: 15°C
Dose rate: 1.10×10^4 r./hr.

Time hr.	Conversion of C_2H_4 %	Selectivity of C_2H_4 %	Yield		*G* Values			$\frac{C_2H_5Cl}{n\text{-}C_4H_9Cl}$
			C_2H_5Cl mol. $\times10^3$	n-C_4H_9Cl mol. $\times10^3$	C_2H_5Cl	n-C_4H_9Cl	$-C_2H_4$	
42.0	8.7	91.2	3.69	2.77	2360	1770	5900	1.33
48.0	10.0	97.3	4.02	3.28	2260	1850	5960	1.23
65.0	21.1	90.9	7.49	7.51	3440	3450	10340	0.997
93.0	23.1	97.9	7.99	9.03	2500	2830	8160	0.885
156.5	28.9	87.7	7.94	9.68	1560	1900	5360	0.820

TABLE VII. DEPENDENCY OF YIELDS ON TIME AND *G* VALUES

Initial pressure of C_2H_4: 368×10^2 mmHg (50 kg./cm²)
Initial pressure of HCl: 83 mmHg
Reaction temperature: 15°C
Dose rate: 3.82×10^4 r./hr.

Time hr.	Conversion of C_2H_4 %	Selectivity of C_2H_4 %	Yield		*G* Values			$\frac{C_2H_5Cl}{n\text{-}C_4H_9Cl}$
			C_2H_5Cl mol. $\times10^3$	n-C_4H_9Cl mol. $\times10^3$	C_2H_5Cl	n-C_4H_9Cl	$-C_2H_4$	
15.0	2.6	84.6	1.14	0.17	607	357	1321	1.70
22.0	3.6	95.1	1.34	1.28	498	476	1450	1.03
42.0	18.4	86.5	4.95	6.50	968	1270	3508	0.761
65.0	30.0	96.2	8.73	11.89	1200	1640	4480	0.734

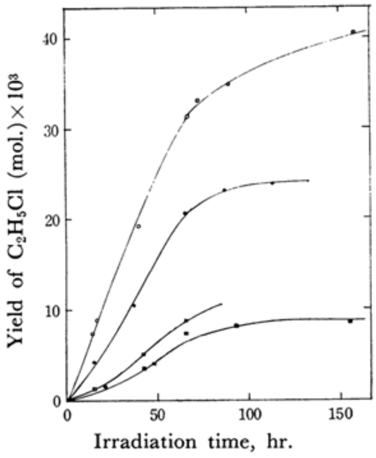

Fig. 1. The relation between irradiation time and yields of C_2H_5Cl at 50, 40 and 15°C.
○: 50°C, Dose rate 1.10×10^4 r./hr.
●: 40°C, Dose rate 1.10×10^4 r./hr.
■: 15°C, Dose rate 1.10×10^4 r./hr.
□: 15°C, Dose rate 3.82×10^4 r./hr.

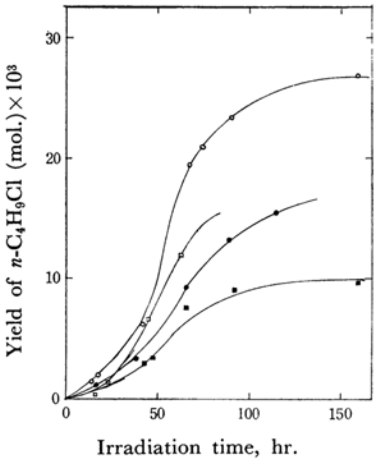

Fig. 2. The Relation between irradiation time and yields of n-C_4H_9Cl at 50, 40 and 15°C.
○: 50°C, Dose rate 1.10×10^4 r./hr.
●: 40°C, Dose rate 1.10×10^4 r./hr.
■: 15°C, Dose rate 1.10×10^4 r./hr.
□: 15°C, Dose rate 3.82×10^4 r./hr.

his co-workers[5)] reported that their synthesis of ethyl chloride by ultraviolet light was a vapor-phase reaction. From these results, it is reasonable for us to conclude that the present reaction, using aqueous hydrochloric acid, is a vapor-phase radical reaction rather than a liquid one. *G* values were calculated on the basis of the assumption that this reaction is vapor-phase one, using total dose absorbed by ethylene.

Table III shows the relation between the yields and the initial pressure of ethylene. The reaction time was 66 hr. 15 ml. of aqueous hydrochloric acid were used in this series. It is evident from these relations that the mole ratios of the products are controlled by the temperature and by the ratio of the initial pressures of ethylene to hydrogen chloride.

The relation between the irradiation time by cobalt-60 gamma-rays and the yields at 50, 40 and 15°C are shown in Figs. 1 and 2. Tables IV, V and VI show the *G* values against the total dose absorbed. The results obtained when the dose rate is changed are given in Table VII.

Since the energy absorbed during the induction period is included, the *G* values in the above results are naturally small when the conversion rate is low. Above $1—2\times10^6$ r., a wax-like or a solid polymer was produced; these were confirmed to be polyethylene by means of a study of their infrared spectra.

When the reaction temperature was above 60°C, viscous decomposition products were found in addition to ethyl chloride and *n*-butyl chloride. This is considered to be attributable to the fact that the reaction, being due to a high temperature, makes the walls of the autoclave tend to corrosion.

Although the selectivity of ethylene to ethyl chloride and *n*-butyl chloride is not quite 100% in some cases in Tables V, VI and VII, it is considered to be practically 100% in all cases, because no product other than ethyl chloride and *n*-butyl chloride was observed. Furthermore, the mole ratio of ethyl chloride to *n*-butyl chloride becomes smaller with an increase in the reaction time. This observation indicates that the partial pressure of hydrogen chloride with respect to the total pressure is decreased more rapidly than that of ethylene in spite of the feeding of hydrogen chloride from the aqueous hydrochloric acid.

The after-effects of the irradiation on yields were practically negligible in the case of 15°C.

The Effect of the Dose Rate on *G* Values.—Effects of the dose rate on the yields can be seen by comparing Tables VI and VII or Figs. 1 and 2. According to the curves in the figures, the *G* values of the consumed ethylene depend on the reaction time. If the logarithm $G(-C_2H_4)$ is plotted against the logarithm of the dose rate at each time, we find that *G* values are proportional to -0.54 powers of the dose rate, as is shown in Fig. 3.

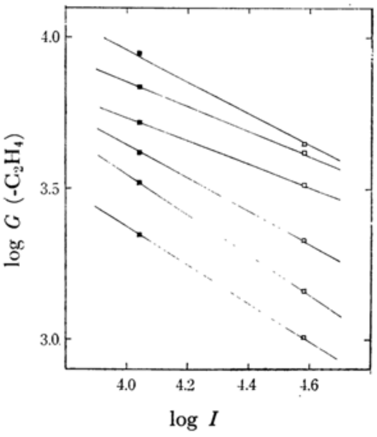

Fig. 3. Dependency of $G(-C_2H_4)$ on dose rate (*I*).

Discussion

Reaction Mechanism.—Since the investigated reaction is guessed to be a vapor-phase radical reaction, it may be presumed that hydrogen and chlorine radicals are initially formed from hydrogen chloride by irradiation and that the reaction proceeds in accordance with the following chain mechanism:

$$HCl \xrightarrow{f(I)} H\cdot + Cl\cdot \tag{1}$$

$$C_2H_4 + Cl\cdot \xrightarrow{k_2} C_2H_4Cl\cdot \tag{2}$$

$$C_2H_4Cl\cdot + HCl \xrightarrow{k_3} C_2H_5Cl + Cl\cdot \tag{3}$$

$$C_2H_4Cl\cdot + C_2H_4 \xrightarrow{k_4} C_4H_8Cl\cdot \tag{4}$$

$$C_4H_8Cl\cdot + HCl \xrightarrow{k_5} C_4H_9Cl + Cl\cdot \tag{5}$$

$$C_4H_8Cl\cdot + C_2H_4 \xrightarrow{k_6} C_6H_{12}Cl\cdot \tag{6}$$

$$C_6H_{12}Cl\cdot + HCl \xrightarrow{k_7} C_6H_{13}Cl + Cl\cdot \tag{7}$$

$$Cl\cdot + Cl\cdot \xrightarrow{k_8} Cl_2 \tag{8}$$

$$H\cdot + C_2H_4 \xrightarrow{k_9} C_2H_5\cdot \tag{9}$$

$$C_2H_5\cdot + HCl \xrightarrow{k_{10}} C_2H_6 + Cl\cdot \tag{10}$$

The addition reaction of the $C_6H_{12}Cl$ radical to C_2H_4 in this reaction mechanism need not be considered, since no products beyond *n*-butyl chloride were obtained.

By applying the stationary-state method, the following equation is obtained:

$$\frac{d(C_2H_5Cl)}{d(n\text{-}C_4H_9Cl)} = \frac{k_3(HCl)}{k_4(C_2H_4)} + \frac{k_3k_6}{k_4k_5} = m \tag{11}$$

This equation shows that the ratio of the reaction rate (*m*) of ethyl chloride to that of *n*-butyl chloride is proportional to the pressure ratio of hydrogen chloride to that of ethylene; that its slope is equal to the ratio of rate constants, k_3/k_4, and that k_6/k_5 is derived from the intercept of the line.

The rates of formation were calculated on the basis of the differential of the formation curves in Figs. 1 and 2, while the depression of ethylene pressure was measured with a gauge. The partial pressure of hydrogen chloride, not being subjectable to direct measurement, was calculated by the use of both Perry's data[9] and the concentration of

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[9] J. H. Perry, "Chemical Engineering Handbook," McGraw-Hill, New York (1950), pp. 166—167.

hydrogen chloride, which in turn was calculated from the yields of ethyl chloride and *n*-butyl chloride. The relation represented by Eq. 11 is illustrated in Fig. 4; the values of k_3/k_4 obtained with a dose rate of 1.10×10^4 r./hr. at 50, 40 and 15°C were 366, 499 and 580 respectively. In the case of a dose rate of 3.82×10^4 r./hr. at 15°C, a value of 568 was obtained.

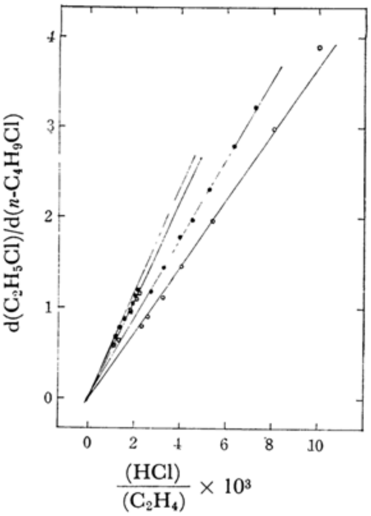

Fig. 4. The relation between ratio of reaction rate (m) and pressure ratio $(HCl)/(C_2H_4)$.
○: 50°C, Dose rate 1.10×10^4 r./hr.
●: 40°C, Dose rate 1.10×10^4 r./hr.
■: 15°C, Dose rate 1.10×10^4 r./hr.
□: 15°C, Dose rate 3.82×10^4 r./hr.

From the fact that these straight lines practically pass through the origin, the value of k_3k_6/k_4k_5 is practically zero; thus, k_6/k_5 approximately equals zero. This calculation agrees well with the fact that nothing beyond *n*-butyl chloride was actually obtained. The logarithms of k_3/k_4 against $1/T$ (T: absolute temperature) gave a straight line according to the Arrhenius equation, as is shown in Fig. 5. From its slope, the difference between activation energies, E_4-E_3, was calculated; its value was 2.29 kcal./mol.

In the case of a dose rate of 1.10×10^4 r./hr., the energies absorbed by ethylene were nearly equal in all cases up to the reaction time of 30 hr.; at this point, a value of 7×10^{19} eV. was obtained. After the pressures of hydrogen chloride and ethylene had been equalized in three cases, the relation between the reaction rates of ethyl chloride and *n*-butyl chloride was found to be as shown in Fig. 6. From the slopes of these straight lines, the apparent activation energies for ethyl chloride and *n*-butyl chloride were calculated to be 6.94 and 8.95 kcal./mol. respectively. The difference between them is 2.01 kcal./mol., which is in good agreement with $E_4-E_3=2.29$ kcal./mol. Evans[10] calculated the activation energy, $E_2=4.5$ kcal./mol., from the distance between atomic centers. Walling and his co-workers[11] calculated the ΔH values in Eqs. 2 and 3 to be -26 and $+5$ kcal./mol. respectively, and suggested that the value of E_3 is a little greater than $+5$ kcal./mol. Our results agree fairly well with these data.

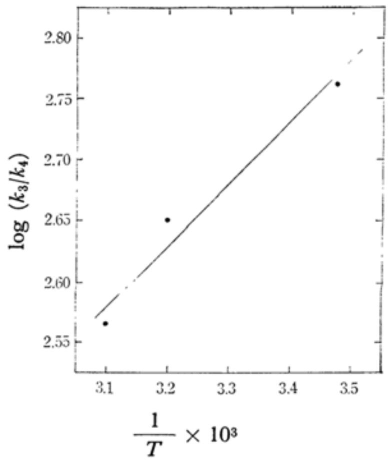

Fig. 5. Logarithms of k_3/k_4 against $1/T$°K.

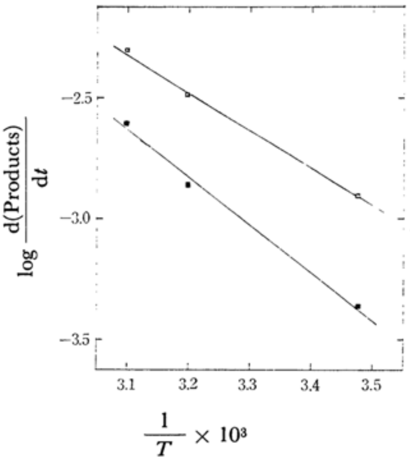

Fig. 6. Logarithms of reaction rates of C_2H_5Cl or n-C_4H_9Cl against $1/T$°K.
□: C_2H_5Cl, Dose rate 1.10×10^4 r./hr.
■: n-C_4H_9Cl, Dose rate 1.10×10^4 r./hr.

Although Vaughan[5] established the formation of ethane, we could not find ethane under our experimental conditions as long as the reaction temperature was kept below 60°C. However, above the reaction temperature of 60°C, small amounts of ethane were observed.

Since the activation energies for the reactions between the H radical and chlorine gas or hydrogen

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[10] M. G. Evans, J. Gergely and E. C. Seaman, *J. Polymer Sci.*, **3**, 866 (1948).

[11] C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957), p. 241.

chloride are rather small, the following equations, 12 and 13, may have occured in the system:

$$H\cdot + Cl_2 \cdots\cdots HCl + Cl\cdot \qquad (12)$$

$$H\cdot + HCl \cdots\cdots H_2 + Cl\cdot \qquad (13)$$

Usually no products from the reaction between ethylene and ethyl chloride and *n*-butyl chloride except polymers were observed, but there were a few cases where small amounts of *s*-butyl chloride were observed. This is presumably due to the isomerization of *n*-butyl chloride to *s*-butyl chloride.

Summary

Ethyl chloride and *n*-butyl chloride have been selectively prepared by the cobalt-60 gamma-ray-induced addition of hydrogen chloride to ethylene. The *G* values of consumed ethylene reached 35000. This reaction has been presumed to be a vapor-phase radical chain reaction, and the proposed reaction mechanism show a good agreement with our experimental results. The activation energies for the production of ethyl chloride and *n*-butyl chloride have been calculated from the rate constants to be 6.94 and 8.95 kcal./mol. respectively.