Isomerization of Alkyl Chlorides and Bromides by Radiation[1]

Masaaki Takehisa, Gerrit Levey, and John E. Willard

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received July 8, 1966*

Abstract: The isomerization reactions induced by γ irradiation of n-C_3H_7Cl, i-C_3H_7Cl, n-C_4H_9Cl, i-C_4H_9Cl, *sec*-C_4H_9Cl, t-C_4H_9Cl, n-C_3H_7Br, and n-C_4H_9Br have been investigated to determine which compounds undergo a hydrogen halide catalyzed chain isomerization and to elucidate further the mechanisms of such isomerizations. n-C_3H_7Cl, n-C_4H_9Cl, and i-C_4H_9Cl show the catalyzed reaction, with high G values, but i-C_3H_7Cl, *sec*-C_4H_9Cl, t-C_4H_9Cl, and the bromides do not. Effects of dose, dose rate, concentration of additives (HCl, HBr, HI, I_2, DPPH, CH_3I), temperature, and phase on G values have been studied. The apparent activation energy, obtained from measurements over the range from -78 to $100°$, is 3 kcal mole^{-1}. Hydrogen bromide, present at 1.2 mole % during the radiolysis of liquid n-C_3H_7Cl, has negligible catalytic effect at 25° but is effective at elevated temperatures, while HI is ineffective, consistent with the relative activation energies for H abstraction by Cl, Br, and I. The ratios of i-C_3H_6TCl to n-C_3H_6TCl produced when liquid n-C_3H_7Cl is radiolyzed in the presence of TCl at -80 and 24° are about 0.8 and 0.4, respectively; these are discussed in relation to the isomerization mechanism. G(isomerization) of n-C_4H_9Cl in both the glassy and polycrystalline states at $-196°$ is less than unity and is quite insensitive to HCl. In the gas phase at 25°, HCl has a similar catalytic effect to that at the same molar concentration in the liquid phase. Radiation energy absorbed by the HCl does not initiate isomerization of the alkyl chloride. Neither HCl nor HBr catalyzes the isomerization of n-C_4H_9Br effectively, but G(isomerization), which is 19 at 25°, rises to 80 at 100°, indicating a chain isomerization occurring by a mechanism not involving hydrogen halide catalysis. The yields of 1,1-, 1,2-, 2,2-, and 1,3-$C_3H_6Cl_2$ from the photolysis and radiolysis of solutions of Cl_2 in n-C_3H_7Cl and i-C_3H_7Cl have been determined to assist in the interpretation of the mechanism of isomerization.

A unique HCl-catalyzed chain reaction involving an intraradical chlorine atom shift has been shown to account for the high yields of i-C_3H_7Cl produced by the radiation-induced isomerization of n-C_3H_7Cl.[2] The evidence indicates that the chain consists of steps 1–4, initiated by a Cl atom produced from the n-C_3H_7Cl by the radiation. The rate of isomerization is proportional

$$n\text{-}C_3H_7Cl + Cl \longrightarrow CH_3CHCH_2Cl + HCl \qquad (1)$$

$$CH_3CHCH_2Cl \rightleftharpoons CH_3CHClCH_2 \qquad (2)$$

$$CH_3CHClCH_2 + HCl \longrightarrow i\text{-}C_3H_7Cl + Cl \qquad (3)$$

$$R + C_3H_6Cl \longrightarrow RC_3H_6Cl \qquad (4)$$

to the concentration of HCl because this determines the probability that a radical will react by (3) rather than (4). Since radicals used up by (3) are regenerated by (1), the steady-state concentration of radicals is independent of the HCl concentration. In accord with this mechanism, the isomerization is eliminated by iodine scavenger, G(isomerization) is inversely proportional to the square root of the radiation intensity, and, when TCl is present, i-C_3H_6TCl is formed at a rate consistent with the rate of isomerization.

The present paper presents the results of work designed to obtain further information on the mechanism of the radical isomerization in n-C_3H_7Cl and on similar reactions in other alkyl halides.

Experimental Section

Materials. The alkyl halides used were reagent grade materials, further purified by careful fractional distillation with a 3-ft Todd still, sometimes preceded by prolonged stirring with concentrated sulfuric acid. Gas chromatographic analyses of the purified compounds showed that they contained less than 0.04 mole % of the isomer for which radiation yields were to be determined. Matheson Chemical Co. HCl was admitted to the vacuum line from a tank through a P_2O_5 tube. It was subjected to repeated freezing and pumping before being stored in a flask on the line.

Sample Preparation and Irradiation. Accurately known volumes of about 0.3 ml of alkyl halides were degassed and distilled through P_2O_5 into 6-mm o.d. Pyrex tubes, in which they were sealed off from the vacuum line. When desired, a known amount of HCl was frozen down in the sample tube, from a metering volume, prior to adding the alkyl halide.

For irradiation the sample tubes were exposed to a cobalt-60 γ-ray source. The dose rate was usually about 3.5×10^{18} ev g^{-1} min^{-1}. Liquid nitrogen, Dry Ice–trichloroethylene, and a thermostated oil bath were used to surround the samples and source for irradiations at temperatures of -196, -78, and 100°, respectively. All other irradiations were done without thermostating at a temperature of approximately 25°.

Analytical Procedures. The yields of isomers were determined by gas chromatography using a silicone oil on firebrick column and a flame ionization detector. Adequate dilution of the samples to be analyzed was obtained with carbon disulfide. Gaseous samples were prepared for aliquoting by freezing down and adding carbon disulfide. The relative sensitivity of the chromatograph for different compounds was determined with known samples, and changes in sensitivity from day to day were also determined with known standards.

HCl yields were determined by iodometry as described earlier.[2,3]

G values were calculated on the basis of Fricke dosimetry[2b] and on the assumption that the ratio of the rate of energy absorption by a sample to that by the dosimeter is equal to the ratio of the number of electrons per gram.

Results

HCl-Catalyzed Isomerization of n-C_4H_9Cl and i-C_4H_9Cl. Dismukes and Wilcox[4] found that the γ-induced isomerizations of n-C_4H_9Cl to *sec*-C_4H_9Cl and of i-C_4H_9Cl to t-C_4H_9Cl occur with G values of 60 and 20, respectively, which are independent of dose in the range of 1.1×10^{21} to 3.6×10^{21} ev g^{-1}. In the same dose range, but at a 10-fold higher dose rate (3.6×10^{18} ev g^{-1} min^{-1}), we also find dose independ-

---

[1] This work has been supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-32 and by the W. F. Vilas Trust of the University of Wisconsin.

[2] (a) H. L. Benson, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **83**, 4672 (1961); (b) H. L. Benson, Jr., and J. E. Willard, **88**, 5689 (1966).

[3] R. J. Neddenriep and J. E. Willard, *J. Phys. Chem.*, **65**, 1206 (1961).

[4] E. B. Dismukes and W. S. Wilcox, *Radiation Res.*, **11**, 754 (1959).

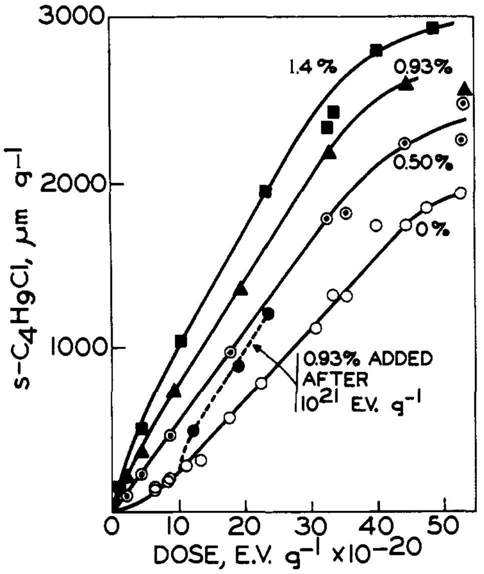


Figure 1. Isomerization of liquid n-C_4H_9Cl to sec-C_4H_9Cl at 25° as a function of radiation dose at high doses. Percentage labels on the curves indicate mole % HCl present at start of irradiation.

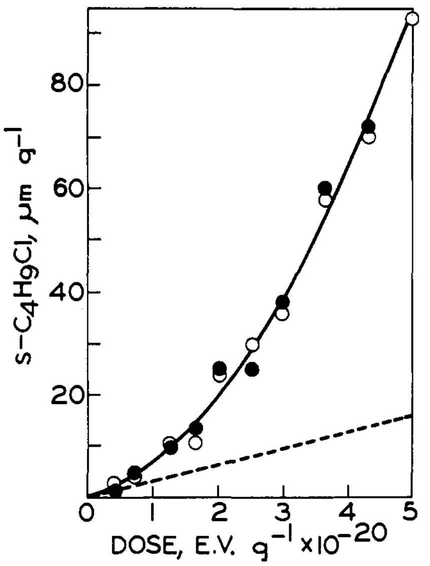


Figure 2. Isomerization of liquid n-C_4H_9Cl to sec-C_4H_9Cl at 25° as a function of radiation dose at low doses.

ence for the rate of isomerization of n-C_4H_9Cl (Figure 1, lowest curve). However, the rate is dose dependent at both lower and higher doses. In the range 0.4×10^{20} to 5×10^{20} ev g^{-1} the yield of the isomer increases approximately as the second power of the absorbed dose (Figure 2), as it does in the isomerization of n-C_3H_7Cl,[2] where the autocatalytic effect has been shown to be caused by the HCl produced during radiolysis. Direct proportionality between G value and average HCl concentrations in the isomerization of n-C_4H_9Cl at low doses is demonstrated by experiments in which known amounts of HCl were added prior to irradiation (Figure 3). The data plotted are average concentrations during the irradiation period. Using $G(\mathrm{HCl}) = 5^{2b}$ to calculate the concentration of HCl built up during irradiation, it may be shown that the rate at any time is the same for HCl produced *in situ* as the initial rate obtained for n-C_4H_9Cl containing an equal concentration of added HCl.

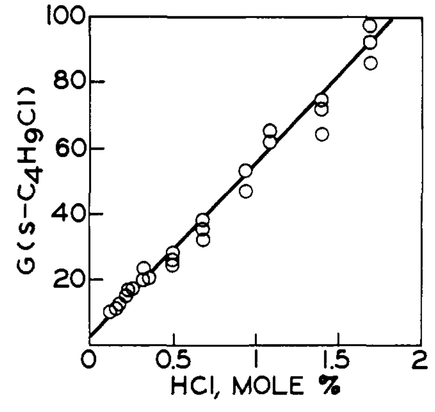


Figure 3. $G(sec$-$C_4H_9Cl)$ from the radiolysis of liquid n-C_4H_9Cl at 25° as a function of HCl concentration.

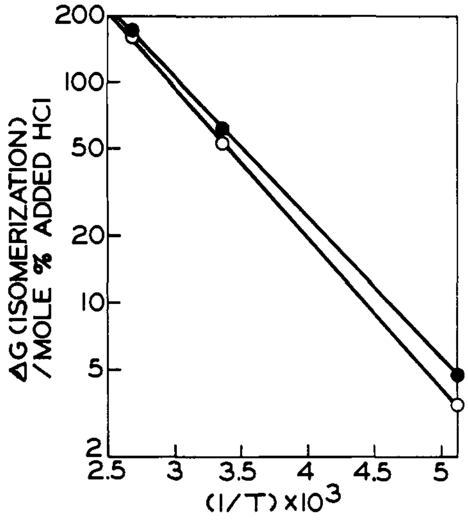


Figure 4. Temperature dependence of HCl-catalyzed isomerizations of liquid alkyl chlorides: ●, n-C_3H_7Cl → i-C_3H_7Cl; ○, n-C_4H_9Cl → sec-C_4H_9Cl.

Similar, less extensive, experiments on the isomerization of i-C_4H_9Cl to t-C_4H_9Cl show qualitatively identical dependence on dose and on concentration of HCl, in the low dose region. It may be concluded that n-C_4H_9Cl, and probably also i-C_4H_9Cl, are similar to n-$C_3H_7Cl^2$ in undergoing radiation-induced isomerization by HCl-catalyzed chain reactions involving intramolecular chlorine atom shifts. At 1.5 mole % HCl the G values for the n-C_4H_9Cl and i-C_4H_9Cl processes at a dose rate of 3.6×10^{18} ev g^{-1} min^{-1} and absorbed dose of 5×10^{19} ev g^{-1} at 25° are about 80 and 20.

The equations for the curve of Figure 2 and for the same system at 100°, as obtained by the least-squares method, are

$$[sec\text{-}C_4H_9Cl] = 3.1n + 3.2n^2 \text{ at } 25° \quad (5)$$

$$= 5.3n + 19.5n^2 \text{ at } 100° \quad (6)$$

where the yields are in μmoles g^{-1} and n is the dose in units of 10^{20} ev g^{-1}. In each case there is a linear term in addition to the square term, suggesting that some isomerization occurs by a process or processes not dependent on the growth of HCl concentration in the alkyl halide during irradiation. The G values indicated

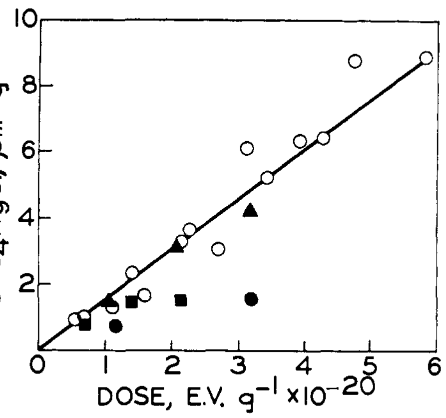


Figure 5. Isomerization of liquid n-C_4H_9Cl to sec-C_4H_9Cl at −78° with and without radical scavengers: ○, pure n-C_4H_9Cl; ▲, n-C_4H_9Cl + 0.85 mole % CH_3I; ■, n-C_4H_9Cl + 0.1 mole % DPPH; ●, n-C_4H_9Cl + 0.25 mole % I_2.

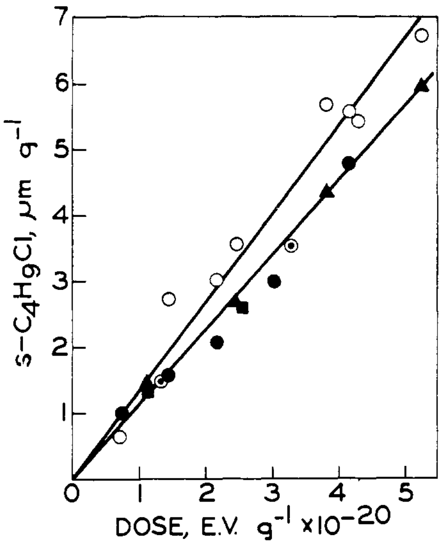


Figure 6. Isomerization of n-C_4H_9Cl to sec-C_4H_9Cl by radiolysis in the solid state at −196°: ○, glassy solid; ▲, polycrystalline solid; ●, glassy solid + 0.1 mole % DPPH; ■, glassy solid + 0.25 mole % I_2; ⊙, glassy solid + 0.85 mole % CH_3I.

for this process are 1.9 at 25° and 3.2 at 100°. The extent of this contribution to the total yield of the isomerization of n-C_4H_9Cl at 25° is indicated by the dotted line of Figure 2.

Temperature Dependence. Figure 4 shows the temperature dependence of the HCl-catalyzed isomerizations of n-C_3H_7Cl and n-C_4H_9Cl. ΔG, plotted on the ordinate, is the change in G value per 1 mole % increase in HCl concentration at the temperature indicated by the abscissa. From these data it appears that the rate-determining step of the HCl-catalyzed isomerization is the same from −78 to 100° and that it is similar for the two compounds. The apparent activation energy is 3 kcal/mole.

The effect of temperature on G(isomerization) of n-C_4H_9Cl is further illustrated by comparison of Figure 5, for irradiation of the liquid at −78°, with Figure 2, for irradiation to the same total dose at 25°. The data of Figure 5 are not adequate to show whether the rate increases with dose or is linear, but the effect of scavengers is consistent with the conclusion that the yield is caused in part by free-radical steps and in part by a nonscavenged step. Better evidence that reactions 1–4 occur even at this temperature is the fact that experiments at five concentrations of added HCl from 0.2 to 1.5 mole % show a linear increase in G(isomerization) from 1.7 at 0.2 mole % HCl to 6 at 1.5 mole % HCl (at a dose of 0.5×10^{20} ev g^{-1}). The concentrations of HCl produced in the experiments of Figure 5 are not known, since G(HCl) has not been determined at −78°.

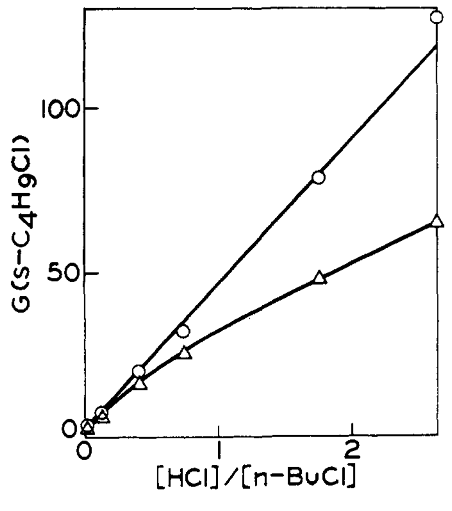


Figure 7. $G(sec$-$C_4H_9Cl)$ from the radiolysis of gaseous n-C_4H_9Cl, as a function of HCl concentration at 25°: pressure of n-C_4H_9Cl, 94 torr for all experiments; dose rate to n-C_4H_9Cl, 2.5×10^{18} ev g^{-1} min^{-1}; total dose to n-C_4H_9Cl, 3.2×10^{20} ev g^{-1}; ○, calculated on the basis of energy absorbed by n-C_4H_9Cl only; △, calculated on the basis of energy absorbed by both n-C_4H_9Cl and HCl.

Solid-State Yields. G(isomerization) for both glassy and polycrystalline n-C_4H_9Cl at −196° is less than unity and is affected very little by HCl. The data of Figure 6 suggest that it may be slightly lower (G = 0.7) in the polycrystalline solid than in the glassy state (G = 0.8), and that radical scavengers added to the glass may reduce the yield to that of the crystalline state. Experiments with initially added HCl gave G values of 1.0 ± 0.1 throughout the range from 0.4 to 1.6 mole % in both glassy and crystalline samples.

In contrast to the slight effect of phase and temperature on G(isomerization) of n-C_4H_9Cl in the absence of HCl, the yields of nonisomeric products of such radiolyses may change dramatically, as shown in Table I for the C_3H_7Cl radiolysis.

Isomerization in the Gaseous State. Radiolysis of n-C_4H_9Cl in the gas phase at 25°, at a pressure of 94 torr, a dose rate of about 2.5×10^{18} ev g^{-1} min^{-1}, and a dose of 3.2×10^{20} ev g^{-1}, gave $G(sec$-$C_4H_9Cl)$ = 2.7. This was increased only to 3.4 by 2 mole % added HCl, in contrast to the large effect of HCl in the liquid phase (Figure 3). With further increase in the HCl concentration, while retaining the n-C_4H_9Cl concentration constant, $G(sec$-$C_4H_9Cl)$ increased linearly (Figure 7), when calculated on the basis of energy absorbed directly by the n-C_4H_9Cl. Similar results were obtained for the isomerization of gaseous n-C_3H_7Cl, using a dose of 0.75×10^{20} ev g^{-1}. The G value in the absence of added HCl was 6.1. In the presence of 75 mole % HCl it rose to 220 (based on energy absorbed by the C_3H_7Cl).

Table I. High-Boiling Radiolysis Products from n-C_3H_7Cl at Various Temperatures

	G values[a]			
	25°	−78°	−196°	−196°[b]
1,2-$C_3H_6Cl_2$	0.59	0.78	0.88	0.76
1,3-$C_3H_6Cl_2$	0.07	0.09	1.4	1.7
sec-$C_6H_{13}Cl$ + 1-Cl-2-Me-pentane	0.39	0.39	0.08	0.04
n-$C_6H_{13}Cl$	0.11	0.11	0.04	0.05
Not identified	0.06	0.02	0.001	
$C_6H_{12}Cl_2$ (A)	0.48	0.17	0.005	
(B)	0.44	0.44	0.01	
(C)	0.72	1[c]	0.03[c]	

[a] Based on the relative yields at 25, −78, and −196° determined in the present work, and normalized to the G values at 25° determined previously.[2b] [b] 0.85 mole % CH_3I was present in the experiments of this column. [c] Relative values for −78 and −196°, not G values; the yield at 25° was not determined in the present work.

Effect of Dose Rate. Comparison of eq 5, obtained for a dose rate of 3.56×10^{18} ev g^{-1} min^{-1}, with the similar equation obtained for a dose rate of 1.14×10^{18} ev g^{-1} min^{-1} ([*sec*-C_4H_9Cl] = $3.67n + 5.19n^2$), indicates that the yield of the first power process varies as $I^{0.85}$ and that of the second-power process as $I^{0.59}$, where I is the absorbed radiation intensity.

These exponents are probably within experimental error of the values of 0.5 and 1 which would be expected if the square term represents production by the mechanism of eq 1–4 and the first power term represents contribution by a mechanism which does not involve radical–radical combination. The square-root dependence on radiation intensity has also been observed for the isomerization of n-C_3H_7Cl.[2]

The G value for increments of *sec*-C_4H_9Cl produced at doses greater than 10^{21} ev g^{-1} at a dose rate of 1.14×10^{18} ev g^{-1} min^{-1} is 28.6 as compared to 25.9 at 3.56×10^{18} ev g^{-1} min^{-1}, indicating an intensity dependence of $I^{0.92}$. This independence of dose rate indicates that most of the reaction chains producing the isomerization are not terminated by radical–radical combination between chain-carrying radicals. Termination may be by combination with olefinic impurities built up in the system as a result of the high dose.

Yields in the Presence of Radical Scavengers. In the presence of 0.25 or 0.5 mole % I_2 or 0.1 mole % diphenylpicrylhydrazyl (DPPH), G(*sec*-C_4H_9Cl) from the radiolysis of liquid n-C_4H_9Cl at 25° in the dose range of 1 to 6×10^{20} ev g^{-1} at a dose rate of 3.6×10^{18} ev g^{-1} min^{-1} was 0.4. The residual reaction must be due to hot-radical reactions or intramolecular rearrangement. The difference between this value and the G of 1.9 in the absence of scavengers which is independent of dose (eq 5, and dotted line of Figure 2) may represent isomerization by thermal radical reactions not involving reaction with HCl. A value of 0.4 for isomerization at 25° in the presence of added I_2 has also been observed for the radiolysis of n-C_3H_7Cl.[2]

A few experiments done under the same dose conditions with 0.85 mole % of CH_3I added gave yields about 0.6 of those shown in Figure 2 for n-C_4H_9Cl without additive. CH_3I is an effective electron scavenger[5] and presumably may also serve as a scavenger for butyl radicals by the process

$$R + CH_3I \longrightarrow RI + CH_3 \qquad (7)$$

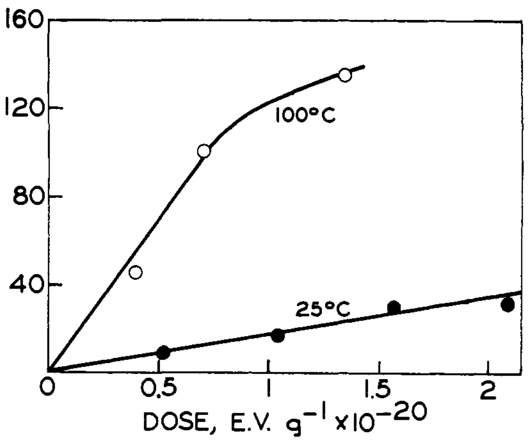


Figure 8. Isomerization of liquid n-C_4H_9Br to *sec*-C_4H_9Br as a function of dose at 25 and 100°: dose rate, 3.5×10^{18} ev g^{-1} min^{-1}.

The effect of scavengers on the n-C_4H_9Cl isomerization at −78° is illustrated in Figure 5. The G values are 0.34, 0.58, and 0.85 in the presence of 0.25, 0.1, and 0.85 mole % I_2, DPPH, and CH_3I, respectively.

Test for Isomerization of *sec*-C_4H_9Cl and *i*-C_3H_7Cl. To evaluate the reversibility of the radiation-induced isomerizations of n-C_4H_9Cl and n-C_3H_7Cl, we have determined G for the reverse isomerizations of *sec*-C_4H_9Cl and *i*-C_3H_7Cl at −196, −78, 25, and 100°. In all cases the value was less than unity. At the two lowest temperatures no isomerization was detected. At the higher temperatures the value rose from zero, without added HCl, to 0.8 with 1.5 mole % added HCl. A dose of 6.9×10^{20} ev g^{-1} at a dose rate of 3.5×10^{18} ev g^{-1} min^{-1} was used.

Photoisomerization of Gaseous n-C_3H_7Cl. Two experiments in which mixtures of 1.5 mole % HCl in gaseous n-C_3H_7Cl (300 torr) were illuminated in quartz at a distance of 4 cm from a quartz-jacketed AH6 mercury arc for 100 and 300 min gave yields of tenths of a per cent of the n-C_3H_7Cl isomerized, indicating that, in the gas phase as in the liquid phase,[2] ionizing radiation is not required for the reaction.

Effect of HBr and HI on the Isomerization of n-C_3H_7Cl. Tests of 1.2 mole % HBr as a catalyst for the isomerization of liquid n-C_3H_7Cl show that it has negligible effect at 25° but that at 160° it increases G(isomerization) from about 10 to several hundred.[6] This is consistent with the fact that the activation energy for abstraction of hydrogen from carbon–hydrogen bonds by Br atoms is much higher than that for Cl atoms. HI showed no catalytic effect even at 160°.

Isomerization of n-C_3H_7Br and n-C_4H_9Br. The radiolysis of liquid n-C_3H_7Br at 25° in the dose range of 0.7 to 2×10^{20} ev g^{-1} at a dose rate of 3.3×10^{18} ev g^{-1} min^{-1} gave an average G(*i*-C_3H_7Br) of 2.1 in agreement with the value of 2.07 reported earlier.[3] In contrast to the results with the alkyl chlorides, neither this value nor the value of $G = 7$ found at 100° was affected by the presence of 1.3 mole % HCl.

Figure 8 shows the formation of *sec*-C_4H_9Br from

---

(5) For examples and references, see (a) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962); (b) R. F. C. Claridge and J. E. Willard, *ibid.*, **87**, 4992 (1965).

(6) The experiments at 160° were done with the liquid sealed in heavy-walled tubing. Relatively negligible isomerization occurred when similar HBr-n-C_3H_7Cl solutions were held at 160° without irradiation.

n-C_4H_9Br at 25 and 100° as a function of dose. The yields at each temperature, in the dose range of Figure 8, increased gradually with increasing HCl concentration in the range from 0 to 1.2 mole %. At 1.2 mole % they are about 1.6 times the value in the absence of HCl and seem to level off.

Products of Radiation-Induced Chlorination of Liquid Alkyl Chlorides. It has been suggested[2] that reaction 2, the isomerization of chloropropyl radical, may be an equilibrium which maintains appreciable concentration of both radicals in the steady state during a radiolysis experiment. Consistent with this hypothesis, both tritiated isopropyl chloride and tritiated n-propyl chloride are formed during the radiolysis of n-C_3H_7Cl containing added TCl (see below). Seemingly inconsistent with the equilibrium hypothesis is the fact that there is negligible radiation-induced isomerization of i-C_3H_7Cl to n-C_3H_7Cl or of sec-C_4H_9Cl to n-C_4H_9Cl, even in the presence of added HCl. However, there is no inconsistency if hydrogen abstraction occurs by reactions 8 and 9 rather than 10 and 11, since the radicals formed by

$$i\text{-}C_3H_7Cl + Cl \longrightarrow CH_3CClCH_3 + HCl \tag{8}$$

$$sec\text{-}C_4H_9Cl + Cl \longrightarrow C_2H_5CClCH_3 + HCl \tag{9}$$

$$i\text{-}C_3H_7Cl + Cl \longrightarrow CH_3CHClCH_2\cdot + HCl \tag{10}$$

$$sec\text{-}C_4H_9Cl + Cl \longrightarrow C_2H_5CHClCH_2\cdot + HCl \tag{11}$$

8 and 9 do not allow for a Cl shift without an H shift.

Fredericks and Tedder[7a] have determined the distribution of products formed when gaseous mixtures containing a ratio of Cl_2:sec-C_4H_9Cl:N_2 of 1:11:360 are illuminated with light absorbed only by the Cl_2, initiating reaction chains of the type

$$Cl_2 \longrightarrow 2Cl \tag{12}$$

$$Cl + C_4H_9Cl \longrightarrow C_4H_8Cl + HCl \tag{13}$$

$$C_4H_8Cl + Cl_2 \longrightarrow C_4H_8Cl_2 + Cl \tag{14}$$

The distribution of dichlorides formed, 1,2:2,2:2,3:1,3, is in the ratio (%) 4:26:51:19 at 35° and nearly the same at 78°. In a similar experiment using liquid sec-C_4H_9Cl containing 2% Cl_2 we have found essentially the same ratio of products except for 1,2-$C_4H_8Cl_2$, which was below our level of detectability. The low relative yield of the 1,2 isomer is consistent with the observed low yield of isomerization of sec-C_4H_9Cl to n-C_4H_9Cl in the radiolysis.

The ratio 1,1:1,2:1,3:1,4 of dichlorides resulting from illumination of Cl_2 in a large excess of N_2 containing n-C_4H_9Cl,[7b] is reported to be 8:26:48:18 (%). We obtain results for the radiolysis in the liquid at −78 to 100°, and for the photolysis in the liquid at −78°, which show the same qualitative trends.

Table II shows relative yields of the dichlorides produced by exposure of liquid n-C_3H_7Cl and i-C_3H_7Cl containing Cl_2 to γ radiation, and to light absorbed by the Cl_2, at different temperatures. These indicate appreciable abstraction of H from the primary C atom during chlorination of i-C_3H_7Cl, thus leaving open the question as to why isomerization does not occur when i-C_3H_7Cl containing HCl is exposed to radiation.

Table II. Products of Chlorination in n-C_3H_7Cl and i-C_3H_7Cl[a]

Radiation	Temp, °C	Relative yields Dichloropropanes 1,1	1,2	2,2	1,3
		n-Propyl Chloride			
γ	−78	0.14	1	0	0.41
	25	0.15	1	0	0.46
	25	0.16	1	0	0.43
	100	0.13	1	0	0.45
Light	35	0.20	1	0	0.50
	−78	0.14	1	0	0.36
		Isopropyl Chloride			
γ	−78	0	0.32	1	Trace[b]
	25	0	0.58	1	Trace[b]
	25	0	0.70	1	Trace[b]
	100	0	0.70	1	Trace[b]
Light	35	0	0.69	1	Trace[b]
	−78	0	0.38	1	Trace[b]

[a] The samples for the experiments of Table II consisted of solutions of about 2 mole % chlorine in liquid propyl chloride, prepared by the usual vacuum-line techniques and sealed in 6-mm o.d. Pyrex tubes which were maintained in the dark until irradiation. Illuminations with an AH6 arc filtered by Pyrex were of 30-min duration, at a distance of 15 cm. γ irradiations were at a dose rate of 3.4×10^{18} ev g^{-1} min^{-1} for 5 min when at 100°, 10 min when at 25°, and 20 min when at −78°. In all of the experiments the chlorine was completely consumed. [b] 0.01 or less.

Ratio of i-C_3H_6TCl to n-C_3H_6TCl from Radiolysis of n-C_3H_7Cl in the Presence of TCl. If both CH_3CHCH_2Cl and $CH_3CHClCH_2$ radicals are present in significant proportions in the steady-state equilibrium represented by reaction 2, and if the activation energies for abstraction of hydrogen from HCl by the two radicals are not too different, radiolysis in the presence of TCl should yield both n-C_3H_6TCl and i-C_3H_6TCl. Four such experiments, summarized in Table III, show both products with the yield of n-C_3H_6TCl being the larger.

Table III. Ratio of Tritiated i-C_3H_7Cl to Tritiated n-C_3H_7Cl Produced in the Radiolysis of Liquid n-C_3H_7Cl in the Presence of 1.6 Mole % HCl (H^3)

Temp, °C	Dose, ev g^{-1} $\times 10^{20}$	Ratio,[a] $\frac{i\text{-}C_3H_6TCl}{n\text{-}C_3H_6TCl}$	G(i-C_3H_7Cl)[b]	G(i-C_3H_7Cl) (H^3)[c]	Isotope effect factor[d]
24	1.6	0.40	98	28.5	3.4
−80	3.4	0.77	7.8	3.2	2.4
97	0.11	0.41	266	91	2.9
−80	6.8	0.77	7.3	2.9	2.5

[a] The i-C_3H_7Cl and n-C_3H_7Cl were separated by gas chromatography and quantitatively trapped. The tritium content was determined by liquid scintillation counting. [b] Based on gas chromatographic analysis for i-C_3H_7Cl. [c] This column shows G(i-C_3H_7Cl) calculated on the assumption that the fraction of the tritium activity found in the form of i-C_3H_6TCl is equal to the fraction of the HCl + TCl which reacted with $CH_3CHClCH_2$ radicals by reaction 3. [d] Ratio of column 4 to column 5.

Discussion

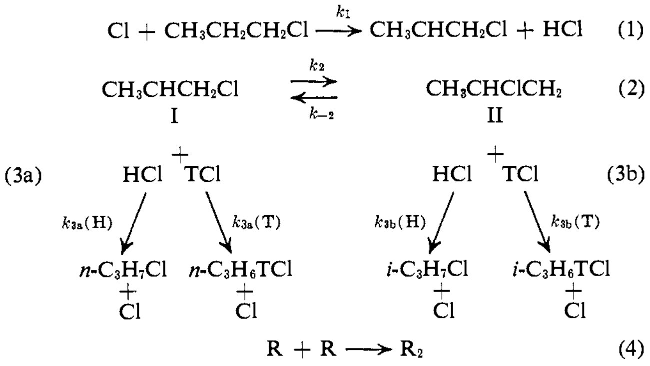
Elementary Steps in the Isomerization. The significant steps in the radiation-induced isomerizations of n-C_3H_7Cl, n-C_4H_9Cl, and i-C_4H_9Cl in the presence of HCl and TCl may be indicated as shown in Scheme I using n-C_3H_7Cl as the example. The activation energies for abstraction of hydrogen from C_2H_6, C_2H_5Cl, and C_3H_8 by chlorine atoms are 1, 1.5, and 0.7 kcal $mole^{-1}$, respectively.[8] It is probable that the value for the reaction with n-C_3H_7Cl is also about 1 kcal $mole^{-1}$. The only fate of Cl atoms in these systems is to abstract

---

(7) (a) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 3520 (1961); (b) P. S. Fredericks and J. M. Tedder, *ibid.*, 144 (1960).

(8) H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, 77, 2629 (1955).

Scheme I



hydrogen. Thus each time a radical is removed by reaction 3 it is replaced by another radical. When the new radical is $CH_2CH_2CH_2Cl$ or CH_3CH_2CHCl (the formation of which are indicated by the data of Table II) instead of CH_3CHCH_2Cl, this is irrelevant with respect to the isomerization, because a n-C_3H_7Cl molecule and a Cl atom are regenerated by reaction with HCl, unless the radical happens to undergo a chain-terminating radical–radical recombination. For a molecule of the isomer product to be produced from a radical formed by step 1, steps 2 and 3 must occur rather than removal of the radical by the competitive step 4 (Scheme I).

Available evidence is not adequate to say whether I or II is the more stable radical. The experiments with added TCl (Table III) indicate that both radicals are present and that the number of TCl molecules reacting with each is the same within a factor of less than 3, but they do not indicate what combination of relative rate constants for (3a) and (3b) and relative concentrations of radicals accomplish this result. The value of $[CH_3CHClCH_2]/[CH_3CHCH_2Cl]$ at the steady state may be larger than unity and the corresponding ratio of rate constants less than unity.

If it is arbitrarily assumed that the rate constants for reactions 3a and 3b are equal, and that the magnitude of the isotope effect for reaction with TCl as compared to HCl is the same for the two isomeric radicals, then the ratio of the stable tritiated isomers formed is equal to the ratio of the two isomeric radicals in the steady state. If the isomeric radicals are in equilibrium at the steady state, then this ratio is the equilibrium constant of the radical isomerization, and the heat of isomerization may be calculated from its variation with temperature. The data of Table III indicate that the ratio of i-C_3H_6TCl to n-C_3H_6TCl changes by less than a factor of 2 between -80 and 97°, while $G(i\text{-}C_3H_7Cl)$ changes by a factor of 35. If the assumptions noted above are correct, the isomerization of chloropropyl radicals is then thermoneutral, within an experimental error of about ± 1 kcal mole^{-1}, and the increase of $G(i\text{-}C_3H_7Cl)$ with increase in temperature is caused primarily by the increased rate of the radical turnover process 3b in competition with chain termination by (4).

The close similarity of the apparent activation energies and also of the absolute rates for the isomerizations of n-C_3H_7Cl and n-C_3H_9Cl suggest that the rate-determining steps are very similar.

It has been reported[9] that an equilibrium mixture of the propyl chlorides contains less thn 0.8% n-C_3H_7Cl. A similar conclusion has been reached by Thomas Lantz of our laboratory on the basis of equilibration with metal chloride catalysts. The addition of HCl to propene gives low yields of n-C_3H_7Cl relative to i-C_3H_7Cl.[10] It has been reported that the heats of combustion of n-C_3H_7Cl and i-C_3H_7Cl are nearly equal.[11]

It is difficult to reconcile the absence of radiation-induced HCl-catalyzed isomerization of i-C_3H_7Cl with the fact that photochlorination of i-C_3H_7Cl produces 0.6 as much 1,2-$C_3H_6Cl_2$ as 2,2-$C_3H_6Cl_2$, since the presence of the 1,2 product indicates that Cl atoms abstract primary H atoms extensively. From the evidence and discussion above it would be expected that the $CH_3CHClCH_2$ radicals formed by Cl atom attack in the presence of HCl would isomerize and, in part, react with HCl to form n-C_3H_7Cl. The dilemma would be resolved if Cl atoms produced by the reaction of radicals with HCl abstract the central H atom of i-C_3H_7Cl much more preferentially than do chlorine atoms produced by the reaction of radicals with Cl_2. There is basis for such a postulate since the reactions of the radicals with Cl_2 are exothermic by some 20 kcal mole^{-1} while those of the radicals with HCl are nearly thermoneutral or endothermic. More than half of the heat of the Cl_2 reaction which goes into kinetic energy is carried by the Cl atom.

We have sought to determine whether "warm" Cl atoms produced in the photochemical chain chlorination of isopropyl chloride, and also of propane, show a different ratio of H abstraction from different bonds from the ratio shown by thermal Cl atoms. For this purpose Cl_2 has been illuminated in the presence of the organic vapor both with and without a larger excess of Ar to serve as moderator. The results are inconclusive, apparently because of variable wall effects in these gas-phase tests. There is no experimental method for distinguishing between the reactions of "warm" and thermal atoms in the liquid phase in these systems. Fredericks and Tedder[7] have found that thermal chlorine atoms are able to cause significant abstraction from all positions in butyl chloride and butane molecules in excess N_2.

Another explanation for the failure of i-C_3H_7Cl to isomerize might be that the radical isomerization equilibrium strongly favors the $CH_3CHClCH_2$ form. The evidence against this is the relatively high yield of n-C_3H_6TCl in the presence of TCl (Table III).

Gas-Phase Isomerization. A comparison of Figure 7 with Figure 3 shows that HCl is a less effective catalyst for the isomerization in the gas phase than in the liquid, on a mole fraction basis. This presumably is because the molar concentration of HCl varies as the first power of the density of reactants while the steady-state molar concentration of radicals (controlled by reaction 4) varies as the square root of the density (for constant mole fraction and constant ev g^{-1} min^{-1} absorbed). Thus, the probability that a radical will encounter an HCl molecule and undergo reaction 3 decreases more with the decrease in density from the liquid to the gas

---

[9] T. I. Crowell and G. L. Jones, Jr., *J. Am. Chem. Soc.*, 73, 3506 (1951).

[10] See, for example (and references therein), (a) F. R. Mayo, *ibid.*, **84**, 3964 (1962); (b) F. R. Mayo, *ibid.*, 76, 5392 (1954); (c) L. E. Swabb and H. E. Hoelscher, *Chem. Eng. Progr.*, **48**, 564 (1952); (d) H. Noller and H. Wolff, *Z. Physik. Chem.* (Frankfurt), 13, 255 (1957); (e) L. G. Brouwer and J. P. Wibant, *Rec. Trav. Chim.*, 52, 1001 (1934).

[11] F. K. Beilstein, "Handbuch der Organischen Chemie," Vol. I, 3rd Suppl., pp 219, 222.

than the probability that a radical will encounter another radical and undergo reaction 4 to end the isomerization chain. The ratio of HCl molar concentrations required to give the same *G*(isomerization) at two different steady-state radical concentrations should equal the ratio of the radical concentrations. Experiments with 90 torr of alkyl chloride required about 130 torr of HCl (60 mole %) to give *G* values (upper curve of Figure 7) equal to those found in the liquid phase at 1 mole %. This is a ratio of molar HCl concentration in the gas to that in the liquid of 0.07, as compared to a ratio of 0.02 estimated for the radical concentrations in the same experiments on the basis of square-root dependence on the density. Considering that the density of the gas is less than 10^{-3} that of the liquid and uncertainties in estimating gas-phase dosage rates, these numbers are in plausible agreement. The deviation is in the direction which would be expected if chain lengths are reduced by wall termination in the gas phase.

The data cannot be explained by energy or charge transfer from the HCl to the alkyl chloride.

Isomerization of *n*-C_4H_9Cl in High-Dose Ranges. The constant value of the rate of isomerization of *n*-C_4H_9Cl in the dose range of about 10×10^{20} to 40×10^{20} ev g^{-1} (Figure 1) suggested that a constant steady-state level of HCl concentration might prevail in this range. Determinations of the yields of HCl up to 10^{22} ev g^{-1} indicate, however, that the differential *G*(HCl) remains constant at a value of about unity from 3×10^{21} to 10^{22} ev g^{-1} (after decreasing from the value of 4.7 which is observed below 10^{21} ev g^{-1}). The fact that *G*(*sec*-C_4H_9Cl) remains constant in this range, while the HCl concentration increases, indicates the appearance of a process which consumes radicals in competition with their reaction with HCl more readily than does radical–radical combination. This must be reaction of the radicals with a radiation-produced impurity, probably an olefin. The HCl concentration produced in the system at 10^{22} ev g^{-1} is about 2.5 mole %, a concentration at which *G*(*sec*-C_4H_9Cl) still increases linearly with added HCl when the HCl is added at the start of an experiment.

Isomerization of *n*-C_3H_7Br and *n*-C_4H_9Br. Wilcox,[12] using the very high dose of 9.5×10^{21} ev g^{-1} with a dose rate of 3×10^{17} ev g^{-1} min^{-1}, has reported a *G* value of 0.2 for the isomerization of *n*-C_4H_9Br to *sec*-C_4H_9Br. The present work indicates (Figure 8) a *G* value of 10 for doses up to at least 1.6×10^{20} ev g^{-1} at a dose rate of 3.5×10^{18} ev g^{-1} min^{-1} at 25°. At 100° and doses below 0.7×10^{20} ev g^{-1}, $G = ca.$ 80 but falls at higher doses. In a recent extensive investigation of the radiolysis of *n*-C_4H_9Br as a function of dose rate, dose, and temperature, Martin and Williams[13] have found that the chain character of the isomerization is more fully manifested at still lower dose rates and doses. Thus, for a dose of 1.3×10^{17} ev g^{-1} and a dose rate of 4.5×10^{15} ev g^{-1} min^{-1} they obtain values of *G*(isomerization) of 187, 466, 965, and 2065 at 16, 38, 61, and 87°, respectively.

At the dose rates and doses we have used, HBr, which is a product of the radiolysis, does not catalyze the isomerization of *n*-C_4H_9Br as HCl catalyzes the isomerization of the chlorides, and added HCl up to 1 mole % has only a small catalytic effect. Likewise, HCl does not catalyze the isomerization of *n*-C_3H_7Br either at 25 or 100°. This indicates either that the observed isomerization cannot occur by an intraradical shift, such as occurs in the case of the chlorides, or that Cl atoms do not abstract H from the β position in alkyl bromides, or that the activation energy for reaction of the radical with HCl is too high to permit a chain reaction. Studies of the photochemical chlorination of *n*-C_4H_9Br[7] indicate that essentially no abstraction of hydrogen by chlorine atoms occurs from the β position of *n*-C_4H_9Br, the ratio of abstraction being 8:0:67:25 from the 1, 2, 3, and 4 positions. This contracts with the chlorination[7] of *n*-C_4H_9Cl where the ratio is 8:26:49:17.

The simplest plausible mechanism for the chain isomerization of *n*-C_4H_9Br involves the steps

$$R + n\text{-}C_4H_9Br \longrightarrow C_2H_5CHCH_2Br + RH \qquad (15)$$

$$C_2H_5CHCH_2Br \longrightarrow C_2H_5CHBrCH_2 \qquad (16)$$

$$C_2H_5CHBrCH_2 + n\text{-}C_4H_9Br \longrightarrow sec\text{-}C_4H_9Br + C_2H_5CHCH_2Br \qquad (17)$$

with the chain being carried by many repetitions of steps 16 and 17. This implies that the $C_2H_5CHBrCH_2$ radical can abstract a β H from *n*-C_4H_9Br more readily than a Cl atom can. The increase in *G* with temperature must result from the activation energies of reactions 16 and 17. A mechanism analogous to that believed to account for the chain isomerization of *n*-C_3H_7Cl,[2a] in which the chain is carried by halogen atom abstraction of β hydrogens, seems to be inconsistent with the photochemical chlorination data[7] noted above.

---

(12) W. S. Wilcox, *Radiation Res.*, 10, 112 (1959).

(13) D. H. Martin, Ph.D. Thesis, University of Tennessee, 1966; T. F. Williams, private communication.