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Evidence on the Elementary Reactions in the Radiolysis of *n*-Propyl Chloride[1,2]

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Abstract: Radiolysis of *n*-C_3H_7Cl by Co^{60} γ rays produces HCl and 19 hydrocarbons and organic chlorides with yields of 0.06 molecule per 100 ev or higher. The major product is *i*-C_3H_7Cl formed by an HCl-catalyzed chain isomerization of *n*-C_3H_7Cl where G(*i*-C_3H_7Cl) increases linearly with increasing HCl concentration.[3] Other major yields are $G(\text{HCl}) = 5$, $G(C_3 \text{ hydrocarbons}) = 4.3$, $G(C_6H_{12}Cl_2) = 1.6$, $G(C_3H_6Cl_2) = 1.0$, $G(H_2) = 1$. With the exception of *i*-C_3H_7Cl, the yields are independent of total dose up to at least 6×10^{20} ev g^{-1}. In the presence of I_2, C_3H_6, or C_2H_4, yields of the hydrocarbons and organic chlorides are all greatly reduced or eliminated and new products are formed. The photolysis of *n*-C_3H_7Cl gives products similar to those from the radiolysis. The data afford evidence on the contributions of the different free-radical processes.

Studies of the radiolysis of *n*-C_3H_7Cl have been limited to the determination of G(HCl exchange),[4] G(HCl),[5] and G(*i*-C_3H_7Cl)[5] as a function of dose at doses greater than 10^{21} ev g^{-1}, and an investigation of the HCl-catalyzed chain-propagated isomerization of *n*-C_3H_7Cl to *i*-C_3H_7Cl at lower doses.[3] The purpose of the present work has been to identify the other products of the radiolysis, to determine the effects of scavengers and of dose on these products, and to compare the products of the photochemical decomposition with those of the radiolysis.

Related work which has been reported includes investigations of the products of the radiolysis of the butyl chlorides[6] and bromides,[7] investigations of scavenger effects in the radiolysis of alkyl iodides,[8] *n*-propyl bromide,[9] and the monohalobenzenes,[10] and investigations of the radiation-induced isomerizations of several alkyl chlorides and bromides.[3b]

Experimental Section

Eastman White Label *n*-C_3H_7Cl was further purified by stirring with concentrated H_2SO_4 for 72 hr, washing with water, drying with $MgSO_4$, and fractional distillation. Gas chromatographic analysis showed a single impurity peak attributable to 0.1 mole % of either *sec*- or *i*-C_4H_9Cl. Samples of the purified *n*-C_3H_7Cl were degassed and distilled under vacuum through P_2O_5 prior to freezing at 77°K and sealing off 5 ml in an annular vessel or 0.3 ml in a 6-mm o.d. glass tube. These irradiation vessels were designed to hold the samples in close proximity to one of two high specific activity Co^{66} sources which gave dose rates on the samples of about 1.4×10^{18} and 4.6×10^{18} ev g^{-1} min^{-1} during the period of this work.

All additives used were degassed, dried, and metered into the sample vessels by vacuum-line techniques.[2] HCl yields were determined by iodometry as described earlier[9,10] using a molar absorbancy index for I_3^- in 1 *M* KI of 2.75×10^4 l. mole^{-1} cm^{-1}

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

[2] Further details are given in the Ph.D. thesis of H. L. Benson, Jr., University of Wisconsin, 1961, available from University Microfilms, Ann Arbor, Mich.

[3] (a) H. L. Benson, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **83**, 4672 (1961); (b) M. Takehisa, G. Levey, and J. E. Willard, *ibid.*, **88**, 5694 (1966).

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[5] R. H. Wiley, W. Miller, C. H. Jarboe, Jr., J. R. Harrell, and J. D. Parish, *Radiation Res.*, **13**, 479 (1960).

[6] E. B. Dismukes and W. S. Wilcox, *ibid.*, **11**, 754 (1959).

[7] J. Wilcox, *ibid.*, **10**, 112 (1959).

[8] See, for example, R. J. Hanrahan and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2434 (1957), and references therein.

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

[10] S. U. Choi and J. E. Willard, *ibid.*, **66**, 1041 (1962).

at 3500 A. Yields of organic products were determined by gas chromatography using helium as the carrier, 40–60 mesh firebrick coated with GE SF-96(40) silicone oil, temperature programming from 25 to 200° at a rate of 3 to 4°/min, and thermal conductivity detection. The sensitivity of the detector for each of the products was determined. Corrections for changes in the sensitivity from day to day were made on the basis of daily runs with standard propane samples. Products were identified by comparison with the emergence times of known samples, or by the increase in peak areas caused by the addition of known compounds to irradiated samples.

The dose rates reported are based on ferrous sulfate dosimetry assuming 15.6 ferrous ions oxidized per 100 ev and assuming a molar absorbancy index for Fe^{2+} of 2238 l. mole^{-1} cm^{-1} at 3050 A at 27°. *G* values were calculated on the assumption that the ratio of energy absorbed per gram of the dosimeter solution to that absorbed per gram of n-C_3H_7Cl is equal to the ratio of the number of electrons per gram of the two.

Photolysis of liquid n-C_3H_7Cl was carried out in a quartz cell with a 1-mm light path and optical faces of 1 cm × 4 cm.

The cell, cooled by an air stream, was exposed to the full light of a quartz-jacketed 1000-w A-H6 mercury arc at a distance of 7 cm. The absorption spectrum of 1 mm of liquid C_3H_7Cl, as determined in this work, begins at 2250 A, increasing to an absorbancy of 1 at 2180 A and 3 at 2105 A. It is greater than 3 at all lower wavelengths to the 1850-A limit of the instrument used.

Results[2]

The γ irradiation of pure n-propyl chloride produces at least the 18 products shown in Table I, plus i-C_3H_7Cl, HCl, and H_2. With the exception of i-C_3H_7Cl,[3] the *G* values are independent of dose up to at least 6×10^{20} ev g^{-1}. At somewhat higher doses the rates of production of the three dichlorohexane isomers decrease and those of hexane, *sec*-hexyl chloride, and an unidentified compound eluting between n-$C_6H_{13}Cl$ and the dichlorohexanes increase. The *G* values of the other products shown in Table I are independent of total dose to 2×10^{21} ev g^{-1} or higher.

Table I. *G* Values for the Products of the Radiolysis of n-C_3H_7Cl with and without Additives. Relative Product Yields in the Photolysis

	Total dose, ev g^{-1} × 10^{-20}					
	5	20	3 to 16[c]	4	6.6	
	Dose rate, ev g^{-1} min^{-1} × 10^{-18}					Photolisys[f]
	1.4	1.4	1.4	1.4	1.4	
	Additive					
	...	...	I_2, 1%	C_3H_6,[d] 1.6%	C_2H_4,[d] 1%	...
CH_4	0.11	0.11	0.02	0.1	*b*	*a*
C_2H_6	0.09	0.09	*b*	*b*	*b*	*a*
C_3H_8 C_3H_6	4.3	4.3	0.6	*b*	*b*	4.3
n-C_6H_{14}	0.13	0.36	*b*	0.3	0.3	...
CH_3Cl	0.23	0.23	0.1	0.1	*b*	0.06
C_2H_5Cl	0.13	0.13	*b*	*a*	2.2	
n-$C_6H_{13}Cl$	0.11	0.11	*a*	0.19	0.1	
sec-$C_6H_{13}Cl$	0.25	0.43	*a*	1.7	0.2	0.14
1-Cl-2-Me-pentane	0.14	0.14	*a*	1.9	0.2	
1,1-$C_3H_6Cl_2$	0.32	0.32	*b*	(0.2)[e]	0.3	0.07
1,2-$C_3H_6Cl_2$	0.59	0.59	*b*	(0.5)[e]	0.5	0.12
1,3-$C_3H_6Cl_2$	0.07	0.07	*a*	*a*	*a*	
$C_6H_{12}Cl_2$ (A)	0.48	0.2	*a*	0.18	(0.2)[e]	0.4
(B)	0.44	0.1	*a*	0.14	(0.2)[e]	
(C)	0.72	0.3	*a*	0.58	(0.4)[e]	0.4
Not identified[g]	0.06	0.41	*a*	0.2	*a*	
Not identified[h]	0.14	0.14	*a*	0.3	*a*	

[a] Below level of detection. [b] Level too low or too poorly resolved for quantitative evaluation. [c] *G* values determined at nine doses in this range in the presence of I_2 were independent of dose up to 16×10^{20} ev g^{-1}, the highest tested. [d] Concentration is that if all of the olefin were in solution. Some may have been in the vapor phase. The vapor/liquid volume ratio was approximately 5. [e] Estimated from trend of values at series of concentration. [f] Numbers are relative, normalized to 4.3 for the C_3 hydrocarbons. [g] Eluted between n-$C_6H_{13}Cl$ and the dichlorohexanes. [h] Eluted following the dichlorohexanes.

The differential *G* values for production of i-C_3H_7Cl increased linearly with dose to about 45 at a dose of 8×10^{20} ev g^{-1} (at a dose rate of 1.4×10^{18} ev g^{-1} min^{-1}) as a result of catalysis of the isomerization by HCl produced in the radiolysis. At higher doses the rate of increase was slower, a value of 70 being attained at 18×10^{20} ev g^{-1}. The $G(C_3$ hydrocarbons) was nearly unchanged in the presence of 2 mole % dissolved[11] HCl, which produce $G(i$-$C_3H_7Cl)$ values of 160.

n-Propyl chloride radiolyzed in the presence of I_2 or C_2H_4 gave products in addition to those listed in Table I. *G* values for these are shown in Tables II and III.

Table II. *G* Values of Products Formed by Reactions of Intermediates with I_2

	Dose,[a] ev g^{-1} × 10^{-20}				
	0.23	0.68	1.4	2.7	...[c]
	I_2, mole %				
	0.1	0.1	1	1	1
	$R^{131}I$[b]				RI[c]
CH_3I	0.08	0.11	0.11	0.14	
C_2H_5I	0.09	0.08	0.09	0.09	
i-C_3H_7I	0.04	0.05	0.07	0.05	
n-C_3H_7I	4.2	4.1	4.0	3.7	3.6
1-Cl-1-I-propane 1-Cl-2-I-propane	2.4	2.6	2.8	2.7	2.0
1-Cl-3-I-propane	0.92	0.84	0.69	0.76	0.6
Not identified[d]	0.03	0.04	0.09	0.27	

[a] Dose rate 1.4×10^{18} ev g^{-1} min^{-1}. [b] Calculated from radio gas chromatography peaks for $R^{131}I$, assuming $G(-{}^1/_2I_2)$, which was found to be 7.8 spectrophotometrically, was all due to formation of organic iodides and none to HI formation. [c] From gas chromatographic RI peaks measured by thermal conductivity in experiments using unlabeled I_2. The *G* values were constant up to 12×10^{20} ev g^{-1} or higher. [d] Emerged from column when temperature reached about 180°. Retention time on column similar to n-$C_6H_{13}I$.

Table III. *G* Values[b] of Products Formed by Reactions of Intermediates with C_2H_4

	C_2H_4, mole %[a]			
	0.2	1.0	3.0	5.0
n-C_4H_{10}	0.06	0.56	0.53	0.6
Not identified[c]	0.06	0.20	0.83	2.3
sec-$C_5H_{11}Cl$	0.21	1.0	2.3	2.5
1-Cl-2-Me-butane	0.17	1.3	3.4	3.6

[a] Total C_2H_4 in gas and liquid phases. [b] Dose of 6.6×10^{20} ev g^{-1} at 1.4×10^{18} ev g^{-1} min^{-1}. [c] Eluted between n-C_6H_{14} and 1,1-$C_3H_6Cl_2$.

The data for HCl production as a function of dose, plotted in Figure 1, indicate that it is formed linearly with a *G* of 5 up to 3×10^{20} ev g^{-1} or somewhat higher, following which the rate decreases, apparently becoming zero at about 14×10^{20} ev g^{-1}. Also plotted in the figure are data we have obtained for the production of HCl from n-C_4H_9Cl. These yield average *G* values of 4.7 and 3.6 for the doses of 3.3×10^{20} and 12.8×10^{20} ev g^{-1}, respectively, in contrast to a value of unity reported by Dismukes and Wilcox[6] for doses

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(11) Determined from the Henry's law constant,[2] 1.38×10^4 torr $= P/N$ at 22°, where P = the pressure of HCl in torr in the vapor and N = the mole fraction in solution.

of 11 × 10^{20} and 36 × 10^{20} ev g^{-1}. The latter workers determined the acid concentration of the irradiated butyl chloride by titrating with NaOH in isopropyl alcohol. It appears that HCl may have been lost either by volatilization in sample transfer or by reaction with the alcohol.

Further experiments on G(HCl) in the radiolysis of n-C_3H_7Cl showed that it is not affected by the presence of 0.05 mole % I_2 in the dose range up to 1.8 × 10^{20} ev g^{-1}. At −75°, G(HCl) is 3.9 up to at least 3.5 × 10^{20} ev g^{-1}. This indicates an apparent activation energy of 0.4 kcal/mole for HCl production.

Earlier work[9] has indicated that H_2 is a product of the radiolysis of n-C_3H_7Cl, with $G(H_2) = 1$ for doses up to 7 × 10^{20} ev g^{-1} or higher. No Cl_2 has been observed as a product.

The last column of Table I lists relative yields of the products formed in a 450-min photolysis of n-C_3H_7Cl under the conditions described in the Experimental Section. The relative values have been normalized to a value of 4.3 for the C_3 hydrocarbons for ease of comparison with the radiolysis yields. The yield of i-C_3H_7Cl on this scale was 14. In an identical experiment with 1 mole % HCl added, the yield of i-C_3H_7Cl increased to 184. The absolute yield of $C_3H_8 + C_3H_6$ in the photolysis experiment of Table I was 35 μmoles.

Discussion

Possible Role of Ionic Species. Values for the G of escape of electrons from recombination with the parent cation[12] during radiolysis of liquid n-C_4H_9Cl, n-C_4H_9Br, and CCl_4 have been determined by electrical conductivity measurements to be 0.27,[13] 0.39,[13] and 0.068,[14] respectively. If $G(e^-)$ in the radiolysis of n-C_3H_7Cl is similar to that for n-C_4H_9Cl, this sets an upper limit of about 0.3 on G(primary ion–molecule reactions) in the work reported here.

Electrons which escape recombination with the parent cation in propyl chloride presumably form n-$C_3H_7Cl^-$ or undergo dissociative capture to form $C_3H_7 + Cl^-$. Use of $^{131}I_2$ scavenger to detect free radicals produced in the radiolysis of 1 mole % n-C_3H_7Cl in liquid n-C_5H_{12} sets an upper limit of 1 for G for dissociative electron capture by the n-C_3H_7Cl.[15] In glassy 3-methylpentane matrices at 77°K, the G value for radical production by dissociative electron capture by alkyl chloride solutes has a saturation value of 1.[16] Propyl radicals formed by dissociative capture will react in the same way as those formed by the decomposition of excited molecules. The ions, Cl^- and n-$C_3H_7Cl^-$, will be neutralized on encounter with cations, possibly with fragmentation.

These facts are all consistent with the conclusion that G(ionic processes) in the radiolysis of liquid n-C_3H_7Cl is not significantly greather than unity and may be much less. Proof that the types of product observed in the radiolysis do not require ionic intermediates is also given by the photochemical experiments (column 7, Table I) in which the maximum energy of the photons (*ca.* 7 ev) was much below the ionization potential (10.7 ev) of n-C_3H_7Cl. A difference in relative amounts of products in the photolysis and radiolysis, as observed, is to be expected, since a wider variety of excited states may be produced by the Compton electrons and δ rays than by the ultraviolet photons.

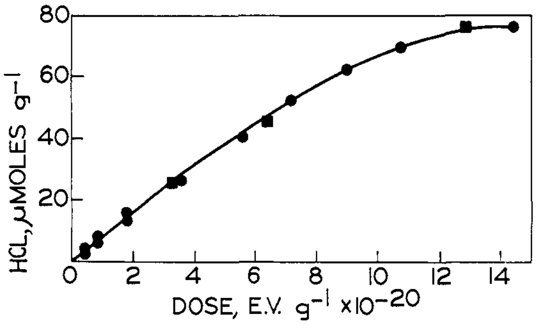

Figure 1. HCl production from liquid n-C_3H_7Cl and n-C_4H_9Cl at 25° as a function of radiation dose: ●, n-C_3H_7Cl; ■, n-C_4H_9Cl.

Role of Radicals. The effect of 1 mole % of added iodine as scavenger in reducing the yields of all products of the radiolysis is that which would be expected if all products are formed predominantly through thermal radical intermediates, with minor portions of the yields of CH_4, C_3 hydrocarbons, and CH_3Cl being formed either by hot-radical or ion–molecule processes. The iodinated products formed (Table II) are consistent with the conclusion that iodine acts as a scavenger for free radicals. Similarly, the effects of added C_3H_6 and C_2H_4 as additives in changing product yields (Table I) and forming new products (Table III) are consistent with the reactions they would be expected to undergo with free radicals.

Elementary Steps. Consideration of the observed products and the effects of additives on their yields indicates that each of the following elementary steps may be involved in the radiolysis of n-C_3H_7Cl. A bold-faced formula indicates that it represents a hot species, *i.e.*, a species born with energy much in excess of the average thermal energy of the system.

$$C_3H_7Cl \longrightarrow \mathbf{C_3H_7Cl} \tag{1}$$

$$\mathbf{C_3H_7Cl} \longrightarrow C_3H_7 + Cl \tag{2a}$$

$$\longrightarrow HCl + C_3H_6 \tag{2b}$$

$$\longrightarrow \mathbf{CH_3} + \mathbf{C_2H_4Cl} \tag{2c}$$

$$\longrightarrow \mathbf{C_2H_5} + \mathbf{CH_2Cl} \tag{2d}$$

$$\longrightarrow CH_3Cl + C_2H_4 \tag{2e}$$

$$\longrightarrow H + C_3H_6Cl \tag{2f}$$

$$(\mathbf{C_3H_7} + \mathbf{Cl}) + M \longrightarrow C_3H_7Cl + M \tag{3}$$

$$\mathbf{R} + C_3H_7Cl \longrightarrow R + C_3H_7Cl \tag{4a}$$

$$\longrightarrow RH + C_3H_6Cl \tag{4b}$$

$$R + C_3H_7Cl \longrightarrow RH + C_3H_6Cl \tag{5}$$

$$R + HCl \longrightarrow RH + Cl \tag{6}$$

$$Cl + CH_3CH_2CH_2Cl \longrightarrow HCl + CH_3CHCH_2Cl \tag{7}$$

$$CH_3CHCH_2Cl \longrightarrow CH_3CHClCH_2 \tag{8}$$

$$C_3H_6Cl + C_3H_7Cl \longrightarrow C_3H_6Cl_2 + C_3H_7 \tag{9}$$

$$2C_3H_6Cl \longrightarrow C_6H_{12}Cl_2 \tag{10}$$

$$2C_3H_7 \longrightarrow C_6H_{14} \tag{11}$$

$$C_3H_7 + C_3H_6Cl \longrightarrow C_6H_{13}Cl \tag{12}$$

$$C_3H_7 + C_3H_6 \longrightarrow C_6H_{13} \tag{13}$$

$$C_3H_6 + HCl \longrightarrow CH_3CHClCH_3 \tag{14}$$

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(16) As shown by esr measurements on γ-irradiated samples by Miriam Shirom in our laboratory.

The maximum energy carried by the hot fragments formed in reactions 2a, c, d, and f is approximately equal to the ionization potential less the energy of the bond broken, *i.e.*, 10.7–3.5 ev in the case of reaction 2a. If this energy were all to go into kinetic energy of the fragments in reaction 2a, the energies of the propyl radical and chlorine atom would be approximately 3.2 and 4.0 ev, respectively. Thus, hot-radical reactions, unsusceptible to scavengers, would be energetically possible.

Propane Formation and C–Cl Bond Rupture. The fact that $G(C_3$ hydrocarbons) is the highest of the initial yields of organic products (4.3) and that $G(HCl)$ is in the same range indicates that the majority of the excited n-C_3H_7Cl molecules probably dissociate either by reaction 2a or 2b (or by dissociative electron attachment). Reaction 2a leads to production of C_3H_8 and HCl by reactions 4b, 5 or 6, and 7. The gas chromatographic separation used in this work did not resolve C_3H_8 and C_3H_6. However, it is possible to estimate an upper limit for the G value for C_3H_6 formation from a consideration of the material balance for thermal propyl radicals. $G(n\text{-}C_3H_7I)$ in the presence of 1 mole % iodine is a measure of thermal C_3H_7 production by the sequence 2a–4a, and the $C_3H_6Cl_2$ yield is a measure of C_3H_7 production by reaction 9. Taking these G values as 3.6 and 1.0 (last column of Table II and column 2 of Table I) indicates a total G for thermal C_3H_7 of 4.6. If n-C_6H_{14} and the $C_6H_{13}Cl$ isomers are formed by reactions 11 and 12, the G for consumption of C_3H_7 radicals in forming them is $2G(n\text{-}C_6H_{14}) + G(C_6H_{13}Cl) =$ *ca.* 0.8. Since the formation of propane from thermal C_3H_7 radicals by reaction 5 is the only other way in which thermal C_3H_7 radicals are consumed at low HCl concentrations, this treatment indicates that the G for propane formation by step 5 is approximately $4.6 - 0.8 = 3.8$.

In the presence of I_2, $G(C_3)$ is 0.6. This hot yield plus the yield for propane formation by thermal processes $(0.6 + 3.8 = 4.4)$ is in good agreement with the experimentally found value of $G(C_3) = 4.3$. The 0.6 hot yield must equal the sum of the yields for C_3H_6 formation by reaction 2b plus C_3H_8 formation by reaction 4b. Changing G values for major products at high doses in both the n-C_3H_7Cl system reported here, and in the analogous bromide[9] and iodide[17] systems, seem to be attributable to a buildup of C_3H_6 concentration.

HCl Formation. Every Cl atom formed by step 2a may be expected to abstract a hydrogen atom from a n-C_3H_7Cl molecule. The activation energy for the process is probably no greater than 1 kcal/mole, as inferred from evidence on related alkanes and chlorides.[18,19] Elemental chlorine has not been reported as a product of the radiolysis of hydrogenous organic chlorides (although 8% of Cl^{38} activated by the $Cl^{37}(n,\gamma)Cl^{38}$ process in n-C_4H_9Cl produces Cl_2[20]).

$G(HCl)$ would be predicted to be equal to $G(C_3) + 2G(C_6H_{14}) + G(C_6H_{13}Cl) - G(C_3H_6Cl_2) = 4.3 + 0.3 + 0.5 - 1.0 = 4.1$, which falls short of the value of 5 found in the present work, suggesting the possibility that some telomer similar to that observed in the radiolysis of n-C_3H_7Br[9] may have been formed, but not detected in the analysis.

The G value of 3.9 for HCl production at −75°, as compared to that of 5 at 25°, indicating an apparent activation energy of 0.4 kcal/mole, suggests that there is some probability that a chlorine atom will recombine with its parent radical (reaction 3) and that this is increased as the walls of the parent cage are strengthened by increase in density as the temperature is reduced. The fact that the activation energy is lower than values normally observed for diffusion (*ca.* 2 kcal $mole^{-1}$) indicates that most of the Cl atoms are born with more than enough energy to escape the parent cage, or that they have a high probability of abstracting hydrogen from adjacent molecules in the cage wall.

Methane, Ethane, Methyl Chloride, and Ethyl Chloride. The yields of CH_4, C_2H_6, CH_3Cl, and C_2H_5Cl (Table I) indicate that the G for primary dissociation by C–C bond rupture (reactions 2c–e) is about 0.3 $(G(C_2H_6) + G(C_2H_5Cl) + G(\text{hot } CH_3Cl))$. In the presence of I_2 the yields of CH_4, C_2H_6, and C_2H_5Cl are reduced to 20% or less of the value in pure n-C_3H_7Cl, indicating that they are produced mainly from thermal radicals by hydrogen abstraction (reaction 5), with a small contribution by hot processes. This is confirmed by the similarity between the G values of the iodides formed (Table II) and the decrease in G values of the corresponding compounds (Table I) caused by I_2 addition.

The fraction of the CH_3Cl yield which is unaffected by I_2 is much larger than the corresponding fraction of the CH_4, C_2H_6, and C_2H_5Cl yield. This may be the result of dissociation of excited n-C_3H_7Cl molecules to form final products by reaction 2e. The $G(CH_3Cl)$ which is eliminated by I_2 is approximately equal to that of the partner product, $G(C_2H_6)$, which is so eliminated.

Dichloropropanes. The reduction of the yields of the three dichloropropane isomers by I_2 indicates that they are formed predominantly by thermal radical reactions of type 9. Small amounts of unscavenged product indicate a minor contribution from hot abstraction. This must involve an ion–molecule process or vibrationally rather than translationally excited radicals, since essentially all of the translational energy from reaction 2f must be carried by the hydrogen atom.

***n*-Hexane and Chlorohexanes.** The yields of n-hexane, the three monochlorohexanes, and the three dichlorohexanes observed are all reduced below the level of detection by 1 mole % added I_2, indicating that they are formed by thermal radical combinations of the type of (10), (11), and (12).

Isopropyl Chloride. Evidence for the HCl-catalyzed production of i-C_3H_7Cl by the sequence of reactions 7, 8, 6, 7, 8, 6, etc., is discussed elsewhere.[3]

Effects of Added Propylene and Ethylene and of High Doses. The effects of added propylene and ethylene (columns 5 and 6 of Table I; Table III) are complex. These additives are radical scavengers which form new radicals, which can in turn combine or abstract. The reduction of the dichloropropane yields by each of these scavengers (Table I) is to be expected, as is the production of pentyl compounds in the system containing added ethylene.

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Several products of the radiolysis of initially pure n-C_3H_7Cl, which are produced in amounts directly proportional to dose at doses less than 10^{21} ev g^{-1}, deviate from this linearity at higher doses. The observed decrease in G values of the dichlorohexanes accompanied by an increase in G values of n-C_6H_{14} and of *sec*-$C_6H_{13}Cl$ is qualitatively what would be expected if C_3H_6, produced by reaction 2b, increases in concentration with increasing dose to become progressively more effective as a radical scavenger.

Formation of Organic ^{36}Cl by γ-Irradiation of $H^{36}Cl$–n-C_3H_7Cl Solutions. It has been reported that the G value for the formation of organically bound Cl from HCl by the irradiation of $HCl(^{36}Cl)$–n-C_3H_7Cl solutions at HCl concentrations of 1 to 4 mole % and at doses of 1×10^{20} to 1×10^{21} ev g^{-1} at a dose rate of 1.4×10^{17} ev g^{-1} min^{-1} is 3.32[4] and is zero order in HCl concentration. Similar experiments which we have done[2] at HCl concentrations from 1 to 3.5 mole % HCl with doses of 4.5×10^{20} ev g^{-1} at a dose rate of 1.3×10^{18} ev g^{-1} min^{-1} give yields which, though not precise, are all in the range of 1.4 to 4.0.

The organic ^{36}Cl species formed must be C_3H_7Cl since the G value of 3 is larger than that of any of the chloride or dichloride products shown in Table I. Johnson and Miller[4] have postulated exchange *via* the steps: $Cl + H^{36}Cl \rightarrow HCl + {}^{36}Cl$; ${}^{36}Cl + C_3H_7Cl \rightarrow C_3H_7{}^{36}Cl + Cl$. Two reasons argue against this mechanism. First, the activation energy for abstraction of hydrogen from C_3H_7Cl by Cl atoms is so low[18,19] that the probability of Cl surviving long enough to undergo the alternative processes would be expected to be small. Second, most attempts to show the occurrence of displacement reactions of halogen atoms in an organic molecule by thermal halogen atoms have yielded negative or inconclusive results.[21]

The reaction $R + HCl \rightarrow RCl + H$ cannot account for the ^{36}Cl incorporation because it is endothermic by some 15 kcal mole^{-1}. Addition of $HCl(^{36}Cl)$ to C_3H_6 seems to be ruled out as an explanation by the high G value which would be required for C_3H_6 formation. The most plausible hypothesis for the "exchange" seems to be the reaction of CH_3CHCH_2Cl radicals with HCl to produce $CH_3CHClCH_2 + HCl$, in competition with $R + HCl \rightarrow RH + Cl$. This is not, however, consistent with the report of zero-order dependence on HCl.[4] Further study of the process is needed.

Comparisons with Other Investigations of the Radiolysis of n-C_3H_7Cl. Values of 3.38,[4] 4.3 ± 0.4,[5] and 5[9] have been reported for G(HCl) from the radiolysis of n-C_3H_7Cl. The two higher values are consistent within experimental error with the value of 5 obtained in the present work.

Wiley and co-workers[5] report finding only "small amounts" of C_3H_8 produced in the radiolysis of n-C_3H_7Cl, in contrast to the $G(C_3)$ of 4.3 reported in this paper, and to the expectation that the yield of C_3 compounds should be close to that of HCl to achieve a material balance. The low yield was probably the result of loss of C_3H_8 while selectively transferring the gaseous products of the irradiation into a gas chromatographic sampling tube with the aid of a Toepler pump and refrigerants. In similar investigations,[22] it has been observed that the solubility of C_3H_8 in C_3H_7Br is too great to allow its separation by selective vaporization at temperatures where the C_3H_7Br vapor pressure is sufficiently low not to interfere with the analysis.

The nature and distribution of organic products containing ^{38}Cl formed by the activation of the Cl in liquid and gaseous n-C_3H_7Cl by the $^{37}Cl(n,\gamma)^{38}Cl$ process, is distinctly different[23] from that shown in Table I, as would be expected from the fact that ^{38}Cl atoms are produced with high kinetic energy, and possibly charge.

Comparison of Radiolysis of n-C_3H_7Cl, n-C_3H_7Br, and n-C_3H_7I. G(C–X rupture) is 5 for n-C_3H_7Cl and n-C_3H_7I, and is probably in the same range for n-C_3H_7Br, while G(C–C rupture) is about 0.3 or slightly lower for all three compounds. Direct radiolytic production of C_3H_6 + HI from n-C_3H_7I occurs, and analogous reactions quite certainly yield C_3H_6 from the bromide and chloride. $G(H_2)$ has been reported as 1.1,[9] 0.5,[9] and 0.3[24] for the chloride, bromide, and iodide, part of which may be unimolecular H_2 elimination, and part H abstraction following H-atom elimination.

Elemental iodine and HI increase linearly with dose in γ-irradiated n-C_3H_7I at low doses. The radicals produced by the primary radiolytic fragmentation react in part with the HI and in part with the I_2 ($R + HI \rightarrow RH + I$; $R + I_2 \rightarrow RI + I$). I_2 is formed by combination of I atoms. An activation energy of the order of 30 kcal mole^{-1} precludes abstraction of H from the solvent by I atoms.

Elemental bromine is not produced in the radiolysis of n-C_3H_7Br at 25°, because Br is able to abstract H from the solvent and because it reacts readily with olefins. HBr is produced at initial rates which increase with temperature but decrease to zero with increasing dose, apparently as a result of competition between addition of Br to olefins, and H abstraction from n-C_3H_7Br. Telomer containing Br is formed as a result of reactions of olefins produced in the system. Propane is formed ($G = 3.5$) as a result of reaction of C_3H_7 radicals with HBr and the solvent.

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