Kinetics of γ-Radiation-Induced Free-Radical Chain Reactions between Alkanes and Chloroolefins. I. Solutions of Tetrachloroethylene in Alkanes

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Abstract: The kinetics of γ-radiation-initiated free-radical chain condensation reactions in solutions of tetrachloroethylene in alkanes, RH (*n*-pentane, cyclopentane, and cyclohexane), resulting in the formation of alkyltrichloroethylenes, RC_2Cl_3, and HCl, have been studied in the temperature range 26–150°. The Arrhenius parameters for the addition of the alkyl radicals, R, to tetrachloroethylene have been determined. In pentane the rate of formation of the condensation products is proportional to the first power of the solute concentration. In cyclohexane, and to a lesser extent in cyclopentane, some deviation from the first-order dependence of the products on tetrachloroethylene concentration is observed at room temperature. At 150° this feature of the kinetics in cyclohexane disappears, presumably due to strong decrease in the steady-state concentration of the cyclohexyltetrachloroethyl radical.

In a recently published work[1] we reported the occurrence of a photochemically induced chain condensation reaction between *n*-pentane and tetrachloroethylene (TCE) yielding pentyltrichloroethylene and hydrogen chloride. This condensation reaction was found to proceed *via* addition of pentyl radicals to TCE followed by subsequent elimination of a chlorine atom from the pentyltetrachloroethyl radical. The findings of the photochemical study lend support to the free-radical nature of a similar condensation reaction in γ-irradiated solutions, postulated by us on the basis of preliminary results.[2] It seemed worthwhile to extend the study of this chain-condensation process by carrying it out in additional alkanes and by investigating the effect of temperature on the yields of the products. The temperature dependence of the yields would presumably allow us to make an estimate of the activation energies involved in the addition of alkyl radicals to TCE.

γ irradiation would seem to offer some significant advantages in this type of study as compared with the more conventional means of generating alkyl radicals. The heating of samples is more easily carried out in the case of radiolysis than in photolysis, and, unlike in photolysis, the rate of alkyl radical generation in radiolysis is almost unaffected by the change in TCE concentration. Furthermore, unlike in systems where alkyl radicals are formed by thermal cleavage of covalent bonds, the change of temperature has no pronounced effect on the rate of generation of radiolytical radicals (chain-initiation step). And finally, since the rate of formation of radicals upon radiolysis is fairly well known, one can easily estimate the kinetic chain length of the condensation process.

Experimental Section

Materials and Procedure. *n*-Pentane, cyclopentane, and cyclohexane of Philips Research Grade were used. Tetrachloroethylene was Matheson spectroquality reagent. The purification of the reagents, the sample preparation techniques, and the analytical methods used in determining the products were similar to those previously reported.[1]

Irradiation of 2-ml samples was carried out with a Co^{60} source (Gammacell 200, Atomic Energy of Canada Ltd.) at a dose rate of 3×10^{17} eV ml^{-1} min^{-1} for all experiments at room temperature. The irradiations at temperatures other than ambient were carried out by placing the sample in a dewar containing a liquid bath maintained at the appropriate temperature. The changes in the temperature of the bath during irradiation were within ±1° at temperatures below 100° and did not exceed 2° at higher temperature.

Results and Discussion

The yields of the main products of the radiolysis of solutions of TCE in *n*-pentane, cyclohexane, and cyclopentane are shown in Tables I–III. The most abundant products are HCl and a derivative of TCE (denoted RC_2Cl_3) in which one chlorine atom is replaced by a radical R formed from the solvent by the loss of a hydrogen atom. Trichloroethylene and monochloro-substituted solvent derivatives were found in lesser yields, and in the case of cyclohexane solutions small yields of pentachloroethane could also be detected. Other chlorine-bearing products which might have been expected in the radiolysis of TCE, such as dichloroacetylene, hexachlorobutadiene, and tetrachloroethane, were not found. The chlorine balance based on product analysis in *n*-pentane and cyclohexane solutions was satisfactory. In cyclopentane solutions the chlorine balance could not be established since one of the expected products, cyclopentyl chloride, could not be determined.

In experiments carried out in cyclohexane the disappearance of TCE was checked against the sum of the products containing three chlorine atoms (Table II). The results clearly indicate that polymerization of TCE does not occur to a significant extent under our experimental conditions.

The formation of trichloroethylene accompanied by an equivalent yield of hydrogen chloride up to a *G* value of about 4 was found in all solvents and has been attributed by us to electron and excitation scavenging by the solute.[3]

Reaction Scheme. The experimental results are discussed in terms of the following reaction scheme in

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[1] A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, 90, 4105 (1968), and references contained therein.

[2] L. A. Rajbenbach and A. Horowitz, *Chem. Commun.*, 769 (1966).

[3] A. Horowitz and L. A. Rajbenbach, *J. Chem. Phys.*, 48, 4278 (1968).

Table I. Major Products of Radiolysis of Solutions of Tetrachloroethylene in *n*-Pentane at 26°

C_2Cl_4, mM	$G(C_{10}H_{22})^a$	$G(C_2H_{11}Cl)^a$	$G(C_2Cl_3H)^b$	$G(C_5H_{11}C_2Cl_3)^a$	$G(HCl)^a$	I/II^c
30.5	1.49	0.8	2.3	1.50	3.4	1.09
61	1.48	1.0	2.9	2.9	5.7	1.13
122	1.47	1.4	3.5	5.9	7.6	0.96
245	1.46	1.5	3.8	11.6	11.4	0.90
368	1.37	1.6	3.9	16.9	16.5	0.88
490	1.35	1.9	4.0	21.8	21.4	0.90
980	0.73	2.3	4.4	33.8	32.5	0.91

[a] Total dose = 7.2 × 10^{19} eV ml^{-1}. [b] Total dose = 4.5 × 10^{18} eV ml^{-1}. [c] I = $G(C_5H_{11}Cl) + G(HCl)$; II = $G(C_2Cl_3H) + G(C_7Cl_3H_{11})$.

Table II. Major Yields in the Radiolysis of Solutions of Tetrachloroethylene in Cyclohexane at 28°

C_2Cl_4, mM	$G(HCl)^a$	$G(c\text{-}C_6H_{11})_2{}^a$	$G(c\text{-}C_6H_{11}Cl)^a$	$G(-C_2Cl_4)^b$	$G(C_2Cl_3H)^c$	$G(C_2Cl_5H)^a$	$G(c\text{-}C_6H_{11}\text{-}C_2Cl_3)$	I/II^d	III/IV^e
25	8.1	1.14	1.47	10.7	2.25	0.3	7.6	0.96	1.03
50	13.4	0.99	2.17	18.8	2.65	0.4	12.7	0.83	0.99
75	18.5	0.88	2.43	26.5	2.80	0.45	18.0	0.80	1.00
100	21.3	0.83	2.64	28.8	2.97	0.50	20.9	0.85	1.00
150	27.4	0.74	3.06	40.1	3.30	0.65	29.6	0.84	1.08
200	32.2	0.71	3.42	45	3.62	0.80	37.8	0.94	1.16

[a] Total dose = 7 × 10^{19} eV ml^{-1}. [b] These determinations are subject to considerable uncertainties since they are derived by measuring the difference between the original and final concentration of the solute. [c] Total dose = 4 × 10^{18} eV ml^{-1}. [d] I = $G(c\text{-}C_6H_{11}C_2Cl) + G(C_2Cl_3H) + G(C_2Cl_5H)$; II = $G(-C_2Cl_4)$. [e] III = $G(c\text{-}C_6H_{11}C_2Cl_3) + G(C_2Cl_3H)$; IV = $G(HCl) + G(C_6H_{11}Cl)$.

Table III. Major Products of Radiolysis of Solutions of Tetrachloroethylene in Cyclopentane at 26°

C_2Cl_4, mM	$G(c\text{-}C_5H_9)_2{}^a$	$G(C_2Cl_3H)^b$	$G(c\text{-}C_5H_9\text{-}C_2Cl_3)^a$	$G(HCl)^a$
25	1.20	1.99	2.62	3.3
50	0.91	2.80	4.42	5.1
75	0.84	3.00	6.71	6.3
100	0.74	3.29	8.60	7.4
150	0.63	3.54	10.4	8.5
250	0.57	3.85	17.0	11.8
500	0.48	4.26	24.1	17.9
1000	0.42	4.40	35.4	31.0

[a] Total dose = 7 × 10^{19} eV ml^{-1}. [b] Total dose = 4 × 10^{18} eV ml^{-1}.

which I represents the radiation intensity, and RH the alkane solvent

Initiation

$$2RH \xrightarrow{k_0I} 2R + \text{products} \tag{1}$$

Propagation

$$R + C_2Cl_4 \longrightarrow RC_2Cl_4 \tag{2}$$

$$RC_2Cl_4 \longrightarrow RC_2Cl_3 + Cl \tag{3}$$

$$Cl + RH \longrightarrow HCl + R \tag{4}$$

Chain termination

$$R + R \longrightarrow R_2 \tag{5}$$

$$R + R \longrightarrow RH + U \tag{6}$$

$$RC_2Cl_4 + R \longrightarrow RC_2Cl_4R \tag{7}$$

$$RC_2Cl_4 + R \longrightarrow RC_2Cl_3 + RCl \tag{8}$$

$$RC_2Cl_4 + R \longrightarrow RC_2Cl_4H + U \tag{9}$$

$$RC_2Cl_4 + RC_2Cl_4 \longrightarrow (RC_2Cl_4)_2 \tag{10}$$

$$RC_2Cl_4 + RC_2Cl_4 \longrightarrow RC_2Cl_5 + RC_2Cl_3 \tag{11}$$

where U denotes the corresponding solvent olefin molecules formed in radical disproportionation reactions 6 and 9.

The initiation step (reaction 1) represents the radiolytical processes in an oversimplified way. A more detailed description of the primary processes occurring in the radiolysis of TCE solutions in *n*-pentane has been presented elsewhere.[3] It should be mentioned that the yield of solute product $G(C_2Cl_3H)$ was found to be somewhat higher than the observed decrease in radiolytic hydrogen yield $\Delta G(H_2)$.[3] This finding may imply a higher yield of pentyl radicals in TCE solutions than in pure *n*-pentane. Since the excess of $G(C_2Cl_3H)$ over $\Delta G(H_2)$ was found to be practically constant in the 0.03–0.5 M concentration range of TCE, the yield of pentyl radicals can be considered invariant within this range of solute concentration.

An alternative propagation mechanism which could account for the experimental results entails the abstraction of hydrogen atom from the solvent by the RC_2Cl_4 radical followed by the breakdown of the products into RC_2Cl_3 and HCl.

$$RC_2Cl_4 + RH \longrightarrow RC_2Cl_4H + R \tag{12}$$

$$RC_2Cl_4H \longrightarrow RC_2Cl_3 + HCl \tag{13}$$

The thermodynamics of step 13 are, however, highly unfavorable in the temperature range 0–150° in which our experiments were carried out, since the activation energy of this reaction exceeds 50 kcal mole^{-1}.[4]

The photochemically induced chain reaction of TCE solutions in *n*-pentane, studied previously, was found to be adequately accounted for in terms of reactions 1–6. However, in the present case there is evidence that the termination steps 5 and 6 are not the only ones occurring. In the radiolytically induced chain reaction the solvent radicals R are formed directly in the initiation step. A measure of the steady-state concentration of the R radicals can be obtained from the yield of the solvent dimer formed in reaction 5. Should termination steps involving the solute (steps 7–11) also occur to a significant extent, one might expect a decrease in the yield of the dimer as the solute concentration increases. Indeed such effects are observed in cyclopentane and cyclohexane solutions (Tables II and III)

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(4) J. C. Hessler, D. W. Setser, and R. L. Johnson, *J. Chem. Phys.*, 45, 3231, 3237 (1966).

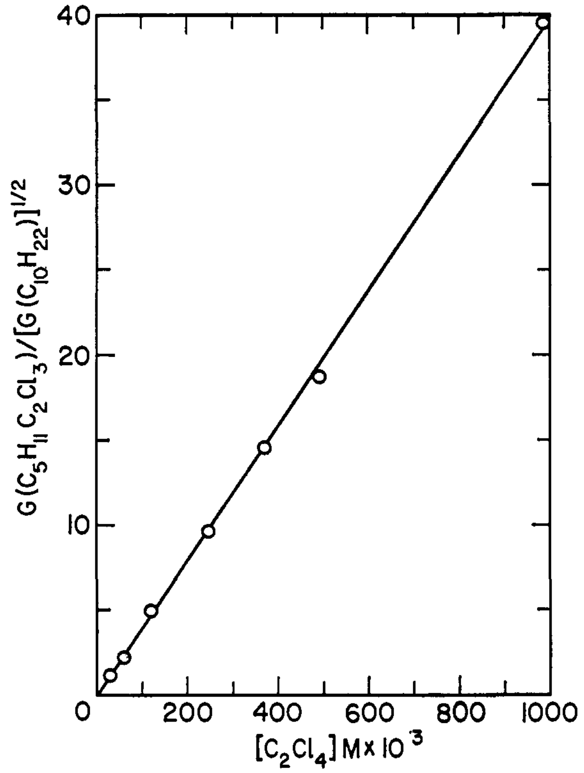

Figure 1. Variation of the product ratio $G(C_5H_{11}C_2Cl_3)/G(C_{10}H_{22})^{1/2}$ with tetrachloroethylene concentration in *n*-pentane solutions.

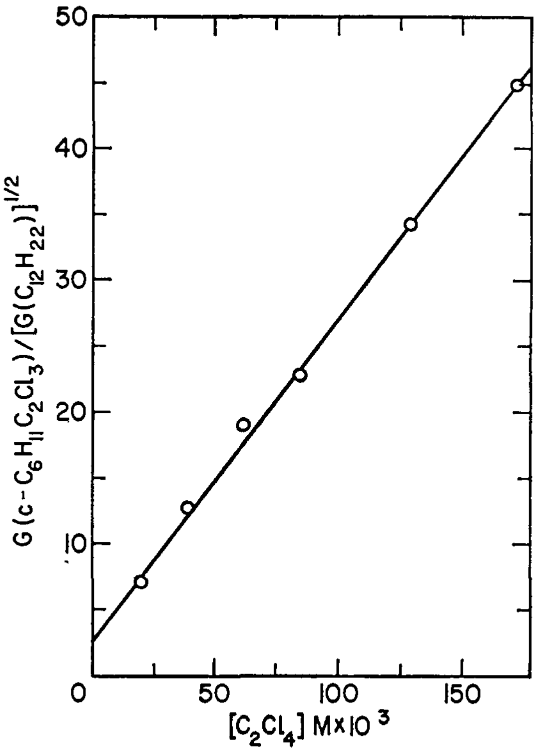

Figure 2. Variation of the product ratio $G(c\text{-}C_6H_{11}C_2Cl_3)/G(C_{12}H_{22})^{1/2}$ with tetrachloroethylene concentration in cyclohexane solutions (because of the appreciable conversion of tetrachloroethylene during these runs the concentrations of solute plotted represent the average of the initial and final concentrations).

but not in *n*-pentane where $G(C_{10}H_{22})$ remains constant up to a concentration of 4×10^{-1} *M* TCE. This finding would suggest that, at least in the case of the cyclic solvents, chain termination steps other than (5) and (6) cannot be ruled out. Superficially the fact that monochloroalkanes are among the products supports at least the occurrence of reaction 8. (However, it will be shown in a later section that chloroalkanes cannot conceivably be formed by radical disproportionation reactions.)

On the other hand, the participation of the RC_2Cl_4 radical in chain termination reactions 7–11 seems hard to reconcile with the fact that this radical is not involved in the abstraction of hydrogen from the solvent (reaction 12), as evidenced by the absence of RC_2Cl_4H among the products, or in a polymerization reaction with TCE (see preceding section). In order to clarify this question we

$$RC_2Cl_4 + (C_2Cl_4)_n \longrightarrow \text{products} \qquad (14)$$

shall first consider the kinetics of RC_2Cl_3 formation in all three solvents in terms of reaction 1-6 only.

Kinetic Treatment of Reactions 1-6. The steady-state treatment of reactions 1-6 yields the following expression for the formation of RC_2Cl_3.

$$\frac{d(RC_2Cl_3)}{dt} = k_2\left[\frac{k_0 I}{2(k_5 + k_6)}\right]^{1/2}[C_2Cl_4] \qquad (15)$$

The fact that the yields of RC_2Cl_3 are not directly proportional to the TCE concentration in the cyclic solvents (Tables II and III), and hence the failure of expression 15 to account for the experimental results is due to the fact that the steady-state concentration of solvent radicals R is not constant with respect to TCE concentration, as has been implicitly assumed in expression 15. However, if we express the steady-state concentration of solvent radicals in terms of the solvent dimer we arrive at the following expression.

$$G(RC_2Cl_3) = k_2\left[\frac{G(R_2)}{2\alpha k_5}\right]^{1/2}[C_2Cl_4] \qquad (16)$$

The proportionality constant $\alpha = 10D/N$, where *D* represents the rate of energy absorption in eV ml^{-1} sec^{-1} and *N* is the Avogadro number, converts the *G* values into the rate of formation in units of mole l.$^{-1}$ sec^{-1}. From Figures 1–3 it can be seen that expression 16 is obeyed over a wide solute concentration range. In the case of cyclohexane, and to a lesser extent cyclopentane, a positive intercept is obtained, suggesting that at least a small part of the RC_2Cl_3 in the cyclic solvents is formed by reactions other than (1)–(4).

The values of the ratios $k_2/(2k_5)^{1/2}$ obtained from the slopes of the straight lines in Figures 1–3 are shown in Table IV. In the photolytic experiments performed previously,[1] we assumed that the rate constant of the interaction of pentyl radicals is equal to that found for ethyl radicals in the liquid phase,[5] namely 3.4×10^9 M^{-1} sec^{-1}. However, very recently Sauer and Mani[6] measured the rate constants of hexyl–hexyl radical interactions and of cyclohexyl–cyclohexyl radical interactions and obtained the values 3.1×10^9 and 2×10^9 M^{-1} sec^{-1}, respectively. These values refer to twice the sum of rate constant of reactions 5 and 6, and in order to obtain k_5 we have to know the ratio of dispro-

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(5) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

(6) M. C. Sauer, Jr., and M. Mani, *ibid.*, **72**, 3586 (1968).

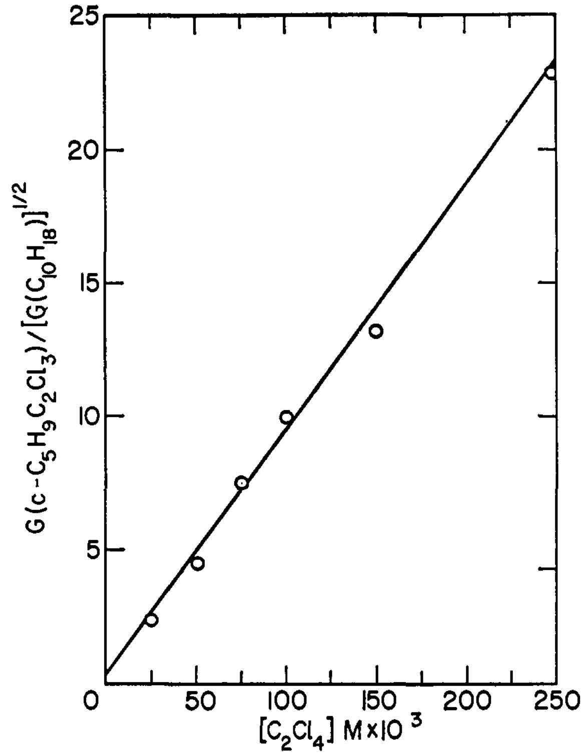

Figure 3. Variation of the product ratio $G(c\text{-}C_5H_9C_2Cl_3)/G(C_{10}H_{18})^{1/2}$ with tetrachloroethylene concentration in cyclopentane solutions.

Table IV. Rate Constants and Arrhenius Factors for the Addition of Alkyl Radicals to Tetrachloroethylene

Radicals	$k_2/(2k_5)^{1/2}$ × 10^{-2}	k_2 × 10^{-2}	$E_2 - E_5/2$, kcal mol^{-1}	Log $[A_2/(2A_5)^{1/2}]$[e]
Pentyl[a]	1.6	6.3[c]		
Pentyl[b]	1.2	4.6[c]	7.1	3.1
Cyclopentyl[b]	2.5	8.0[d]	8.3	3.2
Cyclohexyl[b]	7.3	23.0[d]	6.9	3.3

[a] From photochemical experiments at 25° (see ref 1). [b] Experiments carried out at 26° in the case of pentane and cyclopentane, and at 28° in cyclohexane. [c] Assuming $k_5 = 8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (see ref 6). [d] Assuming $k_5 = 5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (see ref 6). [e] A_2 and A_5 in l. mole^{-1} sec^{-1}.

portionation to combination, k_6/k_5, according to our reaction scheme.

The only published data on the k_6/k_5 ratio for alkyl radicals in the liquid phase are those obtained from the mercury-photosensitized decomposition of *n*-hexane and cyclohexane, where the ratios 1 and 1.3 were found for the hexyl[7] and cyclohexyl[8] radicals, respectively. In the case of cyclopentyl radicals the only available data are those derived from gas-phase experiments,[9] where the ratio was found to be 1. It would seem that no significant error will be introduced in the derivation of k_2 if the ratio k_6/k_5 for the pentyl, cyclohexyl, and cyclopentyl radicals is taken as unity. Assuming that the k_5 values for the cyclopentyl and cyclohexyl radicals are equal, and that those of the pentyl and hexyl radicals are equal, we arrive at the following k_2 values for pentyl, cyclopentyl, and cyclohexyl radicals: 4.6, 8.0, and 23.0 × 10^2 M^{-1} sec^{-1}, respectively. Steric hindrance may account for the difference in k_2 values between cyclic and noncyclic alkyl radicals; however, because of the uncertainties in the k_5 values such considerations are of a rather speculative nature.

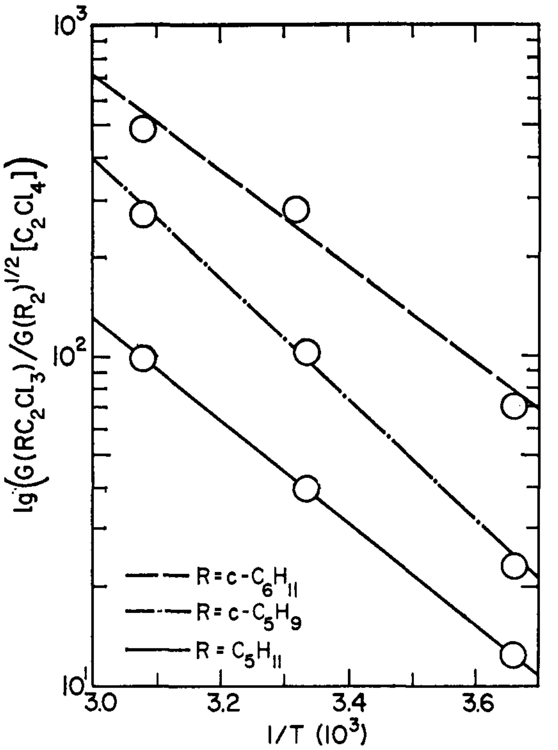

Figure 4. Arrhenius plot for $k_2/(2k_5)^{1/2}$ based on expression 17.

The fair agreement between the k_2 values obtained for pentyl radicals in the photolytic experiments and the radiolytic values arrived at in this work (Table IV) tends to support the contention that in both cases the formation of RC_2Cl_3 follows the same reaction sequence. The slightly lower radiolytic value may be partly due to the fact that a small part of the radiolytic solvent dimer yield could originate from reactions other than 5, such as nonhomogeneous spur reactions[10] and/or ion-molecule reactions.[11] Use of too high a value of $G(R_2)$ in eq 16 would result in too low a value of k_2.

Determination of Activation Energy of Reaction 2. Expressing the k_2 value in eq 16 in terms of the Arrhenius formulation for rate constants, we obtain

$$\log \alpha^{1/2}\left[\frac{G(RC_2Cl_3)}{G(R_2)^{1/2}[C_2Cl_4]}\right] = \log [A_2/(2A_5)^{1/2}] - 0.43(E_2 - E_5/2)\frac{1}{RT} \quad (17)$$

The Arrhenius plots based on eq 17 are shown in Figure 4, and the A and E factors derived from the plot are shown in Table IV.

The G values of the products were determined at 0, 25, and 51°. It was found impracticable to extend the temperature range above 51° since the rapid depletion of TCE at higher temperatures necessitates very short irradiation times, under which conditions the determination of $G(R_2)$ becomes very unreliable.

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(7) R. W. Kunz and G. I. Mains, *J. Amer. Chem. Soc.*, 85, 2219 (1963).
(8) C. E. Klots and R. H. Johnsen, *Can. J. Chem.*, 41, 2702 (1963).
(9) H. E. Gunning and R. L. Stock, *ibid.*, 42, 357 (1964).
(10) T. J. Hardwick, *J. Phys. Chem.*, 64, 623 (1960).
(11) L. Kevan and W. F. Libby, *J. Chem. Phys.*, 37, 2496 (1962).

Determination of k_2 in Solutions of TCE in Cyclohexane at 150°. In the experiments carried out at room temperature we found, as discussed above, that while the simple kinetic expression 16 accounted well for the formation of $C_5H_{11}C_2Cl_3$, it was not entirely satisfactory when applied to cyclohexane and cyclopentane solutions. A plausible reason for this might lie in the somewhat slower rate of chlorine atom splitting (reaction 3) from the c-$C_6H_{11}C_2Cl_4$ and c-$C_5H_9C_2Cl_4$ radicals as compared with their $C_5H_{11}C_2Cl_4$ counterpart. The "longer" lifetime of c-$C_6H_{11}C_2Cl_4$ and c-$C_5H_9C_2Cl_4$ radicals could lead to the occurrence of reactions 7–11 and possibly to interaction between RC_2Cl_4 and TCE (reaction 14).

The activation energy of reaction 2 is about 7–8 kcal mole^{-1} for cyclopentane and cyclohexane (see Table IV), and E_{14} can be assumed to have a comparable value. The radical termination reactions can be expected to have activation energies well below that of reactions 2 and 14.[6,12] An indication of the magnitude of E_3 can be obtained from gas-phase studies on the decomposition of the C_2Cl_5 radical into TCE and a chlorine atom, where an activation energy of 16.8 kcal mole^{-1} has been obtained.[13] Thus a rise in temperature would favor reaction 3, thus depleting the concentration of RC_2Cl_4 radicals, with a consequent suppression of reactions 7–11. This would reduce the complicating features of the kinetic scheme. The results of the experiments carried out in cyclohexane at 150° (Table V) seem to support our assumption. In addition to a pronounced increase in the yield of c-$C_6H_{11}C_2Cl_3$ and HCl, a linear dependence of the products on the concentration of TCE is observed. The k_2 value at 150° can thus be established directly from expression 15. The linearity indicates that the steady-state concentration of cyclohexyl radicals is constant with respect to the solute concentration. From experiments carried out in n-pentane solution at room temperature, we deduce that under such conditions one can expect the steady-state concentration of alkyl radicals to be equal to that in pure solvent. From expression 15 using the value of 4.1×10^9 M^{-1} sec^{-1} for $2(k_5 + k_6)$ at 150°,[14] and by substituting $\alpha G(R)$ for $k_0 I$, the $G(R)$ value for cyclohexyl radicals being taken as 5,[15] we find $k_2 = 4.6 \times 10^4$ M^{-1} sec^{-1}. The k_2 at 150° calculated on the basis of the Arrhenius parameters leads to a value of 2.5×10^4 M^{-1} sec^{-1}. The difference in the two estimates of k_2 lies well within the uncertainty of the derivation of the Arrhenius parameters. We can thus conclude that the kinetic complications encountered in the case of the lower temperature irradiation of the cyclic solutions do not significantly affect the kinetics of RC_2Cl_3 formation and, *ipso facto*, the validity of the Arrhenius parameters.

Table V. Major Products of Radiolysis in Solutions of Tetrachloroethylene in Cyclohexane at 150° [a]

	C_2Cl_4, mM							
	5	10	25	50	100	200	300	400
$G(c\text{-}C_6H_{11}C_2Cl_3)$	33	66	171	356	665	1340	2055	2565
$G(HCl)$	31	68	172	345	672	...	...	...

[a] Total dose = 6.54×10^{17} eV ml^{-1} at dose rate of 2.2×10^{17} eV ml^{-1} min^{-1}.

The kinetic chain length, *i.e.*, the number of product molecules formed per initiating radical, is quite considerable. In 0.4 M TCE in cyclohexane at 150° the chain length is approximately 510, based on a yield of initiating radicals $G(R) = 5$.[15]

Formation of Chloropentane and Chlorocyclohexane. The finding that $C_5H_{11}Cl$ and c-$C_6H_{11}Cl$ are formed with G values of about 2 and 3, respectively (Tables I and II), requires some comment. According to our reaction scheme, the only possible mode of formation of these products is by reaction 8. The fact that in n-pentane solutions at TCE concentrations up to about 0.5 M (where $G(C_5H_{11}Cl) = 1.3$) the yield of the dimer remains constant presents a strong argument against the occurrence of reaction 8. In cyclohexane, however, where $G(c\text{-}C_6H_{11}Cl) = 3.4$ already at 0.2 M TCE the yield of bicyclohexyl is found to be considerably depressed as the TCE concentration increases. This, coupled with the fact that a positive intercept is obtained in the kinetic plot based on reactions 1–6 only (Figure 2) might suggest that, in cyclohexane at least, a part of the c-$C_6H_{11}Cl$ yield does originate from reaction 8. A rough estimate of the yield of c-$C_6H_{11}Cl$ formed by reaction 8 can be obtained by considering the relative possibilities of the occurrence of reactions 8 and 12. Reaction 12 should yield cyclohexyltetrachloroethane, and since the latter compound was not detected, this would place a maximum limit of $G = 0.5$ on its formation.

The relative G values for the formation of $C_6H_{11}Cl$ and $C_8Cl_4H_{12}$ in terms of our reaction scheme are given by

$$\frac{G(RCl)}{G(C_8Cl_4H_{12})} = \frac{k_8[c\text{-}C_6H_{11}]}{k_{12}[c\text{-}C_6H_{12}]} \tag{18}$$

The steady-state concentration of cyclohexyl radicals can be resonably well estimated from the G values of bicyclohexyl and the intensity of the radiation and is found to be $[C_6H_{11}] \sim 1 \times 10^{-8}$ M. The value of k_{12} is not known but one could expect it to be comparable to the rate of abstraction of hydrogen atoms from cyclohexane by CCl_3 radicals. The data of Stone and Dyne[16] on the formation of CCl_3H in the radiolysis of CCl_4 solutions in cyclohexane, coupled with the rate constant of recombination of CCl_3 radicals in the liquid phase[17] (5×10^7 M^{-1} sec^{-1}), enable us to estimate the rate constant of the reaction

$$CCl_3 + c\text{-}C_6H_{12} \longrightarrow CCl_3H + c\text{-}C_6H_{11} \tag{19}$$

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[12] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961).

[13] P. Goldfinger and G. Martens, *Trans. Faraday Soc.*, 57, 2220 (1961).

[14] This value was arrived at by assuming equal activation energies for hexyl–hexyl and cyclohexyl–cyclohexyl radicals interaction. The activation energy of 1.4 kcal mole^{-1} and the value of $2(k_5 + k_6) = 2 \times 10^9$ M^{-1} sec^{-1} at room temperature were taken from ref 6.

[15] (a) R. A. Holroyd and G. W. Klein, *J. Amer. Chem. Soc.*, 84, 4000 (1962); (b) *ibid.*, 87, 4983 (1965). These authors have established the following G values for solvent (R) radical formation in n-pentane, n-hexane, and cyclopentane: 5.4, 5.6, and 4.6, respectively. Since in solutions of 1×10^{-4} to 0.5 M TCE in cyclohexane $G(C_2Cl_3H)$ was found, within experimental error, to be equal to $\Delta G(H_2)$ (A. Horowitz and L. A. Rajbenbach, unpublished results) the yield of radiolytic cyclohexyl radicals in the above range of solute concentration can be taken as constant and equal to that in pure cyclohexane.

[16] J. A. Stone and P. J. Dyne, *Can. J. Chem.*, 42, 669 (1964).

[17] H. W. Melville, J. C. Robb, and R. C. Tutton, *Discussions Faraday Soc.*, **14**, 150 (1953).

yielding a k_{19} value of 2×10^1 M^{-1} sec^{-1}. The value of k_8, the bimolecular radical disproportionation reaction, should not exceed that of k_5 (5×10^8 M^{-1} sec^{-1}).

Making the necessary substitutions in eq 18, we obtain $G(c\text{-}C_6H_{11}Cl) \sim 0.03$. Thus it would seem that the bulk of c-$C_6H_{11}Cl$ is formed by reactions other than those considered in our kinetic scheme. The fact that the addition of cyclohexene to a 0.1 M solution of TCE in cyclohexane increases the G value of c-$C_6H_{11}Cl$ by a factor of 5[18] suggests that secondary reactions between cyclohexene and hydrogen chloride have to be considered as leading to the formation of c-$C_6H_{11}Cl$.

(18) A. Horowitz and L. A. Rajbenbach, unpublished results.

Kinetics of γ-Radiation-Induced Free-Radical Chain Reactions between Alkanes and Chloroolefins. II. Solution of Trichloroethylene in Cyclohexane

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Abstract: The kinetics of the γ-radiation-induced free-radical chain condensation reactions in solutions of trichloroethylene in cyclohexane have been studied in the temperature range 27–150°. The absolute rate constant for the addition of cyclohexyl radical to trichloroethylene at 150° is estimated at 1.28×10^5 M^{-1} sec^{-1}, on the basis of the rate constant ratio obtained from kinetics taken together with alkyl radical combination data. The absolute rate constant for the scission of the chlorine atom from the cyclohexyltrichloroethyl radical is estimated to be 2.1×10^4 sec^{-1} at 150°.

The kinetics of the γ-radiation-induced free-radical chain condensation reactions between tetrachloroethylene (TCE) and alkanes, resulting in the formation of alkyltrichloroethylenes, was described in the preceding paper.[1] The rate constants and the Arrhenius parameters for the addition of the alkyl radicals to TCE were determined. It was thought worthwhile to extend this study to solutions of trichloroethylene (TrCE) in alkanes in order to find whether a similar condensation reaction can be induced, and if so to try and establish the kinetics of the reaction.

Two conditions need to be satisfied *a priori* for the occurrence of a chain condensation reaction between chloro-substituted olefins and alkanes: firstly, a reasonably high affinity of the olefin for the alkyl radical and, secondly, a fast rate constant for the unimolecular decomposition of the newly formed radical yielding a chlorine atom and an olefin. TrCE could be expected to display a greater affinity toward alkyl radical than TCE as evidenced by its greater ease of free-radical polymerization.[2] No prediction could be made as to the ease of the decomposition of the intermediate radical formed by addition of alkyl radical to TrCE. Cyclohexane was chosen as the alkane solvent since it forms predominantly cyclohexyl radicals upon radiolysis, thus eliminating possible complications in the chain-initiation step arising from the possibility of different alkyl radicals attaching themselves to a reactive olefin.

Experimental Section

Materials and Procedure. Cyclohexane (Phillips Research Grade) was used as received. Trichloroethylene (Fisher Reagent Grade) and tetrachloroethylene (Matheson Spectrograde) were distilled under nitrogen. Vapor phase chromatography of the distillates showed them to be free of impurities. Sample preparation and irradiation techniques were identical with those used by us previously.[3] The irradiations were carried out at a dose rate of 3.76×10^{17} and 2.2×10^{17} eV ml^{-1} for experiments at 27 and 150°, respectively. Liquid products were analyzed by gas chromatography (F and M Model 810) using a 12-ft column of 20% Ucon on Haloport W. All but one of the products (cyclohexyldichloroethylene) were identified by comparison of the retention times with authentic samples. Cyclohexyldichloroethylene was identified by mass spectrometry. Hydrogen chloride yields were determined coulometrically using an Aminco-Cotlove chloride titrator.

Results

The yields of the main products of radiolysis at 27°, except for hydrogen which was not measured, are shown in Table I. The most abundant products are hydrogen chloride and cyclohexyldichloroethylene. Only one chromatographic peak was found for the last product. Attempts to resolve this peak, using several different columns, produced no separation into components. Since the Ucon column efficiently separated *cis* and *trans* isomers of c-$C_6H_{11}CH{=}CHCl$,[4] it was concluded that only one isomer of c-$C_6H_{11}C_2Cl_2H$ is formed in the radiolysis. A good balance of mono- and dichloro-substituted products is obtained if the yield of dichloroethylene, which could not be quantitatively separated, is taken as approximately equal to the decrease in radio-

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[1] A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **91**, 4626 (1969), and references contained therein.

[2] (a) T. Alfrey, Jr., and S. Greenberg, *J. Polymer Sci.*, 3, 297 (1948); (b) K. W. Doak, *J. Amer. Chem. Soc.*, 70, 1525 (1948).

[3] (a) A. Horowitz and L. A. Rajbenbach, *J. Chem. Phys.*, 48, 4278 (1968); (b) *J. Amer. Chem. Soc.*, **90**, 4105 (1968).

[4] A. Horowitz and L. A. Rajbenbach, unpublished results.