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

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 $c\text{-}C_6H_{11}Cl$ 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 $c\text{-}C_6H_{11}Cl$ 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 $c\text{-}C_6H_{11}Cl$.

[18] A. Horowitz and L. A. Rajbenbach, unpublished results.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 $1.28 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, 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 $2.1 \times 10^4\ \text{sec}^{-1}$ 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 $c\text{-}C_6H_{11}CH{=}CHCl$,[4] it was concluded that only one isomer of $c\text{-}C_6H_{11}C_2Cl_2H$ 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.

Table I. Major Products of Radiolysis of Solutions of Trichloroethylene in Cyclohexane at 27° [a]

C_2Cl_3H, m*M*	*G*(HCl)	*G*(*c*-$C_6H_{11}Cl$)	*G*($C_8H_{12}Cl_2$)	*G*(*c*-$C_6H_{11})_2$	*G*(−C_2Cl_3H)	I/II [b]
2.5	0.9	0.69	0.81	0.77	...	1.00
5	1.26	0.90	1.33	0.54	...	1.99
7.5	1.43	1.05	1.48	0.47	...	0.97
10	1.54	1.07	1.54	0.47	5.41	0.92
16.6	2.53	1.14	1.80	0.36	...	1.08
25	2.87	1.0	1.93	0.35	7.9	1.01
50	3.28	0.74	2.22	0.35	10.8	0.87
100	4.28	0.66	2.63	0.34	14.3	0.94
250	4.98	0.49	2.71	0.33	...	0.89
500	5.74	0.46	2.79	0.29	...	0.99

[a] Total dose = 6.7 × 10^{19} eV ml^{-1}. [b] I = *G*(*c*-$C_6H_{11}C_2Cl_2H$) + Δ*G*(H_2). The value of Δ*G*(H_2) is taken from ref 5. II = *G*(HCl) + *G*(*c*-$C_6H_{11}Cl$).

lytic hydrogen yield Δ*G*(H_2) in the solution of TrCE in cyclohexane as compared with pure solvent. The Δ*G*(H_2) values for TrCE solutions were reported by us elsewhere.[5] This assumption is based on the equivalence of Δ*G*(H_2) and trichloroethylene found by us in the radiolysis of solutions of tetrachloroethylene in cyclohexane.[4]

The results given in Table II show that there is a pronounced rise in the yields of the condensation products cyclohexyldichloroethylene and hydrogen chloride with increase in temperature of irradiation. The high *G* value of the products clearly indicates the chain mechanism of their production. At higher temperatures the ratio *G*(*c*-$C_6H_{11}C_2Cl_2H$)/*G*(−C_2Cl_3H) was found to increase, indicating that with rise in temperature the condensation reaction becomes the main mechanism by which TrCE is removed from the solution.

Table II. Effect of Temperature on the Yields of the Major Products in the Radiolysis of Solutions of Trichloroethylene in Cyclohexane

C_2Cl_3H, m*M*	Total dose, eV ml^{-1}	Temp, °C	*G*(*c*-C_6H_{11}-C_2Cl_2H)	*G*(HCl)	*G*-(−C_2Cl_3H)
10	1.3 × 10^{19}	80	23.3	...	...
10	6.5 × 10^{19}	115	96.3	...	...
100	2.6 × 10^{19}	50	8.3	9.4	73.1
100	1.3 × 10^{19}	80	65.2	64.8	82.5
100	6.5 × 10^{18}	115	281.0	258.8	339.0

The yields from irradiation at 150° are given in Table III. The results show quite clearly that at 150° the condensation reaction is the only reaction of importance in which the solute is involved. At low concentrations of solute the yields of the products show a good linear dependence on the TrCE concentration.

The results of competitive experiments in solutions containing equimolar concentrations of TrCE and TCE are shown in Table IV. It is seen that in the presence of TrCE there is a drastic decrease in the yield of *c*-$C_6H_{11}C_2Cl_3$, the condensation product of TCE with cyclohexane.

Discussion

Reaction Scheme. The experimental results are discussed in terms of a reaction scheme analogous to that set up for the case of TCE solutions. The radiation intensity is represented by *I*, and the cyclohexane by RH.

Table III. Major Products of Radiolysis of Solutions of Trichloroethylene in Cyclohexane at 150° [a]

C_2Cl_3H, m*M*	*G*(HCl)	*G*(*c*-C_6H_{11}-C_2Cl_2H)	*G*(−C_2Cl_3H)	*G*(HCl)/*G*-($C_8H_{11}Cl_2$)
2.5	50	47.8	...	1.05
5	101	105	...	0.96
7.5	140	146	...	0.96
10	203	216	...	0.94
12.5	247	255	...	0.97
16.6	300	297	...	1.01
25	386	400	408	0.97
50	594	693	720	0.86
100	1101	1099	1237	1.00
250	1743	1648	...	1.06
500	2247	2329	...	0.97

[a] Total dose = 4.3 × 10^{17} eV ml^{-1} for solute concentrations <25 m*M* and 6.54 × 10^{17} eV ml^{-1} for solute concentrations ≥25 m*M*.

Table IV. Yields of Condensation Products in Ternary Solutions of 0.05 *M* Trichloroethylene and Tetrachloroethylene in Cyclohexane [a]

Temp, °C	Total dose, eV ml^{-1}	*G*(*c*-$C_6H_{11}C_2Cl_2H$)	*G*(*c*-$C_6H_{11}C_2Cl_3$)
27	7 × 10^{19}	2.2 (2.6)	0.75 (12.7)
150	6.5 × 10^{17}	610 (693)	197 (356)

[a] Figures in parentheses represent the *G* values of the condensation products in binary solutions at 0.05 *M* concentration of solute.

Initiation

$$2RH \xrightarrow{k_0 I} 2R + H_2 \tag{1}$$

Chain propagation

$$R + C_2Cl_3H \longrightarrow RC_2Cl_3H \tag{2}$$

$$RC_2Cl_3H \longrightarrow RC_2Cl_2H + Cl \tag{3}$$

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

Chain termination

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

$$R + R \longrightarrow RH + \text{cyclohexene} \tag{6}$$

$$RC_2Cl_3H + R \longrightarrow RC_2Cl_3HR \tag{7}$$

$$RC_2Cl_3H + R \longrightarrow RCl + RC_2Cl_2H \tag{8}$$

$$RC_2Cl_3H + R \longrightarrow RC_2Cl_3H_2 + \text{cyclohexene} \tag{9}$$

$$RC_2Cl_3H + RC_2Cl_3H \longrightarrow (RC_2Cl_3H)_2 \tag{10}$$

$$RC_2Cl_3H + RC_2Cl_3H \longrightarrow RC_2Cl_4H + RC_2Cl_2H \tag{11}$$

It should be noted that in reaction 2 two structurally different radicals may be formed, and consequently

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[5] A. Horowitz and L. A. Rajbenbach, *Chem. Commun.*, 1234 (1967).

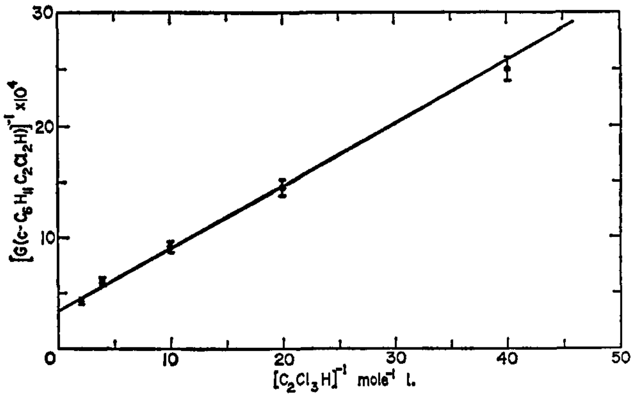

Figure 1. The reciprocal of $G(c\text{-}C_6H_{11}C_2Cl_2H)$ as a function of the reciprocal of C_2Cl_3H concentration.

three isomers may result from reaction 3, namely $c\text{-}C_6H_{11}CHCCl_2$ and *cis* and *trans* isomers of $c\text{-}C_6H_{11}\text{-}CClCHCl$.

Additional reactions which were considered in the radiolysis of solutions of TCE in alkane solvents were

$$RC_2Cl_3H + RH \longrightarrow RC_2Cl_3H_2 + R \quad (12)$$

$$RC_2Cl_3H_2 \longrightarrow HCl + RC_2Cl_2H \quad (13)$$

$$RC_2Cl_3H + C_2Cl_3H \longrightarrow R(C_2Cl_3H)_2 \quad (14)$$

Reactions 12 and 13 could constitute an alternative chain-propagation mechanism. However, the thermodynamics of step 13 in the temperature range 27–150° are considered to be just as unfavorable in TrCE solutions as they were in TCE solutions.[1] The absence of cyclohexyltrichloroethane among the radiolysis products indicates that reaction 12 does not occur to a significant extent.

Room-Temperature Experiments. The kinetics of the γ-radiation-induced condensation between TCE and cyclohexane was found to obey the following expression over the temperature range 27–150°.

$$G(RC_2Cl_3) = k_2\left(\frac{G(R_2)}{2\alpha k_5}\right)^{1/2}[C_2Cl_4] \quad (15)$$

The 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 G values into rates of formation, in units of M^{-1} sec^{-1}.

In the derivation of expression 15 it was assumed that the radical RC_2Cl_4 disappeared from the system mainly by the reaction corresponding to reaction 3, an assumption which was based on the high G values of the condensation product. Accordingly, the kinetics of the chain reaction could be treated in terms of reactions 1-6 only.

In the radiolysis of solutions of TrCE in cyclohexane at 27°, there are two strong indications that the radical $c\text{-}C_6H_{11}C_2Cl_3H$ formed in reaction 2 participates in reactions other than 3 as well, and that the low yields of $c\text{-}C_6H_{11}C_2Cl_2H$ are not due to low k_2 valutes. Firstly, the yield of bicyclohexyl, which can be used as a measure of the steady-state concentration of the cyclohexyl radical, is very pronouncedly reduced even at relatively low concentrations of solute, considerably more so than in the corresponding solution of TCE. This finding would suggest that chain-termination steps 7–11 involving the radical RC_2Cl_3H cannot be neglected. Secondly, the fact that the values of $G(-C_2Cl_3H)$ are considerably higher than the yields of the condensation product suggest the possibility of polymerization of C_2Cl_3H (reaction 14). Thus the experiments at 27° do not lend themselves to treatment by the simple kinetic scheme which was found adequate in analogous experiments in TCE solutions.

Kinetics of Cyclohexyldichloroethylene Formation at 150°. Determination of k_2 and k_3 Values. The radiolysis of TrCE solutions at 150° leads to a drastic rise in the G values of $c\text{-}C_6H_{11}C_2Cl_2H$. This follows the trend observed in TCE solutions at 150° and is most likely due to the same cause, *i.e.*, the relatively high activation energy of reaction 3.

The fact that in experiments carried out at 150° it is only in dilute solutions (up to 1.66×10^{-2} M TrCE) that the yield of $c\text{-}C_6H_{11}C_2Cl_2H$ is first order in solute concentration while at higher concentrations it becomes less than unity suggests that, having ruled out the polymerization, reaction 14 (see Results), we must postulate other chain termination reactions in addition to (5) and (6). However, under the conditions of a long chain the following equality is still valid.

$$\frac{d(RC_2Cl_2H)}{dt} = k_2[R][C_2Cl_3H] = k_3[RC_2Cl_3H] \quad (16)$$

The sum of the steady-state concentrations of the individual radicals in the solution should, under the conditions of a nonbranched chain, remain invariant and equal to the steady-state concentration of cyclohexyl radicals from the irradiated solvent, $[R_0]$. In the absence of polymerization the following relation should hold.

$$[R_0] = [R] + [RC_2Cl_3H] + [Cl] \quad (17)$$

Inherent in expression 17 is the assumption that in analogy with TCE solutions in cyclohexane[1] the yield of radiolytically generated cyclohexyl radicals is unaffected by the presence of TrCE in the concentration range of solute used in this work. In view of the very high values of k_4 (the energy of activation for the reaction of a chlorine atom with a secondary hydrogen atom is 0.6 kcal mole^{-1} [6]), one can consider [Cl] as negligible.

We also have that $[R_0]$ is given by

$$[R_0] = \left|\frac{G(R_0)}{2\alpha(k_5 + k_6)}\right|^{1/2} \quad (18)$$

Combining expressions 16, 17, and 18 we obtain, after suitable arrangement

$$\frac{1}{G(RC_2Cl_2H)} = \left(\frac{2\alpha(k_5 + k_6)}{G(R_0)}\right)^{1/2}[(1/k_3) + (1/k_2[C_2Cl_3H])] \quad (19)$$

The corresponding kinetic plot is shown in Figure 1. From the ratio intercept/slope of the graph, we obtain $k_2/k_3 = 6.1$ M^{-1}. Using the value $2(k_5 + k_6) = 4.1 \times 10^9$ M^{-1} sec^{-1},[7] and assigning $G(R_0) \approx 5$[8] under the

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(6) G. C. Fettis and J. H. Knox, *Progr. Reaction Kinetics*, 2, 1 (1964).

(7) M. C. Sauer, Jr., and M. Mani, *J. Phys. Chem.*, 72, 3586 (1968). These authors give the value of 2×10^9 M^{-1} sec^{-1} for cyclohexyl radicals interaction at room temperature and an activation energy of 1.4 kcal mole^{-1} for hexyl radical interaction in liquid *n*-hexane. Assuming equal activation energy for hexyl-hexyl and cyclohexyl-cyclohexyl radicals interaction we arrive at $2(k_5 + k_6) = 4.1 \times 10^9$ M^{-1} sec^{-1} at 150°.

(8) (a) R. A. Holroyd and G. W. Klein, *J. Amer. Chem. Soc.*, 84, 4000 (1962); (b) *ibid.*, 87, 4983 (1965).

assumption that the radiolytic yield of cyclohexyl radicals in pure cyclohexane at 150° is not significantly different from that observed at room temperature, we obtain from the slope $k_2 = 1.28 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. Hence $k_3 = 2.1 \times 10^4\ M^{-1}\ \text{sec}^{-1}$.

An approximate estimate of k_2 can also be obtained from the competitive experiments in dilute solutions containing equal molarities (0.05 M) of TCE and TrCE (Table IV). Under the conditions of a long chain and in the absence of polymerization reactions we can write

$$\frac{G(c\text{-}C_6H_{11}C_2Cl_2H)}{G(c\text{-}C_6H_{11}C_2Cl_3)} \sim \frac{k_2(C_2Cl_3H)}{k_2(C_2Cl_4)}\frac{[C_2Cl_3H]}{[C_2Cl_4]} \qquad (20)$$

Thus the ratio of the G values of the condensation products at equimolar solute concentrations gives the value $k_2(C_2Cl_3H)/k_2(C_2Cl_4)$, which turns out to be 3.1. Substituting the value $k_2(C_2Cl_4) = 4.63 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ obtained in the preceding paper,[1] we obtain $k_2(C_2Cl_3H) = 1.44 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, in fair agreement with the value $1.28 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ obtained from expression 19.

No quantitative comparison of k_3 values in TrCE and TCE solutions can be made, since in TCE solutions at 150° the yield of the condensation product is first order with solute concentration up to relatively high TCE concentrations (0.4 M^1). Qualitatively, however, this fact implies that the k_3 values are significantly higher in the case of C_2Cl_4 than in C_2Cl_3H.

The Steric Course of the Addition of Cyclohexyl Radical to TrCE. The fact that only one of the isomers of the condensation product is formed could mean either that the cyclohexyl radicals attack exclusively at the site of the monochloro-substituted carbon, in which case only one isomer is possible, or alternatively that they attack at the disubstituted carbon but for some reason only one of the two possible geometrical isomers is formed. The latter explanation seems unlikely in view of our finding[4] that in the radiation-induced condensation of both *cis*- and *trans*-1,2-dichloroethylene with cyclohexane two geometrical isomers are always obtained, indicating that when two isomers are possible they are indeed formed. The former alternative is also supported by the fact that in the study of Cl atom addition to TrCE it has been found[9] that the rate constant for addition of a chlorine atom to the less chlorinated carbon is at least eight times greater than for addition to the other carbon.

The Effect of Chlorine Substitution of Ethylene on the Relative Efficiency of Addition of Alkyl Radicals. The addition of alkyl radicals to substituted olefins is known to be influenced both by steric and by polar effects. If the hydrogen atoms of the olefin are substituted by chlorine atoms, steric hindrance to the addition caused by the presence of bulky chlorine atoms is balanced by the predominantly inductive effect of the halogen substituents, which, by reducing the electron density of the π bond, tends to lower the activation energy for the addition reaction.

We have found that the rate constant for addition of cyclohexyl radicals to TrCE at 150° is approximately three times larger than for the addition to TCE. Since the inductive effect of the chlorine atoms should be, if anything, more pronounced in TCE, the lower affinity of TCE for the cyclohexyl radical can only be attributed to steric hindrance. However, this increase in reactivity accompanying the decrease in chlorine content of the olefin cannot be generalized. A further decrease in chlorine substitution might affect the electronic situation more than the steric one, leading to an over-all decrease in the reactivity of the olefin.

(9) L. Bertrand, J. A. Franklin, P. Goldfinger, and G. Huybrechts, *J. Phys. Chem.*, 72, 3926 (1968).