provided the numerical values of the coefficients and exponential terms.[17] The initial guesses for this computer program were determined according to Prony's method.[18] Having obtained the optimum fit for the experimental data, the six linearly independent equations obtained from the LaPlace transform solution of the cyclic equations were used to determine the six rate constants.

This method using the equilibrium concentrations, exponential terms, and the coefficient, D_1, allowed the determination of the six rate constants from the experimental concentration *vs.* time profile of the rearrangement of only one hydroxy ketone.

(17) R. H. Moore and R. K. Ziegler, "Solution of the General Least Squares Problem with Special References to High Speed Computers," Report LA-2367 (Los Alamos Scientific Laboratory) Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 1963.

(18) F. B. Hilderbrand, "Numerical Analysis," McGraw-Hill, New York, N. Y., 1956, p 378.

Mechanism and Kinetics of Cyclohexyl Radical Addition to Chloroethylenes and of the Subsequent Reactions of the Adduct Radicals

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Abstract: The mechanism and kinetics of the free-radical chain addition reaction between cyclohexane (RH) and chloroethylenes (ECl) have been reinvestigated. The intermediacy of unimolecular β-chlorine scission from the RECl type radicals in the chain propagation sequence has been confirmed. Relative Arrhenius parameters for the addition of R radicals to C_2Cl_4, C_2Cl_3H, and the cis and trans isomers of $C_2Cl_2H_2$ were determined. Arrhenius parameters for Cl atom elimination from $RC_2Cl_2H_2$ and RC_2Cl_3H radicals were evaluated from studies of the temperature dependence of the yields of the saturated and unsaturated addition products.

We have shown[1] that γ irradiation of dilute solutions of chloroethylenes (ECl) in alkanes (RH) leads to a free-radical chain substitution of a chlorine of the chloroethylene by an alkyl radical R. The occurrence of similar substitution reactions has also been observed in other RH–chloroethylene systems where free radicals were generated by decomposition of peroxides,[2-4] photolysis,[5] and pyrolysis.[6] Our kinetic analysis of the substitution reaction was based on a mechanism originally suggested by Schmerling[2] and recently confirmed by Tanner, *et al.*[4] According to this mechanism the following reactions constitute the propagation step of the chain sequence. In recent

$$R\cdot + ECl \longrightarrow RECl\cdot$$

$$RECl\cdot \longrightarrow RE + Cl$$

$$Cl + RH \longrightarrow HCl + R\cdot$$

works we studied the reactions of various chloroethyl radicals in cyclohexane solution.[7,8] It was found that the chloroethyl radicals disappear from the system both by β-chlorine scission and by hydrogen abstraction from the solvent. It would thus appear that in the chloroethylene–alkane system the hydrogen abstraction reaction by the RECl· radicals might have been overlooked by us as a result of its marginal effect in the temperature range at which these experiments were carried out. Furthermore, Tanner, *et al.*,[9] have found that alkyl radicals react with hydrogen chloride in a relatively fast reaction. The importance of this reaction was clearly demonstrated by the above authors in their studies of the chlorovinylation of alkanes.[4] The possibility of a secondary reaction of R and RECl radicals with HCl was not considered by us previously. Because of these facts it seemed to us that further studies of the mechanics and kinetics of the free-radical reactions in the alkane–chloroethylene system are in order. The elucidation of this mechanism appears to be important in view of the potential value of radiolytic techniques for the synthesis of substituted chloroolefins.[10]

Unlike in our previous studies,[1] a competitive kinetic method was used in the present work to obtain the Arrhenius parameters for the addition of cyclohexyl radicals to $C_2Cl_2H_2$, C_2Cl_3H, and C_2Cl_4. This method is free from the somewhat arbitrary assumptions made by us previously[1] in evaluating k_2 at 150°. In the competitive studies the rate of the reaction between cyclohexyl radicals and C_2Cl_4 was used as a standard and therefore it was carefully redetermined.

Experimental Section

Materials and Procedure. Tetrachloroethylene (Matheson Spec-

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(1) (a) A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, 91, 4626 (1969); (b) *ibid.*, 91, 4631 (1969); (c) *ibid.*, 92, 1634 (1970).

(2) L. Schmerling and J. P. West, *ibid.*, 71, 2015 (1949).

(3) F. F. Rust and C. S. Bell, *ibid.*, 92, 5530 (1970).

(4) D. D. Tanner, S. C. Lewis, and N. Wada, *ibid.*, 94, 7034 (1972).

(5) A. Horowitz and L. A. Rajbenbach, *ibid.*, 90, 4105 (1968).

(6) T. J. Hardwick, *Int. J. Chem. Kinet.*, 1, 325 (1969).

(7) A. Horowitz and L. A. Rajbenbach, *J. Phys. Chem.*, 74, 678 (1970).

(8) M. G. Katz, A. Horowitz, and L. A. Rajbenbach, *Trans. Faraday Soc.*, 67, 2354 (1971).

(9) D. D. Tanner and T. N. Bunce, *J. Amer. Chem. Soc.*, 91, 3028 (1969).

(10) A. Horowitz and L. A. Rajbenbach, Proceedings of Symposium on Large Radiation Sources for Industrial Processes, I.A.E.A., Vienna, 1969, p 21.

trograde), trichloroethylene (Fisher, Reagent grade), and *cis-* and *trans*-dichloroethylene (Fluka, puris) were purified by distillation under nitrogen. Glpc analysis of the distillates showed their purity to exceed 99.5%. Cyclohexane (Phillips, Research grade) was used as received. The sample preparation and γ-irradiation techniques were the same as those employed by us previously.[1]

Glpc Analysis. The liquid products were isolated and determined using a 12 ft × 0.25 in. stainless steel column packed with 20% Ucon on Haloport W, maintained at 150°, and a similar column filled with 10% silicon gum rubber, maintained at temperatures ranging from 150 to 200°. A gas chromatograph equipped with a flame ionization detector (Hewlett-Packard Model 7750) was used.

Results

Radiolysis of C_2Cl_4 Solutions in Cyclohexane. The variation of the $c\text{-}C_6H_{11}C_2Cl_3$ yield (given in *G* values, *i.e.*, molecules per 100 eV absorbed) with C_2Cl_4 concentration was studied at two temperatures. The results of these experiments are given in Table I. The experiments which were carried out at low C_2Cl_4 concentrations and which were used in the study of the temperature dependence of $c\text{-}C_6H_{11}C_2Cl_3$ formation are summarized in Table II. In all these experiments the yield of bicyclohexyl, $G(c\text{-}C_6H_{11})_2$, was found to be 1.96 ± 0.05. The saturated addition product $c\text{-}C_6H_{11}C_2Cl_4H$ was not detected even at the highest C_2Cl_4 concentration employed.

Table I. Dependence of $c\text{-}C_6H_{11}C_2Cl_3$ Yields on C_2Cl_4 Concentration in the Radiolysis of C_2Cl_4 Solutions in Cyclohexane at 55 and 100° [a]

	55°		100°	
$[C_2Cl_4]_0$, $M \times 10^3$	$[C_2Cl_4]_{av}$, $M \times 10^3$	$G(RC_2Cl_3)$	$[C_2Cl_4]_{av}$, $M \times 10^3$	$G(RC_2Cl_3)$
25	22.9	21.8	23.2	57.4
50	46.4	38.3	46.7	106
100	93.4	69.8	93.8	194
200	189	119	188	367
300	286	149	285	467
500	479	220	476	744
650			615	1090
800			761	1220
1000			958	1340

[a] At all $[C_2Cl_4]$ the values given in this table are the average of three determinations that were reproducible within 5%. The dose rate in these experiments was 1.90×10^{17} eV ml^{-1} min^{-1}. $[C_2Cl_4]_0$ is the initial concentration and $[C_2Cl_4]_{av}$ the average concentration during the reaction.

Table II. Temperature Dependence of $c\text{-}C_6H_{11}C_2Cl_3$ Yield in the Radiolysis of C_2Cl_4 Solutions in Cyclohexane[a]

Temp, °C	$[C_2Cl_4]_0$, $M \times 10^3$	$G(c\text{-}C_6H_{11}\text{-}C_2Cl_3)$	$k_2/[2(k_6 + k_7)]^{1/2}$,[b] [l./(mol sec)]$^{1/2}$	No. of runs
55	10	10.2	0.112	2
55	20	19.5	0.108	2
70	10	13.5	0.147	2
70	20	26.9	0.150	2
85	10	17.1	0.189	2
85	20	35.9	0.199	2
100	10	21.8	0.238	2
100	20	43.2	0.237	2
100	50	116	0.254	2
125	10	34.5	0.381	2
125	20	70.2	0.385	2
150	10	58.3	0.635	4
150	20	111	0.605	4
			Total no. of runs	30

[a] Dose rate 1.77×10^{17} eV ml^{-1} min^{-1}. [b] Calculated from expression II, $G(R_0)$ taken as 5.7, ref 11.

Radiolysis of Trichloroethylene and *trans*-Dichloroethylene Solutions. In these systems, in addition to the chlorine substitution products, the saturated addition products $c\text{-}C_6H_{11}C_2Cl_3H_2$ and $c\text{-}C_6H_{11}\text{-}C_2Cl_2H_3$ are formed. The saturated products were separated and their structures confirmed by molecular weight determination and mass spectroscopy. In both solutions the temperature dependence of the above product formation was determined. All the experiments were carried out at two solute concentrations, 0.25 and 0.5 *M*. At 150° the radiolytic yields (*G* values) of the unsaturated products were in the range 2000–3000, and about one-tenth of this was at the lowest temperature (75°). The *G* values of the saturated product formation varied between 20 and 50, with a 10% reproducibility. A better reproducibility, of about 5%, was found for the ratios of the yields of the saturated and unsaturated products. Results of a typical set of experiments are given in Table III.

Table III. Yields of $c\text{-}C_6H_{11}C_2ClH_2$ and $c\text{-}C_6H_{11}C_2Cl_2H_3$ in the Radiolysis of *trans*-$C_2Cl_2H_2$ Solutions in Cyclohexane at 135°

[*trans*-$C_2Cl_2H_2$], *M*	I[c]	II[c]	III[c]	(I + II)/III[c]
0.25[a]	472	360	25.9	31.4
0.25[b]	439	351	25.8	30.6
0.5[a]	640	489	35.4	31.9
0.5[b]	627	490	34.1	32.7

[a] Total dose 1.8×10^{18} eV ml^{-1}. [b] Total dose 3.6×10^{18} eV ml^{-1}. [c] I = $G(cis\text{-}c\text{-}C_6H_{11}C_2ClH_2)$, II = $G(trans\text{-}c\text{-}C_6H_{11}C_2ClH_2)$, III = $G(c\text{-}C_6H_{11}C_2Cl_2H_3)$.

The kinetic data obtained from the temperature dependence studies are summarized in Table V (see Discussion).

Radiolysis of Ternary Solutions. Competitive Experiments. Ternary solutions containing, in addition to C_2Cl_4, one of the other chloroethylenes were radiolyzed. The results of a representative set of experiments carried out at 150° are shown in Table IV. The rate constants derived from the temperature-dependence studies over the range 90–150° are summarized in Table VI (see Discussion).

Discussion

Kinetic Scheme. The kinetics of formation of the main products in the radiolysis of cyclohexane solution of chloroethylenes $C_2Cl_nH_{4-n}$ will be discussed in terms of the following reaction scheme. This reac-

Initiation

$$2RH \longrightarrow 2R\cdot + \text{products} \tag{1}$$

Propagation

$$R\cdot + ECl \longrightarrow RECl\cdot \tag{2}$$

$$RECl\cdot \longrightarrow RE + Cl \tag{3}$$

$$RECl\cdot + RH \longrightarrow REClH + R\cdot \tag{4}$$

$$RECl\cdot + HCl \longrightarrow REClH + Cl \tag{4'}$$

$$Cl + RH \longrightarrow HCl + R\cdot \tag{5}$$

Table IV. Results of the Competitive Experiments at 150°

$[C_2Cl_4]_0$, $M \times 10^3$	$[trans\text{-}C_2Cl_2H_2]_0$, $M \times 10^3$	$[cis\text{-}C_2Cl_2H_2]_0$, $M \times 10^3$	$[C_2Cl_3H]_0$, $M \times 10^3$	$G(\text{I + II})/G(\text{III})^a$	$k_2/k_2^{(C_2Cl_4)\,b}$
40	10			0.748	3.05
10	20			0.619	3.12
16		33.5		2.25	1.12
40		67.0		1.88	1.08
40			10	1.28	5.24
10			20	1.01	5.11

[a] I represents the unsaturated product c-$C_6H_{11}C_2ClH_2$ in $C_2Cl_2H_2$ solutions and c-$C_6H_{11}C_2Cl_2H$ in C_2Cl_3H solutions. II denotes the saturated products. III represents c-$C_6H_{11}C_2Cl_3$. [b] Average concentration ratios were used in the calculation of the relative rates.

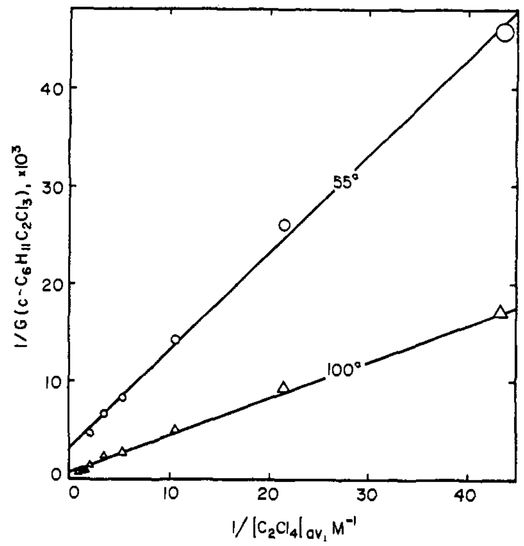

Figure 1. Plot of $1/G$(c-$C_6H_{11}C_2Cl_3$) *vs.* $1/[C_2Cl_4]$. Data from c-C_6H_{12}–C_2Cl_4 mixtures at 55 and 100°.

Termination

$$2R\cdot \longrightarrow R_2 \quad (6)$$

$$\longrightarrow RH + \text{cyclohexene} \quad (7)$$

$$R\cdot + RECl\cdot \longrightarrow REClR \quad (8)$$

$$\longrightarrow RE + RCl \quad (9)$$

$$\longrightarrow REClH + \text{cyclohexene} \quad (10)$$

$$2RECl\cdot \longrightarrow (RECl)_2 \quad (11)$$

$$\longrightarrow RECl_2 + RE \quad (12)$$

tion scheme is almost identical with the one used by us previously,[1] except for the introduction of reactions 4 and 4′. These are the only reactions, in our system, that could account for the formation of the saturated addition products RECIH *via* a chain mechanism.

Tetrachloroethylene Solutions. Determination of A_2 and E_2. In the radiolysis of C_2Cl_4 solutions the formation of the saturated product c-$C_6H_{11}C_2Cl_4H$ could not be detected. A similar observation was made by Tanner, *et al.*[4] Under the conditions of a long kinetic chain, the mechanism outlined thus leads to the following relation[1b]

$$\frac{1}{G(RC_2Cl_3)} = \left[\frac{2\alpha(k_6 + k_7)}{G(R_0)}\right]^{1/2}\left[\frac{1}{k_3} + \frac{1}{k_2[C_2Cl_4]}\right] \quad (I)$$

where $G(R_0)$ is the yield of cyclohexyl radicals in the radiolysis of pure cyclohexane and α is a constant that converts G values into rates of formation in units of mol $l.^{-1}$ sec^{-1}.

It can be seen that our results, plotted in Figure 1, fit well the form of relation I, over a 40-fold variation in the concentration of tetrachloroethylene. Thus the assumptions made in the derivation of this relation seem to be borne out by experiment. Least-squares treatment of the data shown in Figure 1 yields the values of 3.3 and 1.4 l./mol for k_2/k_3 ratios at 55 and 100°, respectively. Consequently, at solute concentrations of $\sim 10^{-2}$ M and temperatures of 55° and above, one can write $k_3 \gg k_2[C_2Cl_4]$. Under such conditions eq 1 reduces, after suitable rearrangement, to the following expression. From expression II

$$G(RC_2Cl_3) = k_2\left[\frac{G(R_0)}{2\alpha(k_6 + k_7)}\right]^{1/2}[C_2Cl_4] \quad (II)$$

the rate constants ratio $k_2/[2(k_6 + k_7)]^{1/2}$ can be evaluated using the known value of $G(R_0)$. We have used the most recent value of 5.7 for $G(R_0)$ as determined at room temperature.[11] The use of this value throughout the temperature range of our experiments is justified by the work of Burns and Reed,[12] who showed that the primary radiolytic events leading to the formation of cyclohexyl radicals in cyclohexane are almost independent of temperature. Our findings that G(bicyclohexyl) values in the experiments summarized in Table II are constant and equal to those in pure cyclohexane are in agreement with the above observation of Burns and Reed, and indicate at the same time that in our system chain termination occurs predominantly *via* reactions 6 and 7. The latter conclusion lends further support to the applicability of eq II to the determination of k_2.

The Arrhenius plot of the average values of the $k_2/[2(k_6 + k_7)]^{1/2}$ ratios at each temperature is shown in Figure 2. Least-squares treatment of all the experimental data (without averaging) yields the values 2.37 ± 0.06 for $\log A_2 - {}^1/_2 \log 2(A_6 + A_7)$ and 5.04 ± 0.10 kcal/mol for $E_2 - {}^1/_2 E_{6+7}$. (As elsewhere in this work, the error limits are the 95% confidence limits 2σ.) In liquids, reactions 6 and 7 can be regarded as diffusion controlled. Accordingly, E_{6+7} corresponds to the activation energy of diffusion, which was found to be 4.54 kcal/mol.[13] Combining this value with the $k_6 + k_7$ value of 1×10^9 l./(mol sec) determined by Sauer and Mani[14] one obtains $\log 2(A_6 + A_7) = 12.66$. Finally, by substitution we obtain $\log k_2 = 8.68 \pm 0.06 - (7300 \pm 100)/2.3RT$ l./(mol sec).

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(11) K. M. Bansal and R. H. Schuler, *J. Phys. Chem.*, **74**, 3924 (1970).

(12) W. G. Burns and C. R. V. Reed, *Trans. Faraday Soc.*, **66**, 2159 (1970).

(13) D. W. McCall, D. C. Douglass, and E. W. Anderson, *Ber. Bunsenges. Phys. Chem.*, **67**, 336 (1963).

(14) M. C. Sauer, Jr., and M. Mani, *J. Phys. Chem.*, **72**, 3586 (1968).

In recent competitive studies in these laboratories $E_2 - E_{13}$ was found to be 1.4 ± 0.1 kcal/mol,[15] where reaction 13 is the reaction between cyclohexyl radical and CCl_4. The activation energy of this reaction, in

$$R + CCl_4 \longrightarrow RCl + CCl_3 \qquad (13)$$

liquid cyclohexane, was found to be 5.8 kcal/mol.[16] The E_2 value of 7.2 ± 0.1 kcal/mol obtained from the above two results is in good agreement with the value 7.3 ± 0.1 kcal/mol found in the present work, and supports the reliability of our method.

The E_2 value obtained by us previously[1a] was higher by about 2 kcal/mol. In retrospect, we attribute this difference to the deficiency of the method used there for the estimation of the steady-state concentration of cyclohexyl radicals. There we used *G*(bicyclohexyl) to determine the above concentration. However, at the C_2Cl_4 concentrations and the temperatures employed in our previous studies, *G*(bicyclohexyl) was considerably lower than in pure cyclohexane and it increased with temperature. Apparently, under these conditions the contribution of nonhomogeneous spur reactions to the bicyclohexyl yield cannot be neglected as was done. Consequently, the method used gave an E_2 value that was not fully corrected for the increase in the steady-state concentration of the cyclohexyl radicals with temperature.

Finally, the $k_3/[2(k_6 + k_7)]^{1/2}$ ratio can be obtained from the intercept of the plots in Figure 1. The values found are (3.1 + 0.7) × 10^{-2} and 0.19 ± 0.09 $[(\text{mol sec})/\text{l.}]^{1/2}$ at 55 and 100°, respectively. The limited data and low accuracy do not justify an attempt at estimating the Arrhenius parameters of the chlorine elimination reaction. Still, our results indicate that E_3 is considerably higher than E_2.

Estimation of Arrhenius Parameters of Reaction 3. In the preceding section it was shown that the method of kinetic analysis used there does not allow accurate determination of k_3 values and of the Arrhenius parameters derived from them. In $C_2Cl_2H_2$ and C_2Cl_3H solutions reaction 14 below is very apt to occur[1b,c] at solute concentrations of about 0.1 *M* and temperatures below 100°, and therefore in this case expression I cannot be applied.

$$RECl\cdot + ECl \longrightarrow R(ECl)_2\cdot \qquad (14)$$

The formation of both chlorine elimination and hydrogen abstraction products in the radiolysis of solutions of *trans*-$C_2Cl_2H_2$ and C_2Cl_3H provides the possibility of an alternative kinetic approach that can be used for the estimation of the Arrhenius parameters of the chlorine elimination reaction. In theory, one expects relation III to apply if reaction 4 is the only route by which the saturated products are formed.

$$k_3/k_4[RH] = G(RE)/G(REClH) \qquad (III)$$

The relatively high *G* values of REClH formation indicate that the contribution of the termination reactions to the formation of these products can be neglected. On the other hand, in view of the compelling evidence[4,9] for the occurrence of reaction 15, it is necessary to

$$R + HCl \longrightarrow RH + Cl \qquad (15)$$

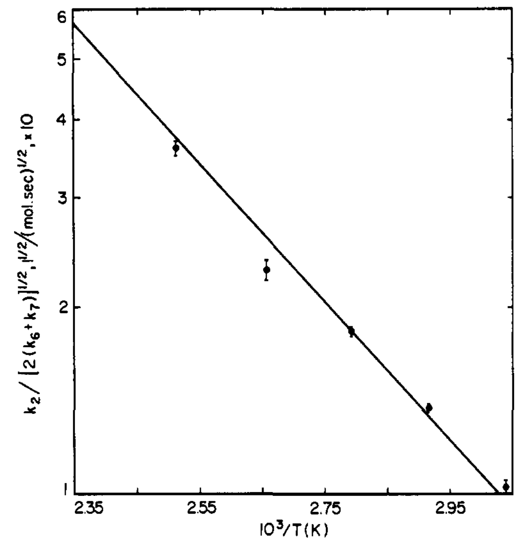

Figure 2. Arrhenius plot of $k_2/[2(k_6 + k_7)]^{1/2}$ (average values only). Data from the low C_2Cl_4 concentration experiments.

consider the possibility that the analogous reaction of RECl radicals (reaction 4′) takes place in our system.

If the saturated products are formed by reaction 4′, then, [RH] being constant, the ratio of the unsaturated to the saturated product yield should increase with HCl concentration. This effect was not observed in our system, as an examination of Table III indicates. The table shows that the ratio of saturated to unsaturated products was not affected by a twofold increase of the applied dose, nor by a threefold increase in HCl concentration as measured by the yield of the unsaturated product. We thus conclude that under our experimental conditions reaction 4′ does not occur. It should be emphasized though that this is not a general argument against the occurrence of reaction 4′. We feel that under different conditions this reaction might take place.

The validity of expression III having been shown, we turn to the results obtained using it. The k_3/k_4 values are summarized in Table V. These values were used in the Arrhenius plots shown in Figure 3. The parameters $E_3 - E_4$ and log A_3/A_4 obtained by least-squares treatment of all the experimental data are 7.7 ± 0.4 kcal/mol and 6.5 ± 0.3 mol/l. for the c-C_6H_{11}-C_2Cl_2H radical and 7.89 ± 0.10 kcal/mol and 6.48 ± 0.06 mol/l. for the c-$C_6H_{11}C_2Cl_2H$ radical, respectively.

From these results the Arrhenius parameters for the chlorine elimination reaction can be estimated

Table V. Rate Constants and Relative Arrhenius Parameters of the Reactions of c-$C_6H_{11}C_2Cl_2H_2$ and c-$C_6H_{11}C_2Cl_3H$ Radicals[a]

	k_3/k_4, mol/l.	
Temp, °C	c-$C_6H_{11}C_2Cl_2H_2$	c-$C_6H_{11}C_2Cl_3H$
75	56.0 ± 1.1	35 ± 0.3
90	78.4 ± 4.8	52.5 ± 1.8
105	129 ± 3	83.8 ± 2.4
120	173 ± 18	119 ± 3
135	259 ± 7	177 ± 3
150	406 ± 13	262 ± 3
Log A_3/A_4, mol/l.	6.5 ± 0.3	6.48 ± 0.06
$E_3 - E_4$, kcal/mol	7.7 ± 0.4	7.89 ± 0.10

[a] Four runs were made at every temperature.

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(15) M. G. Katz and L. A. Rajbenbach, to be submitted for publication.

(16) F. B. Wampler and R. R. Kuntz, *Int. J. Chem. Kinet.*, 3, 283 (1971).

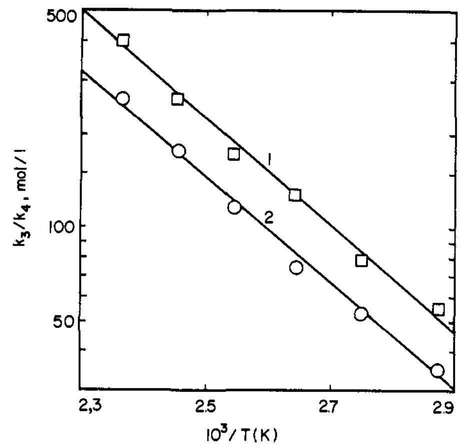

Figure 3. Arrhenius plot of k_3/k_4: (1) for c-$C_6H_{11}C_2Cl_2H_2$; (2) for c-$C_6H_{11}C_2Cl_3H$.

assuming that the Arrhenius parameters for hydrogen abstraction from alkanes are rather insensitive to the change in the chlorine content of the alkyl radicals. In the absence of reliable liquid-phase data, gas-phase results will be used, assuming that in nonpolar solvents such as cyclohexane the change of phase does not have a significant effect on the Arrhenius parameters of the hydrogen abstraction reaction.

The Arrhenius parameters for hydrogen abstraction from cyclohexane (reaction 16) were recently

$$CCl_3 + c\text{-}C_6H_{12} \longrightarrow CCl_3H + c\text{-}C_6H_{11} \qquad (16)$$

determined in the gas phase. The values found were $\log A_{16}$ l./(mol sec) = 8.79 and E_{16} = 10.70 kcal/mol.[17] These values are in good agreement with the recently recalculated data of Tedder, *et al.*,[18] on the abstraction of hydrogen from *n*-butane. Assuming that the Arrhenius parameters of reactions 4 and 16 are equal, we obtain the following rate expressions for reaction 3: $\log k_3 = 15.3 - 18{,}600/2.3RT$ for the c-$C_6H_{11}C_2Cl_2H_2$ radical and $\log k_3 = 15.3 - 18{,}400/2.3RT$ for the c-$C_2H_{11}C_2Cl_3H$ radical. The close correspondence between the two expressions may be fortuitous, mainly because of the underlying assumption that E_4 and A_4 are equal for the two radicals. As a result of the uncertainties involved both in the experimental measurements and in the values used for the Arrhenius parameters of reaction 4, we estimate that the parameters derived could be in error by about an order of magnitude for the preexponential coefficients and about 1 kcal/mol for the activation energies of the chlorine elimination reaction.

The activation energy of about 18.5 kcal/mol for reaction 3 is comparable to the value of 20.7 kcal/mol found in gas-phase studies for chlorine atom elimination from 1,2-dichloroethyl radicals.[19] The magnitude of the A_3 parameters falls within the range of the presently accepted values for unimolecular reactions.[20] In terms of the transition state theory, the finding that the A_3 values are in excess of the "normal" value of $10^{13.5}$ indicates a significant gain in entropy of activation in the transition state for chlorine elimination.

Incidentally, the A_3 values found by us cannot be reconciled with the bimolecular mechanism suggested by Rust and Bell[3] for the formation of the chlorine elimination products, thus providing further support for Tanner's[4] arguments against that mechanism.

Addition of Cyclohexyl Radical to Chloroethylenes. Competitive Studies. In the radiolysis of dilute ternary systems of two chloroethylenes, A and B, in cyclohexane, the olefins can be taken to be consumed only by reaction with R radicals. Under such conditions the relative rates of addition of R radicals to the chloroethylene will be given by

$$\frac{k_2^{(A)}}{k_2^{(B)}} = \frac{\log [A]/[A]_0}{\log [B]/[B]_0} \qquad (IV)$$

where $[A]_0$ and $[B]_0$ denote the initial concentrations. Our experimental conditions lead to low conversions and therefore the above relation can be reduced to the following

$$\frac{k_2^{(A)}}{k_2^{(B)}} = \frac{G(PA)[B]_{av}}{G(PB)[A]_{av}} \qquad (V)$$

where PA and PB are the products formed from the two chloroethylenes.

Table VI summarizes the relative rate constants obtained with the use of expression V for c-C_6H_{11} radical addition, where k_2 for tetrachloroethylene is used as a reference. The relative Arrhenius parameters derived from the rate constants are given in Table VII.

Table VI. Relative Rates of Cyclohexyl Radical Addition to Chloroethylenes

Temp, °C	$k_2/k_2^{(C_2Cl_4)}$		
	cis-$C_2Cl_2H_2$	*trans*-$C_2Cl_2H_2$	C_2Cl_3H
90	1.11 ± 0.05	3.05 ± 0.09	5.76 ± 0.11
105	1.29 ± 0.05	3.10 ± 0.09	5.51 ± 0.26
120	1.09 ± 0.02	3.09 ± 0.18	5.45 ± 0.15
135	1.10 ± 0.02	2.99 ± 0.10	5.30 ± 0.16
150	1.10 ± 0.03	3.07 ± 0.10	5.11 ± 0.07
150[a]	0.87 ± 0.2	2.50 ± 0.40	4.10 ± 0.6[b]

[a] Calculated from results of ref 1, with an estimated error. [b] Corrected for the change in the C_2Cl_3H concentration of the experiments in ref 1b.

Table VII. Relative Arrhenius Parameters for the Addition of c-C_6H_{11} Radicals to Chloroethylenes

Chloroethylene	*cis*-$C_2Cl_2H_2$	*trans*-$C_2Cl_2H_2$	C_2Cl_3H
Log A_2 − log $A_2^{(C_2Cl_4)}$	0.042 ± 0.09	0.45 ± 0.11	0.42 ± 0.09
$E_2 - E_2^{(C_2Cl_4)}$, kcal/mol	0.0 ± 0.2	−0.05 ± 0.2	−0.55 ± 0.15

Table VI also gives the ratios of k_2 values at 150° derived from direct determinations of k_2.[1] In general, the agreement between these ratios and those obtained in the present work is good. The differences of approximately 25% probably reflect the uncertainty in k_2 values derived from eq I.

The replacement of hydrogen atoms in ethylene by

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(17) M. L. White and R. R. Kuntz, *Int. J. Chem. Kinet.*, 3, 127 (1971).

(18) (a) H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *ibid.*, 4, 249 (1972); (b) J. A. Kerr and M. J. Parsonage, *ibid.*, 4, 243 (1972).

(19) G. Huybrechts, J. Kathinhabwa, G. Martens, M. Nejszaten, and J. Obbregts, *Bull. Soc. Chim. Belg.*, 81, 65 (1972).

(20) See, for example, S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Government Printing Office, Washington, D. C., 1970, pp 28–29.

the bulky chlorine atoms would be expected to decrease the reactivity, due to steric hindrance. On the other hand, the inductive effect of chlorine atoms on the π-bond electron would tend to facilitate the addition of nucleophilic alkyl radicals. The overall effect of chlorine substitution is reflected in the reactivity order: $C_2Cl_3H >$ *trans*-$C_2Cl_2H_2 >$ *cis*-$C_2Cl_2H_2 > C_2Cl_4$. The data in Table VII would seem to indicate that the steric and inductive effects influence both the activation energy and the preexponential factor.

Mechanistic Partition of the Solvolysis of Cyclohexyl Tosylate

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Abstract: The substitution and elimination products from the solvolysis of cyclohexyl tosylate have been quantitatively apportioned into direct and rearranged components by examination of the reactions of cyclohexyl-*1-d* and cyclohexyl-*2,2,6-d_3* (1 H trans to 6 H) tosylates. The substitution product (cyclohexyl ester) comes from two sources: (1) direct substitution at the 1 position exclusively with inversion, and (2) rearrangement *via* a hydride shift with subsequent substitution at a carbon adjacent to the original 1 position. The elimination product (cyclohexene) likewise is composed of material formed before and after hydride shift. The direct substitution product decreases from 80% in buffered acetic acid to 60% in formic acid, and to about 50% in trifluoroacetic acid, with the remainder composed entirely of hydride-shifted material. No direct substitution with retention was detected, although the question could not be fully resolved for trifluoroacetolysis. The elimination product is formed in acetic acid with <5% hydride shift, in formic acid with 15% shift, and in trifluoroacetic acid with 50% shift. Rearrangement in the elimination process thus lags behind that in the substitution process except in trifluoroacetic acid. The results are discussed in terms of rate-determining formation of an intimate ion pair, followed by partitioning into the various reaction pathways. When the amounts of all the various product components from acetolysis were assessed, the product distribution proved to be essentially identical with that from *trans*-4-*tert*-butylcyclohexyl tosylate.

Considerable effort has been devoted to the study of the solvolysis mechanism of substituted cyclohexyl arenesulfonates.[2] The process of solvolysis results in products formed by substitution (cyclohexyl esters) and by elimination (cyclohexene). A significant portion of these products arises from substitution or elimination that follows a 2,1-hydride shift. In order to detect this type of rearrangement in the cyclohexyl series, a positional label must be installed in the ring. Thus an alkyl group in the 4 position would be found in the 3 position of rearranged material obtained from substitution. Separation and analysis of the positional isomers permit a direct determination of the amount of rearrangement. In order to determine the stereochemistry of the substitution component of the reaction, the system is in further need of a diastereomeric label, *e.g.*, an alkyl group at the 4 position with known stereochemistry with respect to the arenesulfonate leaving group. Thus a complete analysis of the reaction components requires determination of the overall ratio of substituton to elimination, of the proportion of rearranged to unrearranged products, and of the stereochemistry of the substitution component.

A diastereomeric label that permits a complete analysis of all the reaction components is the 4-*tert*-butyl group. The solvolysis of *cis*- and *trans*-4-*tert*-butylcyclohexyl arenesulfonates was first studied by Winstein and Holness[2a] and more recently with more reliable analytical accuracy by Whiting and coworkers.[2d] The trans isomer, for example, on acetolysis gives 0.4% of the *trans*-4-alkyl ester (substitution, unrearranged, retention), 19.5% of the *cis*-4-alkyl ester (substitution, unrearranged, inversion), 2.0% of the 3-alkyl esters (substitution, rearranged), 73.6% of the 4-alkylcyclohexene (elimination, unrearranged), and 5.6% of 1- and 3-alkylcyclohexenes (elimination, rearranged). The ene/ester ratio therefore is 79.2:21.9, the unrearranged/rearranged ratio is 93.5:7.6, and the inversion/retention ratio (1 position) is 19.5:0.4.

Although the diastereomeric label is an effective device to dissect the reaction pathways of substituted cyclohexyl arenesulfonates, the question naturally arises as to the nature of the solvolysis of the totally unsubstituted (except at the 1 position) cyclohexyl arenesulfonate. The alkyl-substituted derivatives may be poor models for the unsubstituted material for several reasons. The bulky *tert*-butyl group, although having the advantage of freezing the ground state into a known conformation, by the same token imparts some ground-state distortion. X-Ray structures are

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[2] For leading references, see (a) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 77, 5562 (1955); (b) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, 87, 1382, 1383 (1965); (c) J. L. Mateos, C. Perez, and H. Kwart, *Chem. Commun.*, 125 (1967); (d) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968); (e) M. Tichy, J. Hapala, and J. Sicher, *Tetrahedron Lett.*, 3739 (1969); (f) J. E. Nordlander and T. J. McCrary, Jr., *J. Amer. Chem. Soc.*, **94**, 5133 (1972).