tained from the Radiochemical Centre (Amersham, England) and were used without purification.

A. Determination of Isomeric Distributions. A solution of the reactants was prepared in aqueous acetic acid (80%, by volume), the resulting concentrations being about 1 *M* in the aromatic substrate and *ca.* 0.65 *M* in chlorine. The solution (10 ml) was then mixed with a sample containing about 50 μCi of $^{36}Cl_2$ and a small amount of Cl^- (5%) as an impurity. The latter step was carried out by sealing together the ampoules of the reagents and breaking an internal glass seal, according to standard procedures. The resulting solution was allowed to stand in the dark at room temperature for periods from 8 weeks to 2 years. The reaction mixture was then added to about 200 mg of each of the three inactive monochloro derivatives of the aromatic substrate, and treated with a solution of sodium sulfite in order to remove the unreacted chlorine. The organic materials were extracted several times with petroleum ether (bp 30–60°); the combined organic layers were washed with a solution of inactive sodium chloride and finally dried over sodium sulfate. After removal of the solvent, the residue was analyzed by preparative gas chromatography, using separated glass traps directly inserted into the detector block of a Model B (or Model D) Fractovap (Carlo Erba, Milan) to collect the individual fractions. The separations were carried out in 6 mm i.d. stainless steel columns, with helium as the carrier gas, under the following conditions.

Chlorinated Products from Benzonitrile. A mixed column (1 m long), containing 7.4 g of diisodecyl phthalate modified Bentone 34 (20% w/w on Celite) and 5.6 g of diisodecyl phthalate (20% w/w on Celite), was used at 175°.

Chlorinated Products from Nitrobenzene. A mixed column (1.3 m long), containing 10.2 g of diisodecyl phthalate modified Bentone 34 (25% w/w on Chromosorb) and 8 g of diisodecyl phthalate (25% w/w on Chromosorb), was used at 150°.

Chlorinated Products from Benzotrifluoride. An 8 m long column packed with tricresyl phosphate (25% w/w on Chromosorb W), was used at 150°.

The radioactivities of the purified fractions collected at the outlet of the gas chromatograph were measured with a Mark I Nuclear Chicago scintillation spectrometer, and the gas chromatographic purification was repeated until a constant value for the specific activity of each product was reached.

Because of the low conversion, it is possible that radiation damage produced within the reaction mixture by the tracers could promote radiolytic processes, responsible to some extent for the formation of the labeled chlorobenzonitriles. A rough calculation, however, shows that this is not the case, since the dose received by the system is, at most, 3000 rads. At this level of radiation damage, taking into account the dilution of the active chlorine, only a chain process with an exceedingly high energetic yield could contribute significantly to the observed yields.

B. Competitive Experiments. (i) Relative Chlorination Rates of Benzonitrile and Benzotrifluoride. Solutions containing benzonitrile (*ca.* 0.87 *M*), benzotrifluoride (*ca.* 0.19 *M*), and $^{36}Cl_2$ were prepared as previously described. After being allowed to stand for several weeks, the reaction mixture was added to known amounts of each of the six monochloro derivatives of the two aromatic substrates, and treated in the usual way. The residue was analyzed by preparative gas chromatography, using a 6 mm i.d. column (3 m long) packed with Apiezon L grease, 25% w/w on silanized Chromosorb W, with helium as the carrier gas. The temperature was kept at 140° until the benzonitrile peak emerged, then raised to 220° at a rate of 44° per min. In this way, separate fractions were obtained, containing the isomeric chlorobenzonitriles and chlorobenzotrifluorides, respectively. Relative rates of chlorination were determined by the radioactivities of these two fractions, allowance being made for the different initial concentrations of the two substrates.

(ii) Relative Chlorination Rates of Benzonitrile and Nitrobenzene. Solutions containing benzonitrile (*ca.* 0.24 *M*), nitrobenzene (*ca.* 0.91 *M*), and $^{36}Cl_2$ were prepared and treated as above, using the same column. The temperature was kept at 150° until the nitrobenzene peak emerged, then raised to 220° at the rate of 44° per min. Two fractions were obtained containing the isomeric chloronitrobenzenes and chlorobenzonitriles, respectively. Relative rates of chlorination were calculated as before.

Acknowledgments. Thanks are due to Mr. D. Carrara for his skillful assistance.

Reversible Hydrogen Abstraction. The Mechanism of Trichlorovinylation

Dennis D. Tanner,* Stephen C. Lewis,[1] and Naoto Wada[2]

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received February 3, 1972*

Abstract: The mechanism of the reaction of tetrachloroethylene with *n*-hexane and cyclohexane has been reinvestigated. The reaction has been shown to proceed by a free-radical chain mechanism involving reversible hydrogen abstraction by atomic chlorine as the product-determining process. The anomalous results obtained by comparing the isomer distributions for chlorination and chlorovinylation reactions have been accounted for by the differences in the chain-transfer rates of the alkyl radicals with molecular chlorine on the one hand, and tetrachloroethylene and hydrogen chloride on the other. The chlorination of cyclohexane with carbon tetrachloride was found, unlike the chlorovinylation reaction, to proceed without detectable reversal of the radicals formed during the reaction with the chloroform produced in the reaction.

The peroxide-initiated reaction of polychloroethylenes (Ia, b, and c) with various saturated hydrocarbons was reported by Schmerling and West[3] to give chlorovinylated alkanes. These authors proposed a free-radical chain mechanism which involves the chlorine atom as the chain-carrying species (Scheme I).

The mechanism, which involves a β scission of the carbon–chlorine bond (eq 2) and a product-determining abstraction of an alkyl hydrogen by atomic chlorine (eq 3), would predict that the final distribution of chlorovinylated products would be determined by the selectivity of atomic chlorine. Rust and Bell[4] have recently reported their investigation of the free-radical chlorovinylation of *n*-hexane using compounds

---

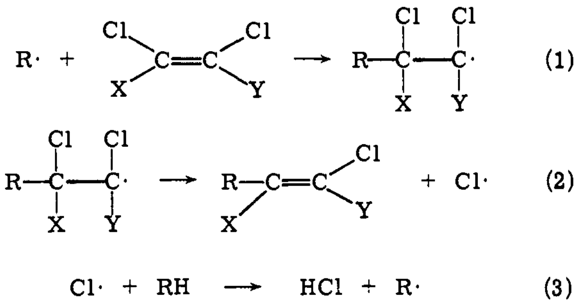
[1] University of Alberta Postdoctoral Fellow, 1970–1971.

[2] University of Alberta Postdoctoral Fellow, 1971–1972.

[3] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, 71, 2015 (1949).

[4] F. F. Rust and C. S. Bell, *ibid.*, **92**, 5530 (1970).

Scheme I



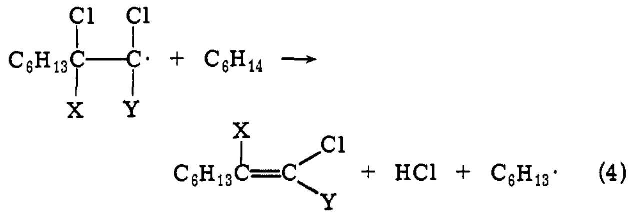
Ia, X = Y = H
Ib, X = H; Y = Cl
Ic, X = Y = Cl

Ia–c. These authors found that the isomer distributions of chlorovinylation products obtained using these substrates were significantly different from the distribution obtained for the chlorination of hexane with molecular chlorine (see Table I). The product-determining species in the chlorovinylation reactions showed an apparent primary to secondary selectivity/H which is higher than that for atomic chlorine. On this basis the mechanism of Schmerling and West was rejected and the authors proposed that the mechanism for chlorovinylation proceeded *via* the intermediacy of a chloroalkyl radical which serves as the chain-carrying species (eq 4).

Table I. Relative Reactivities of the Hydrogens in Hexane[a]

Hexane	$h\nu$, 65° Cl_2	*cis*-CHCl= CHCl	CHCl= CCl_2	CCl_2= CCl_2
CH_3	0.35	0.06	0.04	Trace
CH_2	1.15	1.97	1.68	4.24
CH_2	1.0	1.0	1.0	1.0

[a] The above data are taken from ref 4.



Recently we have observed several examples of high apparent selectivity in radical substitution reactions where the chain-carrying species was the chlorine atom.[5,6] A selectivity higher than that attributable to chlorine atoms can be observed if the chain-transfer step (eq 5) has an activation energy, E_a^{Tr}, equal to or

$$R\cdot + M\text{-}Cl \xrightarrow{E_a^{\mathrm{Tr}}} RM + Cl\cdot \qquad (5)$$

greater than that necessary for the reversal of the abstraction reaction by chlorine atoms, eq 6. The activa-

$$RH + Cl\cdot \underset{E_a^{-ab}}{\rightleftarrows} R\cdot + HCl \qquad (6)$$

tion energy for the reaction of an alkyl radical with hydrogen chloride (E_a^{-ab}) has been estimated from bond strength data to vary from $E_a \simeq 5$ kcal/mol for a primary radical to ~10 kcal/mol for a secondary radical to ~14 kcal/mol for a tertiary radical.[5] Since the magnitude of the rate constants for the reverse reaction (eq 6) would be in the opposite order to those for the abstraction reactions (eq 6), the more energetic radicals would be converted back to starting material at a faster rate than the more stable radicals (*i.e.*, if reversal is taking place) and the products finally found would be those of the least energetic radicals. An examination of the products of such a reaction would show an anomalously high selectivity.

This situation, in principal, should take place in the free-radical substitution reaction of alkanes with molecular chlorine. However, the rate of transfer of an alkyl radical with molecular chlorine is too fast for a competitive transfer reaction with hydrogen chloride to be observed experimentally.

An investigation of one of the chlorovinylation reactions of Schmerling and West was undertaken to test for the reversibility of chlorine atom abstraction as a possible explanation for the results obtained by Rust and Bell. The results of this investigation are reported in this paper.

Results

Substitution Reactions of Hexane. The chlorination (125°) and the chlorovinylation (125°) of hexane, with molecular chlorine and with tetrachloroethylene, were carried out using the method reported by Rust and Bell.[4] The characterized products were analyzed by glpc and the product ratios and yields are listed in Table II. The compounds listed were the only volatile products observed and the percentage yields were calculated by adding known amounts of *o*-dichlorobenzene and using standard calibration curves to determine the molar amounts of the products formed in the reactions.

A series of identical reactions between tetrachloroethylene and hexane was carried out with and without added hydrogen chloride and the reactions were quenched after varying lengths of time. Analysis of the reaction mixtures showed, for the reactions without added hydrogen chloride, a gradual change in the ratios of the three products produced. The changes in the product ratios could be correlated with the changes in the percentage of reaction. The reactions run with added hydrogen chloride did not show this change. The results of the analysis of the three chlorovinylation products, 1,1,2-trichloro-1-octene (II), 1,1,2-trichloro-3-methyl-1-heptene (III), and 1,1,2-trichloro-3-ethyl-1-hexene (IV), produced in the reactions carried out without added hydrogen chloride are listed in Table III, while the results of the reactions with added hydrogen chloride are listed in Table IV.

The reaction products II, III, and IV were shown to be stable, and irreversibly formed, by placing a known mixture of these materials in a reaction mixture of cyclohexane, *tert*-butyl peroxide, an internal standard (*o*-dichlorobenzene), and tetrachloroethylene. The chlorovinylation of the cyclohexane was carried out and an analysis of the reaction mixture showed that, within the accuracy of analysis, the absolute amounts of II, III, and IV remained unchanged.

---

[5] D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, 91, 3028 (1969).

[6] N. J. Bunce and D. D. Tanner, *ibid.*, 91, 6096 (1969).

Table II. Isomer Distribution for the Substitution Products of *n*-Hexane

Reaction	Reactant	Product ratios	Product	Yield, %[a]
1–2	Cl_2	1.02	$CH_3(CH_2)_4CH_2Cl$	32.6 ± 2.0
		1.11	$CH_3(CH_2)_3CHClCH_3$	35.5 ± 1.1
		1.00	$CH_3(CH_2)_2CHClCH_2CH_3$	31.9 ± 1.4
3–4	$CCl_2{=}CCl_2$	0.12	$CH_3(CH_2)_5CCl{=}CCl_2$ (II)	0.5 ± 0.06
		3.88	$CH_3(CH_2)_3CH(CCl{=}CCl_2)CH_3$ (III)	16.3 ± 0.06
		1.00	$CH_3(CH_2)_2CH(CCl{=}CCl_2)CH_2CH_3$ (IV)	4.2 ± 0.03

[a] The values reported are average values of the listed reactions. The errors are averages of the deviations of three or more analyses.

Table III. The Variation of the Product Composition with Percentage Reaction for the Reaction of Hexane with Tetrachloroethylene

Reaction	Conversion, %	Product composition, %[a] II	III	IV
5–6	0.2	9.6	67.2	23.3
7–8	0.4	6.5	70.5	23.2
9–10	2.4	3.5	76.9	19.6
11–12	3.3	2.6	78.0	19.5
13–14	5.0	2.7	78.5	18.9
15–16	9.0	2.2	79.2	18.7
17	14.7	2.2	78.6	19.3
3	20.4	2.3	78.6	19.2
4	21.6	2.3	77.1	20.6

[a] Values reported are averages of three or more analyses. The reproducibility of all the analyses was greater than 2.5% of the value reported. Reactions that are listed at the same conversion percentage did not vary more than ±0.5% and are reported as average values.

Table IV. Product Composition Compared with Percentage Conversion for the Reaction of Hexane with Tetrachloroethylene with Added Hydrogen Chloride (5.9 Mol %)

Reaction	Conversion, %	Product composition, %[a] II	III	IV
18–19	0.3	2.4	79.7	17.9
20	10.9	1.7	80.2	18.1
21	17.1	2.3	78.0	19.7

[a] Values reported are averages of three or more analyses. Reactions that are listed at the same conversion percentage did not vary more than ±0.5% and are reported as average values.

The Stability of 1,1,2,2-Tetrachlorohexane. One of the possible products from the reaction of tetrachloroethylene and hexane that one might infer from the mechanism proposed by Rust and Bell[4] was 1,1,2,2-tetrachlorooctane. A model compound 1,1,2,2-tetrachlorohexane (V) was synthesized. A predetermined amount of V was added to the reaction mixture of hexane and tetrachloroethylene, the reaction was carried out, and a product analysis of the reaction mixture showed that the three chlorovinylation products, II, III, and IV, had been formed in their expected ratios, and that the added V had remained unchanged.

The Chlorovinylation of Cyclohexane. The reaction of a 6:1 mixture of cyclohexane–tetrachloroethylene containing 5 mol% of *tert*-butyl peroxide gave a 25% yield of 1,1,2-trichloro-2-cyclohexylethene (VI).

Deuterium Scrambling Reactions during Chlorovinylation. The *tert*-butyl peroxide initiated reaction of tetrachloroethylene and a 1:1 mixture of cyclohexane–perdeuteriocyclohexane gave a 36.7% yield of the corresponding chlorovinylated cyclohexanes after 21 hr (reaction 22) and a 25.0% yield after 17 hr (reaction 23). The unsubstituted starting alkanes were isolated from the reaction mixture by preparative glpc and were subjected to mass spectral analysis. A comparison of the mass spectra of cyclohexane and perdeuteriocyclohexane before the reaction with that of the reisolated mixture after the reaction is listed in Table V.

An identical reaction mixture containing no *tert*-butyl peroxide was subjected to the same reaction conditions (125° for 16.8 hr); glpc analysis showed no chlorovinylation products and a mass spectral analysis of a reisolated mixture of the substrate was identical with that of one taken before the reaction was carried out. The decomposition of *tert*-butyl peroxide in a mixture of perdeuteriocyclohexane and cyclohexane was carried out in a manner identical with the above reaction. Reisolation and analysis of the mixture of alkanes showed that <7% of the amount of scrambling that was observed in the chlorovinylation reactions had taken place in the control reaction.

A 1:1 mixture of *n*-hexane–perdeuteriocyclohexane was subjected to the *tert*-butyl peroxide initiated chlorovinylation reaction with tetrachloroethylene. The reaction yielded 11% of the three products resulting from the substitution of hexane and a 14% yield of the chlorovinylation product of perdeuteriocyclohexane. The unsubstituted starting materials were isolated by preparative glpc and subjected to mass spectral analysis. A comparison of the mass spectral analysis for the hexane and perdeuteriocyclohexane before and after the reaction is given in Table VI. When the reaction between tetrachloroethylene and the mixture of perdeuteriocyclohexane and hexane was repeated without added peroxide no chlorovinylation products could be detected and the mass spectral analysis of the perdeuteriocyclohexane and hexane was the same before and after being subjected to the reaction conditions (125° for 16 hr).

Discussion

The isomer distribution of chlorination products formed in the peroxide-initiated chlorination of *n*-hexane at 125° was found to be similar to that reported by Rust and Bell[4] for the photochlorination at 65°. However, as expected, the amount of 1-chlorohexane formed was increased at the higher temperature. The relative reactivities per hydrogen (125°) for the chlorination and trichlorovinylation products can be compared for substitution at carbons 1, 2, and 3: 0.68, 1.11, and 1.00 for chlorination and 0.08, 3.88, and 1.00 for chlorovinylation. The differences observed in the reactivity of the hydrogens in hexane with the two reagents could have several explanations. One possibility, the most obvious, was that the chlorovinylation and chlorination reactions proceed by mechanisms having two different abstraction species, a chloroalkyl

Table V. Isotopic Composition of the Parent Ions from Cyclohexane and Deuterated Cyclohexane before and after Chlorovinylation[a]

Reaction	Compound	M^+, %													% yield of trichlorovinyl compound
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	
22	C_6H_{12} (before reaction)	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	C_6D_{12} (before reaction)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	4.2	6.6	88.8	36.7
	$C_6H_nD_{12-n}$ (after reaction)	5.5	11.3	12.9	10.0	5.7	2.8	2.0	3.3	6.6	10.8	13.3	11.0	4.7	
23	C_6H_{12} (before reaction)	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	C_6D_{12} (before reaction)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	4.2	6.6	88.8	25.0
	$C_6H_nD_{12-n}$ (after reaction)	33.5	11.9	2.3	0.5	0.1	0.0	0.0	0.0	0.3	1.0	4.2	13.5	32.7	

[a] Values reported are corrected for ^{13}C natural abundance.

Table VI. Isotopic Composition of the Parent Ions from Hexane and Deuterated Cyclohexane before and after Chlorovinylation[a]

Reaction	Compound	M^+, %															% yield of trichlorovinyl compound
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	
24	Hexane																
	before reaction	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	after reaction	76.9	18.4	3.9	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.8
	Cyclohexane																
	before reaction	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	4.2	6.6	88.8			
	after reaction	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.8	7.3	24.2	66.2			13.6
25	Hexane																
	before reaction	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	after reaction	69.2	23.1	6.3	1.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	10.6
	Cyclohexane																
	before reaction	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	4.2	6.6	88.8			
	after reaction	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.7	2.4	10.5	27.1	59.1			13.9

[a] Values reported are corrected for ^{13}C.

radical and a chlorine atom. The second possibility was that the reactivity observed was due to the selectivity of the same abstracting radical, but, as proposed in the introductory statement, that in the chlorovinylation reaction a competitive chain-transfer process was competing for the alkyl radicals. The radicals once formed, by the abstraction of hydrogen by atomic chlorine in their kinetically determined distribution, are fated to react in one of two mechanistically distinct paths (see Scheme II).

Scheme II

$$(CH_2CH_2CH_3)_2 + Cl\cdot \rightleftarrows CH_3(CH_2)_4CH_2\cdot + HCl \qquad (7)$$

$$(CH_2CH_2CH_3)_2 + Cl\cdot \rightleftarrows CH_3(CH_2)_3\dot{C}HCH_3 + HCl \qquad (8)$$

$$(CH_2CH_2CH_3)_2 + Cl\cdot \rightleftarrows CH_3(CH_2)_2\dot{C}HCH_2CH_3 + HCl \qquad (9)$$

$$R\cdot + Cl_2C{=}CCl_2 \longrightarrow RCCl_2CCl_2\cdot \qquad (10)$$

$$RCCl_2CCl_2\cdot \longrightarrow RCCl{=}CCl_2 + Cl\cdot \qquad (11)$$

The first of these is a reaction with hydrogen chloride to regenerate hexane and a chlorine atom (eq 7–9) and the second the addition of an alkyl radical to tetrachloroethylene to form the radical precursors of the chlorovinylation products (eq 10).

The kinetics of cyclohexyl radical addition to tetrachloroethylene have been investigated at several temperatures[7] and a value of 7–8 kcal/mol has been assigned to the activation energy for this process. Since this value is comparable to the value of the estimated activation energy for primary (≥ 5 kcal/mol) and secondary (≥ 10 kcal/mol) radicals reacting with hydrogen chloride, it is not unlikely that competitive transfer reactions will occur. The primary radical will return to starting material by transfer with hydrogen chloride at a faster rate (eq −7) than the secondary radicals (eq −8 and −9), and, therefore, more of the secondary radicals

---

[7] A. Horowitz and L. A. Rajbenbach, *J. Amer. Chem. Soc.*, **91**, 4626 (1969).

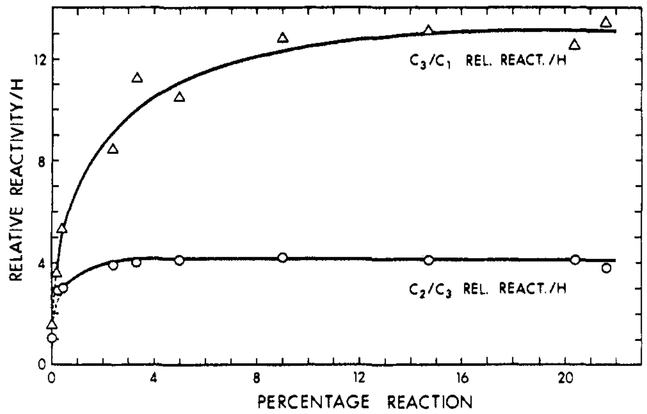


Figure 1. Relative reactivity/H *vs.* percentage reaction of the C_3/C_1 and C_2/C_3 hydrogens in the trichlorovinylation of *n*-hexane.

will be able to go forward to give the products of substitution (eq 10 and 11). Furthermore, the relative rate of a radical's reversal compared to its addition reaction will be proportional to the ratio of transfer agents $[HCl]/[C_2Cl_4]$. At the beginning of the reaction no hydrogen chloride is present for reversal and the products (II, III, and IV) should be formed in the ratio determined by chlorine atom abstraction. As the reaction continues the ratio $[HCl]/[C_2Cl_4]$ becomes larger and reversal with hydrogen chloride becomes more important, resulting in a change in the product distribution where secondary substitution products are formed at the expense of the primary substitution product. This trend can be recognized by a comparison of the product distribution at varying per cent reaction; the results are listed in Table III. Concentration conditions at the end of the reaction can be simulated by the initial addition of hydrogen chloride to the reaction. The product distribution at low conversion under these conditions was the same as the final distribution at the end of the gradually changing reaction (Table IV). For this to be true a very great sensitivity to hydrogen chloride concentration must exist in these relative transfer reactions. The apparent relative reactivity of the hydrogens at C_1, C_2, and C_3 as a function of per cent reaction is plotted in Figure 1.

The C_3/C_1 and C_2/C_3 relative reactivity/H values at 0% reaction are extrapolated to 1.5 and 1.1. The ~~extrapolated values are those for the C_3/C_1 and C_2/C_3~~ reactivities determined for the chlorination of hexane with molecular chlorine at 125°. It is seen that there is a very great sensitivity to hydrogen chloride concentration since at approximately 5% reaction the reversible reactions seem to dominate completely the product distribution.

The reversible hydrogen abstraction having been implied kinetically was confirmed chemically. The chlorovinylation of a mixture of cyclohexane and perdeuteriocyclohexane showed an extensive amount of scrambling of deuterium into the unsubstituted cyclohexane and protium into the deuteriocyclohexane (Table V). A lower limit on the number of exchanges per act of substitution (E/S) could be calculated from the yield of the products and the number of exchanged atoms. The ratio, E/S, represents a minimum value for the number of exchanges since any exchange into or out of the same position is not detected by our experimental method. The same value of $E/S \simeq 7$ was obtained from reactions 22 or 23, reactions differing in yield by 30%. This observation would only be true for reactions where reversibility was a controlling factor in the early stages of the reaction.

Reversible abstraction during the chlorovinylation of *n*-hexane was further substantiated by an examination of the deuterium scrambling which takes place when a mixture of perdeuteriocyclohexane and hexane was competitively reacted. The ratio $E/S \simeq 7$ was likewise obtained for incorporation of deuterium into the unsubstituted hexane and for protium incorporation into the unsubstituted cycloalkane.

Having established that a reversible hydrogen abstraction of chlorine atoms is a controlling factor in the isomer distribution obtained in the reaction of tetrachloroethylene with hexane, there was no evidence available to form a basis for the rejection of the chlorine atom chain. The possibility still existed, however, that the chlorinated alkyl radical was the chain-carrying species (eq 12) and that it had a selectivity that was similar to the chlorine atom.

A reasonable estimate for the energetics involved in the undefined process proposed by Rust and Bell, eq 4, could be obtained by dividing the reaction into two, more chemically plausible, separate processes, eq 12 and 13. Thermodynamic calculations[8] can be used for

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

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

the two reactions, 12 and 13, to estimate that an abstraction–elimination such as eq 4 would have an activation energy in excess of 13 kcal/mol. It, therefore, appears to be unlikely that such a process would play a significant role in a chain propagation sequence.

The process represented by eq 13 could be eliminated as a possible step in the trichlorovinylation mechanism by the observation that the model compound V was stable under the reaction conditions.

Therefore, both on theoretical and on chemical grounds a mechanism involving a reversible chlorine atom chain, Scheme II, must be preferred. This mechanism for chlorovinylation has only been established for the reactions of tetrachloroethylene, the reaction showing the largest effects from reversibility, but presumably the same processes are, to a lesser degree, controlling the isomer distributions obtained in the chlorovinylation reactions of *cis*-1,2-dichloroethylene and trichloroethylene with alkanes.[4]

The isomer distribution observed by Rust and Bell[4] for the peroxide-initiated chlorination of hexane with carbon tetrachloride could possibly have been influenced by a reversal of the radicals formed with the chloroform produced in the reaction. Chlorination of

$$CCl_3 + RH \rightleftarrows HCCl_3 + R\cdot$$

$$R\cdot + CCl_4 \longrightarrow RCl + CCl_3$$

mixtures of cyclohexane and perdeuteriocyclohexane showed no scrambling. Reactions between cyclo-

---

[8] Values for the calculations were taken as $D(CHCl_2CCl_2{-}H) = 95.9$ kcal/mol (J. A. Franklin and G. H. Huybrechts, *Int. J. Chem. Kinet.*, 1, 3 (1969)); $C_2Cl_5\cdot \rightarrow C_2Cl_4 + Cl\cdot$, $\Delta H = 16.8$ kcal/mol (see Franklin and Huybrechts); $D(H{-}Cl) = 102.2$ kcal/mol (T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958, p 271); $D(n\text{-}C_3H_7{-}H) = 98.0$ kcal/mol (J. A. Kerr, *Chem. Rev.*, 66, 465 (1966)).

hexane and carbon tetrachloride run in the presence of deuteriochloroform, likewise, showed no incorporation of deuterium into the recovered starting material. The isomer distribution observed[4] in the case of the chlorination reactions of carbon tetrachloride is therefore due to the selectivity of the trichloromethyl radical.

Experimental Section

Materials. *n*-Hexane and cyclohexane, Phillips research grade, were used without further purification, after checking their purity by glpc analysis and potassium iodide–acetic acid. Perdeuteriocyclohexane (99%) was obtained from Merck Sharp and Dohme (Canada) Ltd.

Tetrachloroethylene was obtained from Matheson Coleman and Bell, spectroquality grade, and was purified prior to use by fractional crystallization followed by distillation from phosphorus pentoxide. Its purity was checked by glpc analysis.

tert-Butyl peroxide (K & K Laboratories Inc.) was used as supplied.

Anhydrous hydrogen chloride was obtained from Matheson of Canada Ltd. and was distilled prior to use.

Glpc Analysis. For the chlorovinylation reactions both preparative isolation of products and their analytical determinations were carried out using a 10 ft × $^1/_4$ in. stainless steel column packed with 10% SE-30 on acid-washed Chromosorb W. An Aerograph Model 1520 gas chromatograph equipped with a thermal conductivity detector was used for this work. Quantitative analyses of these reaction mixtures were carried out using a 10 ft × $^1/_8$ in. stainless steel column packed with 5% SE-30 on acid-washed Chromosorb W.

Quantitative analyses of the chlorination products of *n*-hexane with molecular chlorine were carried out using a Carlo-Erba Fractovap gas chromatograph equipped with a flame ionization detector and a 300 ft × 0.01 in. stainless steel capillary column (68°) coated with a FFAP liquid phase.

The product yields were determined in the usual manner[9] from standard calibration curves using an added standard, *o*-dichlorobenzene.

Unless otherwise indicated, the reaction products were identified by comparing their ir and/or nmr spectra and glpc retention times with those of authentic materials.

Mass Spectra. When gas chromatography was carried out coupled directly to a mass spectrometer (gc–mass spectroscopy), the spectrometer used was an AEI MS-12 in conjunction with an Aerograph Hy-Fi Model III gas chromatograph. For the deuteration studies, mass spectra were obtained using an AEI Model MS-9, and the molecular ions were used to estimate the extent of hydrogen–deuterium exchange. The standard corrections were applied for ^{13}C natural abundance.

The Chlorination of Hexane with Molecular Chlorine. In a compartmentalized reaction vessel separated by a break seal was placed, in one compartment, a carbon tetrachloride solution of molecular chlorine (0.1 *M*, 1 × 10^{-3} mol) and, in the other compartment, a solution of *n*-hexane (0.86 g, 1 × 10^{-2} mol) and *tert*-butyl peroxide (0.003 g, 2 × 10^{-5} mol). The solutions were degassed and the reaction vessel was thermostated at 125°. The break seal was broken and the solutions were mixed, while the reaction was kept at 125° in the thermostated oil bath. After 30 min the colorless solution was removed from the reaction tube and washed successively with aqueous solutions of sodium thiosulfate, potassium carbonate, and then with water. The organic layer was dried over anhydrous sodium sulfate. Distillation of the bulk of the carbon tetrachloride left a mixture which when subjected to glpc analysis (FFAP, capillary column) was shown to contain unreacted hexane, residual carbon tetrachloride, and the three isomeric monochlorinated hexanes.

The monochlorinated hexanes were identified by a comparison of their retention times on several columns (FFAP, SE-30) with those of the authentic materials which were prepared from the corresponding alcohols by the method of Bunnett.[10]

1,1,2,2-Tetrachlorohexane (V). The tetrachloride was prepared by the method of Hennion[11] from 1-hexyne. The complex reaction mixture was fractionated by preparative glpc (SE-30, programmed from 60 to 150°) and then V was identified from its spectral properties and microanalysis: nmr (CCl_4) τ 4.06 (s, 1 H), 7.70 (deformed t, 2 H), 8.2–8.9 (m, 4 H), and 9.11 (deformed t, 3 H). *Anal.* Calcd for $C_6H_{10}Cl_4$: C, 47.06; H, 6.54. Found: C, 47.24; H, 6.65.

The Reaction of Tetrachloroethylene with *n*-Hexane. Aliquot samples of a 6:1:0.02 mixture of hexane, tetrachloroethylene, and *tert*-butyl peroxide were degassed and sealed in Pyrex ampoules. The ampoules were placed in a thermostat at 125° for the appropriate times (0.1–47 hr). The reaction mixtures were removed from the tubes, washed with water, dried over anhydrous sodium sulfate, and subjected to analysis by glpc (see Table III).

The reactions were quantitated by adding known amounts of *o*-dichlorobenzene and determining the yields of the products formed by the use of standard calibration curves constructed for the products and the standard. The three products, 1,1,2-trichloro-1-octene (II), 1,1,2-trichloro-3-methyl-1-heptene (III), and 1,1,2-trichloro-3-ethyl-1-hexene (IV), were formed under the optimum conditions (16 hr) in 21% yield in a ratio of 0.12:3.88:1.00. Other volatile materials detected by glpc represented less than 1% of the product mixture.

The three substitution products were eluted from the glpc column in the order IV, III, and II and could be collected preparatively. An analysis of a mixture of the three isomers was: calcd for $C_8H_{13}Cl_3$: C, 44.57; H, 6.09; Cl, 49.34. Found: C, 44.68; H, 5.93; Cl, 49.02.

The structures of the three isomers were assigned on the basis of their nmr and mass spectra, and by a comparison of the nmr chemical shifts and coupling constants of the three isomers with those of the corresponding three chlorohexanes.

1,1,2-Trichloro-1-octene (II) showed the following characteristics: nmr (CCl_4) τ 7.43 (t, J = 7 Hz, 2 H), 8.20–8.90 (m, 8 H), 9.08 (deformed t, 3 H). The mass spectrum showed parent peaks at *m/e* (M^+) 214, 216, 218, 220, $(M)^+$ 214.0076 (calcd for $C_8H_{13}Cl_3$, 214.0084).

1,1,2-Trichloro-3-methyl-1-heptene (III) showed the following: nmr (CCl_4) τ 6.60–7.10 (m, 1 H), 8.30–9.30 (m, 12 H). The mass spectrum showed parent peaks at *m/e* (M^+) 214, 216, 218, and 220 in the proper ratio for a trichlorinated hydrocarbon.

1,1,2-Trichloro-3-ethyl-1-hexene (IV) showed the following: nmr (CCl_4) 6.80–7.20 (m, 1 H), 8.35–8.90 (m, 6 H), 8.90–9.30 (m, 6 H). The mass spectrum showed parent peaks at *m/e* (M^+) 214, 216, 218, and 220 in the proper ratio for a trichlorinated hydrocarbon. A significant series of peaks (20% of base) was *m/e* $(M - C_2H_5)^+$ 185, 187, 189, and 191, while the base peaks $(M - C_3H_7)^+$ were *m/e* 171, 173, 175, and 177.

Reactions of hexane and tetrachloroethylene were carried out in the above manner with added (0.043 *M*) 1,1,2,2-tetrachlorohexane (V). After the reactions were carried out for 15 or 40 hr a weighed amount of a standard, *o*-dichlorobenzene, was added and the mixture was analyzed by glpc. In both reactions the concentration of 1,1,2,2-tetrachlorohexane was unchanged while the proportions of the products II, III, and IV were similar to those obtained previously in reactions run without added V. A control experiment which did not contain peroxide showed that none of the substitution products was formed and that V, likewise, remained unchanged.

Reactions of hexane and tetrachloroethylene were carried out with added (0.065 mmol/ml) hydrogen chloride, a 1:20 mol ratio to tetrachloroethylene. The reactions were carried out and analyzed in the usual manner and the results are listed in Table IV.

The Reaction of Tetrachloroethylene with Cyclohexane. The reaction of cyclohexane with tetrachloroethylene was carried out in the same manner as was the reaction of hexane with tetrachloroethylene. A single reaction product was formed which could be isolated by preparative glpc, 1,1,2-trichloro-2-cyclohexylethene (VI): nmr (CCl_4) τ 6.90–7.23 (m, 1 H), 8.05–9.00 (m, 10 H). *Anal.* Calcd for $C_8H_{11}Cl_3$: C, 45.00; H, 5.20; Cl, 49.80. Found: C, 45.29; H, 5.06; Cl, 49.65.

The Reaction of Tetrachloroethylene with Cyclohexane and Perdeuteriocyclohexane. A solution of a 1:1:0.66:0.06 mixture of cyclohexane–perdeuteriocyclohexane–tetrachloroethylene–*tert*-butyl peroxide was allowed to react in a sealed degassed Pyrex ampoule at 125° for 21 hr. The reaction mixture was subjected to preparative glpc (SE-30, 70°) and the unsubstituted cyclohexane and perdeuteriocyclohexane were collected as a mixture and subjected to mass spectral analysis. A comparison of the analysis of the cycloalkanes before and after reaction is given in Table V, reaction 22. The conversion of the tetrachloroethylene to VI and its

---

(9) D. D. Tanner and P. B. van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967).

(10) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968).

(11) G. F. Hennion and C. E. Welsh, *ibid.*, **62**, 1367 (1940).

deuterated analogs was determined to be 36.7% by a comparison of the standardized glpc calibration curve of VI and added *o*-dichlorobenzene.

The reaction and its product analysis were repeated using a 1:1:0.66:0.025 mol ratio mixture of reactants. A reaction carried out for 17 hr gave a 25% yield of chlorovinylation products. The analytical results are listed in Table V, reaction 23.

A control experiment carried out without added peroxide showed no exchange had taken place in the recovered starting materials and that no chlorovinylation products were formed.

The Reaction of Tetrachloroethylene with *n*-Hexane and Perdeuteriocyclohexane. A reaction mixture having a 1:1:0.33:0.017 mol ratio of *n*-hexane–perdeuteriocyclohexane–tetrachloroethylene–*tert*-butyl peroxide was allowed to react for 16 hr in the previously described manner. Glpc analysis with the added standard showed that for duplicate experiments a 25% yield (14% cyclohexyl substituted and 11% hexyl substituted) of substituted starting materials was produced. Preparative glpc (SE-30, 55°) of the reaction mixture allowed the isolation of the unsubstituted cyclohexanes and *n*-hexanes. The mass spectral analyses of these recovered materials are listed in Table VI.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. VII. Self-Reactions of Iminoxy Radicals[1]

J. L. Brokenshire,[2] J. R. Roberts,[3] and K. U. Ingold*

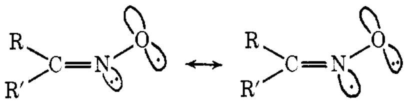
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

Received January 12, 1972

Abstract: The silver oxide oxidations of a number of oximes in benzene solution have been examined. The reaction probably involves the intermediate formation of iminoxy radicals. Rather complex mixtures of products are generally produced because of the instability of some of the initially formed iminoxy radical dimers. Iminoxy radicals can dimerize by N–N, N–O, and O–C coupling. The kinetics and rate constants for the decay of a wide variety of photochemically generated iminoxy radicals have been measured by epr spectroscopy. Under the conditions of the decay experiments the radicals are in equilibrium with "unstable" dimers. For unhindered dialkyliminoxy radicals the equilibrium is rapidly established and lies in favor of the dimers. Decay is first order. For the majority of diaryliminoxy, alkylaryliminoxy, and hindered dialkyliminoxy radicals the equilibrium favors the radicals or else is only slowly established and decay is second order. A unified reaction scheme is proposed but in view of the complexities of the iminoxy radical self-reactions the precise interpretation of the measured decay rate constants and activation parameters is uncertain.

Since their identification by Thomas[4] in 1964, a very large number of iminoxy radicals, $RR'C{=}NO\cdot$, have been prepared by numerous workers using a variety of experimental techniques.[5–15]

Interest in these radicals has centered almost exclusively on their electron paramagnetic resonance (epr) spectra which are characterized by a large splitting, ~30 G, due to nitrogen. This indicates that there is significant spin density on nitrogen in an orbital with considerable s character. Calculations[11,12] have indicated that 41 ± 5% of the unpaired spin is on an orbital whose p/s ratio is 6.1 ± 0.7, the CNO angle being about 139°. The radicals are best represented by the canonical structures



The unpaired electron is in a π type orbital which lies in the nodal plane of the C–N π bond. Iminoxy radicals are therefore described as σ radicals to distinguish them from the more common class of π radicals in which the unpaired electron is in an orbital perpendicular to the nodal plane of the molecular π system. Frequently, both isomeric iminoxy radicals are observed, regardless of which of two geometrically isomeric oximes is oxidized. The configuration stability of the radical is therefore not as great as that of the parent oxime. The hyperfine splitting patterns for protons in iminoxy radicals show two types of effect. There is a long-range interaction which is greatest when the proton, the iminoxy group, and the intervening atoms are coplanar and there is a shorter range interaction that appears to occur directly across space, as opposed to through the bonds.

Despite the number of epr studies of iminoxy radicals there has been only one report on the kinetics of their self-reactions. Gilbert and Norman[8a] mixed equimolar concentrations of oxime and lead tetra-

---

[1] Issued as NRCC No. 12815. Part VI: G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972).

[2] NRCC Postdoctorate Fellow 1969–1971.

[3] NRCC Postdoctorate Fellow 1970–1972.

[4] J. R. Thomas, *J. Amer. Chem. Soc.*, 86, 1446 (1964).

[5] B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 234 (1964).

[6] (a) H. Lemaire and A. Rassat, *Tetrahedron Lett.*, 2245 (1964); (b) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964).

[7] W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965).

[8] (a) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966); (b) *ibid.*, 722 (1966); (c) *J. Phys. Chem.*, 71, 14 (1967); (d) *J. Chem. Soc. B*, 981 (1967); (e) *ibid.*, 123 (1968).

[9] (a) J. W. Lown, *ibid.*, 441 (1966); (b) *ibid.*, 644 (1966).

[10] I. Miyagawa and W. Gordy, *J. Chem. Phys.*, 30, 1950 (1959).

[11] M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); 2276 (1965).

[12] W. M. Fox and M. C. R. Symons, *J. Chem. Soc. A*, 1503 (1966).

[13] L. Burlamacchi and E. Tiezzi, *Gazz. Chim. Ital.*, **99**, 1313 (1969).

[14] B. C. Gilbert and W. M. Gulick, Jr., *J. Phys. Chem.*, 73, 2448 (1969).

[15] B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, **93**, 3290 (1971).