1967

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Recommended Citation

Haffley, Philip Gene, "Photochlorination of aliphatic hydrocarbons " (1967). *Retrospective Theses and Dissertations*. 3393.
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PHOTOCHLORINATION OF ALIPHATIC HYDROCARBONS

by

Philip Gene Haffley

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirments for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967

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LITERATURE SURVEY

Walling reviews the literature up to 1957 on free-radical reactions in his book, Free Radicals in Solution, and quite recently an excellent review of solvent effects in free-radical reactions has been published by Huyser in Advance in Free-Radical Chemistry (1, 2). The photochlorination of hydrocarbons is the most extensively studied reaction with respect to solvent effects.

The photochlorination reaction has the following free-radical chain mechanism:

$$Cl_2 \longrightarrow 2Cl\cdot \qquad (1)$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \qquad (2)$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad (3)$$

A primary deuterium isotope effect has been observed for the abstraction reaction (eq. 2), (3). Neither carbon skeleton rearrangements nor hydrogen migrations occur in the alkyl radicals during photochlorinations, and thus the site of the chlorine in the alkyl chloride produced (eq. 3) is the site of abstraction of the hydrogen atom by the chlorine atom (eq. 2), (3a, 4). The reactivities of the various carbon-hydrogen bonds toward abstraction by a chlorine atom can, therefore, be measured by a quantitative comparison of the amounts of the various alkyl chlorides produced. All possible products are always formed (4). However, under the conditions employed in this present study, aromatic hydrogens are not attacked. A solvent effect in the photochlorination reaction will manifest itself by a change in the composition of the alkyl chlorides produced.

The possibility of a solvent effect in the photochlorination reaction was first suggested by Russell and Brown in 1954, and evidence of a solvent effect in the chlorination of 2,3-dimethylbutane was first reported in 1957 by G. A. Russell (5, 6). A more complete study of the solvent effect in the chlorination of 2,3-dimethylbutane was reported in 1958 (7). It was shown that aromatic solvents greatly increased the selectivity of the chlorine atom. Russell demonstrated that there was no preferential scavenging of an intermediate alkyl radical by the aromatic solvent by establishing that the hydrogen chloride and alkyl chloride were formed in a 1:1 molar ratio. He also provided evidence that the solvent effect observed actually involved the hydrogen atom abstraction reaction by a study of the deuterium isotope effect both in the absence (isotope effect, 1.3) and presence (isotope effect, 1.8) of a complexing solvent. This result also indicated a greater degree of bond breaking in the transition state in complexing solvent.

Only aromatic solvents and some solvents which contain a hetero-atom such as sulfur have an appreciable effect on the relative reactivities of the tertiary, secondary, and primary carbon-hydrogen bonds toward a chlorine atom. There is a very good correlation between the effect of an aromatic solvent on the relative reactivities and the electron density of the aromatic nucleus. Thus there is a good linear correlation between the relative reactivities and both the log of the relative basicities of the solvent and the Hammett σ (meta) constants for the substituent on the benzene nucleus. These facts suggest an equilibrium between the chlorine atom and a π-complex of the chlorine atom and an aromatic nucleus, (eq. 4). Russell estimated that at 25°C in 8 M benzene at least 91%, and probably more, of the chlorine atoms involved


(4)

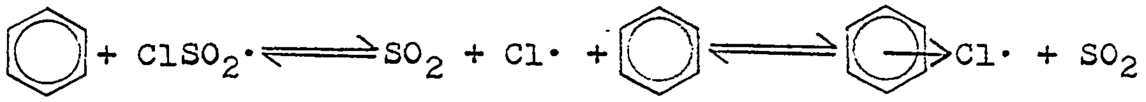
$$Cl\cdot + S{=}C{=}S \rightleftharpoons S{=}C(Cl){-}S\cdot \qquad (5)$$

in hydrogen abstraction are complexed with the aromatic solvent (7). It has been postulated that in the case of carbon disulfide as a solvent the chlorine atom forms a sigma complex which is the principle chlorinating agent (eq. 5), (2).

The hydrogen abstracting species in sulphuryl chloride chlorinations, which are more selective than molecular chlorine, is thought to be the chlorosulphonyl radical

$$\cdot SO_2Cl + RH \longrightarrow SO_2 + HCl + R\cdot \qquad (6)$$

(eq. 6), (5). Evidence supporting the existence of the chlorosulphonyl radical has been provided by Kharasch and Zavist (8). Russell demonstrated that the $\cdot SO_2Cl$ radical is less stable than the aromatic π-complexed chlorine atom and that the equilibrium of the chlorosulphonyl radical and an aromatic compound lies in the direction of the π-complexed chlorine atom (eq. 7), (9). In 8 M benzene $k_{3°}/k_{1°}$ for the



(7)

reaction at 25°C of 2,3-dimethylbutane with SO_2Cl_2 is 53 and with Cl_2 is 49 as compared to a relative reactivity of 12 for neat 2,3-dimethylbutane with $SO_2 Cl_2$ and 4.2 for neat 2,3-dimethylbutane with Cl_2.

Walling and Mayahi reported in 1959 that cyclopropane could complex chlorine atoms (10). However, in 1962 it was subsequently reported that the results which lead to this conclusion could not be repeated and that the presence or absence of cyclopropane had no effect on the photochlorination of 2,3-dimethylbutane or n-butane (11). They did observe that chlorine in its attack on cyclopropane apparently effected a radical displacement on carbon to produce 1,3-dichloropropane while attack of chlorine on cyclobutane produced no ring opening products. Since the strain energy of the cyclobutane is almost as large as cyclopropane, this indicated that there might be some type of interaction of the chlorine atom with cyclopropane (11). Perhaps an interaction similar to that of chlorine with an olefin is occurring and is like the chlorine-olefin complex collapsing to an addition product (addition across the sigma bond of cyclopropane).

Walling and Wagner recently reported the detailed study of the effect of solvent on chlorinations with t-butyl hypochlorite (12). Here the hydrogen abstracting species is thought to be the t-butoxy radical (eq. 8). They found a

$$(CH_3)_3C\text{-}O\cdot + RH \longrightarrow (CH_3)_3C\text{-}OH + R\cdot \tag{8}$$

$$R\cdot + (CH_3)_3C\text{-}O\text{-}Cl \longrightarrow RCl + (CH_3)_3C\text{-}O\cdot \tag{9}$$

$$R'(CH_3)_2C\text{-}O\cdot \longrightarrow (CH_3)_2C{=}O + R'\cdot \tag{10}$$

smaller effect of solvent than in the case of chlorinations with molecular chlorine with both aromatic and non-aromatic polar solvents having an effect on the relative reactivity. The greatest effect of solvent was on the decomposition reaction (eq. 10), (12, 13). This work is extensively discussed by Huyser (2).

In the chlorination of alkyl side chains on aromatic hydrocarbons, the relative reactivity, k_α/k_β, toward "free" chlorine atoms can be determined only by diluting the aromatic hydrocarbon with a non-complexing solvent and extrapolating the relative reactivity to zero aromatic concentration. When this measurement was made, it was found that the phenyl group activates the α-hydrogen atoms to about the same extent as a methyl group (14). This is most probably due to a small extent of bond-breaking in the transition state which would not permit the resonance interaction of the phenyl ring to contribute very much to the stability of the transition state. Russell and Brown have estimated from the competitive chlorination of toluene and cyclohexane that the extent of bond breaking in the transition state is approximately 10 percent (5). Another factor which probably detracts from the activation of the α-hydrogens is the inductive electron-withdrawing properties of the phenyl ring.

In chlorination reactions where there is not a great amount of bond-breaking in the transition state (ca. 10%) the effect of an electron-withdrawing polar group is to decrease the reactivity of the α-hydrogens and the hydrogens on adjacent carbon atoms (1, 5, 15). In radical reactions where there is more bond-breaking, such as brominations, the effect of the electron-withdrawing group is to decrease the activation energy for attack of the α-hydrogen due to a weakening of the carbon-hydrogen bond (15g). This has been discussed in terms of the following transition states (16, 17, 18):

$$X\cdot + RH \longrightarrow [\underset{I}{R:H\cdot X} \longleftrightarrow \underset{II}{R^{+}\cdot HX:^{-}} \longleftrightarrow \underset{III}{R\cdot H:X}] \longrightarrow R\cdot + HX$$

According to the Hammond postulate when X· is very reactive, the transition state will resemble the reactants (structure I), and when X· is less reactive, the transition state will resemble products (structure III), (19). A complexing solvent stabilizes the chlorine atom and thus should make the transition state for hydrogen abstraction more like structure II. This should increase the importance of resonance stabilization of the transition state and at the same time might increase the polar effect for hydrogens two or more carbon atoms away due to the increasing polar nature of the transition state.

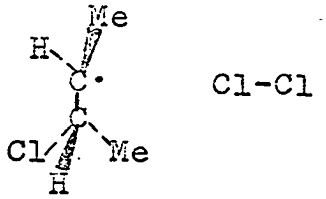
Complexing the chlorine atom has little effect on the relative reactivities of hydrogen atoms near a polar group although it has a considerable effect on the relative reactivities of hydrogen atoms in the same molecule which are sufficiently far away (10, 17, 20, 21). Some representative data is given below:

	CH_3 -	CH_2 -	CH_2 -	CH_2Cl	
Relative Reactivity	1.0	2.6	1.2	0.3	Cl· in aliphatic solvent
	1.0	3.7	1.7	0.45	Cl· in 7.5 M benzene
	1.0	8.1	2.4	0.5	Cl· in 11.1 M carbon disulfide

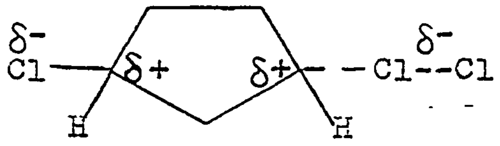
Russell has evaluated the above data and drawn the following conclusion (17): "Relative reactivities that are determined mainly by the availability of electrons in the carbon-hydrogen bond are not particularly sensitive to solvent effects while relative reactivities that are determined mainly by the stabilities of the incipient free radicals are very sensitive to changes in solvent."

Tedder et al. have recently published results which demonstrate that close comparison between gas phase chlorinations and liquid phase studies are not justified (22, 15f). Their results indicate that the polar effect in the chlorination of heptanoyl fluoride does not extend beyond two carbon atoms in the gas phase but in the liquid phase it extends at least five carbon atoms. For chlorinations in both the gas and liquid phase it has been generally concluded that the differences in reactivity of the various carbon-hydrogen bonds in a molecule containing an electron-withdrawing group are mainly due to differences in activation energy (15, 16, 21, 23).

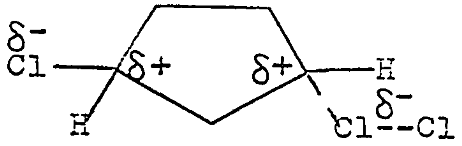
Fredricks and Tedder have pointed out the importance of hyperconjugative stabilization on the reactivities of the various carbon-hydrogen bonds and also have noted a stereochemical preference for the attack of chlorine on the 2-chlorobutyl radical to yield erythro-2,3-dichlorobutane (15a, 15b, 15c). This result has been explained as a preference for the chlorine molecule to approach the alkyl radical from the side opposite to the chlorine already in the molecule. This of course assumes that the radical is mainly in the conformation given below:



A similar explanation has been advanced by Russell and Ito to explain their results in the chlorination of chlorocyclopentane (24). They found that the cis/trans ratio could be influenced by polar solvents such as nitrobenzene or acetonitrile but was relatively unaffected by complexing solvents such as benzene or carbon disulfide. They concluded that in the case of chlorocyclopentane the preponderance of trans product was probably due to an unfavorable interaction of parallel dipoles in the transition state leading to cis products. This kind of explanation does not give a clear prediction in the case of the chlorination of chlorocyclohexane which is more complicated due to the flexibility of the six-membered ring. The data of Russell and Ito on the chlorination of chlorocyclohexane in carbon tetrachloride at 40° C are compared in Table 1 with the results of Little, Chang, and Zurawic which were presented by Huyser (2). Since the results of Little <u>et</u> <u>al</u>. were a personal communication to Huyser in 1965, no experimental details are available. However, the results certainly are different from the chlorocyclopentane results of Russell and Ito, where complexing



cis transition state



trans transition state

Table 1. Effect of solvent on cis-trans ratios in the photochlorination (at 40° C) of substituted cyclohexane

Substrate	Solvent	Relative reactivity				Cis/trans ratio		
		1	2	3	4	2	3	4
Chlorocyclohexane[a]	CCl_4	0.36	0.44	0.79	1.0	0.086	0.80	0.89
Cyclohexane carboxylic acid[b]	CCl_4	0.34	0.43	0.83	1.0	0.91	0.65	1.44
	C_6H_6	0.21	0.29	0.85	1.0	0.91	0.96	1.37
	CS_2	0.46	0.28	0.86	1.0	0.83	0.36	1.72
Methylcyclohexane carboxylate[b]	CCl_4	0.47	0.60	1.01	1.0	0.79	0.74	1.21
	C_6H_6	0.34	0.38	0.97	1.0	1.00	0.91	1.30
	CS_2	0.57	0.44	1.05	1.0	0.97	0.71	0.80

[a] Russell and Ito (24)

[b] Little, Chang, and Zurawic (2)

solvents had no effect on the cis/trans ratios, and point out the need for further work on the cyclohexane system.

INTRODUCTION

Several workers have deduced that the reactivity of the tertiary carbon-hydrogen bonds in 2,2,4-trimethylpentane and 2,4-dimethylpentane must be abnormally low from rate and product studies (25). However, only in the case of 2,2,4-trimethylpentane has anyone directly measured the reactivity of the tertiary hydrogen atoms (25f). The series of methylpentanes--2,4-dimethylpentane, 2,2,4-trimethylpentane, and 2,2,4,4-tetramethylpentane--were, therefore, chlorinated in several solvents to obtain direct evidence on this point and to observe the effect of solvent on the reactivity of the tertiary hydrogens.

Since 2,5-dimethylhexane has approximately "normal" reactivity, it was used in the study of the effect of temperature on the rates of attack of chlorine in several complexing solvents on carbon-hydrogen bonds. This study was undertaken in order to check the hypothesis that complexing solvents stabilize the chlorine atoms and, thereby, make them more selective by increasing the difference in the energy of activation for attack on the various types of carbon-hydrogen bonds. Isobutyronitrile, propionitrile, toluene and α-chlorotoluene were chlorinated over a temperature range to obtain data on the energies of activation for attack of chlorine in complexing and non-complexing solvents on compounds containing a polar group. Finally, adamantane was chlorinated in carbon tetrachloride, 4 M benzene, and 12 M carbon disulfide to see if the tertiary hydrogens were as reactive as or more reactive than "normal" toward abstraction by chlorine atoms.

The various mixtures of alkyl chlorides were analyzed by gas-liquid partition chromatography (glpc) and identified by synthesis of authentic samples or collection of sufficient material by preparative glpc for subsequent identification by spectral methods. The extent of chlorination was limited to 10 mole percent or less in order to exclude polychlorination. It has been demonstrated that the products of a photochlorination are a true measure of the initial site of attack by chlorine atoms (3a, 4).

The methylpentanes and 2,5-dimethylhexane were also photochlorinated competitively in the presence of cyclohexane. The relative rates of attack on the two hydrocarbons were calculated by means of the equation

$$\frac{k_1}{k_2} = \frac{\log \frac{[R_1H]_f}{[R_1H]_i}}{\log \frac{[R_2H]_f}{[R_2H]_i}}$$

where $[\ ]_i$ represents the initial concentration and $[\ ]_f$ the final concentration. By use of the following expression the reactivity of the primary hydrogens (X) relative to cyclohexane may be calculated:

$$\frac{k_1}{k_c}(12) = (\#p)(X) + \frac{2^\circ}{1^\circ}(\#s)(X) + \frac{3^\circ}{1^\circ}(\#t)(X).$$

The k_1/k_c is the rate of attack on a hydrocarbon relative to cyclohexane; #p, #s, and #t are the number of primary, secondary, and tertiary hydrogen atoms in the molecule; and $2^\circ/1^\circ$ and $3^\circ/1^\circ$ are the relative reactivities of the hydrogens within the molecule.

The purpose of these calculations is to demonstrate the validity of the comparison of relative reactivities within one molecule with those of another. If the primary hydrogens of two molecules have the same reactivities relative to a standard, then the comparison of $3^\circ/1^\circ$ or $2^\circ/1^\circ$ ratios will be valid.

RESULTS AND DISCUSSION

Photochlorination of Methylpentanes

Solutions of 2,4-dimethylpentane, 2,2,4-trimethylpentane and 2,2,4,4-tetramethylpentane were chlorinated to the extent of ca. 5%, and the composition of the monochlorides formed were analyzed by gas-liquid partition chromatography (glpc). These results are summarized in Table 2. The glpc peaks were identified by comparison of the relative retention times of authentic samples of the primary and tertiary chloropentanes. The peak remaining was then assumed to be the secondary chloride. The only exception was the assignment of the monochlorides of 2,2,4,4-tetramethylpentane. In this case the peak due to the primary chloride was assigned on the basis of: (1) the order in which the peaks came off the column--in all other instances the order was tertiary then secondary and finally primary and (2) the relative size of the two peaks produced from chlorination of a carbon tetrachloride solution. Since there are nine primary hydrogens to one secondary hydrogen and normal $k_{2°}/k_{1°}$ is ca. 2.6, the peak due to the primary chloride should be at least three times larger than the peak due to the secondary chloride. An indication that this assignment is correct is provided by the fair agreement of these results with those of Backhurst who chlorinated 2,2,4,4-tetramethylpentane in the gas phase and reported 20% of the secondary chloride formed (26).

Table 2. Composition of monochlorides formed in the chlorination of methylpentanes at 40° C

Solvent		Chlorides (% of total monochlorides)		
		Primary	Secondary	Tertiary
		2,4-Dimethylpentane		
CCl_4[a]		55.1	22.9	22.0
		55.5	23.0	21.5
		54.3	23.2	22.5
	Average	55.0	23.0	22.0
4 M C_6H_6[a]		33.5	30.2	36.3
		33.4	30.6	36.0
		33.1	30.9	36.0
	Average	33.3	30.6	36.1
12 M CS_2[b]		10.5	35.8	53.7
		11.1	35.2	53.7
		12.3	36.5	51.2
		9.6	35.0	55.4
	Average	10.8	35.6	53.6
		2,2,4-Trimethylpentane		
CCl_4[a]		70.6	24.6	4.8
		70.6	24.6	4.8
		70.2	24.4	5.4
		70.1	24.4	5.5
		67.4	26.0	6.6
		67.4	26.0	6.6
	Average	69.4	25.0	5.6

[a] Ca. 5 mole % chlorination.

[b] Ca. 2 mole % chlorination.

Table 2 (continued).

Solvent		Chlorides (% of total monochlorides)		
		Primary	Secondary	Tertiary
4 M C_6H_6[a]		50.5	39.7	9.8
		49.5	40.9	9.6
		51.1	40.1	8.8
	Average	50.4	40.2	9.4
12 M CS_2[b]		19.3	59.8	20.9
		20.7	57.1	22.2
		20.8	55.8	23.4
		22.6	51.5	25.9
		22.1	53.0	24.9
	Average	21.0	55.5	23.5
		<u>2,2,4,4-Tetramethylpentane</u>		
CCl_4[a]		81.8	18.2	
		82.6	17.4	
		81.1	18.9	
	Average	81.8	18.2	
4 M C_6H_6[a]		52.5	47.6	
		52.0	48.0	
		51.5	48.5	
	Average	52.0	48.0	

Competitive chlorinations with cyclohexane were performed in carbon tetrachloride, benzene, and carbon disulfide solutions. The relative reactivities of cyclohexane and the methylpentanes, summarized in Table 3, are based on the rates of disappearance of the two hydrocarbons as measured by glpc.

Table 3. Competitive photochlorination of methylpentanes with cyclohexane at 40° C

Solvent	Pentane, M		Cyclohexane, M		$\frac{k_{pentane}}{k_{cyclohexane}}$[a]
	Initial	Final	Initial	Final	
			2,4-Dimethylpentane		
CCl_4	0.970	0.825	1.006	0.804	0.72
	0.970	0.811	1.006	0.792	0.74
	1.00	0.874	1.00	0.834	0.74
	1.00	0.825	1.00	0.771	0.74
	1.00	0.816	1.00	0.757	0.73
	1.00	0.827	1.00	0.779	0.76
4 M C_6H_6	2.30	1.96	2.74	2.16	0.67
	2.30	2.16	2.74	2.50	0.69
	2.30	2.18	2.74	2.52	0.64
	2.30	2.14	2.74	2.49	0.75
12 M CS_2	1.00	0.909	1.008	0.860	0.61
	1.00	0.916	1.008	0.868	0.59
	1.00	0.856	1.00	0.791	0.66
	1.00	0.860	1.00	0.789	0.64
	1.00	0.840	1.00	0.755	0.62

[a] Calculated by the expression,

$$\frac{k_{pentane}}{k_{cyclohexane}} = \frac{\log \frac{[pentane]_f}{[pentane]_i}}{\log \frac{[cyclohexane]_f}{[cyclohexane]_i}}$$

Table 3 (continued).

Solvent	Pentane, M		Cyclohexane, M		$\frac{k_{\text{pentane}}}{k_{\text{cyclohexane}}}$[a]
	Initial	Final	Initial	Final	
			<u>2,2,4-Trimethylpentane</u>		
CCl_4	1.00	0.865	1.07	0.899	0.83
	1.00	0.860	1.07	0.881	0.77
	1.00	0.862	1.07	0.875	0.73
	1.10	0.919	1.12	0.887	0.78
4 M C_6H_6	1.62	0.959	3.41	1.54	0.66
	1.62	0.880	3.41	1.43	0.70
12 M CS_2	1.00	0.796	1.00	0.922	0.32
	1.00	0.820	1.00	0.936	0.43
	1.00	0.734	1.00	0.896	0.36
	1.00	0.850	1.00	0.937	0.40
			<u>2,2,4,4-Tetramethylpentane</u>		
CCl_4	0.452	0.409	0.456	0.387	0.63
	0.452	0.381	0.456	0.344	0.61
4 M C_6H_6	0.608	0.565	0.608	0.474	0.29
	0.608	0.518	0.608	0.362	0.31

The "normal" relative reactivity of a primary alkyl hydrogen atom relative to a cyclohexane hydrogen atom at 40° C is 0.35-0.45 in aliphatic solvents. This relative reactivity for the "normal" hydrocarbon, 2,3-dimethylbutane, decreases to 0.20 in 4 M benzene and to ca. 0.05 in 12 M carbon disulfide (7, 17). That the primary hydrogen atoms of

2,4-dimethyl- and 2,2,4-trimethylpentane have normal reactivities is apparent from an inspection of the data of Table 4. It is, therefore, permissible to discuss the reactivities of secondary and tertiary hydrogen atoms relative to primary hydrogen atoms within the methylpentanes and to compare these reactivities with "normal" reactivities. At 40°C in an aliphatic liquid phase a "normal" tertiary to primary relative reactivity is ca. 4 (7, 17). This value increases to 16 in 4 M benzene and to ~200 in 12 M carbon disulfide. Table 5 demonstrates that the secondary hydrogen atoms in 2,4-dimethylpentane and 2,2,4-trimethylpentane are quite normal but that the tertiary hydrogen atoms have an unusually low reactivity, particularly in the solvents that complex chlorine atoms. In 2,2,4-trimethylpentane the

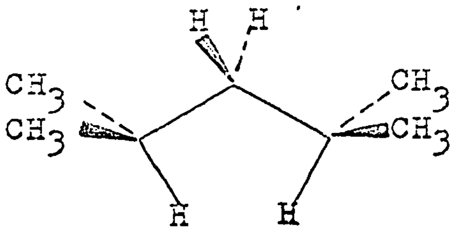
Table 4. Reactivities of primary hydrogen atoms relative to a cyclohexane hydrogen atom at 40° C

	Solvent		
Hydrocarbon	CCl_4	4 M C_6H_6	12 M CS_2
"Normal"	0.35-0.45	0.20	0.05
2,4-Dimethylpentane	0.41	0.23	0.067
2,2,4-Trimethylpentane	0.44	0.27	0.064
2,2,4,4-Tetramethylpentane	0.34	0.11	-----

Table 5. Relative reactivities of hydrogen atoms

Hydrocarbon	Solvent CCl_4	 4 M C_6H_6	 12 M CS_2
	Secondary to Primary		
"Normal"	2-3	5-6	20-25
2,4-Dimethylpentane	2.5 ± 0.1	5.5 ± 0.1	20 ± 1
2,2,4-Trimethylpentane	2.7 ± 0.1	6.0 ± 0.1	20 ± 2
	Tertiary to Primary		
"Normal"	3.5-4.2	16-20	200-225
2,4-Dimethylpentane	2.4 ± 0.1	6.5 ± 0.1	30 ± 1
2,2,4-Trimethylpentane	1.2 ± 0.2	2.8 ± 0.1	17 ± 2

tertiary hydrogen atom is somewhat less than 30% as reactive as expected in carbon tetrachloride solution. Toward the chlorine atom complexed in 4 M benzene solution, the tertiary hydrogen is about 15% as reactive as expected while toward the chlorine atom in 12 M carbon disulfide solution the reactivity is less than 10% of the expected value. This result is explicable in terms of the preferred conformation expected for 2,4-dimethylpentane (I) and 2,2,4-trimethylpentane (II) on the basis of elementary consideration of nonbonded interactions. Although nonbonded interactions would be relieved by attack of chlorine atoms at the secondary or tertiary hydrogen atoms to give a planar radical, it is apparent that the free-radical site is not sufficiently developed in the transition state for this effect to be



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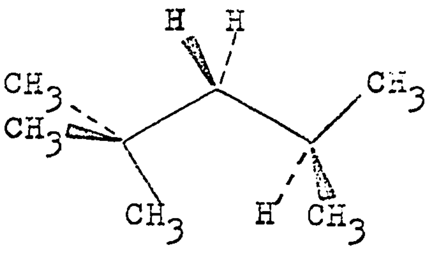


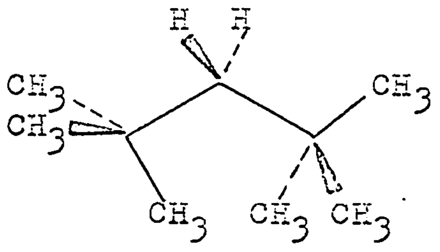
II

important. The molecular geometry leaves the methylene group open to attack by the chlorine atom or a complexed chlorine atom. The methine hydrogens cannot be easily attacked, particularly if the chlorine atom must approach along the axis of the carbon-hydrogen bond. The increased importance of this effect when the chlorine atom is complexed with benzene or carbon disulfide may be due to the lowered reactivity of the chlorine atom (requiring closer approach to the carbon-hydrogen bond) or to the increased bulk of the complex.

Fuller and Hickinbottom attempted to demonstrate the effect of steric bulk in the chlorination of 2,2,4-trimethylpentane (25f). They used various N-alkyl-N-chlorosulphonamides and initiated the reaction at 85°C with benzoyl peroxide. However, their results indicated that in each case the only chlorinating agent was the chlorine atom and with each N-alkyl-N-chlorosulphonamide they observed the same relative reactivity, 1:3.3:2.5.

They also photochlorinated 2,3,4-trimethylpentane with molecular chlorine at 20° C (27). They observed that the interior methine carbon-hydrogen bond at position three had a higher relative reactivity ($k_{3°}/k_{1°} = 4.2$) than the methine carbon-hydrogen bonds at the two and four positions ($k_{3°}/k_{1°} = 2.4$). These results of Fuller and Hickinbottom are in perfect agreement with the results presented in this thesis. The conformation of 2,3,4-trimethylpentane should be similar to structure I with a methylene hydrogen replaced by a methyl group. This would predict that the methine carbon-hydrogen bond at the three position should be essentially normal, which it is, and that the methine carbon-hydrogen bonds at the two and four positions should be less reactive than normal, which they are.

For 2,2,4,4-tetramethylpentane we might expect a preferred conformation, III. In III the methylene group is



III

not particularly hindered and a normal reactivity is observed. The value of $k_{sec\text{-}H}/k_{cyclohexane\text{-}H}$ is 0.68 in carbon tetrachloride and 0.91 in 4 M benzene. In carbon tetrachloride the primary hydrogens are about as reactive as normal primary hydrogen atoms ($k_{prim-H}/k_{cyclohexane-H} = 0.34$), but in 4 M benzene this value is 0.11 instead of the expected 0.2. This suggests hindrance to methyl attack in III due to the crowding of three methyl groups at the back of the molecule.

Insertion of a second methylene group between the tertiary or quaternary centers reduced the crowding at the back of these molecules and normal reactivity of methine hydrogen atoms is observed in 2,5-dimethylhexane and 2,2,5-trimethylhexane in carbon tetrachloride solutions (25e).

Chlorination of 2,5-Dimethylhexane

Solutions of 2,5-dimethylhexane in 12 M carbon disulfide, 6 M fluorobenzene, and several concentrations of benzene were chlorinated to the extent of 10 mole percent or less at temperatures ranging from -35° C to 60° C. The composition of the monochlorides formed were analyzed by glpc and are presented in Table 6. The glpc peaks were identified by comparison of the retention times of authentic samples of the tertiary chloride and a mixture of the tertiary and secondary chlorides. The primary chloride was collected by preparative glpc and identified by p.m.r.

Competitive chlorinations of 2,5-dimethylhexane and cyclohexane were performed in carbon tetrachloride, 6 M fluorobenzene, 6 M benzene, and 12 M carbon disulfide. These results are presented in Table 7. The reactivity of the

Table 6. Composition of monochlorides formed in the chlorination of 2,5-dimethylhexane

Temperature (°C)	Percent chlorination	Chlorides (% of total monochlorides)		
		Tertiary	Secondary	Primary
		Neat		
60	5	24.2	35.6	40.2
	5	24.0	34.9	41.1
40	5	24.1	35.3	40.6
	5	24.7	35.7	39.6
20	5	24.1	35.7	40.2
	5	23.8	37.3	38.9
	5	24.3	34.5	41.2
0	5	24.4	36.5	39.1
	5	25.8	35.1	39.1
-19	3	26.1	35.6	38.3
	3	25.9	36.0	38.1
-35	3	27.0	35.2	37.8
	3	27.6	34.7	37.7
		4 M Benzene		
60	7	36.3	33.6	30.1
	7	37.6	34.7	27.7
40	7	39.5	34.2	26.3
	7	39.3	34.4	26.3
20	7	43.6	33.2	23.2
	3	43.3	33.5	23.2
0	7	47.1	31.9	21.0
	3	47.1	32.1	20.8

Table 6 (continued).

Temperature (°C)	Percent chlorination	Chlorides (% of total monochlorides)		
		Tertiary	Secondary	Primary
		6 M Fluorobenzene		
60	5	39.1	36.6	24.3
	10	39.0	37.4	23.6
40	5	42.1	36.6	21.6
	5	41.1	35.6	23.3
20	5	47.2	34.5	18.3
	2	46.7	33.7	19.6
	5	44.9	34.3	20.8
0	5	49.2	33.2	17.6
	5	48.6	33.3	18.1
-19	5	54.6	31.1	14.3
	10	54.1	31.3	14.6
-35	10	57.3	30.0	12.7
	10	57.1	30.1	12.8
		6 M Benzene		
60	5	44.3	34.0	21.7
	5	43.2	33.2	23.6
40	5	47.2	33.8	19.0
	5	46.3	33.6	20.1
20	5	52.3	30.4	17.3
	5	52.0	32.1	15.9
	5	52.3	31.2	16.5
0	3	56.1	30.6	13.3
	3	55.2	30.3	14.5
	5	55.5	31.1	13.4

Table 6 (continued).

Temperature (°C)	Percent chlorination	Chlorides (% of total monochlorides)		
		Tertiary	Secondary	Primary
		8 M Benzene		
60	8	49.9	34.1	16.0
	8	49.6	34.2	16.1
	5	49.0	32.8	18.2
	3	49.4	33.6	17.0
40	8	53.5	32.5	13.9
	8	52.2	32.6	15.2
	8	53.3	32.5	14.2
20	8	57.1	32.0	10.9
	8	57.3	31.5	11.2
	8	57.4	31.3	11.3
0	5	61.7	29.2	9.1
	5	61.3	29.4	9.3
		12 M Carbon Disulfide		
40	1	60.8	30.9	8.3
	10	65.1	32.8	8.1
20	3	67.2	28.3	4.5
	3	64.7	29.2	6.1
	5	65.4	29.2	5.4
	5	66.0	28.3	5.7
	5	66.9	28.3	4.8
10	5	65.5	28.9	5.6
	5	66.8	28.2	5.0

Table 7. Competitive chlorination of 2,5-dimethylhexane with cyclohexane

Solvent	2,5-Dimethylhexane, M		Cyclohexane, M		$\frac{k_{2,5\text{-dimethylhexane}}}{k_{\text{cyclohexane}}}$
	Initial	Final	Initial	Final	
CCl_4	1.108	0.707	1.093	0.634	0.82
	1.108	0.731	1.093	0.661	0.83
	1.025	0.736	1.111	0.738	0.82
	1.025	0.750	1.111	0.751	0.80
	1.025	0.667	1.111	0.668	0.84
	1.025	0.685	1.111	0.680	0.82
6 M C_6H_5F	1.620	1.337	1.510	1.144	0.70
	1.620	1.402	1.510	1.235	0.73
	1.620	1.205	1.510	1.060	0.83
	1.612	1.330	1.518	1.157	0.72
	1.612	1.360	1.518	1.195	0.74
	1.612	1.330	1.518	1.170	0.75
	1.612	1.253	1.518	1.110	0.82
6 M C_6H_6	1.620	1.404	1.730	1.408	0.70
	1.620	1.373	1.730	1.399	0.77
	1.620	1.348	1.730	1.349	0.74
	1.620	1.289	1.730	1.292	0.78
	1.620	1.385	1.730	1.400	0.74
	1.620	1.396	1.730	1.424	0.77
12 M CS_2	0.781	0.575	1.269	0.879	0.84
	0.781	0.480	1.269	0.683	0.79
	0.781	0.525	1.269	0.777	0.82
	0.781	0.464	1.269	0.725	0.93

primary hydrogens of 2,5-dimethylhexane compared to cyclohexane hydrogens, data in Table 8, were calculated by combining the data in Tables 6 and 7 as discussed previously. It is apparent from Table 8 that the primary hydrogens have normal

Table 8. Reactivities of primary hydrogen atoms relative to a cyclohexane hydrogen atom at 40°C

Solvent	2,5-Dimethylhexane	"Normal"
CCl_4	0.33	0.35
6 M C_6H_5F	0.17	----
6 M C_6H_6	0.15	0.20 (4 M C_6H_6)
12 M CS_2	0.068	0.05

reactivity, and the relative reactivities of the hydrogens in 2,5-dimethylhexane can, therefore, be compared with previous data.

It was expected on the basis of the overall reactivity of 2,5-dimethylhexane toward phenyl radicals in carbon tetrachloride solution that the tertiary hydrogens would have normal reactivity (25e). However, this appears to be true only in non-complexing solvents. In Table 9 are compared the

Table 9. Comparison of 40°C of tertiary to primary ratio of 2,3-dimethylbutane and 2,5-dimethylhexane

Solvent	2,3-Dimethylbutane	2,5-Dimethylhexane
Neat	3.9	3.65
4 M C_6H_6	17.0	9.0
8 M C_6H_6	40.0	22.0
12 M CS_2	200	46.0

3°/1° relative reactivities at 40°C of 2,5-dimethylhexane and 2,3-dimethylbutane. In aromatic solvents the tertiary hydrogens of 2,5-dimethylhexane are only ca. 50% as reactive and in carbon disulfide only ca. 25% as reactive as normal. The possible consequences of this apparent steric hindrance in complexing solvents will be discussed later.

The effect of solvent on hydrogen abstraction by chlorine has been rationalized in terms of ground and transition state solvation as well as in terms of repulsion curves between the chlorine atom and the carbon-hydrogen bonds (12, 21). A possible schmatic energy diagram is shown in Figure 1. The complexed chlorine atom is shown as stabilized relative to the "free" chlorine atom, and the activation energy for hydrogen abstraction is further increased by the effects of solvent on the transition state, i.e., greater amount of bond breaking, and finally, the difference in activation energy between abstraction of a primary and tertiary hydrogen is increased.

The data presented in Table 10 in terms of relative reactivities were calculated from the data in Table 6 and plotted against 1/T in Figures 2 and 3. From these Arrhenius plots, the difference in the energy of activation for abstraction of a tertiary or secondary hydrogen from that of a primary hydrogen, (E_p-E_t) or (E_p-E_s) can be calculated.

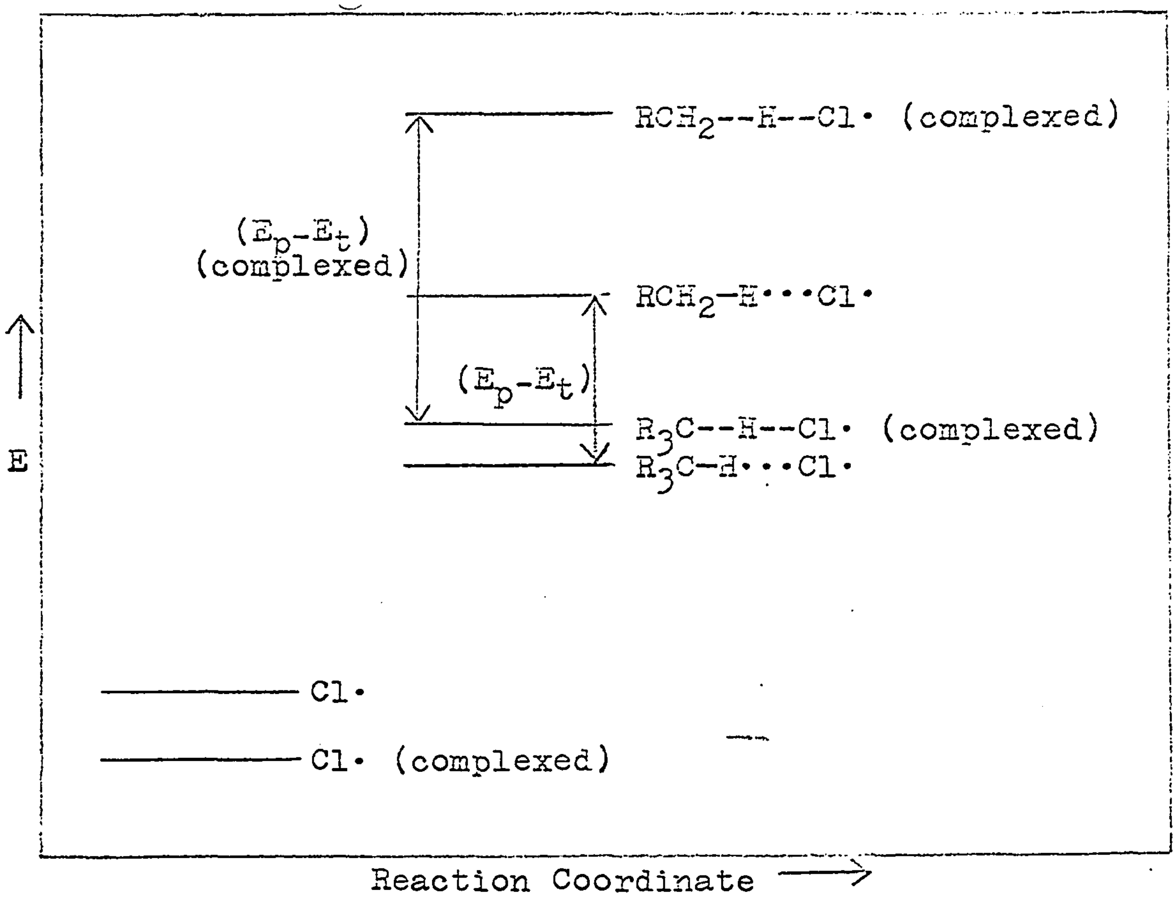


Figure 1. Schematic diagram of changes with solvent in activation energy for hydrogen abstraction by chlorine atoms

Table 10. Relative reactivities of hydrogen atoms in 2,5-dimethylhexane

	Temperature					
Solvent	60°C	40°C	20°C	0°C	-19°C	-35°C
			Secondary to Primary			
Neat	2.60 ± 0.08	2.65 ± 0.05	2.68 ± 0.12	2.75 ± 0.07	2.80 ± 0.04	2.77 ± 0.09
4 M C_6H_6	3.54 ± 0.21	3.91 ± 0.03	4.31 ± 0.09	4.60 ± 0.10	----	----
6 M C_6H_5F	4.62 ± 0.13	4.80 ± 0.20	5.24 ± 0.32	5.61 ± 0.10	6.46 ± 0.18	7.04 ± 0.26
6 M C_6H_6	4.46 ± 0.24	5.19 ± 0.20	5.64 ± 0.30	6.65 ± 0.30	----	----
8 M C_6H_6	6.01 ± 0.34	6.80 ± 0.25	8.55 ± 0.27	9.55 ± 0.31	----	----
12 M CS_2	----	11.7 ± 0.8	16 ± 2	16 ± 1 (10°C)	----	----
			Tertiary to Primary			
Neat	3.56 ± 0.09	3.65 ± 0.10	3.60 ± 0.12	3.85 ± 0.13	4.07 ± 0.04	4.34 ± 0.21
4 M C_6H_6	7.69 ± 0.47	9.00 ± 0.05	11.2 ± 0.2	13.5 ± 0.4	----	----
6 M C_6H_5F	9.75 ± 0.2	11.1 ± 0.5	14.1 ± 1.0	16.5 ± 0.3	22.4 ± 0.6	26.8 ± 1.6
6 M C_6H_6	11.6 ± 0.7	14.4 ± 0.6	18.9 ± 0.8	24.2 ± 1.0	----	----
8 M C_6H_6	17.7 ± 1.0	22.0 ± 1.0	30.9 ± 0.7	40.1 ± 1.1	----	----
12 M CS_2	----	46 ± 3	75 ± 9	75 ± 5 (10°C)	----	----

Figure 2. Arrhenius plot of $2^\circ/1^\circ$ relative reactivities of hydrogen atoms in 2,5-dimethylhexane

A. Neat
B. 4 M C_6H_6
C. 6 M C_6H_5F
D. 6 M C_6H_6
E. 8 M C_6H_6
F. 12 M CS_2

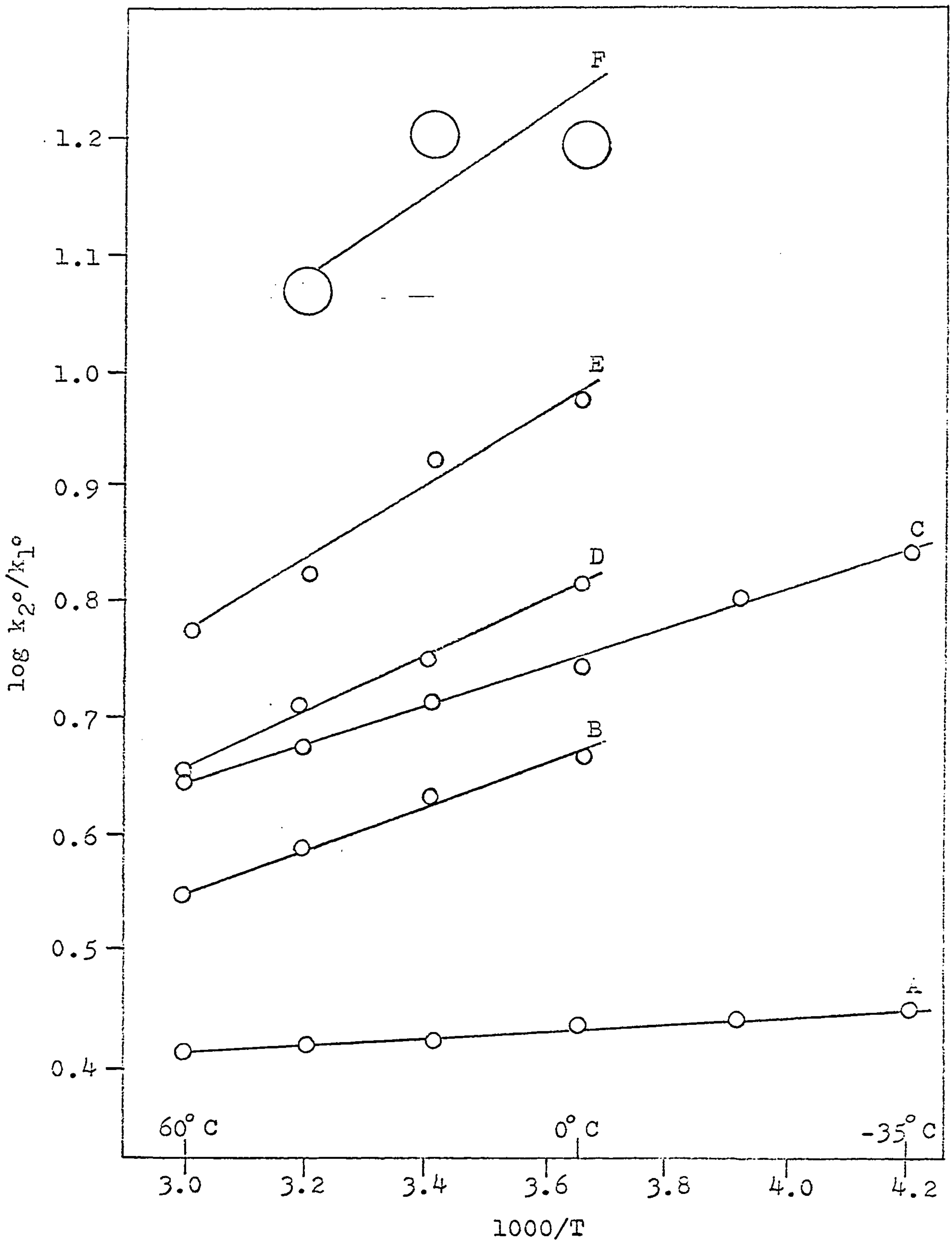

log $k_2°/k_1°$
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
F
E
D
C
B
A
60° C
0° C
-35° C
3.0
3.2
3.4
3.6
3.8
4.0
4.2
1000/T

Figure 3. Arrhenius plot of 3°/1° relative reactivities of hydrogen atoms in 2,5-dimethylhexane

A. Neat

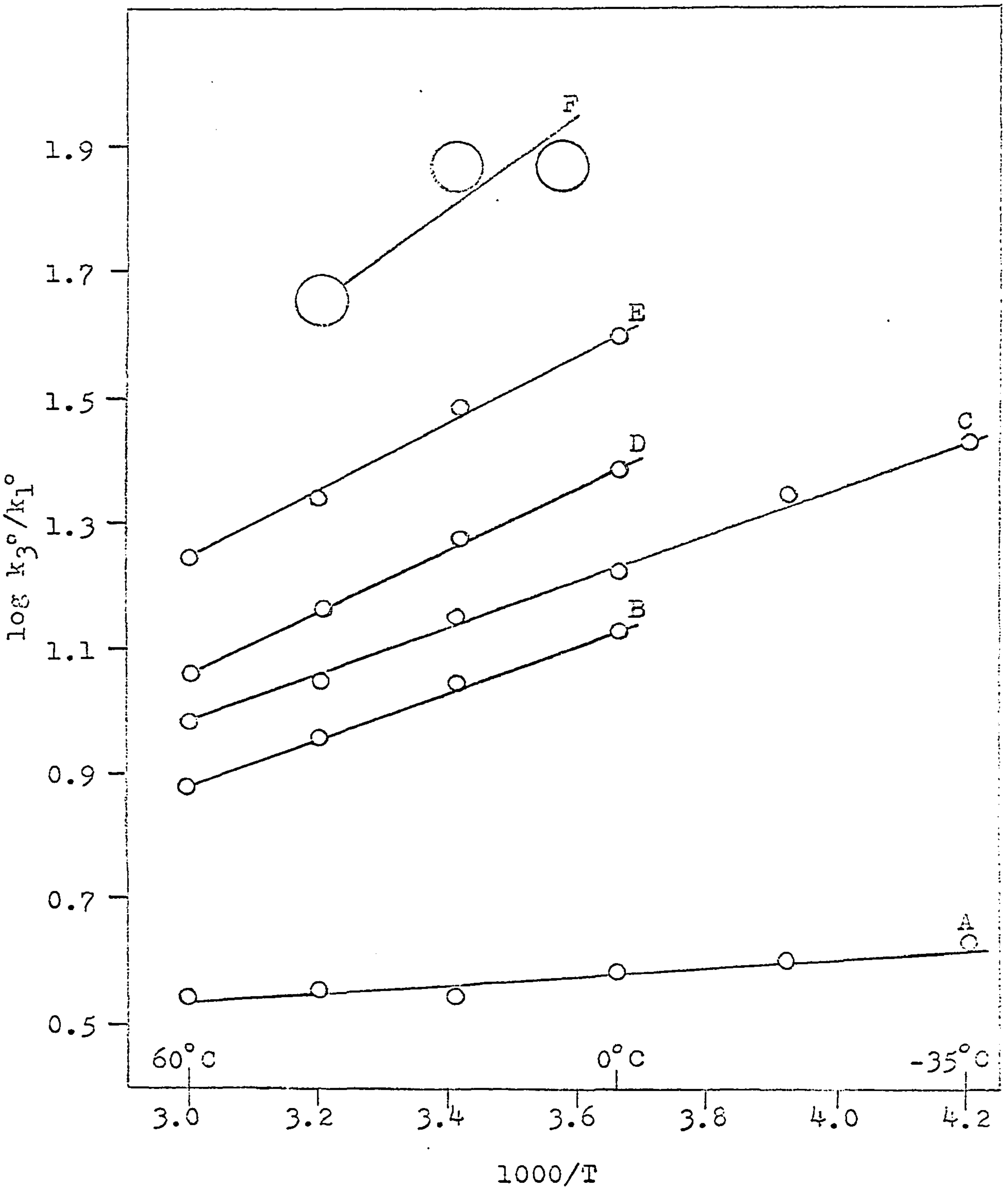
B. 4 M C_6H_6

C. 6 M C_6H_5F

D. 6 M C_6H_6

E. 8 M C_6H_6

F. 12 M CS_2


F
E
D
C
B
A
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
log k_3°/k_1°
60°C
0°C
-35°C
3.0
3.2
3.4
3.6
3.8
4.0
4.2
1000/T

These results are presented in Table 11 along with the entropy terms, log A_t/A_p and log A_s/A_p. The trends in (E_p-E_t)

Table 11. Activation parameters calculated from Figures 2 and 3

Solvent	E_p-E_t (Kcal.)	$\log \frac{A_t}{A_p}$	E_p-E_s (Kcal.)	$\log \frac{A_s}{A_p}$
Neat	0.33 ± 0.13	+0.32 ± 0.09	0.01 ± 0.01	+0.42 ± 0.01
C_6H_6 (4 M)	1.69 ± 0.26	-0.22 ± 0.17	0.80 ± 0.25	+0.03 ± 0.16
C_6H_5F (6 M)	1.73 ± 0.20	-0.16 ± 0.13	0.70 ± 0.10	+0.20 ± 0.09
C_6H_6 (6 M)	2.24 ± 0.30	-0.41 ± 0.15	1.09 ± 0.30	-0.06 ± 0.22
C_6H_6 (8 M)	2.45 ± 0.25	-0.37 ± 0.16	1.37 ± 0.22	-0.12 ± 0.17
CS_2 (12 M)	~3.2	----	~2	----

and (E_p-E_s) are presented schematically in Figure 4. It is apparent that the observed effects are consistant with the previously proposed mechanism of the action of complexing solvent on chlorine atom abstraction of hydrogen. The energy of activation for attack on a primary hydrogen increases in complexing solvents more rapidly than that on a secondary or tertiary hydrogen which results in the observed increase in

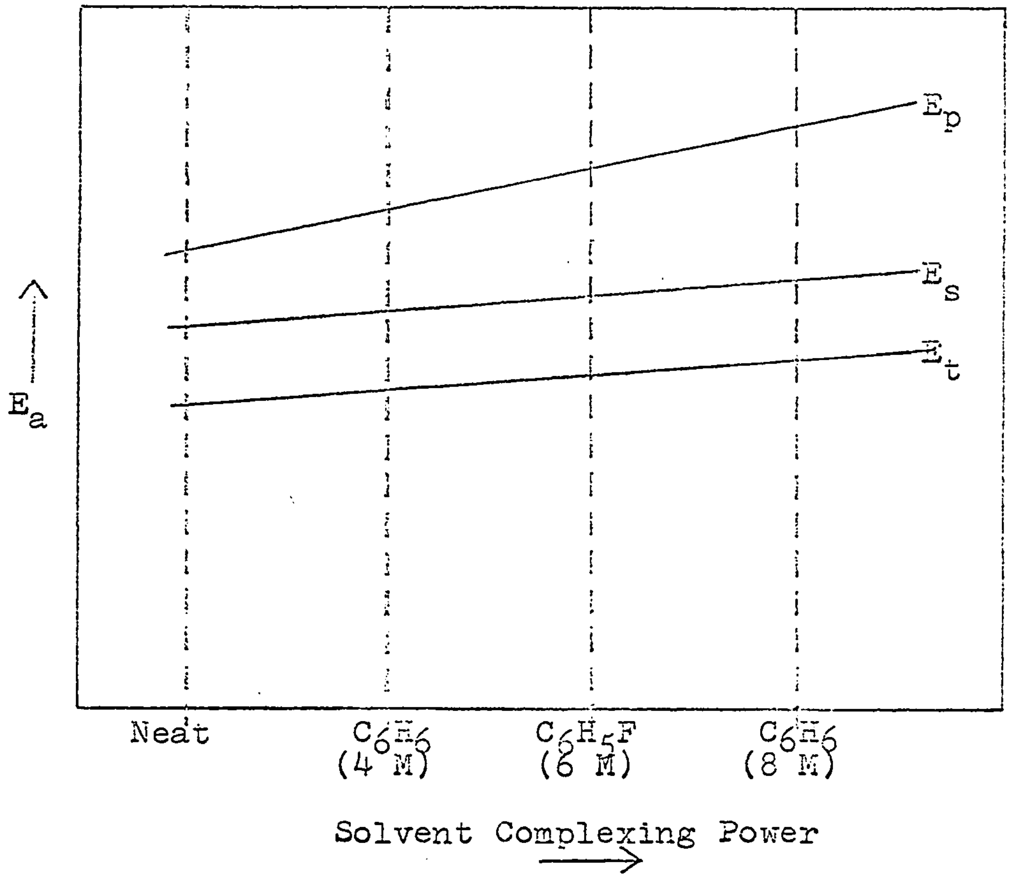


Figure 4. Schematic diagram of the trend in energy of activation with increasing complexing power of the solvent in the chlorination of 2,5-dimethylhexane

the selectivity of the chlorine atom. That the energy of activation for hydrogen abstraction increases in complexing solvents was indicated qualitatively by the slower rate of reaction of aromatic solutions. Solutions with aromatic solvents, especially 8 M benzene, tended to become yellow with unreacted chlorine if the chlorine was admitted too rapidly. Neat 2,5-dimethylhexane did not become yellow colored even at the fastest rate of addition of chlorine.

It would have been expected on the basis of the previous arguments that (E_s-E_t) should also have increased with the complexing ability of the solvent. However, this was not observed, and instead (E_s-E_t) was an almost constant 1 Kcal. in aromatic solvents. This is possibly due to the steric hindrance for attack on the tertiary hydrogens in complexing solvents which would increase the activation energy. Since the secondary hydrogens, if they are at all, are much less sterically hindered, this steric hindrance should decrease the difference between E_s and E_t. This apparently fortuitously results in the ca. 1 Kcal. constant difference in E_s and E_t in aromatic solvents.

Log A_t/A_p and log A_s/A_p for carbon disulfide solutions were not calculated because of the greater uncertainty in these results. Chlorinations of carbon disulfide solutions could not be carried out below 10°C because of the apparent insolubility of 2,5-dimethylhexane at lower temperatures. The trend in the difference in the entropy of activation as log A_t/A_p or log A_s/A_p follows in an inverse fashion the trend in (E_p-E_t) and (E_p-E_s). Often, though not always, the change in the enthalpy of activation is paralleled by a corresponding change in the entropy of activation with changes in solvent or some other variable in a reaction or a series of reactions. When the plot of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ or E_a versus log A is linear and the ranges in the enthalpies and entropies of activation are large compared to the experimental error, this is evidence that an isokinetic temperature, β, exists (28). At the

$$\Delta H^{\ddagger} = \beta \Delta S^{\ddagger} + \Delta H_o^{\ddagger}$$

isokinetic temperature changes in solvents would have no or little effect on the rate of reaction. This is observed in the case of t-butyl hypochlorite chlorinations where the isokinetic temperature is in the range of the temperatures studied (12). Although the range in log A in the chlorination of 2,5-dimethylhexane is not very large compared to the uncertainty, an isokinetic plot (Figure 5) gives a straight line, and thus this reaction appears to follow the isokinetic relation. The isokinetic temperature calculated from the slope of this plot is ca. 600°K.

Walling has recently suggested that the data for the chlorination of 2,3-dimethylbutane in 4 M chlorobenzene is not consistant with a simple charge-transfer interpretation of the solvent effect (12). He based his suggestion on (E_p-E_t) and

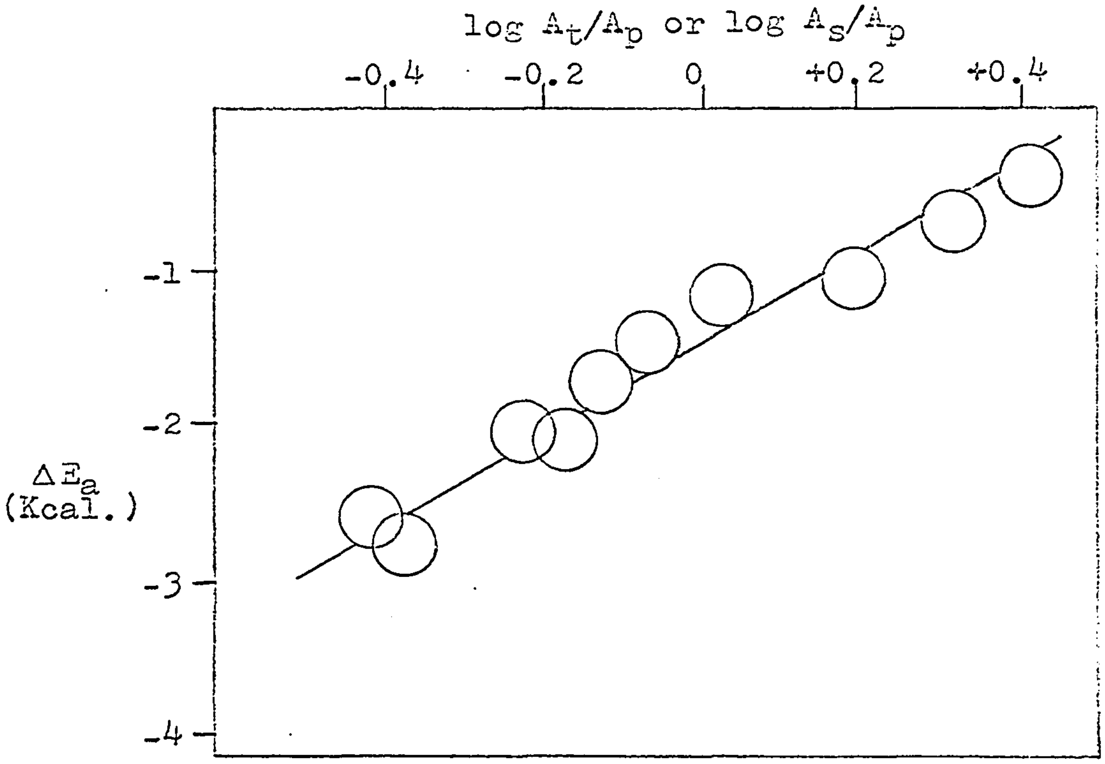


Figure 5. Isokinetic relationship in the effect of solvents on 3°/1° and 2°/1° ratios in the chlorination of 2,5-dimethylhexane

log A_t/A_p calculated from three points which have only a 30°C temperature range (7). It seems likely because of the small temperature range that a possible error in one of the three points could easily lead to an erroneous value of (E_p-E_t) and log A_t/A_p. An isokinetic plot is shown in Figure 6 for the chlorination of 2,3-dimethylbutane in four solvents. In particular the data on the chlorinations in 4 M chlorobenzene does not seem to fit. Although the data is insufficient to establish an isokinetic relationship, if the chlorination of 2,5-dimethylhexane exhibits such a relationship, then the chlorination of 2,3-dimethylbutane probably also does. Leffler has discussed the interpretation of isokinetic plots and suggests that deviation of a point from an established isokinetic plot indicates that that reaction has a different mechanism or a significantly different transition state (28). This is not likely in this case, and it probably indicates only that the values calculated for the energy and entropy of activation in 4 M chlorobenzene are not accurate.

An attempt was made to use bromobenzene and chlorobenzene as solvents in the present studies, but they proved unsatisfactory. Chlorobenzene has an identical retention time as 2,5-dimethyl-2-chlorohexane on all of the glpc columns tried, and bromobenzene was attacked by chlorine producing chlorobenzene. This latter reaction has been studied by Miller and Walling, and Walling and Wagner have reported that

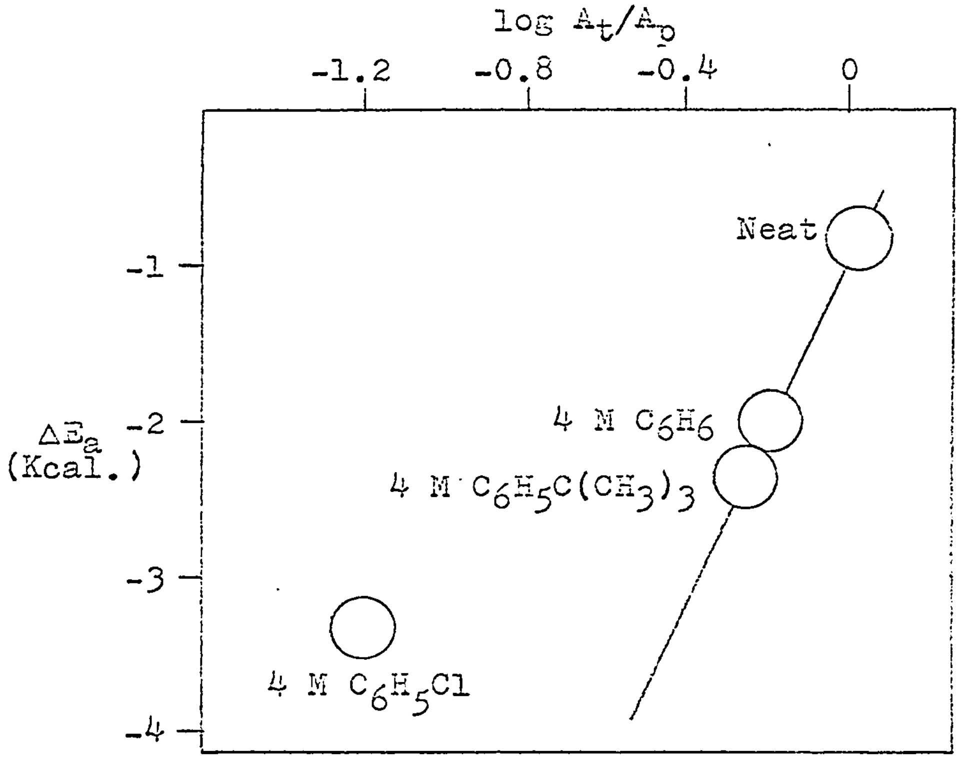


Figure 6. Isokinetic relationship in the effect of solvents on $3^\circ/1^\circ$ ratio in the chlorination of 2,3-dimethylbutane

chlorobenzene was produced in t-butyl hypochlorite chlorinations in bromobenzene (12, 29).

Effect of Solvent on the Photochlorination of Compounds Containing a Polar Group

The chlorine atom is a very electrophilic species. For this reason in molecules containing a polar group it preferentially attacks electron rich carbon-hydrogen bonds. All of the data in the literature can be correlated by a consideration of the electrophilic nature of the chlorine atom and the inductive electron withdrawing powers of the various polar groups (7). Complexing solvents have very little effect on the reactivity of carbon-hydrogen bonds near a polar group. This has been demonstrated by the chlorination of various halo alkanes and compounds containing sundry other polar groups (7, 10, 15, 24, 30). One would expect that the complexed chlorine atom would be less electrophilic than a "free" chlorine atom and should, therefore, be less subject to a polar effect. Perhaps because of the increased amount of bond-breaking and thus a transition state more like

$$\overset{\delta+}{R}\cdot H\overset{\delta-}{Cl}:,$$

the decreased electrophilic nature of the complexed chlorine atom is balanced by the increase in the polar character of the transition state. Whether or not this explanation is correct, the result is that the reactivity of the carbon-hydrogen bond near the polar group, but not α to the polar group, are not affected by complexing solvents. Complexing solvents do affect the reactivity of α-hydrogens. The possibility of resonance stabilization of the incipient radical α to a polar group has been demonstrated by both Russell and Tedder (7, 15, 24). However, the effect is not large due to the small extend of bond breaking in the transition state. Russell and Ito have recently published some results on the chlorination of chlorocyclohexane which illustrate both effects. The reactivity of the α-hydrogen of chlorocyclohexane compared to cyclohexane increased from 0.20:1.0 in carbon tetrachloride to 0.46:1.0 in carbon disulfide, while the relative reactivity of the β-hydrogens, 0.36:1.0, did not change with solvent (24).

Photochlorination of propionitrile and isobutyronitrile

Both propionitrile and isobutyronitrile were chlorinated to the extend of 10 mole percent or less, neat and in 8 M benzene over a range of temperatures. Propionitrile was also chlorinated in 12 M carbon disulfide. The identity of the glpc peaks was confirmed by a comparison of the retention times of authentic samples of the chloroalkyl nitriles. The composition of the monochlorides formed are given in Tables 12 and 13. The Arrhenius plots are illustrated in Figures 7 and 8. The results of the photochlorination of propionitrile are very similar to previously published results on

Table 12. Composition of monochlorides formed in the chlorination of propionitrile

Temperature (°C)	Chlorides (% of total monochlorides)		Relative Reactivity β/α
	α	β	
	<u>Neat</u>		
60	25.9	74.1	1.85 ± 0.06
	27.0	73.0	
40	24.9	75.1	2.01
	24.9	75.1	
20	24.0	76.0	2.10 ± 0.25
	21.4	78.6	
	26.8	73.2	
	<u>8 M Benzene</u>		
60	37.1	62.9	1.11 ± 0.02
	37.8	62.2	
40	36.2	63.8	1.17 ± 0.02
	36.5	63.5	
20	34.9	65.1	1.20 ± 0.05
	36.5	63.5	
	<u>12 M Carbon Disulfide</u>		
40	41.3	58.7	0.94 ± 0.02
	41.9	58.1	
20	40.3	59.7	1.05 ± 0.05
	39.2	60.8	
	37.2	62.8	
0	42.3	57.7	1.0 ± 0.1
	37.6	62.4	

Table 13. Composition of monochlorides formed in the chlorination of isobutyronitrile

Temperature (°C)	Chlorides (% of total monochlorides) α	β	Relative Reactivity α/β
	Neat[a]		
60	30.1	69.9	2.67 ± 0.07
	31.0	69.0	
	31.1	68.9	
40	27.4	72.6	2.40 ± 0.14
	30.2	69.8	
	28.7	71.3	
	27.7	72.3	
20	27.0	73.0	2.26 ± 0.04
	27.1	72.9	
	27.7	72.3	
0	22.4	77.6	1.74 ± 0.02
	22.8	77.2	
	8 M Benzene[b]		
60	51.9	48.1	6.58 ± 0.12
	52.1	47.9	
	52.9	47.1	
40	56.8	43.2	7.56 ± 0.30
	54.8	45.2	
20	58.0	42.0	8.56 ± 0.27
	59.6	40.4	

[a] $E_\beta - E_\alpha = -1.13$; $\log A_\alpha/A_\beta = +1.17$

[b] $E_\beta - E_\alpha = +1.28$; $\log A_\alpha/A_\beta = -0.02$

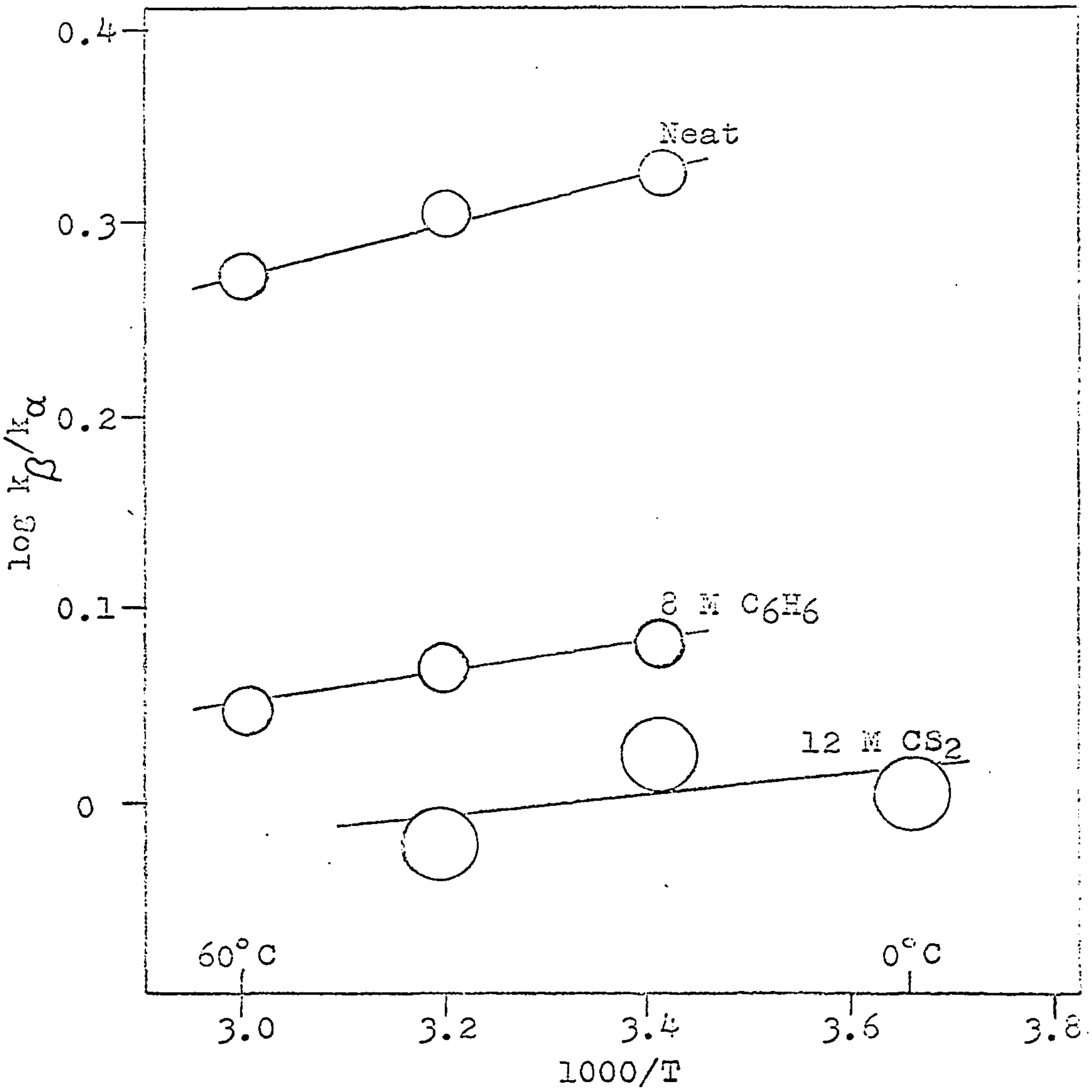


Figure 7. Arrhenius plot of the photochlorination of propionitrile

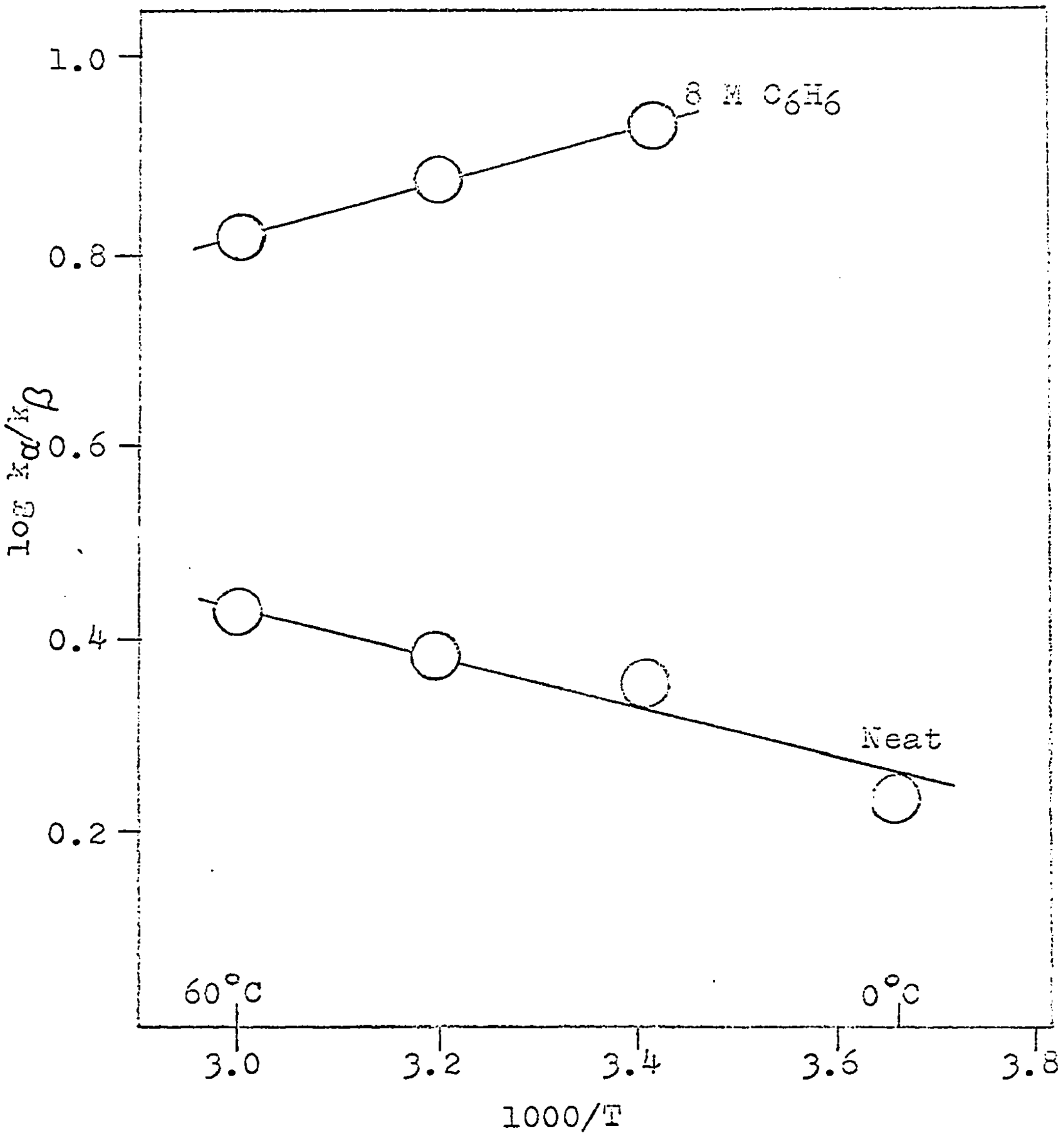


Figure 8. Arrhenius plot of the photochlorination of isobutyronitrile

other compounds (15, 24). The reactivity of the α-hydrogen changes only to a small extent with solvent. The β-hydrogen atom is more reactive by a factor of ca. 2 in neat propionitrile, and the α- and β-hydrogens are approximately equally reactive in 12 M carbon disulfide. The data on the photochlorination of isobutyronitrile, on the other hand, provides a more striking illustration of the possible importance of resonance stabilization on the reactivity of the carbon-hydrogen bond α to a polar group. Attack on the β-hydrogen is favored by an energy of activation of ca. 1 Kcal. in neat isobutyronitrile, but in 8 M benzene attack on the α-hydrogen is favored by ca. 1 Kcal. This is the first example in the literature where ΔE_a for attack on two different carbon-hydrogen bonds has reversed with solvents. These trends in energy of activation are illustrated in Figure 9. The assumption has been made that the primary hydrogens of propionitrile and isobutyronitrile have approximately equal reactivity in order to put both results in one figure. That this is a reasonable assumption is demonstrated by the similarity of the reactivities of the primary hydrogens of various compounds given earlier in this thesis. The illustration as drawn indicates that the energy of activation for attack on a secondary hydrogen α to a cyano group is less than that on a tertiary hydrogen α to a cyano group. These are the actual average values observed and would seem to discredit the previous assumption since this would not be the expected order.

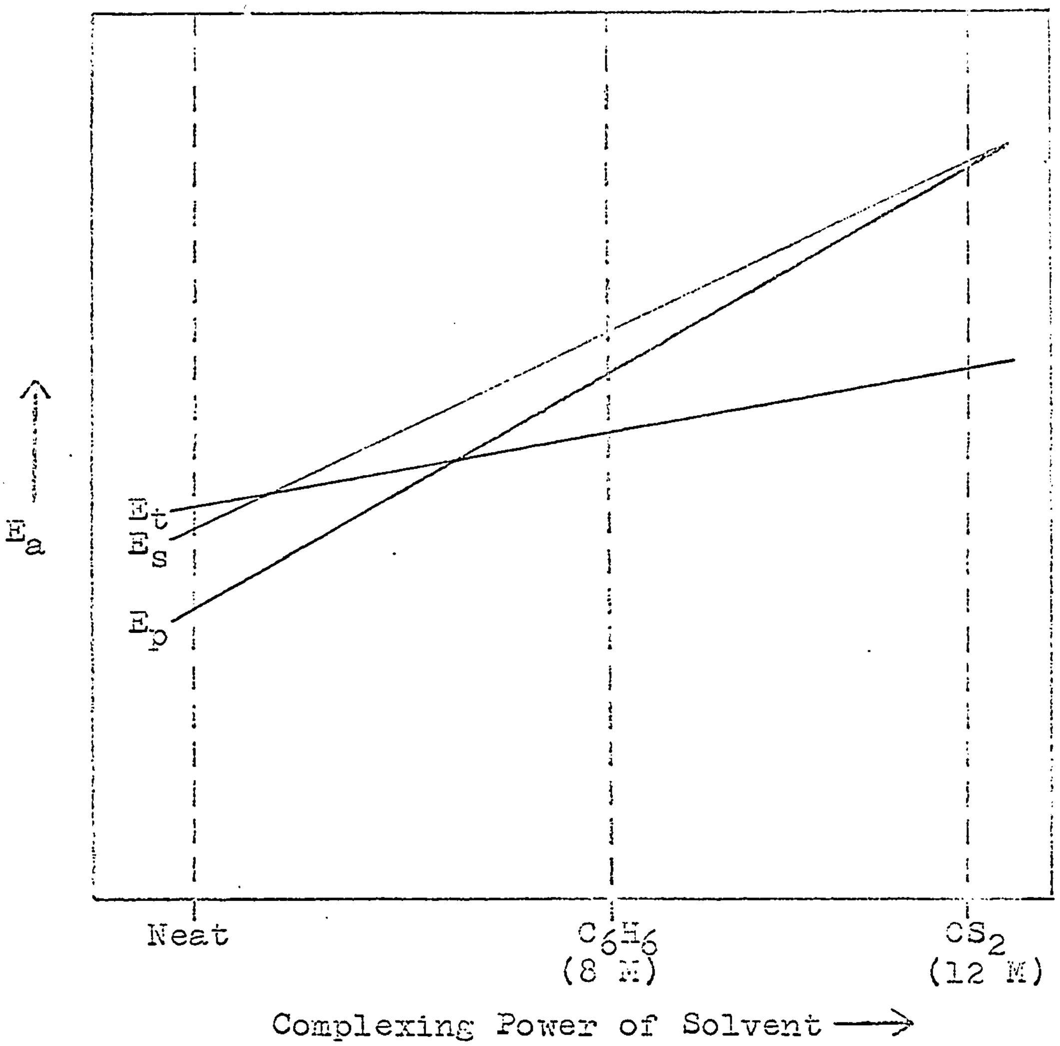
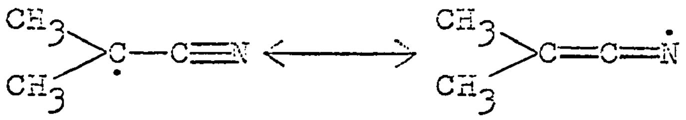


Figure 9. Schematic diagram of the trend in energy of activation with increasing complexing power of the solvent on the chlorination of propionitrile and isobutyronitrile

However, the uncertainty in these results is sufficient that these two energies of activation are approximately equal and their relative order then could easily be the reverse of that shown. The increase in reactivity of the α-hydrogens in complexing solvent is most probably due to the greater extent of bond breaking in the transition state in complexing solvents which would increase the importance of resonance in the stabilization of the transition state:



The inductive and hyperconjugative contributions of the methyl group undoubtably are also important. This is illustrated by the greater increase in selectivity of isobutyronitrile (factor of 3.2) compared with propionitrile (factor of 1.8) on going from neat to 8 M benzene solution.

A very interesting feature of the chlorination of isobutyronitrile is the control exerted by the difference in the entropy of activation. Although attack on the β-carbon-hydrogen is favored by ca. 1 Kcal. in neat isobutyronitrile, the α-carbon-hydrogen bond is 2.4 times as reactive at 40°C due to a log A_α/A_β of ca. 1.2. When the chlorination was carried out in 8 M benzene the relative reactivity, k_α/k_β, increased by a factor of three due to the energy of activation now favoring attack on the α-carbon-hydrogen bond by ca. 1 Kcal. Log A_α/A_β in 8 M benzene is approximately zero.

It has been assumed by current theories that differences in activation energy are the principle reason for the different reactivities of various carbon-hydrogen bonds toward halogen atoms (23). These present results point out that entropies of activation can be important and should not be neglected in any consideration of the reactivities of carbon-hydrogen bonds. Entropy also has a noticeable effect on the competitive photochlorination of toluene and α-chlorotoluene.

Photochlorination of toluene and α-chlorotoluene

Solutions of α-chlorotoluene and toluene in carbon tetrachloride (2.2 M total aromatic concentration) and 7.3 M chlorobenzene (9.5 M total aromatic concentration) were competitively chlorinated at 60° C, 40° C, and 20° C. The relative reactivities were calculated by measuring the disappearance of the two reactants and are presented in Table 14. The Arrhenius plots are illustrated in Figure 10. $E_{\phi CH_2Cl}-E_{\phi CH_3}$ increased from ca. 0 Kcal. to ca. 2 Kcal. in 9.5 M aromatic solution while the relative reactivity, $k_{\phi CH_3}/k_{\phi CH_2Cl}$, at 40° C actually decreased 30% from 10.3 to 6.9. Once again the importance of entropy is emphasized.

It was thought at first that the comparison of toluene and α-chlorotoluene would be like a comparison of methane and methyl chloride since the phenyl ring is common to both. However, this is not so since that would predict that $E_{\phi CH_2Cl}-E_{\phi CH_3}$ should decrease in complexing solvents. A

Table 14. Competitive photochlorination of α-chlorotoluene with toluene

Temperature (°C)	α-Chlorotoluene, M		Toluene, M		$\frac{k_{toluene}}{k_{\alpha\text{-chlorotoluene}}}$
	Initial	Final	Initial	Final	
		Carbon Tetrachloride			
60	2.056	1.907	0.101	0.049	10.0
	2.050	1.951	0.101	0.061	10.9
	2.048	1.964	0.101	0.064	10.9
				Average	10.6 ± 0.3
40	2.040	1.942	0.103	0.063	10.3
	2.056	1.917	0.101	0.050	10.3
				Average	10.3
20	2.036	1.967	0.106	0.074	10.3
	2.052	1.881	0.106	0.042	11.1
				Average	10.7 ± 0.4
		7.3 M Chlorobenzene			
60	2.037	1.876	0.0995	0.0617	5.8
	2.038	1.875	0.0995	0.0600	6.1
				Average	6.0 ± 0.2
40	2.034	1.915	0.0995	0.0672	6.6
	2.033	1.916	0.1045	0.0692	7.1
				Average	6.9 ± 0.3
20					
20	2.049	1.846	0.1045	0.0363	10.0
	2.048	1.083	0.1045	0.0357	8.4
				Average	9.2 ± 0.8

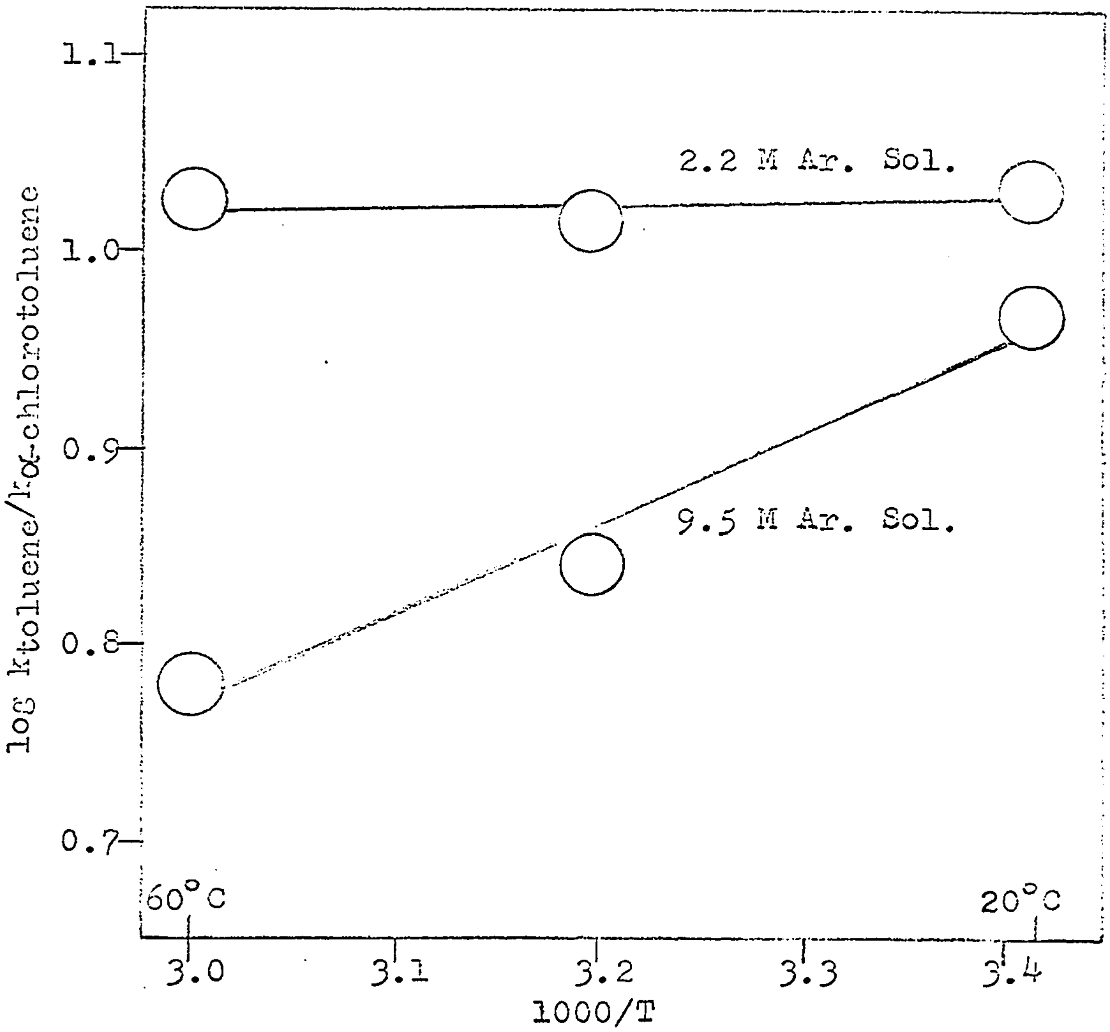
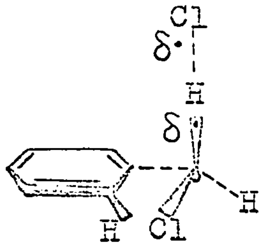
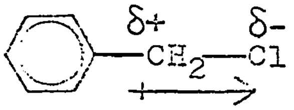


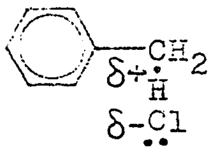
Figure 10. Arrhenius plot of the competitive photochlorination of toluene and α-chlorotoluene

possible explanation is that the phenyl rings do not have an equal opportunity to interact in the transition state. Russell, Ito, and Hendry have observed that complexing solvents do not activate the series--toluene, ethylbenzene, and cumene--in a constant manner. The explanation was offered that possible steric hindrance decreased the activation in cumene and ethylbenzene compared to toluene (14). It is apparent from the figure below that the developing radical center which is becoming sp^2 forces the Cl into the plane of the benzene ring and thus causes some interaction with the ring hydrogens which might cause the radical center to tilt slightly out of the plane of the benzene ring. The net effect would be a less effective interaction of the phenyl ring and the radical center. Since the resonance interaction due to the phenyl ring is much more important than that of the chlorine atom and it is not equal in the two compounds, complexing solvents might be expected to increase $E_{\phi CH_2Cl}-E_{\phi CH_3}$. Even though $E_{\phi CH_2Cl}-E_{\phi CH_3}$ does increase in 7.3 M chlorobenzene, the relative reactivity, $k_{\phi CH_3}/k_{\phi CH_2Cl}$ decreases by 30%.



A possible rationalization for this entropy effect is as follows: Solvation by chlorobenzene in the ground and transition state of α-chlorotoluene should be similar due to the dipole already present in the molecule. Solvation of the toluene by chlorobenzene, however, should be more ordered in the transition state than in the ground state due to the polar nature of the transition state in complexing solvent and the relatively little dipole in the ground state. This would





result in a greater increase in entropy upon going from the ground to transition state for toluene and for α-chlorotoluene in 7.3 M chlorobenzene where the resonance interaction is important.

These results demonstrate that relative reactivities alone are not always sufficient for an understanding of what is occurring in the transition state of free radical halogenations.

Photochlorination of Adamantane

Applequist and Kaplan have performed a series of experiments designed to measure the relative stability of alkyl radicals. Their results indicate that the tertiary adamantane radical is more stable than the tert-butyl radical (31). They suggested that the extra stabilization of the adamantyl radical relative to t-butyl might be just inductive or perhaps a special type of delocalization. A special delocalization by overlap in the interior of the adamantane molecule of a p orbital and the backside of the sp^3 tertiary orbitals has been postulated by several workers to explain both the p.m.r. spectra of adamantyl ion and the fine structure in the e.s.r. spectrum of the adamantane radical anion (32). However, the latter result has been disproven by M. T. Jones, who demonstrated that an identical e.s.r. spectrum could be obtained from the benzene radical anion (33). Benzene is a common impurity in adamantane which is difficult to completely remove. Jones showed that the amount of benzene impurity present in adamantane is sufficient to have produced the observed spectrum.

On the basis of these results adamantane was investigated to determine if the tertiary hydrogens were unusually reactive toward chlorine atoms. It was hoped that if there were any extra stabilization of the incipient tertiary radical compared to a normal tertiary radical it would manifest itself, especially in complexing solvents, by increased reactivity. Smith and Williams have demonstrated that the selectivity of the tertiary hydrogens compared to the secondary hydrogens of adamantane are affected by solvent (34). Unfortunately they did not give the concentration of the complexing solvents that they used, and the results in carbon tetrachloride were complicated by polychlorination.

Adamantane was photochlorinated at 40°C in carbon tetrachloride, 4 M benzene, and 12 M carbon disulfide to the extent of 10 mole percent or less. The composition of the monochlorides formed were analyzed by glpc and are presented in Table 15. The two chloroadamantanes were collected by preparative glpc and identified by p.m.r. The first peak was assigned to 1-chloroadamantane on the basis of the following p.m.r. spectrum: two broad singlets at 1.7δ and 2.1δ with a relative area of 2:3. The second peak was then assigned to 2-chloroadamantane on the basis of the following p.m.r.

Table 15. Composition of monochlorides formed in the chlorination of adamantane at 40°C

Solvent	Chlorides (% of total monochlorides)		Relative Reactivity $3^\circ/2^\circ$
	Tertiary	Secondary	
CCl_4	43.6 42.7 42.3 39.8	56.4 57.3 57.7 60.2	2.20 ± 0.16
4 M C_6H_6	53.0 52.8 53.5	47.0 47.2 46.5	3.38 ± 0.05
12 M CS_2	62.2 61.9 61.4 62.0	37.8 38.1 38.6 38.0	4.87 ± 0.07

spectrum: a complex hash from 1.3δ to 2.3δ with a relative area of 14 and a complex multiplet from 4.0δ to 4.2δ with a relative area of one. Adamantane was also chlorinated competitively with cyclohexane. These results are in Table 16.

Table 16. Competitive photochlorination of adamantane with cyclohexane

Solvent	Adamantane, M		Cyclohexane, M		$\frac{k_{adamantane}}{k_{cyclohexane}}$
	Initial	Final	Initial	Final	
CCl_4	0.447	0.316	0.534	0.386	1.07
	0.447	0.346	0.534	0.417	1.04
	0.447	0.328	0.534	0.416	1.25
				Average	1.12 ± 0.08
4 M C_6H_6	0.446	0.246	1.131	0.896	2.54
	0.446	0.310	1.131	0.972	2.40
	0.446	0.348	1.131	1.009	1.68
				Average	2.21 ± 0.35
12 M CS_2	0.445	0.3385	1.869	1.755	4.44
	0.445	0.3530	1.869	1.703	2.56
	0.445	0.3645	1.869	1.748	3.00
	0.445	0.3175	1.869	1.742	4.94
				Average	3.74 ± 0.95

The data in Tables 15 and 16 were combined to produce Table 17. It is clear from the data in Table 17, which compares the reactivity of the secondary and tertiary hydrogens of adamantane to cyclohexane and "normal" 3°/2° ratios, that the tertiary hydrogens have completely normal reactivities and exhibit no unusual stabilization in free radical chlorinations.

Table 17. Relative reactivities of the hydrogen atoms of adamantane compared to cyclohexane

Solvent	$\frac{2^\circ\text{-Adamantane}}{\text{Cyclohexane}}$	$\frac{3^\circ\text{-Adamantane}}{\text{Cyclohexane}}$	$\frac{3^\circ}{2^\circ}$ "Normal"
CCl_4	0.65 ± 0.07	1.43 ± 0.27	1.5-2.0
4 M C_6H_6	1.04 ± 0.17	3.52 ± 0.63	3.0-4.0
12 M CS_2	1.42 ± 0.37	6.94 ± 1.9	~10

The secondary hydrogens also have normal reactivities except in carbon tetrachloride solutions where they appear to be slightly less reactive than normal. It is interesting to note that a relative reactivity of 0.66 is predicted for the ratio 2°-adamantane/cyclohexane, if it is assumed that either the axial or equatorial hydrogens of cyclohexane are twice as reactive toward chlorine atoms as the other and that the secondary hydrogens of adamantane resemble the less reactive hydrogens. However, this calculation is probably fortuitous since the secondary hydrogens have normal reactivities in 4 M benzene and 12 M carbon disulfide.

EXPERIMENTAL

Apparatus and Procedure

The apparatus used for the chlorination of methylpentanes has been described by Ito (35). The modified apparatus used for the temperature studies of the chlorination of 2,5-dimethylhexane is shown schematically in Figure 11. Before the reaction was started, chlorine gas was condensed in the liquid chlorine reservoir by use of a dry ice-acetone bath. Then the material to be chlorinated was placed in the jacketed reaction flask under an ice water or dry ice and carbon tetrachloride condenser and degassed with pre-purified nitrogen, which was introduced into the system through a drying tube containing glass beads coated with phosphorous pentoxide. The jacketed reaction flask was connected by Tygon tubing to a Haake circulator and temperature regulator which maintained the various temperatures from 0°C to 60°C within ± 0.05°C. Lower temperatures were obtained by passing a coolant liquid, ethanol, through a copper coil immersed in dry ice-carbon tetrachloride bath (-19°C) or a dry ice-chlorobenzene bath (-35°C). After the solution had been degassed and the correct temperature obtained, the dry ice-acetone bath was lowered and a measured amount of chlorine was allowed to vaporize and pass through a capillary tip near the bottom of the reaction flask. The reaction was illuminated with a 200 watt unfrosted tungstem lightbulb placed approximately 4 cm.

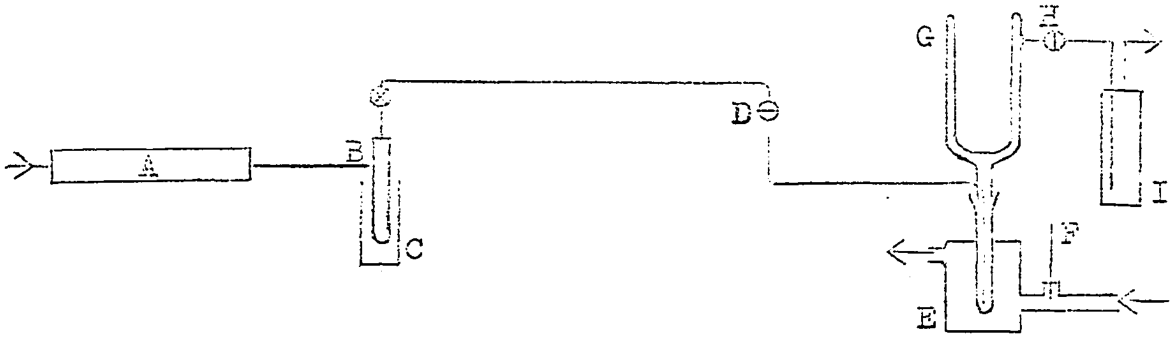


Figure 11. Photochlorination apparatus

A: drying tube

B: calibrated glass tube with tapered joint and Teflon stopcock

C: dry ice-acetone bath

D: spherical joints

E: jacketed reaction flask with a tapered joint

F: thermometer

G: condenser

H: spherical joints

I: gas trap (10% KOH)

from the reaction flask. After the reaction was complete, the solution was degassed to remove the hydrogen chloride which was subsequently trapped in a 10% potassium hydroxide solution.

Analytical Procedure

The alkanes anc chloroalkanes were analyzed by gas-liquid chromatography in an instrument using a hot wire thermal conductivity gauge. Chloropentanes and chlorohexanes were analyzed at 50°C using a 100 m. x 1/16 in. i.d. copper Golay column coated with polyproplyene glycol. The α- and β-chloroisobutyronitriles as well as the α- and β-chloropropionitriles were analyzed on a 1 m. decyl pthalate column with the temperature programmed from 70°C to 150°C. The 1- and 2-chloroadamantanes were analyzed at 160°C on a 5 ft. SF96 column. The isomeric halides were assumed to have equal reactivity with the thermal conductivity dector, and this was verified in the case of the α- and β-chloroisobutyronitriles.

The conditions for the analysis of the competitive chlorinations are given in Table 18. All of the competitive chlorinations such as 2,5-dimethylhexane versus cyclohexane were determined by measuring the disappearance of the two reactants.

Table 18. Conditions for the analysis of competitive chlorinations

Reactants	Temperature	Column
2,4-Dimethylpentane vs. cyclohexane	70° C	4.2 m. polyphenyl ether
2,2,4-Trimethylpentane vs. cyclohexane	50° C	4.2 m. polyphenyl ether
2,2,4,4-Tetramethylpentane vs. cyclohexane	90° C	4.2 m. polyphenyl ether
2,5-Dimethylhexane vs. cyclohexane	50° C	2 m. di-2-ethylhexyl-sebacate + 1 m. polypropylene glycol
Toluene vs. α-chlorotoluene	75° C	1 m. SF96
Adamantane vs. cyclohexane	programmed 60° C-180° C	3.1 m. polypropylene glycol

Reagents

The 99 mole percent 2,4-dimethyl- and 2,2,4-trimethylpentane obtained from Phillips 66 and the National Bureau of Standards 99.9 mole percent 2,2,4,4-tetramethylpentane were used without further purification. Isobutyronitrile (Eastman Kodak Co., practical grade) and α-chlorotoluene (Matheson, Coleman, and Bell) were distilled through a Vigreux column prior to chlorination. The 2,5-dimethylhexane (Columbia Organic Chemical Co.) and Eastman spectro grade cyclohexane were used without further purification. Adamantane was obtained from Gallard-Schlesinger Chemical Corp. The solvents carbon disulphide (Mallinckrodt), carbon tetrachloride (Matheson, Coleman, and Bell), fluorobenzene (Pierce Chemical Co.), and benzene (J. T. Baker Chemical Co.), were passed through silica gel and stored over Molecular Sieves. Toluene (Matheson, Coleman, and Bell) and propionitrile (Eastman Organic) were used without further purification. The 3-chloropropionitrile was obtained from Eastman Organic.

Synthesis of Haloalkanes

2,4,4-Trimethyl-1-chloropentane

Hydroboration of 2,4,4-trimethyl-1-pentene according to the procedure of H. C. Brown (36), and subsequent oxidation with hydrogen peroxide and sodium hydride produced 2,4,4-trimethyl-1-pentanol. After preliminary purification, the crude alcohol was dissolved in dry ether and a slight excess of thionyl chloride was added. The mixture was stirred for several hours and then refluxed on a steam bath for one hour. Water was added to destroy excess thionyl chloride, and then the ether layer was separated and dried. The resulting chloro compound had a retention time identical to the third peak of the halopentanes prepared by photochlorination of 2,2,4-trimethylpentane.

2,4,4-Trimethyl-2-chloropentane

This compound was prepared by the addition of hydrogen chloride gas at 0°C to neat 2,4,4-trimethyl-1-pentene. The reaction was essentially quantitative according to analysis by glpc.

2,4-Dimethyl-1-chloropentane

The 2,4-dimethyl-1-pentanol from K & K Laboratories was purified by distillation and reacted neat with thionyl chloride. Water was added to destroy excess thionyl chloride, and the organic layer was separated and dried. Analysis by glpc showed only some starting material and a peak with identical retention time to the third peak of the halopentanes prepared by photochlorination of 2,4-dimethylpentane.

2,4-Dimethyl-2-chloropentane

Addition of hydrogen chloride to 2,4-dimethyl-2-pentanol produced the chloropentane in greater than 95% yield by glpc analysis.

2,5-Dimethyl-2-chlorohexane

Addition of hydrogen chloride to 2,5-dimethyl-2-hexanol from K & K Laboratories at 0°C produced the chlorohexane in greater than 95% yield. The p.m.r. spectrum (which consisted of a doublet at 0.95δ with a relative area of six and a singlet which overlaped with a broad multiplet at 1.55δ with a combined relative area of eleven) was consistant with the structure of 2,5-dimethyl-2-chlorohexane. This compound had an identical glpc retention time as the first peak of the halohexanes prepared by photochlorination of 2,5-dimethylhexane.

2,5-Dimethyl-3-chlorohexane

Several attempts were made without success to make pure 2,5-dimethyl-3-chlorohexane from 2,5-dimethyl-3-hexanol purchased from K & K Laboratories. Thionyl chloride and the neat alcohol, the alcohol in ether, or the alcohol in pyridine produced a mixture of two compounds. Since the glpc retention times of the two components of the mixture were identical with the first two peaks from the chlorination of 2,5-dimethylhexane and the first peak was identified as due to 2,5-dimethyl-2-chlorohexane, the second component and the second glpc peak were presumably 2,5-dimethyl-3-chlorohexane.

2,5-Dimethyl-1-chlorohexane

Since 2,5-dimethyl-3-chlorohexane could not be obtained in a pure state for positive identification of the second glpc peak, the third glpc, which was sufficiently distant from the other two peaks (relative glpc retention times = 1.0:1.08:1.64), was collected by preparative glpc and identified by a p.m.r. spectrum as 2,5-dimethyl-1-chlorohexane. The p.m.r. spectrum consisted of a doublet at 3.4δ and a hash from 0.95δ to 1.5δ. Since the signal at 3.4δ was a doublet and not a more complex multiplet, the compound was identified as the 1-chloro- and not the 2-chlorohexane.

β-Chloroisobutyronitrile

This compound was prepared by the method given by Colongo and Guyot (37). Hydrogen chloride was added to an ether solution of methacrylonitrile until saturated and was allowed to stand overnight. Distillation resulted in the isolation of 99% pure β-chloroisobutyronitrile, b.p. 175°C. The p.m.r. spectrum, a doublet at 3.65δ with relative area two, a sextet at 3.05δ with relative area one, and a doublet at 1.40δ with relative area three, was consistant with the structure of β-chloroisobutyronitrile.

α-Chloroisobutyronitrile

Spinning band distillation of the mixture resulting from the photochlorination of isobutyronitrile in benzene resulted in 99% pure α-chloroisobutyronitrile, b.p. 114-115°C, literature b.p. 114-116°C (38). The p.m.r. spectrum, a singlet at 1.95δ, was consistant with the structure of α-chloroisobutyronitrile.

SUMMARY

The series of methylpentanes--2,4-dimethylpentane, 2,2,4-trimethylpentane, and 2,2,4,4-tetramethylpentane--were chlorinated in carbon tetrachloride, 4 M benzene, and 12 M carbon disulfide solutions. The composition of the monochlorides formed were determined by gas-liquid partition chromatography (glpc). The reactivity of the tertiary carbon-hydrogen bonds was abnormally low especially in complexing solvents. This was interpreted as being due to steric hindrance. The increased importance of the steric hindrance when the chlorine atom is complexed with benzene or carbon disulfide was attributed to either the lowered reactivity of the chlorine atom (requiring closer approach to the carbon-hydrogen bond) or to the increased bulk of the complex.

Temperature studies on the reactivity of the various carbon-hydrogen bonds in 2,5-dimethylhexane were carried out in several solvents. It was found that there was a larger spread in the energies of activation for attack by a chlorine atom on the various kinds of carbon-hydrogen bonds in the solvents in which the chlorinations were more selective. These results are consistant with the formation of a complex between the chlorine atom and an aromatic ring which results in a less reactive and, thereby, a more selective chlorine atom as previously postulated by G. A. Russell (6, 7).

Propionitrile and isobutyronitrile were chlorinated over a temperature range, neat and in 8 M benzene. When chlorinated neat, the β-carbon-hydrogen bond had a lower energy of activation for attack by a chlorine atom than the α-carbon-hydrogen bond due to the polar effect of the electron-withdrawing cyano group. In the case of propionitrile in 8 M benzene the difference in energy of activation was decreased but still favored attack on the β-carbon-hydrogen bond. However, in the case of isobutyronitrile changing from no solvent to a 8 M benzene solution effected a reversal in ΔE_a and the energy of activation favored attack on the α-carbon-hydrogen bond by ca. 1 Kcal. These results were attributed to increased bond breaking in the transition state in 8 *M* benzene, which increased the importance of the resonance contribution of the cyano group on the incipient radical and thus lowered the energy of activation. Even though the energy of activation in neat isobutyronitrile favored attack on the β-carbon-hydrogen bond by ca. 1 Kcal., the α-carbon-hydrogen bond was preferentially attacked by a factor of ca. 2.5.

The possible importance of entropy of activation was again emphasized by the results of the competitive chlorination of α-chlorotoluene and toluene. Toluene carbon-hydrogen bonds were more reactive than the α-chlorotoluene carbon-hydrogen bonds by a factor of ca. 10 in ~2 M aromatic solutions, while in ~9 M aromatic solution they were more reactive by only a factor of ca. 7 despite the fact that ΔE_a changed from ca. 0 Kcal. to ca. 2 Kcal. in favor of attack on toluene.

Finally, adamantane was chlorinated in carbon tetrachloride, 4 M benzene, and 12 M carbon disulfide to determine if the tertiary carbon-hydrogen bonds were unusually reactive towards chlorine atoms. The carbon-hydrogen bonds of adamantane had normal reactivities.

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ACKNOWLEDGMENTS

The author wishes to express appreciation to Dr. G. A. Russell for the suggestion of this problem and his helpful comments during the course of this investigation. The author also extends sincere thanks to his wife, who typed this thesis.