

THE LIQUID-PHASE PHOTOCHEMICAL HALOGENATION  
OF ISOBUTANE AND ITS MONOHALO DERIVATIVES

By

PREM SAGAR JUNEJA

Bachelor of Science

Panjab University, Chandigarh

Panjab, India

1959

Submitted to the Faculty of the Graduate College of  
the Oklahoma State University  
in partial fulfillment of the requirements  
for the degree of  
DOCTOR OF PHILOSOPHY  
May, 1967

JAN 10 1968

THE LIQUID-PHASE PHOTOCHEMICAL HALOGENATION  
OF ISOBUTANE AND ITS MONOHALO DERIVATIVES

Thesis Approved:

*Ernest M. Rodnitz*

Thesis Adviser

*John E. Moore*

*O. Stewart Haver*

*E. J. Eisenbaum*

*D. D. Durham*

Dean of the Graduate School

658877

## ACKNOWLEDGMENTS

I wish to express my gratitude to Professor E. M. Hodnett, research adviser, for his invaluable guidance, patience and confidence in the author which provided all the inspiration needed during the course of my graduate work and the preparation of this thesis. Grateful acknowledgment is made to Dr. O. C. Dermer, for suggestions and reading the manuscript; to Dr. S. E. Schepple for his criticism and helpful discussions. Thanks are also due to Dr. Rex L. Elmore, a former colleague, for his help in the early stages of my graduate work; to Miss Olamay Chen, without whose help the storage of tritiated isobutane would have been quite inconvenient.

Acknowledgment is made to the U. S. Atomic Energy Commission (Contract No. AT (11-1)-1049), the Chemistry Department, Research Foundation and the Graduate College, all of Oklahoma State University, for financial support.

Finally, I wish to thank Bhabha Atomic Research Center, Trombay, (formerly A.E.E.T.), Bombay (Government of India) for the study leave granted to the author.

## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION . . . . .	1
II. HISTORICAL . . . . .	2
III. INTRODUCTION OF THE EXPERIMENTAL WORK . . . . .	23
Objectives and Plan of the Study . . . . .	23
Kinetics of Chlorination of 2-methylpropane-2- <u>t</u> . . . . .	26
Assay for Tritium . . . . .	32
IV. EXPERIMENTAL . . . . .	34
Materials . . . . .	34
Identification of Products . . . . .	34
General Procedure of Halogenation . . . . .	35
Product Analysis in the Chlorination of Isobutyl Chloride . . . . .	36
Preparative-scale Chlorination of Isobutyl Chloride . . . . .	36
Quantitative vpc Analysis of Products in Competitive Chlorinations . . . . .	37
Preparation of 1,2-Dichloro-2-methylpropane via Addition of Chlorine to Isobutylene . . . . .	38
Preparation of 1-Chloro-2-Bromo-2-methylpropane Peroxide-Catalyzed Addition of Hydrogen Bromide to Methallyl Chloride . . . . .	39
Addition of Bromine to Isobutylene in the Dark . . . . .	40
Chlorination of <u>tert</u> -Butyl Bromide . . . . .	40
Chlorination of Isobutyl Bromide . . . . .	41
Bromination of <u>tert</u> -Butyl Chloride . . . . .	41
Bromination of Isobutyl Chloride . . . . .	42
Preparation of 2-Methylpropane-2- <u>t</u> . . . . .	42
Assay of Isobutane- <u>t</u> . . . . .	45
Reference Compound for Measuring Activity of Isobutyl Chloride . . . . .	46
Preparation of Tritiated Isocrotyl Chloride . . . . .	47
Specific Radioactivity of Isocrotyl Chloride . . . . .	48
Tritium Assay of the Reaction Products . . . . .	51
Photochlorination of 2-Methylpropane-2- <u>t</u> . . . . .	53
Specific Radioactivity of Hydrogen Chloride . . . . .	55

Chapter	Page
IV. RESULTS AND DISCUSSION . . . . .	58
BIBLIOGRAPHY . . . . .	91

LIST OF TABLES

Table	Page
I. Relative Reactivities of C-H Bonds in Saturated Hydrocarbons toward Chlorine Atoms . . . . .	4
II. Vpc Retention Times and nmr Data for the Chloro Bromo Derivatives of Isobutane . . . . .	43
III. Initial Specific Radioactivity of Isobutane and Isocrotyl Chloride . . . . .	50
IV. Vapor Pressures of Some Compounds at Different Temperatures . . . . .	57
V. Relative Reactivities of Tertiary and Primary Hydrogen Atoms of 2-Methylpropane at 24° . . . . .	59
VI. Ratio of Reactivities of Tertiary and Primary Hydrogen Atoms in Some Hydrocarbons . . . . .	60
VII. Relative Reactivities of Hydrogen Atoms in the Chlorination of Isobutyl Chloride in CCl <sub>4</sub> at 24° . . . . .	62
VIII. Chlorination of Isobutyl Chloride in Carbon Tetrachloride at -15±0.5° . . . . .	63
IX. Competitive Chlorination of Isobutane and Isobutyl Chloride . . . . .	64
X. Competitive Chlorination of Isobutane and <u>tert</u> -Butyl Chloride . . . . .	68
XI. Solvent Effects in the Photochlorination of Isobutyl Chloride . . . . .	70
XII. Solvent Effects in the Competitive Photochlorination of Isobutyl Chloride and <u>tert</u> -Butyl Chloride . . . . .	71
XIII. Final Specific Radioactivity of Isobutane (E106A', E106B) . . . . .	81
XIV. Final Specific Radioactivity of Isobutane and Isobutyl Chloride (E106C) . . . . .	82

Table	Page
XV. Final Specific Radioactivity of Isobutane, Runs E107A and E107B . . . . .	85
XVI. Reactants Used in the Chlorination of 2-Methylpropane-2- <u>t</u> . . . . .	87
XVII. Assays of Isobutane and Isobutyl Chloride for Secondary Isotope Effect . . . . .	89

LIST OF FIGURES

Figure	Page
1. Appartus for Transferring Isocrotyl Chloride- <u>t</u> from an Ampule into an Ionization Chamber . . . . .	49
2. Appartus for Trapping Hydrogen and Tritium Chlorides . .	56



## CHAPTER I

### INTRODUCTION

The purpose of this investigation is to gain a better insight into the different factors which control the relative rates of substitution of different hydrogen atoms in a hydrocarbon and its derivatives bearing electronegative groups. Another objective of this undertaking is to explore the neighboring group effect of bromine and chlorine substituents in the liquid-phase photochemical chlorination and bromination of chloro- and bromo-derivatives of isobutane. Variation of "relative reactivities" with the nature of the solvent was studied at different concentrations of an aromatic and a non-aromatic "complexing solvent" in order to understand the relative importance of polar and hyperconjugative interactions in the photochlorination of isobutyl and tert-butyl chlorides. Primary and secondary tritium isotope effects in the photochemical reaction between chlorine and 2-methylpropane-2-t were studied so that a better knowledge regarding the nature of the transition state in such reactions could be gained.

## CHAPTER II

### HISTORICAL

Since the discovery of the triphenylmethyl (trityl) radical by Gromberg in 1900 (41) and the subsequent work of Taylor (144) and Paneth (98) on the role of radicals as transient intermediates in chemical reactions the chemistry of free radicals has come a long way. The progress made in this field may be gauged from the number of monographs that have appeared in the last twenty years (105, 138, 140, 148, 153, 162, 167). Free-radical halogenation constitutes an important phase in the chemistry of atoms and radicals. Because of the nature of the subject dealt with in this thesis, the historical background presented here will be restricted to the literature which has some bearing on this study.

Although chlorination of certain aliphatic compounds was carried out as far back as the nineteenth century (17, 83, 121), the first pioneering experiments of chlorination were conducted by Hass and coworkers (44, 45). These authors reviewed the older data and as a result of their own precise measurements on chlorination of aliphatic hydrocarbons, they formulated a number of rules which may be used to predict qualitatively the results of chlorination.

The free-radical chlorination of hydrocarbons occurs in the vapor phase at high temperatures thermally or at low temperatures photochemically or in the presence of radical sources such as azomethane (151).

In the liquid phase the reaction may be initiated by radicals formed from the decomposition of compounds such as benzoyl peroxide (151). The facile dissociation of chlorine by visible light of short wave length, however, makes the photochemical reaction most attractive. Besides the halogen elements, many halogen compounds such as sulfuryl chloride, N-halo amides and N-halo imides, and tert-butyl hypohalites have been employed for halogenation studies.

The chain mechanism of photochemical chlorination was proposed by Pease and Walz (101) and by Yuster and Reyerson (171) and was later substantiated by Kharasch and associates (9). An identical mechanism operates for atomic bromination (59).

A very pronounced inhibition by traces of oxygen was noted in the thermal chlorination of methane (101). A similar behavior was observed by Richie and Winning. (106) Presumably in the presence of oxygen, the normal substitutive step ( $R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$ ) is replaced by  $R\cdot + O_2 \longrightarrow R-OO\cdot$ . Actually the presence of large amounts of oxygen in the system may result in a halogen-induced auto-oxidation rather than chlorination of the organic substrate (120). The inhibitory action of oxygen may also be due to the formation of the transient species  $ClO$  which subsequently decomposes to chlorine and oxygen (102, 122, 123, 124). Peroxide-sensitized chlorination of a number of hydrocarbons and halo alkanes employing sulfuryl chloride was investigated by Kharasch and Brown (60) and found to be sensitive to oxygen.

Photochemical bromination differs from photochemical chlorination in certain aspects. Thus bromination of toluene and phenanthrene was markedly accelerated by traces of oxygen (61, 62, 63), an effect which is contrary to what has been observed for chlorination. The enhancement

in the rate of bromination in the presence of oxygen is obvious from the fact that light-catalyzed bromination of cyclopropane in the absence of oxygen took 200 hrs. for 47% reaction whereas in the presence of oxygen, the same reaction was 100% complete in only 2 hrs. (64). The presence of oxygen was found to be essential to achieve a good photochemical reaction between bromine and neo-pentane (65). Liquid-phase bromination of certain hydrocarbons, however, was impeded by oxygen at high pressures (59). The energetics of bromination and chlorination also differ considerably. Attack of a chlorine atom on a C-H bond is a strongly exothermic, low-activation-energy process, whereas the bromine-atom attack is endothermic except in reactions involving very weak C-H bonds. The endothermic character of bromination is borne out by the high selectivity observed for this reaction. For instance, only secondary bromides were found when n-pentane was photobrominated (66). No reaction between neopentane and bromine in the liquid phase at room temperature (65) and exclusive formation of tert-butyl bromide in the vapor-phase bromination of isobutane (22, 59) also demonstrate the selectivity of the bromine reaction. Many other examples of the differences in selectivity of chlorine and bromine atoms are in the literature (107, 108, 110). Reversibility of the hydrogen abstraction process, i.e., the attack of alkyl radicals on the hydrogen bromide produced within the reaction, is another feature exhibited only by bromination reactions (156).

The correlation between structure and reactivity of different C-H bonds in a molecule has been explored by many workers since the classical data of Hass and coworkers appeared. The ease of substitution of a hydrogen atom by a halogen atom is generally discussed in terms of "relative reactivity" which may be defined as the ratio of rates of

substitution at different positions in a molecule corrected for the number of hydrogen atoms available at these sites. The relative reactivities are generally obtained by halogenating a compound to low conversions (to avoid complications due to polyhalogenation) and determining the relative amounts of isomeric mono-substituted products.

The relative reactivities of C-H bonds derived from the data of Hass et al. (45) on the vapor- and liquid-phase chlorination of saturated hydrocarbons are shown in Table I.

TABLE I

Relative Reactivities of C-H Bonds in  
Saturated Hydrocarbons Toward Chlorine Atoms

Temperature	Primary	Secondary	Tertiary
600°	1	2.1	2.6
500°	1	2.4	3.2
400°	1	2.7	3.8
300°	1	3.2	4.4
200°	1	3.7	5.4
100°	1	4.3(2.0)*	7.0(3.0)
50°	1	4.8(2.9)	- (4.5)
0°	1	- (4.5)	- (7.0)
-50°	1	- (7.2)	-(11.8)

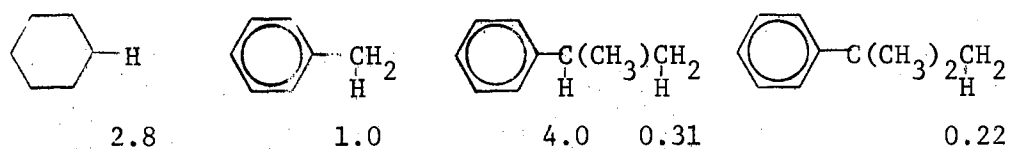
\*Values in parentheses are for liquid-phase reactions.

The effects of many variables such as temperature, reactant concentration, light intensity, presence of water vapor, and surface area on the photochemical gaseous-phase chlorination of isobutane were investigated by Taft and Stratton (142, 143).

Anson, Fredricks and Tedder (2) studied halogenation of n-butane and isobutane at various temperatures in the vapor phase. These authors employed gas chromatography for the determination of reaction products rather than fractional distillation. The reactivity ratios of tertiary

and primary hydrogen in isobutane and secondary and primary hydrogen in n-butane for chlorination at 31° were reported as 5.16 and 3.89 respectively.

Lower selectivity of substitution is observed when chlorination is carried out in the liquid phase (non-complexing medium) as was originally noted by Hass et al. (values in parentheses in Table I) The same conclusion may be derived from the data of Brown and Russell (10, 11) on liquid-phase chlorination of cyclohexane, toluene and some alkylbenzenes as shown below:



The lower selectivity in the liquid phase is presumably due to high rates of reactions involving chlorine atoms. For instance, in the case of isobutane, the rate constant is  $6.13 \times 10^{10}$  at 100° (103, 104) which is comparable to the rate of diffusion of chlorine atoms. Hence a chlorine radical that collides with any part of the hydrocarbon structure would probably stay there owing to the surrounding solvent long enough for reaction even though more reactive sites are available elsewhere (154). Very recently Tedder and coworkers have reported (34) chlorination of n-hexane both in the vapor-phase with nitrogen as the diluent and in the liquid-phase in carbon tetrachloride medium. The relative rates of substitution at the primary and secondary positions are expressed by the rate equations,

$$\left(\frac{k_s}{k_p}\right)_{\text{gas}} = 2.2 \pm 0.6 \exp (214 \pm 127/RT)$$

$$(k_s/k_p)_{\text{liquid}} = 0.8 \pm 0.2 \exp (597 \pm 20/RT)$$

These results, therefore, indicate that the greater selectivity in gas-phase chlorination at normal temperatures is due to the ratios of the pre-exponential factors in the rate expressions. Actually the activation energy differences for attack at the primary and secondary positions are greater in the liquid phase. It is believed that the difference in the gas- and liquid-phase chlorination is not only due to the solvent-cage effect as suggested by Walling but arises at least partially from the solvation of the chlorine atom. These authors have postulated the formation of a weak charge-transfer complex between the chlorine atom and the solvent even though the latter does not have any  $\pi$  electrons.

The relative rates of substitution of different hydrogen atoms are very much influenced by the presence of certain functional groups, although different radicals are affected in different ways by a particular substituent. The different rates of attack on methane, ethane and the halogenated methanes by methyl radicals, and chlorine atoms provide evidence for this effect (39, 72, 149). Although the C-H bond in methyl chloride is 4.4 times as reactive as that of methane (103, 104), the chlorination of ethyl chloride at 208° (152) yields 80% of 1,1-dichloroethane, which means that relative reactivities of hydrogen atoms in ethyl chloride with respect to those of ethane are about 0.47 for  $\alpha$  and about 0.08 for  $\beta$ . The change in the relative reactivities when liquid ethyl chloride is chlorinated near its boiling point is insignificant; the product is still mainly (70%) 1,1-dichloroethane (20). The lowering of reactivity of C-H bonds in the neighborhood of halogen substituents has been reported (12, 19, 20, 25, 26, 27, 48, 55, 60, 87, 152) for many haloalkanes both in the vapor and liquid phase. The peroxide

catalyzed chlorination of tert-butyl chloride with sulfuryl chloride (85) and competitive photochemical chlorination of tert-butyl chloride and 2,3-dimethylbutane (113) provide further examples in which the retarding influence of the chlorine atom is felt.

The product distribution in the chlorination of a series of carboxylic acids and related compounds, chiefly from the investigations of Bruylants et al. (14, 15) and Hertog and collaborators (50, 51), confirms that C-H bonds  $\alpha$  to carbonyl and similar groups are considerably deactivated. Poor reactivity of C-H bonds  $\alpha$  to the carbonyl or acid chloride group is apparent from the fact that acetic acid, acetyl chloride (14) and acetonitrile (15) all fail to undergo vapor-phase photochemical chlorination under conditions where other members of the series react readily. Acetyl chloride does not react with sulfuryl chloride (12, 13) and the butyl esters of formic acid, acetic acid, and trifluoroacetic acid when chlorinated in the gas phase show appreciable deactivation of the 1- and 2- positions (102). Similar observations have been made by other workers (35, 67, 96, 99, 118, 133).

This inevitably means that in deciding the relative reactivities of different hydrogen atoms in a molecule towards attack of  $\text{Cl}\cdot$ , the polar properties of any functional group present must be considered in addition to the bond strengths. To obtain a more quantitative picture of the significance and the magnitude of inductive effect in radical chlorination, Kooyman and Van Helden (46) and Walling and Miller (156) conducted competitive chlorinations of substituted toluenes. The former employed sulfuryl chloride as the chlorine atom source whereas photochlorination with elemental chlorine was used by the latter. The data obtained by these workers show that the relative rates of chlorination of the



substituted toluenes obey the Hammett  $\rho\sigma$  relation. Van Helden and Kooyman (46) also carried out competitive chlorination (using sulfuryl chloride) on a series of substituted tert-butyl compounds,  $X-C(CH_3)_3$  and obtained further evidence for the importance of polarity in the form of a good correlation between reactivity and the ionization constants of the corresponding acids,  $XCH_2-COOH$ .

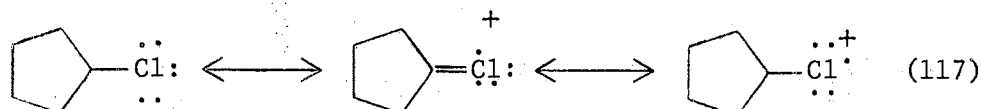
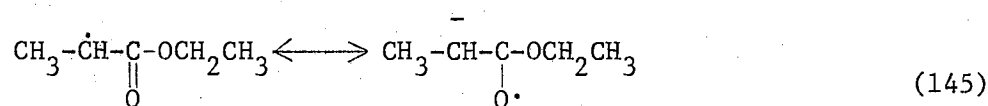
The property of these substituents which impedes chlorination at adjacent positions is considered largely polarity (12, 50, 51, 133, 155) although other factors do play important roles. Because of its strong electrophilic character, the chlorine atom preferentially attacks points of high electron density. Because groups such as  $-Cl$ ,  $-COCl$  and  $-\overset{O}{\parallel}C-OR$  are electron-withdrawing, the electron density along the chain is decreased, the maximum effect being exerted in the immediate vicinity of the substituent. This in turn makes each carbon-hydrogen bond less susceptible to attack by the chlorine atom, the effect decreasing with increasing distance from the substituent.

Another important factor that must be taken into account is the resonance stabilization of the incipient alkyl radical (13). For instance, the order of substitution,  $3^\circ > 2^\circ > 1^\circ$ , which is the same as the experimentally determined order of C-H bond strengths, can be rationalized in terms of the resonance stabilization of the incipient radical through hyperconjugation.



This argument then suggests that the reactivity of primary atoms themselves would vary from molecule to molecule depending upon the amount of hyperconjugative resonance, which is controlled by the extent and

nature of substitution at adjacent carbon atoms. Such a variance has actually been observed in the rates of chlorination of the primary hydrogen atoms in *n*-butane, isobutane and neopentane, which decrease in that order (48). The relatively smaller degree of deactivation of the hydrogens of substituted carbon is interpreted as due to the participation by  $\Pi$  electrons or non-bonded p electrons, which results in the added contribution to resonance stability as shown below.



Thus at the substituted carbon, the resonance and polar effects oppose each other.

Tedder (145) has rationalized in some detail the hydrogen abstraction from aliphatic compounds in terms of differences in activation energy which according to him is controlled by: (a) the strength of the H-X bond that is formed, (b) the strength of the R-H bond which is broken, (c) the repulsion between the incoming radical X $\cdot$  and the substrate molecule RH, and (d) the repulsion between the new radical R $\cdot$  and the new molecule HX.

Rust and Vaughan (152) noticed that the yield of 1,2-dichloroisomer in the chlorination of *n*-propyl, isopropyl, *n*-butyl, and *sec*-butyl chlorides decreased considerably as the temperature was raised especially above 300 $^{\circ}$ . They called this phenomenon the "vicinal effect", a term

earlier used by Tischenko (147) to describe the retardation of hydrolysis of 1,2-dichlorides because of the proximity of the chlorine atoms. Ash and Brown (12, 13) reasoned that the decreased rate of substitution at the positions close to the halogen atom in the case of high-temperature gas-phase chlorination is caused by the instability of the intermediate radical,  $\dot{\text{R}}\text{CH}-\text{CH}_2\text{Cl}$ , which tends to eliminate the chlorine atom to form the corresponding olefin,  $\text{R}-\text{CH}=\text{CH}_2$ . These arguments are supported by other instances of radical instability. Exclusive formation of allyl chloride rather than the addition product in the chlorination above  $300^\circ$  of propylene (45) is attributed to the decomposition of the  $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{Cl}$  radical. Formation of vinyl chloride in good yield when a small quantity of chlorine is added to ethylene chloride above  $300^\circ$  (139) provides further evidence of the unstable nature of chloroalkyl radicals at higher temperatures.

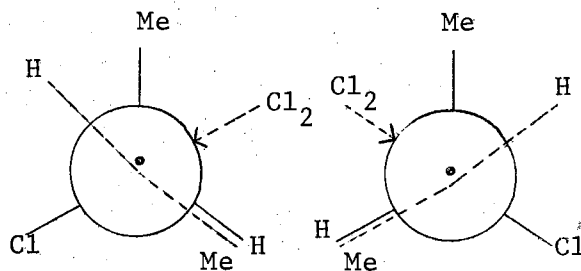
No case involving the "vicinal effect" in the liquid-phase chlorination of alkyl chlorides has so far been reported, presumably because of the lower temperatures commonly employed. Disproportionation of  $\text{CH}_3\dot{\text{C}}\text{H}-\text{CH}_2-\text{Br}$  to give allyl bromide was proposed by Kharasch et al. (68) to explain the 45% yield of 1,2,3-tribromopropane in the bromination of *n*-propyl bromide. The formation of 1,2-dichlorobutane in the chlorination of *n*-bromobutane was ascribed (26, 27) to the breakdown of the *n*-bromoalkyl radical  $\text{CH}_2\text{Br}-\dot{\text{C}}\text{H}-\text{CH}_2\text{CH}_3$  at temperatures as low as  $35^\circ$ . The 1-chloro-2-butyl radical also decomposed but at  $150^\circ$ .

Although experimental evidence for the existence of alkyl radicals as transient species during halogenation was the primary motive of Kharasch et al. (9) in carrying out the chlorination of optically active (+)-1-chloro-2-methylbutane, the complete loss of asymmetry to

yield optically inactive 1,2-dichloro-2-methylbutane indicated significantly, that the carbon atom bearing on odd electron either assumes a planar  $sp^2$  configuration or is pyramidal and there is rapid interconversion of the two pyramidal forms as in the ammonia molecule.

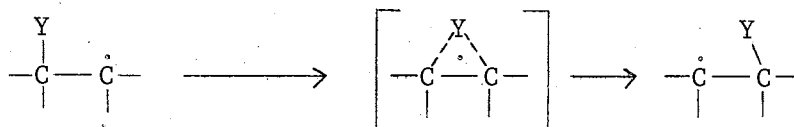
The conformation of radicals has been investigated by spectral methods but unfortunately it has not been proven unambiguously whether typical organic radicals are planar or slightly pyramidal. The ultraviolet, infrared, Raman, and electron paramagnetic resonance (EPR) spectra for the methyl radical have all been recorded and analyzed to determine its conformation (optical spectra (52, 53); EPR spectra (56, 57)). However none of the methods can distinguish between a planar conformation and one in which there is a  $10$  to  $15^\circ$  deviation from planarity.

The halogenation of the 2-halogenobutanes yielded both of the expected 2,3-dihalobutanes, threo and erythro, but not in equal amounts (26, 37, 145) which implies a stereospecific reaction between the intermediate  $CH_3CHX-\dot{C}H-CH_3$  radical and the halogen molecule. Conformational effects rather than a halogen-bridge formation were invoked by these authors to rationalize this stereospecificity. Assuming nearly planar  $sp^2$  configuration for the tervalent carbon, the free rotation of the bonds on tetrahedral carbon was suggested to give a preferred conformation in which the methyl group of the tervalent carbon lies above and close to the hydrogen atom of the tetrahedral carbon.



Since the approach of the incoming halogen is easier from the side opposite to the substituent halogen atom, the erythro isomer is formed. This is supported by the fact that the size of the halogen substituent has a greater effect on the relative proportions of the two stereoisomers than the reactivity of the attacking species does. A similar explanation was offered by Kooyman and Vegter (73), who observed predominant formation of the 2-exohalide in the halogenation of bicyclo (2,2,1) heptane (norbornane). The reactions of free radicals are influenced by steric inhibition of resonance as noted by Kooyman and Strang (74) who found that trichloromethyl radicals attack m- or p-cymene about five times as fast as o-cymene whereas the attack on hexaethylbenzene was only about half as fast as that on ethylbenzene, although hexamethylbenzene was attacked eight times as fast as toluene. Resonance stabilization of the incipient benzyl radical can occur only if the radical is planar, and this is not possible in either o-cymene or hexamethylbenzene.

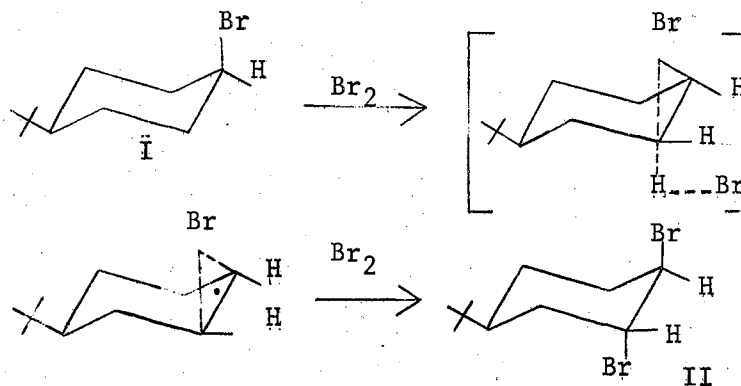
The facile 1,2-migration of chlorine in polyhalogenoalkyl radicals has been demonstrated in a series of publications by Russian workers (28 to 31, 71, 75 to 79, 88 to 95). The radicals studied were generated through homolytic addition of hydrogen bromide, bromotrichloromethane, bromine, thiophenol and alkyl mercaptans to  $XCCl_2CY=CH_2$  with  $X=Cl, F, H,$  or  $CH_3$  and  $Y=H, Cl, Br,$  or  $CH_3$ , as well as by the homolytic peroxide-catalyzed dimerization of  $CCl_{3-n}F_nCY=CH_2$  with  $n = 1$  or  $2$ . The reaction of diazomethane with polychloromethanes such as carbontetrachloride and chloroform (150) and the radiation-induced isomerization of n-propyl chloride to isopropyl chloride (4, 166) are all considered to involve a 1,2-chlorine shift. Non-classical bridged radical as depicted below:



has been postulated by many investigators for the transition state during 1,2 radical rearrangements. As no quantum mechanical assessment for such a transition state is available, the arguments for and against the idea of a bridged intermediate are based solely on indirect experimental evidence. Thus the stereospecific nature of the peroxide-catalyzed addition of hydrogenbromide to 1-bromocyclohexene and to 1-methylcyclohexene, yielding cis-1,2-dibromocyclohexane and cis-1-methyl-2-bromocyclohexane respectively, was first noted by Goering et al. (36) They proposed a bridging or a resonating bromine atom holding both carbons of the double bond in a fixed conformation until hydrogen abstraction completes the structure from the side opposite to the bromine bridge. Although no rearrangement was observed in the chlorination of isobutyl bromide, chlorination of isopropyl bromide gave 15% 1-bromo-2-chloropropane. tert-Butyl bromide when treated with tert-butyl hypochlorite at  $-78^{\circ}$  produced 92% of rearranged product, i.e., 1-bromo-2-chloro-2-methylpropane (134). Thaler (146) obtained identical relative reactivities of secondary hydrogens in the chlorination and bromination respectively of n-butyl bromide and n-butyl chloride. The values are identical to those reported by Walling and Mayahi (157) in the photochlorination of n-butyl chloride at  $68^{\circ}$  and show deactivation of secondary hydrogens next to the substituted carbon. On the contrary, bromination of n-butyl bromide and 2-bromobutane gave a much greater reactivity ratio for the secondary hydrogens adjacent to the carbon atom bearing the bromine atom. Similarly cyclopentyl and cyclohexyl bromides were found to yield 90% trans-1,2-dibromo isomers

although cyclohexyl chloride produced only 10% of the vicinal dihalide derivative. Neighboring group participation by the bromine substituent resulting in the stabilization of the transition state through delocalization of the unpaired odd electron especially in bromination (high activation energy process) relative to chlorination (low activation energy) was advanced by Thaler (146) to rationalize the enhanced reactivity in the above cases. Furthermore, the ability of bromine and the inability of chlorine substituent to behave as a good neighboring group was considered to be related to the greater size and polarity of the former.

Formation of optically active (-)-1,2-dibromo-2-methylbutane in the photobromination of active (+)-1-bromo-2-methylbutane (135) although photochlorination of the corresponding chloride gave only racemic products (9) has been interpreted as arising from a bromine bridged intermediate. Since photochlorination of the same bromide gave an optically inactive product, it was assumed that the bridged radical is trapped by tert-butyl hypobromite or bromine but opens to permit rotation before reacting with tert-butyl hypochlorite or chlorine. Stereoselective photobromination of (+)-1-chloro-2-methylbutane to form (-)-2-bromo-1-chloro-2-methylbutane (135) was considered to result from the selective opening of the chlorine-bridged intermediate on the tertiary carbon. Further evidence in favor of bromine participation in the transition state is provided in the photobromination of cis-4-bromo-tert-butylcyclohexane (I) (with bromine in the axial position) to form trans-3-cis-4-dibromo-tert-butylcyclohexane (II) in high preponderance (136).



The liquid-phase photochemical bromination of (+)-1-cyano-2-methylbutane proceeds with high selectivity at the tertiary carbon to yield (+)-2-bromo-1-cyano-2-methylbutane (42). In this case it is hard to conceive of any neighboring group effect by the cyano substituent. It was argued that the reaction of the initially formed pyramidal radical with bromine is fast enough to compete with the relatively slow racemization process. Furthermore  $\cdot\text{Br}_3$  was thought to be the hydrogen abstractor rather than the free bromine atom,  $\text{Br}\cdot$ .

Both the "normal" and "abnormal" products were reported by Haag and Heiba (43) who repeated the reaction between tert-butyl bromide and tert-butyl hypochlorite at  $-78^\circ$ . Elimination of  $\text{Br}\cdot$  from the classical  $(\text{CH}_3)_2\text{CBr}\dot{\text{C}}_2$  radical followed by its readdition to the isobutylene so generated was suggested to cause the formation of 1-bromo-2-chloro-2-methylpropane. The supposedly free bromine atoms were trapped with allene to produce bromochloropropene in good yield. EPR spectra of bromoalkyl radicals analyzed by Abell and Piette (1) do not permit an unequivocal conclusion in favor of the bridged character of the intermediates although they are consistent with the bridged structure.

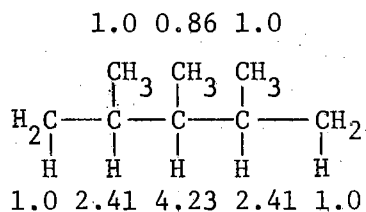
Vapor-phase bromination and chlorination of 2,2,4,4-tetramethylpentane (3) were found to give only normal substitution products, though



Kharasch had earlier reported (69, 70) formation of a rearranged product, 2-bromo-2,3,4,4-tetramethylpentane.

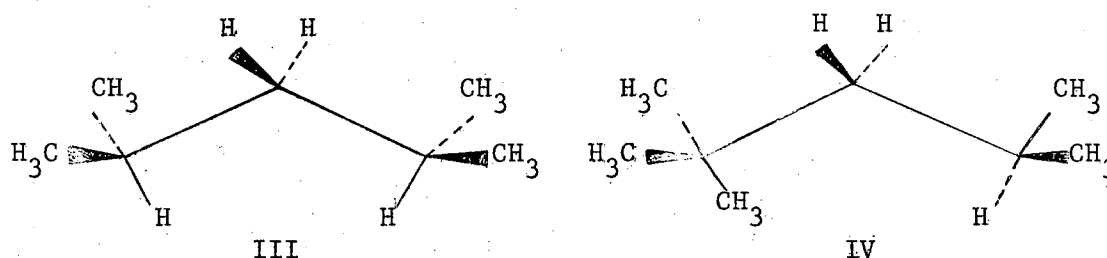
Lower reactivity of 2,2,4-trimethylpentane, in contrast to the statistically identical 2,3,3-trimethylpentane, when chlorinated with N,2,4,6-tetrachloroacetanilide (6) or attacked by tert-butoxy radicals (8) is considered to stem from the shielding of the tertiary hydrogen in 2,2,4-trimethylpentane by the methyl groups. This view is supported by the chlorination data on other hindered hydrocarbons such as 2,2,4,4,6- and 2,2,4,6,6-pentamethylheptane (6).

Steric interaction between the incoming chlorine atom and the chlorine substituent explains the predominant yield of erythro dichlorohexanes from the chlorination of 2-chloro- and 3-chlorohexane (19). The significance of steric factors in chlorination can be appreciated from the different reactivities possessed by the three tertiary hydrogens in 2,3,4-trimethylpentane. Furthermore the methyl group on the third carbon is less reactive than the other four (32).

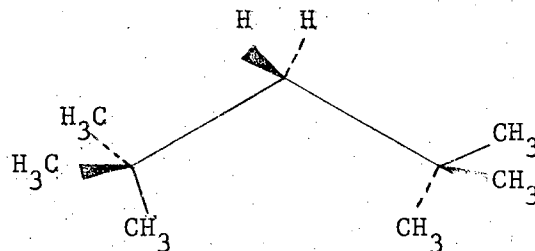


Russell and Brown (109), however, reported identical reactivities for the three tertiary hydrogens. The isopropyl groups shield the methyl group against the attacking species but at the same time enhance inductively the reactivity of the tertiary hydrogen on carbon 3. In the photo- or sulfuryl-chloride chlorination of 2,2,4-trimethylpentane (33) the tertiary hydrogen was found to be less reactive than the secondary hydrogen, a remarkable deviation from the usual order ( $3^\circ > 2^\circ > 1^\circ$ ) of

hydrogen reactivities in alkanes. The very low reactivity of the tertiary hydrogens of 2,4-dimethylpentane, 2,2,4-trimethylpentane and 2,2,4,4-tetramethylpentane towards attack by a free or complexed chlorine atom has been explained in terms of specific conformations possessed by these hydrocarbons in which the tertiary hydrogens are shielded from radical attack (119). The preferred conformations expected for 2,4-dimethylpentane and 2,2,4-trimethylpentane on the basis of non-bonded interactions are shown as structures III and IV respectively.



In each case the geometry of the molecule leaves the methylene group open to attack whereas the abstraction of the tertiary hydrogen is difficult because of steric hindrance in the approach of the attacking species. Steric control becomes apparent when the bulk of the chlorine atom is increased due to complexation with the solvent, for under these conditions, the tertiary hydrogens became even less reactive. A similar conformational effect is manifested by 2,2,4,4-tetramethylpentane (V), in



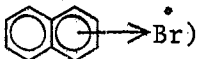
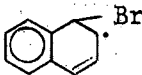
which 1,3 dimethyl interactions lead to poor reactivity of the primary hydrogens especially towards complexed chlorine atom.

A very profound solvent effect in a liquid-phase chlorination was first reported by Russell in 1957 (111). He noted that certain solvents, particularly aromatic compounds, rendered liquid-phase chlorination a highly selective reaction. A number of articles have appeared since then, all confirming the original observation (47, 112 to 117). That the predominant substitution of the  $\alpha$ -hydrogens in the chlorination of alkyl arenes is most likely due to complexation of chlorine atom was demonstrated by Russell and Ito (118), who found that the ratio of abstraction of  $\beta$ -hydrogens relative to that of  $\alpha$ -hydrogens from both ethylbenzene and cumene increased when the reactants were diluted with a non-complexing solvent. Assuming an equilibrium between the complexed and free chlorine atoms dilution with an inert solvent increases the concentration of uncomplexed chlorine atoms and hence the possibility of attack on other than benzylic hydrogens becomes greater.

The product distribution for mono-chlorination of n-hexanoyl chloride is also influenced by the nature of the solvent (49). Similar results were obtained by Walling and Mayahi (157), who noticed that the increase in selectivity of the chlorine atom in solvents with  $\Pi$  electrons is also reflected in activation energy differences. Russell (113) showed that the variation in selectivity of chlorination in aromatic solvents could be related to their basicity. No appreciable solvent effects were, however, observed by Sherman and Williams (126) on the relative rates of  $\alpha$ -hydrogen abstraction by tert-butoxy radicals, although other workers have demonstrated solvent effects to a smaller extent for competitive hydrogen abstractions by tert-butoxy radical (100, 158, 160, 161).

The simplest and most plausible explanation of these effects suggested by Russell involves the formation of a charge-transfer complex

between the electrophilic radical and electron-rich solvents such as aromatic hydrocarbons or carbon disulfide. Walling and his associates (158, 159), however, feel that the solvent modifies the nature not only of the ground state of the attacking radical but also of the transition states of the reactions involving the complexed radical.

Because of the high selectivity observed in bromination reactions, the isomer distribution methods cannot be employed fruitfully to determine the effects of the medium on bromine atoms. Retardation of the rate of side chain bromination of toluene in the presence of naphthalene was attributed by Mayo and Hardy (84) to inhibition of the chain-propagation step because of the competing addition reaction. Recently it has been proposed (168) that the hydrogen abstraction might not be by a bromine radical but rather by  $\pi$ -complexed (  $\rightarrow \text{Br}^\bullet$ ) or  $\sigma$ -complexed () bromine atoms, a possibility which should result in the retardation actually observed.

Study of reactions employing substrates specifically labeled with deuterium and tritium (isotopes of hydrogen) has become a powerful tool to elucidate reaction mechanism (37). An equilibrium or kinetic isotope effect is termed as "primary" when the bond to the isotopic atom is directly involved in the rate-determining step of a reaction. Before Lewis and Boozer (80) and Shiner (127), working with different solvolytic systems reported independently that deuteration beta to the leaving group could affect the reaction rate, it was generally assumed that isotopic differences of any significance in equilibrium or kinetic rate constants were to be expected only in reactions in which a bond to an isotopic atom is either broken or formed. Such isotope effects on rate and equilibrium constants, occurring although a bond to the isotopic atoms is

neither ruptured nor produced, are called "secondary". The primary as well as the secondary effects of hydrogen isotopes, mostly deuterium, have been measured and interpreted for a large number of ionic reactions (18, 38, 86). Reactions in which the normal and isotopic hydrogen are abstracted by radical species have also been reported, although relatively few in number. Thus the effect of methyl deuteration on the rate of air oxidation of cumene in chlorobenzene at 65° was studied by Boozer et al. (7) using azobisisobutyronitrile as the initiator. With 2,4-dinitrophenol as the inhibitor, the value of  $k_H/k_D$  for two samples of deuterocumene was 1.19 and 1.27, indicating the retarding influence of the deuterium atoms on the abstraction of tertiary hydrogen atom. The secondary deuterium effect observed in the radical addition of  $\cdot\text{CH}_3$  and  $\cdot\text{CF}_3$  to a number of deuterated olefins was considered by Szwarc and associates (24) as insignificant. An appreciable primary isotope effect ( $k_H/k_D=2.0$ ) was reported by Brown and Russell (10) in the liquid-phase photochlorination of toluene- $\alpha$ -d at 80°. Assuming equal reactivities for the primary hydrogens, the tertiary hydrogen of 2-methylpropane was 1.8 times as reactive as the tertiary deuterium atom of 2-methylpropane-2-d (10) Competitive photochlorination of monodeuterotoluene and undeuterated toluene was carried out by Walling and Miller (156). They reported  $k_H/k_D = 2.08$  at 69.5° for the reaction in the vapor phase in its own liquid phase, and in the solvents benzene and *o*-dichlorobenzene. A lower value,  $k_H/k_D=1.99$ , was obtained in carbon tetrachloride whereas sulfuryl-chloride chlorination gave  $k_H/k_D=2.105$ . The intramolecular isotope effects,  $k_H/k_D$ , for chlorination of  $\text{C}_6\text{H}_5\text{CH}_2\text{D}$  and  $\text{C}_6\text{H}_5\text{CHD}_2$  at 77° were respectively 1.30 and 1.39 (165). A much higher value of  $k_H/k_D=4.54$  to 5.26 was reported by Wiberg and Slauch (165) for the photobromination of

isotopic toluenes in carbon tetrachloride at 77°. The deuterium isotope effect in the photochlorination of 2-methylpropane-2-d at -15° was found to increase from 1.3-1.5 in the liquid substrate to 1.6-2.1 in chlorobenzene (5.9M) (112). The presence of acetic acid, acetonitrile, benzene, and benzonitrile was found to have no influence on the  $\alpha$ -deuterium kinetic isotope effect for the formation of methyl radicals in the decomposition of  $\alpha$ -methyl- $\alpha$ -trideuteriomethylbenzyl hypochlorite ( $C_6H_5C(CH_3)(CD_3)O-Cl$ ) (172).

## CHAPTER III

### INTRODUCTION TO THE EXPERIMENTAL WORK

#### Objectives and Plan of the Study

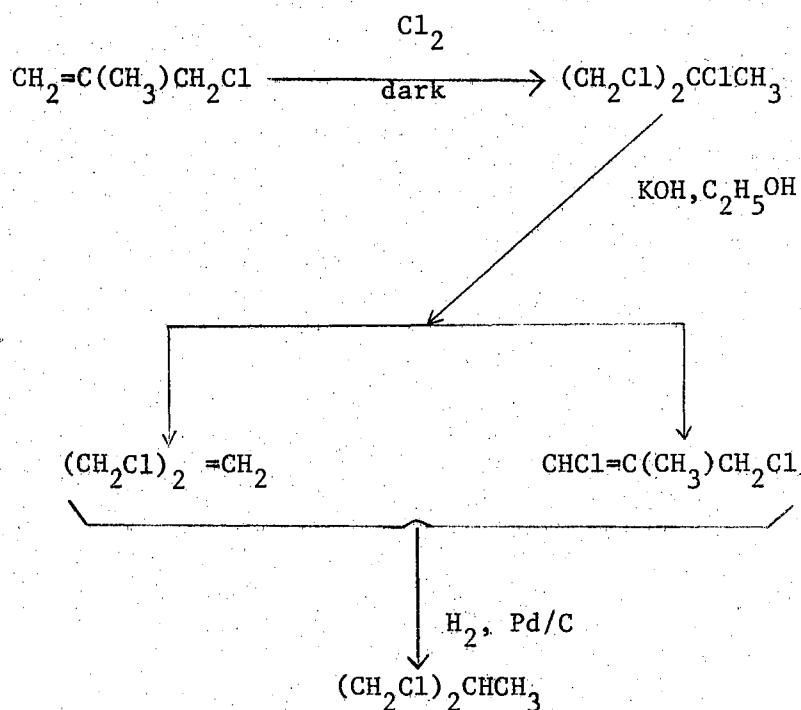
The present investigation was undertaken for a number of reasons which are presented in this section. Much of the earlier work deals with gas-phase chlorination, employing conventional analytical methods for the analysis of reaction products. Only in recent years has attention been diverted to liquid-phase photochemical chlorination. In the past, polar and resonance effects have been generally considered together whenever the rationalization of chlorination pattern of different substrates was needed.

Although there is convincing evidence for the neighboring group effect of bromine substituent in radical reactions, the participation of chlorine atom in identical reactions is still a controversial question. Much information is known on the deuterium isotope effects in both ionic and radical reactions, but virtually nothing has been reported to date regarding the primary and secondary tritium isotope effects in free-radical reactions. In the light of these statements, it is easier to understand the objectives of the present study which are summarized below.

Liquid-phase photochemical chlorination at 24° of 2-methylpropane and its monochloro derivatives has been investigated individually as

well as competitively in order to obtain further information on the relative importance of inductive and hyperconjugative effects. The reactions were carried out both in carbon tetrachloride and in carbon tetrachloride containing varying concentrations of a  $\pi$  electron-rich solvent so as to ascertain the effect of the reaction medium on the relative rates of hydrogen abstraction in isobutyl chloride and tert-butyl chloride. Justification for the empirical correlation suggested by Russell (113) between the polar properties of a substituent and the solvent effect was also sought.

Pure dichloro isomers of isobutane were needed to verify the structures of the disubstitution products formed in the photochlorination of isobutyl and tert-butyl chloride. An unsuccessful attempt was made to synthesize 1,1-dichloro-2-methylpropane by the reaction of phosphorus pentachloride with isobutyraldehyde (97). Preparation of 1,3-dichloro-2-methylpropane according to the following scheme





was considered but later abandoned owing to foreseen difficulties such as hydrogenolysis of the intermediate allylic chlorides.

Pure dichloro isomers were hence obtained with relative ease from the preparative-scale chlorinations of isobutyl chloride (see experimental section) and their identities verified by their nuclear magnetic resonance spectra. The 1,2-dichloro isomer was prepared also from the addition of chlorine to isobutylene. Its retention time and nmr spectrum correspond exactly to those recorded for the 1,2-dichloro derivative formed in the chlorination of isobutyl chloride.

Photobromination of isobutyl and tert-butyl chlorides and photochlorination of isobutyl and tert-butyl bromides was carried out to help clarify the status of the controversial halogen-bridged intermediate which has been suggested to intervene in the free-radical 1,2-rearrangements (134, 135, 136). The structural assignments to the various chloro bromo products resulting in these reactions were made by comparing their vpc and nmr data with authentic samples synthesized by unambiguous means. Thus 1-chloro-2-bromo-2-methylpropane, a compound observed in the photobromination of isobutyl chloride as well as in the photochlorination of isobutyl bromide, was obtained by ionic addition of hydrogen bromide to methallyl chloride. Peroxide-catalyzed addition of hydrogen bromide to methallyl chloride gave 1-chloro-3-bromo-2-methylpropane which is also one of the products in the reaction between isobutyl bromide and chlorine. Synthesis of 1,2-dibromo-2-methylpropane, a sole product of bromination of tert-butyl chloride as well as a minor component from bromination of isobutyl chloride, was achieved by adding bromine to isobutylene in dark.

The photochemical chlorination of 2-methylpropane-2-t in

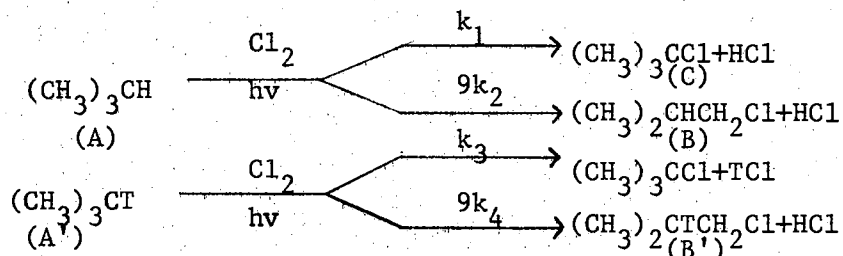
"complexing" and "non-complexing" media was included in this work in order to examine the ionic character of the transition state as well as the role of hyperconjugative interactions stabilizing such a transition state. Isomerization of methallyl chloride to isocrotyl chloride in the presence of sulfuric acid containing tritiated water gave tritiated isocrotyl chloride which was used as a reference substance to determine the specific activity of isobutyl chloride produced in the photochlorination of isobutane-2-t.

In this thesis the portion which deals with the determination of polar effects of the chlorine substituent, solvent effects and the ability of halogen atoms to form bridged intermediates is simpler both kinetically as well as experimentally. It involves irradiation of a known amount of a particular substrate with a predetermined quantity of chlorine or bromine in a solvent system of known composition. This is followed by qualitative and quantitative gas chromatographic analysis of the reaction mixture.

The kinetics of that part which deals with the tritium isotope effects are somewhat more involved and will be presented at this stage.

#### Kinetics of Chlorination of 2-Methylpropane-2-t

2-Methylpropane-2-t for the "isotope effects" study was prepared by the acid hydrolysis of tert-butyl Grignard reagent in the presence of tritiated water (see details under experimental section). The chlorination of isobutane may be indicated as below:



Letting

$A_o$  = Initial concentration of unlabeled isobutane.

$A'_o$  = Initial concentration of labeled isobutane.

$A$  = Concentration of unlabeled isobutane at time  $t$ .

$A'$  = Concentration of labeled isobutane at time  $t$ .

$B$  = Concentration of unlabeled isobutyl chloride.

$B'$  = Concentration of labeled isobutyl chloride.

$C$  = Concentration of tert-butyl chloride.

One may write the rate equations as:

$$-\frac{dA}{dt} = (9k_2 + k_1)[A][Cl_2]$$

or 
$$-\frac{dA}{A} = [Cl_2](9k_2 + k_1)dt \quad [I]$$

Similarly

$$-\frac{dA'}{dt} = [A'] [Cl_2] (9k_4 + k_3)$$

or 
$$-\frac{dA'}{A'} = [Cl_2] (9k_4 + k_3)dt \quad [II]$$

Dividing the Equation I by Equation II and integrating the resulting expression yields

$$\frac{\ln(A/A_o)}{\ln(A'/A'_o)} = \frac{9k_2+k_1}{9k_4+k_3}$$

or 
$$\frac{\ln(A'/A'_o)}{\ln(A/A_o)} = \frac{9k_4+k_3}{9k_2+k_1}$$

Subtracting unity from both sides of this equation gives

$$\frac{\ln(A'/A'_o)}{\ln(A/A_o)} - 1 = \frac{9k_4+k_3}{9k_2+k_1} - 1$$

or 
$$\frac{\ln(A'/A'_o) - \ln(A/A_o)}{\ln(A/A_o)} = \frac{9k_4+k_3}{9k_2+k_1} - 1$$

$$\text{or} \quad \frac{\ln\left(\frac{A'/A_o}{A/A_o}\right)}{\ln(A/A_o)} = \frac{9k_4+k_3}{9k_2+k_1} - 1$$

$$\text{or} \quad \frac{\ln\left(\frac{A'/A_o}{A/A_o}\right)}{\ln\left(\frac{A}{A_o}\right)} = \frac{9k_4+k_3}{9k_2+k_1} - 1$$

$$\text{or} \quad \frac{\ln(N'_A N'_{A_o})}{\ln(A/A_o)} = \frac{9k_4+k_3}{9k_2+k_1} - 1 \quad \text{[III]}$$

In the Equation III

$$N_{A'} = \frac{A'}{A'+A} \approx \frac{A'}{A} = \text{Final specific radioactivity of isobutane.}$$

$$N_{A_o} = \frac{A_o}{A_o+A_o} \approx \frac{A_o}{A_o} = \text{Initial specific radioactivity of isobutane.}$$

Further

$$\frac{dB}{dt} = 9k_2[A][Cl_2] \quad \text{[IV]}$$

$$\frac{dB'}{dt} = 9k_4[A'][Cl_2] \quad \text{[V]}$$

Dividing the Equation IV by Equation V and integrating the resulting expression gives

$$\frac{B'}{B} = \frac{k_4}{k_2} \cdot \frac{A'}{A}$$

For low extents (1 to 5%) of reaction, i.e., for small t, A and A' are not much different from their initial values. Hence one may write

$$\frac{B'}{B} = \frac{k_4}{k_2} \cdot \frac{A_o'}{A_o}$$

$$\text{or} \quad N_{B'} = \frac{k_4}{k_2} \cdot N_{A_o'}$$

$$\text{or} \quad \frac{k_2}{k_4} = \frac{N_{A_o'}}{N_{B_o'}} \quad \text{[VI]}$$

where  $N_{B'}$  denotes the specific activity of isobutyl chloride produced in

the reaction and  $N_{A_0}$ , is the initial specific activity of isobutane. In a similar manner

$$\frac{dc}{dt} = k_1[A][Cl_2] + k_3[A'] [Cl_2] \quad [VII]$$

$$\frac{dB}{dt} = 9k_2[A][Cl_2] \quad [VIII]$$

Once again for small extents of the reaction, one obtains from Equations VII and VIII

$$\frac{C}{B} = \frac{k_1[A] + k_3[A']}{9k_2[A]} \quad \text{Under these conditions the}$$

term  $k_3[A']$  will be relatively small and hence may be neglected

$$\therefore \frac{C}{B} \approx \frac{k_1[A]}{9k_2[A]}$$

or

$$\frac{k_1}{9k_2} = \frac{C}{B} \quad [IX]$$

where  $C/B$  is the ratio of the amounts or concentrations or tert-butyl chloride and isobutyl chloride.

The ratio  $k_1/k_2$  determined from chlorination of unlabeled isobutane can be used directly in these equations. To determine the primary isotope effect,  $k_1/k_2$ , from equation III, in addition to the values for  $k_1/k_2$  and  $k_4/k_2$  two other parameters, namely the initial and final specific radioactivities of isobutane and the extent of the reaction, are also required. With reference to expression III, the extent of chlorination should be held somewhere in the range of 40% to 60% in order that the difference in the initial and final specific activities of isobutane be large enough to be measured accurately. The final concentration of isobutane cannot be obtained by subtracting the amount of chlorine added from the initial weight of isobutane because chlorine under these conditions is consumed not only by monochlorination but also by di- and poly-substitution.

The method considered best is based on the assumption that the ratio of peak heights of isobutane and an internal standard (the solvent in these cases) is proportional to the concentration of the hydrocarbon. By employing liquified chlorine rather than its solution in carbon tetrachloride, any error because of dilution could be minimized. To check the accuracy of this assumption, six samples each containing a known amount of isobutane in carbon tetrachloride were analyzed under identical vpc conditions. A linear relation was observed between the concentration of isobutane and the ratio of the peak heights for isobutane and carbon tetrachloride in the range of concentrations of isobutane that would be employed in the actual experiments.

As will be discussed in the next chapter, reliable values for the final specific radioactivity or the final concentration of isobutane could not be obtained. Therefore, the use of the equation III to determine the primary isotope effect had to be abandoned. A different approach which did not require a high extent reaction had to be devised.

The rate expressions for the formation of tritium chloride and hydrogen chloride are:

$$d(\text{Tcl}) = k_3(A')dt \quad [\text{X}]$$

$$d(\text{HCl}) = 9k_4(A')dt + (K_1+9k_2)A dt \quad [\text{XI}]$$

Since the hydrogen chloride formed from the tritiated isobutane molecules will be very little as compared to the amount arising from the chlorine attack on unlabeled isobutane, the factor  $9k_4(A')$  in equation XI may be omitted. Therefore, equation XI reduces to

$$d(\text{HCl}) = (k_1+9k_2)(A)dt \quad [\text{XII}]$$

Dividing X by XII, one obtains

$$\frac{d(\text{TCl})}{d(\text{HCl})} = \frac{k_3 A' dt}{(k_1 + 9k_2) A dt} \quad [\text{XIII}]$$

The concentrations of labeled and unlabeled molecules at any time  $t$  is related to the corresponding initial concentrations by the exponentials XIV and XV

$$A' = A'_0 e^{-(k_3 + 9k_4)t} \quad [\text{XIV}]$$

$$A = A_0 e^{-(k_1 + 9k_2)t} \quad [\text{XV}]$$

Substituting these relations in XIII,

$$\frac{d(\text{TCl})}{d(\text{HCl})} = \frac{k_3 A'_0 e^{-(k_3 + 9k_4)t} dt}{(k_1 + 9k_2) A_0 e^{-(k_1 + 9k_2)t} dt}$$

Integration of both sides and rearranging yields

$$\frac{\text{TCl}}{\text{HCl}} = \frac{k_3 A'_0 [e^{-(k_3 + 9k_4)t} - 1]}{(k_1 + 9k_2) A_0 [e^{-(k_1 + 9k_2)t} - 1]} \quad [\text{XVI}]$$

For small values of  $t$  (i.e., at low extents of reaction), the exponential functions may be substituted by the first two terms in their corresponding expansions. Hence one obtains,

$$\frac{\text{TCl}}{\text{HCl}} = \frac{k_3 A'_0}{(k_1 + 9k_2) A_0} \quad \text{or} \quad N_{\text{HCl}} = \frac{k_3}{(k_1 + 9k_2)} \times N_{A_0} \quad [\text{XVII}]$$

The relation between rate constants  $k_1$  and  $k_2$  is easily obtained from the chlorination of unlabeled isobutane. The specific radioactivity of hydrogen chloride is another unknown parameter to solve equation XIII in order to obtain "primary isotope effect" (i.e.,  $k_1/k_3$ ).

The secondary isotope effect is represented by the ratio  $k_2/k_4$ . The final specific radioactivity of isobutane and isobutyl chloride is determined by the flow ionization method (details in Chapter IV) whereas

the initial specific radioactivity of isobutane and the isocrotyl chloride (reference compound) is obtained by the static ionization technique.

In order to determine the secondary isotope effect ( $k_2/k_4$  of equation VI), the extent of chlorination was increased to 4-5% because the concentration of isobutyl chloride in those runs which had a lower extent of reaction (1 to 3%) was too low to permit an accurate tritium assay.

#### Assay for Tritium

Tritium, the radioactive isotope of hydrogen, decays to helium-3 with the emission of a beta particle. Tritium has a half-life of 12.5 years and its emitted beta particle has an average energy of 0.018 Mev (154). Its determination, therefore, suffers from the handicap of the low energy of the beta particles. The maximum beta energy of 18.9 Kev, corresponding to a calculated range of 0.9 mg. per square cm. (82) precludes the use of end-window counters owing to appreciable loss of energy.

Measurement with high efficiency is more readily attained if the disintegration takes place within the active volume of the detector. Two "internal-counting" devices, a vibrating-reed electrometer and a liquid scintillation counter, were available for this investigation. Because of the low efficiency generally obtained with scintillation counting techniques, the vibrating-reed electrometer was preferred for rapid routine analysis.

The vibrating-reed electrometer used was an Applied Physics Corporation Model 30. In this method, a known amount of the sample is introduced into an ionization chamber in the gaseous state along with a gas



such as methane which has a relatively low ionization potential. The ionization chamber consists of a gas-tight metal shell with a central electrically insulated electrode. Depending upon the ionization chamber, a potential of 90-300 volts d.c. is applied across the two electrodes. The energy which is released from the disintegration of tritium ionizes the methane. The charged particles, essentially between the plates of a condenser, produce what is commonly known as an ion current. This current although only  $10^{-13}$ - $10^{-16}$  amperes is applied across a resistance of  $10^{10}$ - $10^{12}$  ohms. The resulting potential drop across the resistance, after proper amplification, is then measured on a strip-chart recorder. This is a very sensitive method and has been found to be reproducible to  $\pm 1\%$  (170).

## CHAPTER IV

### EXPERIMENTAL

#### Materials

Isobutane (unlabeled) and chlorine from the Matheson Company were used without further purification. Spectroscopy-grade carbon tetrachloride (Eastman) was employed. The benzene used in this work was obtained from J. T. Baker Company as their reagent grade; gas chromatographic analysis showed that it contained no more than 0.4% impurities, of which 0.33% was toluene. Carbon disulfide was also a reagent grade from J. T. Baker Company and was gas-chromatographically pure. The purest grade of isobutyl chloride from Eastman Kodak Company was rectified in a column packed with glass helices and only the middle fraction, b.p. 68° at 746 mm., was used. tert-Butyl chloride (0.02%) and n-butyl chloride (0.3%) were the only impurities detected by vpc. tert-Butyl chloride was prepared from tert-Butyl alcohol and concentrated hydrochloric acid (156); its purity by vpc was 99.5%. Eastman reagent grade isobutyl and tert-butyl bromide (97.9% and 99.6% respectively by gas chromatography) were used in this work. n-Butyl bromide (1.8%) was the major impurity in isobutyl bromide.

#### Identification of Products

Analysis of the samples for qualitative and quantitative characterization of the products was done on an Aerograph Model A-90P gas

chromatograph using a 15 ft. by  $\frac{1}{4}$  in. aluminum column containing Resoflex-728 (30% on firebrick) as the stationary phase. Helium was used as the carrier gas for all vpc analyses. The nmr spectra were obtained with a Varian A-60 nuclear magnetic resonance spectrometer; carbon tetrachloride was used as the solvent (unless otherwise specified) and tetramethylsilane as the internal standard.

#### General Procedure of Halogenation

Weighed quantities of the compound or compounds (except isobutane) dissolved in an appropriate solvent or mixtures of solvents was taken in a Pyrex reaction tube and a known amount of chlorine or bromine dissolved in carbon tetrachloride (it was dissolved in carbon disulfide when the solvent effect in pure carbon disulfide was studied) was added. The transfer of isobutane was done on the vacuum line by measuring a predetermined volume of the gas at a definite temperature and pressure. The gas was thoroughly dissolved in the solvent(s) by alternate cooling with a liquid nitrogen bath and warming of the reaction tube. The solutions were degassed twice on the vacuum line, closed with a stopcock, and irradiated for 30 minutes with a 200-watt incandescent bulb (unless otherwise mentioned) placed at a distance of 2 ft. The tube was opened and the reaction mixture was shaken gently with a small amount of solid sodium bicarbonate. The products were dried overnight with Drierite and analyzed by gas chromatography; the peak area (peak height times width at half peak height) being assumed to be proportional to the concentration of products (125). The work up of the reaction mixtures from the experiments designed to trap the hydrogen chloride and tritium chloride for counting purposes being somewhat different from the general procedure will be described separately. To eliminate any effect of

extraneous light, the upper third of the reaction tubes was painted black in addition to the precaution of preparing the samples in complete darkness.

#### Product Analysis in the Chlorination of Isobutyl Chloride.

In addition to the peaks corresponding to the unreacted alkyl halide and carbon tetrachloride (solvent), four peaks were observed on the gas chromatograms. The component immediately following the air peak was identified as isobutane by vpc. comparison with a sample of pure isobutane. The possibility that this component was isobutylene which might be formed from decomposition of unreacted isobutyl chloride, was ruled out since the retention time of isobutylene under the same conditions was greater. Moreover, no decomposition products were detected when isobutyl chloride was injected into the gas chromatograph. The isomeric dichloro compounds, i.e., 1,1-dichloro-2-methylpropane, 1,2-dichloro-2-methylpropane, and 1,3-dichloro-2-methylpropane, followed the solvent peak in the order of their boiling points, their retention times being 5.75 min., 6.5 min., and 16.4 min. respectively. A similar correspondence between boiling points and retention times has been observed (146) for the isomeric dibromo derivatives of n-butane.

#### Preparative-scale Chlorination of Isobutyl Chloride.

A solution of 2.2 g. of chlorine in 20 ml. of carbon tetrachloride was added during two hours to a stirred solution of isobutyl chloride (3.52 g.) in 2 ml. of carbon tetrachloride, the mixture being irradiated continuously with a 100-watt uv lamp (General Electric). After washing first with an aqueous 5% sodium bicarbonate solution and then with distilled water, the reaction mixture was dried over Drierite. After

removal of the solvent by fractional distillation, the pot residue of di- and trichloro derivatives was subjected to preparative gas chromatography in order to isolate the dichloro isomers, which were purified by a second vpc fractionation and their nmr spectra taken.

The nmr spectrum of 1,1-dichloro-2-methylpropane shows the six equivalent primary hydrogen atoms represented by a doublet at  $\tau$  8.88,  $J = 6.25$  cps, the methine hydrogen by a doublet at  $\tau$  4.31,  $J = 3.75$  cps and the tertiary hydrogen as a multiplet centered at  $\tau$  7.80. The spectrum of 1,2-dichloro-2-methylpropane has only two signals: one at  $\tau$  8.33 corresponds to the six methyl hydrogens and the other at  $\tau$  6.3 represents the two methylene protons. The spectrum of the 1,3-dichloro isomer is similar to that of the 1,1-dichloro compound exhibiting a doublet at  $\tau$  8.88,  $J = 6.50$  cps due to the interaction of the methyl hydrogen atoms with the tertiary proton, a doublet at  $\tau$  6.41,  $J = 5.75$  cps for the splitting of the four equivalent methylene hydrogens by the  $3^\circ$  hydrogen, and a multiplet with mean  $\tau$  7.77 for the tertiary hydrogen atom.

#### Quantitative vpc Analysis of Products in Competitive Chlorinations.

Competitive chlorination of isobutane with isobutyl or tert-butyl chloride yields a mixture containing mono- and dichloro derivatives of isobutane. In order to correct for any difference in the thermal conductivity response of the detector to monochlorides and dichlorides, the apparatus was calibrated by analyzing standard mixtures of tert-butyl chloride, 1,2-dichloro-2-methylpropane, and 1,3-dichloro-2-methylpropane in carbon tetrachloride, keeping the concentrations of the components very nearly equal to those found in actual experiments. Using the relation

$$\frac{\text{Peak Area of } \underline{\text{tert-Butyl Chloride}}}{\text{Peak Area of 1,2 (or 1,3) Dichloride}} \times n = \frac{\text{Moles of } \underline{\text{tert-Butyl Chloride}}}{\text{Moles of Dichloro Compound}}$$

the average values of the calibration factor, n, from two runs are 1.21 and 1.23. Values of 0.98 and 0.92 obtained for calibration with the 1,3-dichloro isomer vs. 1,2-dichloro compound being not far from unity, the three isomeric dichlorides were assumed to have identical thermal conductivities. The ratio of tert-butyl chloride and isobutyl chloride formed in the photochlorination of isobutane alone was used to calculate the amount of isobutyl chloride formed from isobutane in the competitive runs. The overall effect of this contribution on the concentration of isobutyl chloride taken in comparative experiments (Table VI) was regarded as negligible.

In the experiments involving competitive chlorination of isobutyl and tert-butyl chloride, 1,2-dichloro-2-methylpropane being a common product of chlorination, the relative reactivity of the tertiary hydrogen compared to the primary hydrogen on the substituted or unsubstituted carbon obtained in the chlorination of isobutyl chloride alone was employed to determine the amount of 1,2-dichloro isomer (in terms of units of area) from isobutyl chloride. This value when subtracted from the total area under the 1,2-dichloro peak gives the amount (in terms of units of area) of this isomer arising from tert-butyl chloride.

#### Preparation of 1,2-Dichloro-2-methylpropane via Addition of Chlorine to Isobutylene.

Carbon tetrachloride (10 ml.) and 6.5 ml. of liquified isobutylene were placed in a three-neck flask cooled in an ice bath and equipped with a dropping funnel and a water-cooled condenser. A solution of

chlorine in carbon tetrachloride (30 ml.) containing 0.113 g. of chlorine per ml. of solution was added to the flask during 15 minutes in complete darkness. After the addition, the flask was removed from the ice bath and the mixture stirred for 15 minutes. After washing with 30 ml. of 5% potassium bicarbonate and then with 30 ml. of distilled water, the organic layer was dried over Drierite. After removing the solvent by fractional distillation, the pot residue (3 ml.) was distilled completely in a micro unit. The distillate was fractionated by preparative vpc so as to obtain pure 1,2-dichloro-2-methylpropane.

#### Preparation of 1-Chloro-2-bromo-2-methylpropane.

Methallyl chloride (Eastman practical grade, containing 7% isocrotyl chloride) (15 ml.) and 66 g. of 48.8% aqueous hydrogen bromide were placed in a flask covered with aluminum foil to exclude light and the mixture was stirred in the dark at room temperature for 7.5 hrs. The organic layer was washed with aqueous sodium bicarbonate solution and then with distilled water. The mixture was extracted with ether which was then dried over Drierite and the ether was evaporated. Analysis of this mixture showed that 90% of it was one component. The mixture was distilled under reduced pressure and the major product isolated by vpc.

#### Peroxide-Catalyzed Addition of Hydrogen Bromide to Methallyl Chloride.

Dry hydrogen bromide (21) was prepared by dropping 48% aqueous hydrobromic acid on phosphorous pentoxide and passing the vapors through a trap containing more phosphorous pentoxide. Nitrogen gas was used to provide an inert atmosphere and also to sweep the acid vapors into 10 ml. of methallyl chloride containing 200 mg. of benzoyl peroxide cooled

in an ice bath. The solution was washed with aqueous sodium bicarbonate solution and extracted with ether. The ether extract was dried with Drierite and the solution warmed to about 40° in order to evaporate the ether. The residue was distilled under reduced pressure. Vpc analysis of the distillate showed three products: 1-chloro-2-bromo-2-methylpropane, 15.5%; 1-bromo-3-chloro-2-methylpropane, 81.5%; and an unidentified compound, 3%. The structures were assigned on the basis of their nmr spectra.

#### Addition of Bromine to Isobutylene in the Dark.

A saturated solution of isobutylene (CP grade, Matheson Co.) in carbon tetrachloride was placed in a 50 ml. round bottom flask which was covered with aluminum foil. Liquid bromine (0.4 ml) was added dropwise as the mixture was stirred with a magnetic stirrer. At the end of the addition, the reaction mixture was analyzed by vpc which showed that it contained two products: 1,2-dibromo-2-methylpropane, 85%; and methallyl bromide, 15%. The major product was isolated by preparative gas chromatography and its nmr spectrum recorded.

#### Chlorination of tert-Butyl Bromide.

tert-Butyl bromide (0.6 g.) and 0.12 g. of chlorine in 2 ml. of carbon tetrachloride were irradiated at room temperature until the yellow color of chlorine disappeared; the reaction mixture was then treated as described under General Procedure. Analysis by gas chromatography indicated a single product that had a retention time identical to that of the major product from the chlorination of isobutyl bromide. Injections of mixtures of this component with 1-chloro-2-bromo-2-methylpropane gave two peaks. The nmr spectrum of this compound is similar to that of



1-chloro-2-bromo-2-methylpropane but the chemical shifts for the two signals (6 protons and 2 protons) in the former differ significantly from those in the latter compound. This product is hence assumed to be 1-bromo-2-chloro-2-methylpropane. The chlorination of tert-butyl bromide was relatively faster than the halogenation of other alkyl halides reported here.

#### Chlorination of Isobutyl Bromide.

Gas chromatographic analysis of the products from a particular run involving the reaction of isobutyl bromide (0.63 g.) and chlorine (0.12 g.) showed three peaks: (a) 1-bromo-3-chloro-2-methylpropane, 33%, confirmed by comparison of its retention time and its nmr spectrum with that of the major product obtained by the anti-Markovnikov addition of hydrogen bromide to methallyl chloride described earlier; (b) 1-bromo-2-chloro-2-methylpropane, 59%, was identical with the product obtained by chlorinating tert-butyl bromide; and (c) 1-chloro-2-bromo-2-methylpropane, 8%, was identical with the main product obtained by the addition of hydrogen bromide to methallyl chloride in the dark as well as the chief product of bromination of isobutyl chloride. A complete resolution of 1-chloro-2-bromo-2-methylpropane and 1-bromo-2-chloro-2-methylpropane could not be achieved although separation to allow estimation of the relative proportions of the two isomers was obtained.

#### Bromination of tert-Butyl Chloride .

This reaction was found to be extremely slow which is understandable in terms of the low reactivity of bromine as well as the primary hydrogens of tert-butyl chloride. In a typical run, liquid bromine (0.4 g.) was added to a solution of tert-butyl chloride (1.69 g.) in 2 ml. of

carbon tetrachloride. After being degassed, the solution was irradiated with ultraviolet light (100-watt, General Electric) for 36 hrs. Since the solution still retained the color of bromine, aqueous potassium iodide was added to it followed by the addition of aqueous sodium thio-sulfate till the solution was free of unreacted bromine. The mixture was then extracted with ether. The ether solution was dried with Drierite and the ether was evaporated. Analysis of the residue indicated only one product in addition to the unreacted chloride and the solvent. This component was characterized as 1,2-dibromo-2-methylpropane by its identity (nmr spectra and retention times on two different columns at different temperatures and carrier gas flow) with the product obtained by the ionic addition of bromine to isobutylene.

#### Bromination of Isobutyl Chloride.

The principle product (98-99%) from this reaction (0.84 g. of isobutyl chloride and 0.3 g. of bromine in 1 ml. of carbon tetrachloride) was found to be 1-chloro-2-bromo-2-methylpropane. This compound was identical in retention time and nmr spectrum with the 1-chloro-2-bromo-2-methylpropane which was formed by the addition of hydrogen bromide to methallyl chloride in the dark. 1,2-Dibromo-2-methylpropane (0.4%) was also detected from this reaction.

Retention times (vpc) and nmr data for the different chloro bromo derivatives of isobutane are presented in Table II.

#### Preparation of 2-methylpropane-2-t.

The method described by Whitmore and Badertscher (164) for preparing tert-butyl Grignard reagent was employed. A few crystals of iodine were placed in a three-neck round-bottom 300-ml. flask equipped with a

TABLE II

VPC Retention Times and nmr Data for the  
Chloro Bromo Derivatives of Isobutane

<u>Compound</u>	<u>Retn. Time (a)</u>	<u>Chem. Shift</u>	<u>Multi- plicity</u>	<u>Inten- sity</u>
1-chloro-2-bromo-2-methylpropane	7 m. 30 sec.	$\tau$ 8.17	Singlet	6H
		6.13	Singlet	2H
1-bromo-2-chloro-2-methylpropane	8 m.	8.3	Singlet	6H
		6.37	Singlet	2H
1-bromo-3-chloro-2-methylpropane <sup>(b)</sup>	13 m. 12 sec.	6.46	Triplet	4H
		8.86	Doublet	3H
1-2-dibromo-2-methylpropane	20 m. 54 sec.	7.8	Multiplet	1H
		8.13	Singlet	6H
		6.15	Singlet	2H

(a) vpc analysis at column temperature 112° with a carrier gas flow of 50 ml./m.

(b) The triplet at  $\tau$  6.46 in the spectrum of this compound seems to result from the overlap of the two doublets, one for each pair of methylene protons, since integration shows the triplet in the intensity ratio of 1:2:1. The triplet was not resolved even when the nmr spectrum was recorded using hexadeuterioacetone as the solvent.

magnetic stirrer, pressure-equalizing separatory funnel and a Frederick condenser through which water at  $0.5^{\circ}$  was circulated. Magnesium turnings (8.16 g., 1/3 mole) that had been washed twice with anhydrous ether were added to the flask. The bottom of the flask was warmed with a match till iodine vapors started coming through the magnesium turnings. The flask was then allowed to cool. Pure tert-butyl chloride (31.8 g., 1/3 mole) that had been left 4-5 days over calcium chloride was dissolved in 42 ml. of anhydrous ether (anhydrous grade from J. T. Baker Co. dried over sodium metal). A portion (4 ml.) of this ether-halide mixture was added. The reaction started immediately. About 20 ml. of dry ether were added directly into the flask. A major portion (50 ml.) of the ether-halide mixture was added at a rate never greater than 1 drop per two seconds. The remaining ether solution of tert-butyl chloride was diluted with 25 ml. of ether and added at the aforementioned rate. The total time for all additions was 8.5 hrs. Less than 0.5 g. of magnesium turnings were left unreacted at this stage. The mixture was stirred for an additional 1.5 hrs. One hundred lambdas of tritiated water (specific radioactivity, 171 mc./g.,) was dissolved in 1.5 ml. of reagent-grade isopropyl alcohol (Baker) and the solution diluted with 10 ml. of anhydrous ether. The solution was added dropwise to the Grignard reagent.

The cylinder was rinsed with 2 ml. of ether which was then added to the flask. Distilled water (25 ml.) containing 4 drops of concentrated hydrochloric acid (11.7 N) followed by another 15 ml. of water were next added. During all of these additions, the evolved gas after passing through the cold condenser was condensed into a trap held at  $-78^{\circ}$  (dry ice-acetone bath). The ether in the reaction flask was refluxed for 1 hr.

Vpc analysis of the liquid condensate in the trap showed isobutane and ether in the ratio 3:1. This solution was distilled slowly through a Frederick condenser at  $0.5^{\circ}$ . About 4 ml. of the liquid that always condensed back into the flask and comprised mainly of ether (90%) was discarded. The distillate contained nearly 16% ether. The isobutane was freed from ether by passing it through 10% sulfuric acid solution and a trap packed with cotton, anhydrous calcium chloride, and potassium hydroxide pellets. The process was repeated three times. Vpc analysis of the purified isobutane-2-t (25 ml. of liquid) indicated the presence of two contaminants: isobutylene (3.47%) and ether 0.62%. No further purification was done.

#### Assay of Isobutane-2-t

The initial specific radioactivity of the isobutane is required not only for evaluating the secondary isotope effect but also because it will serve as a standard when the radioactivity of unreacted isobutane from the large-extent reaction is needed to solve equation III. Isobutane-2-t after being freed from non-condensable components is put in a small glass bulb of predetermined volume (10.70 ml.) at a measured temperature and pressure. With the aid of a mercury Toepler pump, the gas is then transferred into a pre-evacuated ion chamber. The chamber is then filled with methane gas at atmospheric pressure. The different stopcocks on the vacuum line are manipulated so that there is little chance of the radioactive isobutane diffusing back into the line. The ionization chamber, after being removed from the vacuum line, is mounted on the preamplifier head of the vibrating-reed electrometer. With a potential of 360 volts d.c. across the chamber and a  $10^{11}$  ohms resistor,

a value in millivolts is directly recorded on the strip-chart recorder. A background reading is taken in a similar fashion by filling the chamber with only methane gas. The difference in these two measurements is the reading for the sample alone. The specific activity of the sample is then calculated in the following manner.

$$\text{Specific Radioactivity } (\mu\text{c./mmole}) = \frac{8.75 \times 10^{11} \frac{\mu\text{c.}}{\text{amp}} \times \frac{\text{millivolt reading}}{\text{resistance (ohms)}}}{\frac{\text{sample weight (mg.)}}{\text{millimolecular weight (mg./mmole)}}$$

In this expression, the factor  $8.75 \times 10^{11} \mu\text{c./amp.}$  is the reciprocal of the product of the number of coulombs per disintegration ( $3.1 \times 10^{-17}$ ) and the value for the microcurie ( $3.7 \times 10^4 \text{ d./sec.}$ ). The initial specific activity of isobutane determined in this manner is given in Table III.

#### Reference Compound for Measuring Activity of Isobutyl Chloride.

Radioactive isobutyl chloride would be the desired standard substance to determine the specific radioactivity of isobutyl chloride which is formed in the photochlorination of 2-methylpropane-2-t. Since the position of tritium in the reference compound is of no importance, it was planned to obtain tritiated isobutyl chloride by hydrogenating methallyl chloride with tritium, the latter being generated by electrolysis of tritiated water. However, preliminary attempts to hydrogenate methallyl chloride over ruthenium/carbon catalyst (in water) or on palladium/carbon (no solvent) resulted mainly in the hydrogenolysis of the carbon-chlorine bond followed by the ionic addition of hydrogen chloride to the double bond of the resulting isobutylene or the starting material. Isocrotyl chloride failed to undergo any reduction, including

hydrogenolysis, over palladium/carbon catalyst. The most direct way to obtain radioactive isobutyl chloride was to collect it by vpc fractionation of a reaction mixture from the large-extent chlorination of isobutane-2-t. The method was not adopted because of a limited supply of isobutane-2-t and the time consuming process of vpc fractionation. Isocrotyl chloride, which has a boiling point and vpc retention time (72.2°, 3 min.) very close to those of isobutyl chloride (68.9°, 2 min. 42 sec.) furnished an alternative provided the former could be labeled with tritium. The isomerization of methallyl chloride with sulfuric acid to give an equilibrium mixture containing 93% of isocrotyl chloride along with 7% of the starting material has been reported (16). Since methallyl chloride was readily available, its isomerization with sulfuric acid containing a known amount of tritiated water provided a novel method of incorporating tritium into the isomeric allylic chlorides. Pure tritiated isocrotyl chloride was obtained by fractionating the equilibrium mixture on the gas chromatograph as described below.

#### Preparation of Tritiated Isocrotyl Chloride.

The procedure of Hearne and coworkers (16) for the acid catalyzed isomerization of methallyl chloride to isocrotyl chloride was followed for this preparation. Methallyl chloride (48 ml., practical grade) was placed in a three-neck, 200 ml. round-bottom flask provided with a magnetic stirrer, a thermometer, and a dropping funnel containing 6.12 g. of 80% sulfuric acid. Fifty lambdas of tritiated water (specific radioactivity, 170 mc./g.) was added to the acid. The flask was immersed up to the level of methallyl chloride in a water bath. The acid was added dropwise for 30 minutes, the mixture being stirred continuously. The temperature of the mixture remained between 25°-26°. A brown layer

separated at the bottom. The flask was then removed from the water bath and warmed with a heating mantle with continued stirring for 2.5 hrs., maintaining the temperature at 40° throughout. The mixture was transferred into a separatory funnel and allowed to stand overnight. After removing the acid layer, the upper organic layer was washed with 10 ml. of 5% aqueous sodium bicarbonate and then with 20 ml. of water in two 10 ml. portions. The solution was dried overnight with anhydrous sodium sulfate. After filtering off sodium sulfate, the filtrate was distilled and the slightly turbid distillate collected in the boiling range 58°-72° was dried over sodium sulfate. This fraction (25 ml.) was found by vpc analysis to contain isocrotyl chloride and methallyl chloride in the ratio 93.6:6.4. Pure isocrotyl chloride was obtained by preparative gas chromatography (column temperature 75°, carrier gas flow 100 ml./min.) of this mixture.

#### Specific Radioactivity of Isocrotyl Chloride-t.

The procedure developed by Wilzbach et al. (169) for preparing a gaseous sample for assay involves the reduction of the compound to methane and hydrogen by heating it with water at 640° in the presence of finely divided zinc and nickel oxide. Although this method is reported (169) to be very accurate and reproducible, it is time-consuming and requires extra precautions such as precise regulation of oven temperature and preparation of strain-free glass seals. Because of the appreciable vapor pressure of isocrotyl chloride at room temperature, it was decided to use the compound directly and assume that none of it would condense inside the chamber under the experimental conditions employed.

Fifteen to twenty milligrams of the liquid is drawn up into a warmed, weighed ampule one end of which has previously been drawn into



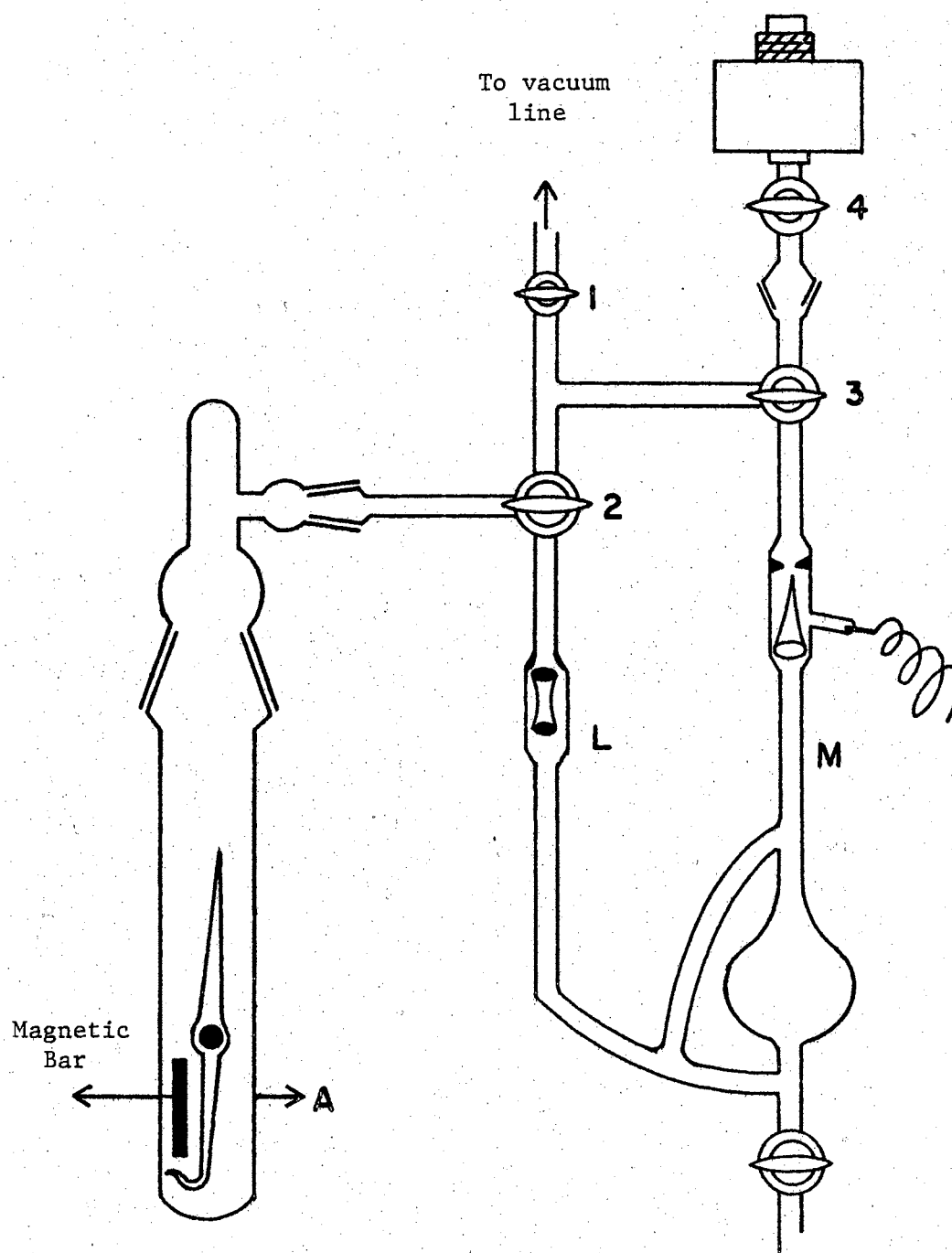


Figure 1. Apparatus for Transferring Isocrotyl Chloride-t from an Ampule into an Ionization Chamber

TABLE III

Initial Specific Radioactivity of Isobutane and Isocrotyl Chloride

Compound	Run	Specific Radioactivity, $\mu\text{c./mmole}^{(a)}$	Ave. <sup>(c)</sup>
Isobutane <sup>(b)</sup>	1	60.00	59.92 $\pm$ 0.13
	2	60.09	
	3	59.07	
Isocrotyl Chloride	1	9.74	9.69 $\pm$ 0.03
	2	9.67	
	3	9.65	

- a. Since the measurements on the two compounds were made on quite different dates, these values have been normalised to a single time.
- b. The values for isobutane have been corrected for non-radioactive impurities, i.e., isobutylene (3.47%) and diethyl ether (0.62%).
- c. With standard deviations.

a fine break-off tip. The open end of the ampule is then sealed in a micro flame and the ampule is reweighed on a micro balance. The weight of the sample is given by the difference in the two weighings. This ampule is then placed carefully inside a Pyrex tube A (Figure 1) along with a magnetic bar. Through a Pyrex elbow, tube A is connected to the vacuum line. By operating stopcock 2, tube A is evacuated to 1 micron. The stopcock 2 is then rotated so that it connects tube A to the arm L of the mercury Toepler pump. The stopcock 3 is positioned in such a manner that the ion chamber and the arm M of the Toepler pump are directly connected. Thus the Toepler pump, ionization chamber and tube A are isolated from the vacuum line. With the help of an external magnet, the magnetic bar in the tube A is moved up and down a few times until the tip of the ampule is broken. The sample is then completely transferred to the ion chamber by operating the Toepler pump. In every cycle of the Toepler pump, mercury is pushed up to the base of stopcock 4. About 10-12 cycles were deemed sufficient for complete transfer. The chamber is then filled with methane gas at atmospheric pressure and radioactivity measured as described earlier. The specific radioactivity of the isocrotyl chloride used is given in Table III.

#### Tritium Assay of the Reaction Products.

The amount of radioactive isobutyl chloride formed in the low-extent chlorination of isobutane-2-t is so small that its separation by preparative vpc for assay purposes was very difficult. A single instrument which could separate the reaction products and assay them for radioactivity in a continuous manner was highly desirable. Such a system devised by coupling a standard vpc unit with a flow-type ion

chamber has been used (23) successfully in this laboratory. The spherical flow chamber employed is made by Applied Physics Corporation and has a volume of 250 ml. The shell is insulated from the preamplifier of the electrometer by means of a standard-taper ceramic adapter and from the gas chromatograph (Aerograph model A-90-P) with glass insulator. An insulated rod passes through the center of the steel tube on which the chamber is mounted. A potential of 90 volts d.c. is applied to collect the ions. The chamber is heated by means of two hemispherical heating mantles fitted tightly around it. To avoid any condensation of the vapors entering the ion chamber, the temperature of the latter, measured with an iron-constantan thermocouple is maintained about 50° above the column temperature. The metallic tube and the joints which connect the chamber to the chromatograph outlet are also heated with a heating tape.

Removal of one substance from the chamber prior to the entry of the next was achieved by supplementing the helium flow with an argon flow rate of 2.5 l. per minute. Argon gas enters through a T connection between the gas chromatograph and the ionization chamber. The use of argon was preferred because of its low ionization potential. To measure and maintain a constant flow rate of argon, a flow meter was inserted between the chamber and the gas cylinder. This method simply involves the separation of the different components of the reaction mixture on a gas chromatograph column followed by the passage of each separated compound through the ion chamber in order to determine its radioactivity.

The final specific radioactivity of isobutane from each run was determined by comparison with isobutane itself, the radioactivity of the latter having been predetermined by the static method. Isocrotyl chloride was employed as the reference standard for isobutyl chloride.

The principle involved in the method may be elaborated by an example. To obtain the specific radioactivity of isobutyl chloride, a sample of isocrotyl chloride of known specific radioactivity is first injected into the gas chromatograph. The ratio of the peak height or peak area on the electrometer recorder to the corresponding peak height or peak area on the recorder attached to the gas chromatograph is proportional to the specific radioactivity of the standard. This is followed by the analysis of the reaction mixture in an identical manner.

All the variables such as column temperature and helium and argon flow rates must be kept constant. Multiple assays of the standard and the unknown, injected alternately, were carried out to minimize any instrumental variations in this technique. Because of greater reproducibility and accuracy, peak heights rather than peak areas were actually employed. Since the specific radioactivity of the standard is known, the specific radioactivity of the unknown is calculated by comparing the peak height ratios for the sample and the standard. The data in Tables XII, XIII, XIV, and XVI were obtained by this method.

#### Photochlorination of 2-Methylpropane-2-t.

A known volume of tritium-labeled isobutane measured at a definite temperature and pressure was condensed into previously degassed carbon tetrachloride or benzene. After dissolving the gas in the solvent in the manner described under General Procedure, the reaction tube was removed from the vacuum line and 0.25 ml. of the solution was withdrawn for measuring the initial specific radioactivity of isobutane. A pre-calculated amount of chlorine in carbon tetrachloride solution was added to the reaction tube and the mixture again degassed on the vacuum

line. After irradiation of the sample, the still unopened reaction tube was reattached (A in Figure 2) to a yoke on the vacuum line. At the B was attached a centrifuge tube containing 60 mg. of quinoline dissolved in 1 ml. of carbon tetrachloride. After the quinoline solution had been degassed, stopcocks  $S_3$  and  $S_2$  were closed. Stopcock  $S_1$  was opened for 5-10 minutes after which the reaction tube was cooled to  $-78^\circ$  (dry ice-acetone) for 15-20 minutes. Stopcock  $S_1$  was then closed. By opening  $S_2$  and cooling the trap with liquid nitrogen, the acid vapors were condensed into the quinoline solution. After repeating this process 4 times, stopcock  $S_1$  was closed and  $S_2$  opened. The trapping tube was alternately warmed to room temperature and cooled with liquid nitrogen to insure complete reaction of the acid and quinoline. Finally the trap was cooled with a liquid nitrogen bath, stopcock  $S_2$  was closed and the tube and stopcock were disconnected from the yoke. After allowing the solution to warm to room temperature,  $S_2$  was opened and the adapter removed. Since the quinoline salt was lighter than carbon tetrachloride, the latter could not be removed by decantation or by centrifugation. Most of the carbon tetrachloride was, therefore allowed to evaporate. The salt was stirred with about 1 ml. of anhydrous ether and the mixture centrifuged (International Equipment Co., Model CL). The ether layer was removed with a capillary pipette. Washing of the salt with ether to remove carbon tetrachloride and excess quinoline was repeated twice.

Another tube containing 3 ml. of carbon tetrachloride or benzene was now attached to side B of the yoke. Most of unreacted isobutane-2-t was recovered in a manner identical to the one described for trapping the acid vapors. The reaction tube was then disconnected from the

vacuum line and the reaction mixture, after treating with a few crystals of solid sodium bicarbonate, was assayed for the final specific radioactivities of isobutane and isobutyl chloride.

#### Specific Radioactivity of Hydrogen Chloride .

As mentioned in Chapter III, specific radioactivity of hydrogen chloride formed in the photochlorination of tritiated isobutane is needed in order to determine "primary isotope effect" in this reaction. Preliminary work indicated that hydrogen chloride and isobutane could not be separated by gas chromatography and hence the flow method for determining specific radioactivity of hydrogen chloride had to be ruled out. It was found that quinoline gave a crystalline white hydrochloride. Higher vapor pressure of hydrogen chloride at  $-78^{\circ}$  as compared to that of other components in the reaction mixture (Table IV), made it possible to separate radioactive hydrogen chloride from the reaction mixture on the vacuum line and trap it as quinoline hydrochloride by distilling it into carbon tetrachloride solution of quinoline as described earlier.

A weighed amount of dry quinoline salt was dissolved in absolute alcohol and the total volume of the solution made to 5 ml. A measured volume of this solution was then counted on a Tri-Carb liquid scintillation spectrometer (Packard, Model 314).

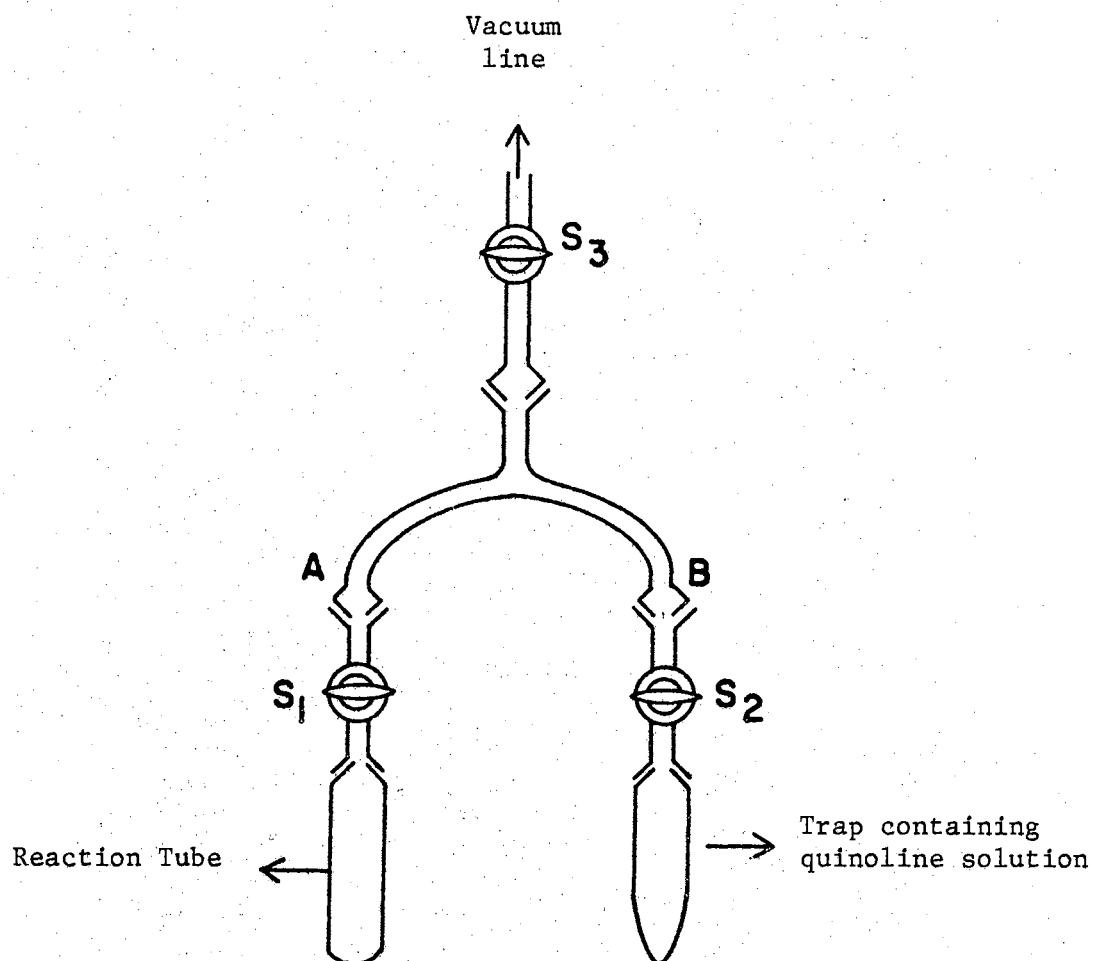


Figure 2. Appartus for Trapping Hydrogen and Tritium Chlorides



TABLE IV

Vapor Pressures of Some Compounds at Different Temperatures (54)

Compound	m.p.	1mm.	10mm.	40mm.	100mm.	400mm.	760mm.
Isobutane	-145 <sup>o</sup>	-109.2	-86.4	-68.4	-54.1	-27.1	-11.7
Isobutyl chloride	-131.2	- 53.8	-24.5	- 1.9	16.0	50.0	68.9
<u>tert</u> -Butyl chloride	- 26.5	solid	solid	-19.0	- 1.0	32.6	51.0
Carbon tetra- chloride	- 22.6	- 50.0	-19.6	4.3	23.0	57.8	76.7
Hydrogen chloride	-114.3	-150.8	-135.6	-123.8	-114.0	-95.3	-84.8

## CHAPTER V

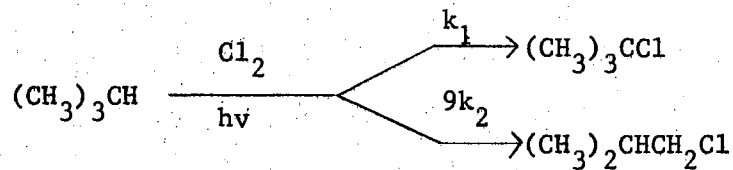
### RESULTS AND DISCUSSION

Preliminary work on the photochlorination of isobutane indicated the formation of dichloro substitution products if the extent of reaction was allowed to exceed 5 mole percent. To avoid any complications due to such polychlorination, the extent of reaction in all the experiments designed to determine relative reactivities was limited to 3 mole percent. Very inconsistent results were obtained from runs that were made without any protection from the laboratory lights and day light. This problem was solved when the samples were prepared and handled (prior to irradiation) in complete darkness, using light only from an infrared lamp.

The characterization of the products, i.e., isobutyl and tert-butyl chlorides, was achieved by adding authentic samples of these compounds to the reaction mixture before gas chromatographic analysis. Thermal conductivity responses of the isomeric monochlorides were assumed identical. The reactivity of the tertiary hydrogen relative to the primary hydrogen atom obtained through quantitative estimation of the products by vpc is shown in Table V. The value of  $3.5 \pm 0.15$  for the reactivity ratio of tertiary to primary hydrogen agrees with values reported for 2,3-dimethylbutane and 2,3,4-trimethylpentane at room temperature (Table VI).

TABLE V

Relative Reactivities of Tertiary and Primary  
Hydrogen Atoms of 2-Methylpropane at 24°



Expt. No.	Isobutane g.	Chlorine g.	$k_1/k_2^a$
47A	0.2000	0.0049	3.80±0.04
47B	0.1795	0.0049	3.41±0.01
48A	0.1996	0.0049	3.41±0.08
48B	0.1913	0.0049	3.38±0.02
Ave.			3.50±0.15

a. Average of 5 or 6 analyses of the same run.

TABLE VI

Ratio of Reactivities of Tertiary and Primary  
Hydrogen Atoms in Some Hydrocarbons

Compound	Reaction Temperature °C	Rel. Reactivity (3°/1°)	Reference
2-Methylpropane	24	3.5±0.15	
2,3-Dimethylbutane	25±0.1	3.5±0.2	109
2,3-Dimethylbutane	25	4.2	113
2,3-Trimethylpentane	25±0.1	3.4±0.2	109

Pure isobutyl chloride was subjected to photochemical chlorination at 24° in carbon tetrachloride solution, the extent of reaction being held between 2 and 2.5 mole percent. The results are summarized in Table VII.

Table VIII contains the results of photochlorination of isobutyl chloride at -15°. Much greater selectivity of chlorine atoms at lower temperatures is evident from comparison of  $k_1/k_3$ ,  $k_3/k_2$  and  $k_1/k_2$  in Tables VII and VIII. This is in keeping with the general energetics of reactions involving attack by chlorine atom.

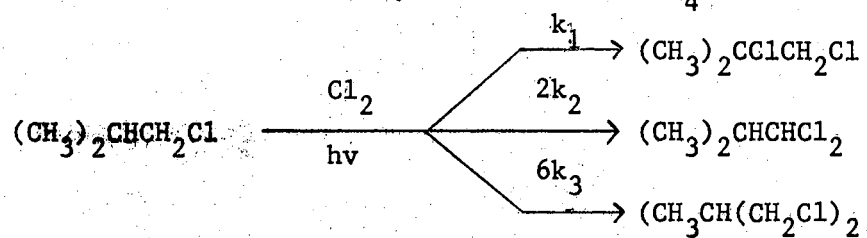
As detailed in the preceding chapter, electron-withdrawing groups retard the substitution by chlorine atom of hydrogens in the proximity of such groups. Therefore, the reactivity ratio of 4.54 for tertiary to primary hydrogen atoms in the chlorination of isobutyl chloride seems unexpectedly high compared to the values for unsubstituted hydrocarbons (Table VI).

These results may be occasioned by either the higher reactivity of tertiary hydrogen or the poor reactivity of the primary hydrogens of isobutyl chloride relative to the corresponding hydrogens of isobutane. Before a definite choice between these two possibilities, the first of which is unprecedented, could be made, it was considered imperative to chlorinate isobutane and isobutyl chloride on a competitive basis. The results from these experiments are given in Table IX.

As is evident from the data in Table IX, both the tertiary and the primary hydrogens of isobutyl chloride are less reactive than the corresponding hydrogens of isobutane. The tertiary hydrogen atom in isobutyl chloride is substituted 4.54 times as rapidly as a hydrogen atom on carbon 3 of isobutyl chloride (Table VII) although the ratio of

TABLE VII

Relative Reactivities of Hydrogen Atoms in the Chlorination of Isobutyl Chloride in  $\text{CCl}_4$  at  $24^\circ$



Expt. No.	Isobutyl Chloride, g.	Chlorine, g.	$k_1/k_3^a$	$k_3/k_2^a$	$k_1/k_2^a$
43A	0.4239	0.0067	4.40±0.06	1.36±0.02	6.00±0.10
43B	0.4244	0.0067	4.53±0.07	1.38±0.02	6.23±0.09
44A	0.4233	0.0067	4.56±0.05	1.35±0.02	6.16±0.07
44B	0.4239	0.0067	4.66±0.12	1.32±0.02	6.16±0.17
Ave.			4.54±0.07	1.35±0.02	6.14±0.07

<sup>a</sup>Each value is the average of 5 or 6 analyses of the same run.

TABLE VIII

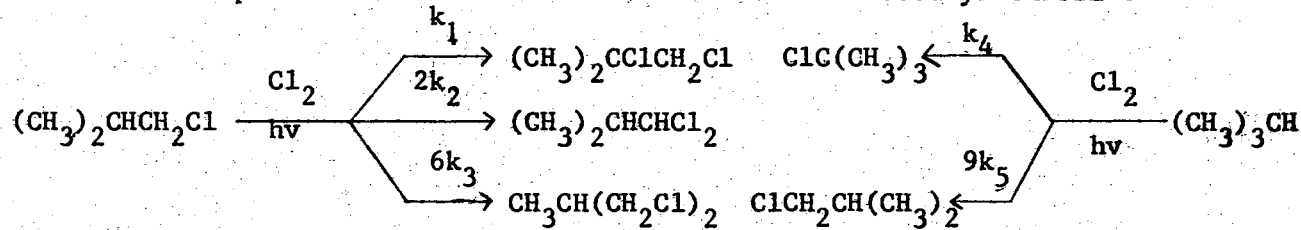
Chlorination of Isobutyl Chloride in Carbon  
Tetrachloride at  $-15 \pm 0.5^\circ$

Expt. No.	Isobutyl Chloride, g.	Chlorine, g.	$k_1/k_3^a$	$k_3/k_2^a$	$k_1/k_2^a$
61A	0.4282	0.0067	$5.74 \pm 0.10$	$1.46 \pm 0.04$	$8.40 \pm 0.07$
61B	0.4259	0.0067	$5.63 \pm 0.14$	$1.52 \pm 0.03$	$8.53 \pm 0.13$
62A	0.4245	0.0067	$5.65 \pm 0.07$	$1.50 \pm 0.04$	$8.45 \pm 0.13$
62B	0.4236	0.0067	$5.64 \pm 0.06$	$1.51 \pm 0.02$	$8.51 \pm 0.17$
Ave.			$5.67 \pm 0.05$	$1.50 \pm 0.02$	$8.48 \pm 0.05$

<sup>a</sup>Each ratio is the average of 5 or 6 analyses of the same run.

TABLE IX

## Competitive Chlorination of Isobutane and Isobutyl Chloride



Expt. No.	Isobutane, g.	Isobutyl Chloride, g.	Chlorine, g.	$k_4/k_1^a$	$k_5/k_3^a$	$k_5/k_2^a$
49	0.2004	0.4226	0.01	1.38±0.03	1.82±0.06	2.46±0.05
51	0.2000	0.4226	0.01	1.25±0.01	1.70±0.02	2.23±0.06
53A	0.2007	0.4224	0.01	1.34±0.03	1.74±0.04	2.30±0.04
53B	0.2007	0.4242	0.01	1.36±0.02	1.70±0.04	2.33±0.03
54A	0.2015	0.4252	0.01	1.30±0.02	1.64±0.07	2.24±0.04
54B	0.2014	0.4243	0.01	1.34±0.02	1.72±0.06	2.27±0.03
Ave.				1.33±0.04	1.72±0.04	2.30±0.06

<sup>a</sup>Each value in a particular experiment is the average of 5 or 6 analyses.



reactivities of the tertiary and primary hydrogen atoms of isobutane under similar conditions is only 3.5 (Table V). The competitive experiments, however, indicate that the tertiary hydrogen atom of isobutyl chloride is only 0.75 times as reactive as the tertiary hydrogen atom of isobutane whereas the primary hydrogens on the substituted and unsubstituted carbon atoms of isobutyl chloride are respectively 0.43 and 0.58 times as reactive as a primary hydrogen of isobutane. The inductive effect of the chlorine atom situated on carbon 1 of isobutyl chloride should be greater on carbon 2 than on carbon 3 since this effect is known to fall off rapidly along a carbon chain. Therefore, the amount of deactivation felt at tertiary hydrogen should be greater than that at the methyl hydrogens. This trend is shown, for instance, by the relative reactivities to chlorination of the hydrogen atoms of n-hexane and n-hexyl chloride. The relative reactivities of the hydrogens on carbon 1 through 4 of n-hexane are reported (19) to be 1.00, 2.45, 2.60, and 2.60; those for n-hexyl chloride are 0.16, 0.83, 1.23, and 2.17. The hydrogen atoms on carbon 1 through carbon 4 of n-hexyl chloride are therefore, 0.16, 0.34, 0.48, and 0.83 respectively as reactive as the hydrogen atoms on the corresponding carbon atoms of n-hexane.

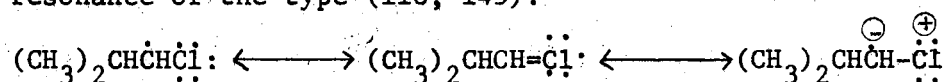
Singh and Tedder (132) have observed that in the vapor-phase chlorination of n-butyl esters of formic, acetic and trifluoroacetic acids, the reactivity of secondary C-H bonds on carbon 3 relative to primary hydrogens on carbon 1 of the n-butyl moiety is very nearly equal to that found in the gas-phase chlorination of n-butane. This implies that no inductive effect is exerted by the ester function on carbon 3 of n-butyl chain.

Any neighboring group participation of the chlorine substituent would enhance the stability of the tertiary radical,  $\text{CH}_3-\dot{\text{C}}(\text{CH}_3)\text{CH}_2\text{Cl}$ , but it does not offer any explanation for the considerable deactivation observed at the unsubstituted carbon.

The small tendency of the terminal methyl group in butyryl chloride towards attack by chlorine atom was attributed by Bruylants and coworkers (14, 15) to a cyclic conformation of the acid chloride in which the deactivating influence of the chlorocarbonyl group on the  $\gamma$ -position was enhanced, probably through some sort of "field effect". These results were, however, later contradicted by Hertog and collaborators (50). Any preferred conformation of isobutyl chloride in which there is considerable interaction between the chlorine and the methyl hydrogens would tend to lower the rate of substitution at these positions. Unfortunately, on the basis of the available data, any arguments for and against such a possibility must be taken with reservations.

The stability of the radical  $\dot{\text{C}}\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$  is mainly provided by the hyperconjugative effect of the tertiary C-H bond. Since the tertiary C-H bond has its electron density lowered because of the strong inductive effect of the substituent chlorine, the electron pair becomes much less available for hyperconjugation, as a result of which the activation energy for the formation of  $\dot{\text{C}}\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$  radical is increased.

The electronegative nature of the chlorine substituent renders the C-H bonds of the substituted carbon less susceptible to attack by the chlorine atom. However, the radical  $(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{HCl}$  gains some stability from resonance of the type (118, 145).

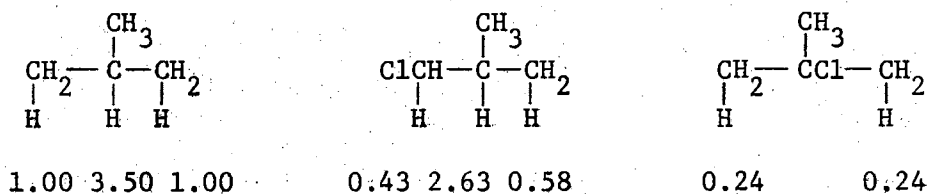


Hence, the activation energies for the formation of  $\dot{\text{C}}\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$  and  $(\text{CH}_3)_2\dot{\text{C}}\text{HCH}_2\text{Cl}$  radicals are nearly equal. Consequently only a small difference is observed in the reactivities of the primary hydrogen atoms on the substituted and unsubstituted carbon atoms of isobutyl chloride.

The low reactivity of the  $1^\circ$  hydrogens of tert-butyl chloride as compared to the methyl hydrogens of 2,3-dimethylbutane obtained through competitive chlorination was attributed by Russell (113) to the strong inductive effect of the chlorine substituent. As a part of the present investigation, mixtures containing known amounts of isobutane and tert-butyl chloride and limited amounts of chlorine were irradiated at  $24^\circ$ . Knowledge of the initial concentrations of the reactants and the relative proportions of their chlorination products determined quantitatively by vpc permits a comparison of the rate constants for the individual reactions occurring simultaneously in the mixture. Data from four different runs are collected in Table X.

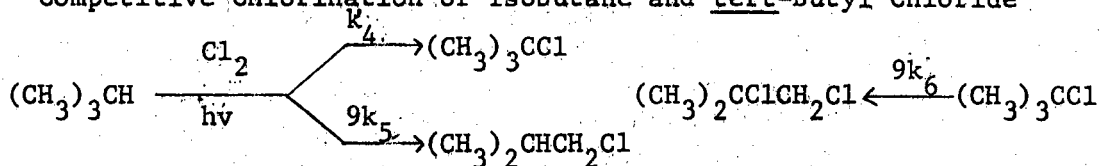
Although concentration effects, if any, in these reactions are known to be insignificant (128), it was considered advisable to maintain the concentrations of the reactants in a series of competitive runs (Tables IX and X) as nearly constant as possible experimentally.

The relative reactivities of individual hydrogen atoms in isobutane, isobutyl chloride and tert-butyl chloride derived from the competitive chlorinations may be shown in the following manner.



From these values the tertiary hydrogen of isobutyl chloride as compared

TABLE X

Competitive Chlorination of Isobutane and tert-Butyl Chloride

Run	Isobutane, g.	<u>tert</u> -Butyl Chloride, g.	Chlorine, g.	$k_5/k_6^a$
56A	0.2012	0.8264	0.01	4.18±0.10
56B	0.2013	0.8293	0.01	3.99±0.04
57A	0.2017	0.8364	0.01	4.23±0.05
57B	0.2015	0.8310	0.01	4.20±0.08
Ave.				4.15±0.06

<sup>a</sup>Each value is the average of five or six analyses of the same run.

to its methyl and methylene hydrogens should be respectively 4.53 and 6.12 times as reactive.

These values are in very good accord with values of 4.54 and 6.14 obtained by direct chlorination of isobutyl chloride itself. The ratio 1.35 of reactivity of primary hydrogens on the unsubstituted and substituted carbons is the same value which is obtained independently. (Table VII).

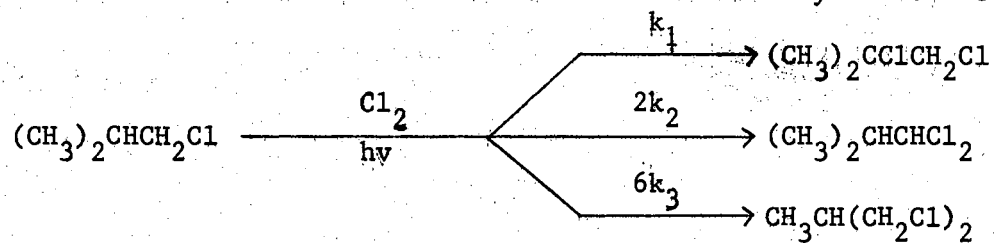
The overall reactivity of isobutyl chloride relative to tert-butyl chloride calculated from the relative reactivities of the individual hydrogen atoms of the two compounds is 3.23. When isobutyl chloride and tert-butyl chloride were chlorinated competitively (0.42 g. of tert-butyl chloride, 0.43 g. of isobutyl chloride and 0.017 g. of chlorine in a total volume of 4 ml.) and the dichloro products determined by vpc, a value of  $3.11 \pm 0.04$  for the ratio of overall reactivities of the two compounds was obtained.

The change in the relative reactivities with the variation of the nature of the medium was evaluated by photochlorinating isobutyl chloride at  $24^{\circ}$  in mixtures of carbon tetrachloride and carbon disulfide and in mixtures of carbon tetrachloride and benzene. It was believed that these experiments would help to obtain information regarding the ionic character of the transition state in the hydrogen abstraction process. The results appear in Table XI. Mixtures of tert-butyl chloride and isobutyl chloride were also chlorinated under these same conditions using mixtures of the same solvents. The data from these runs are given in Table XII.

As pointed out in the first chapter, certain solvents, especially those with  $\pi$  electrons, have pronounced effect on the selectivity of

TABLE XI

Solvent Effects in the Photochlorination of Isobutyl Chloride



Isobutyl Chloride g.	Chlorine, g.	Solvents	Concn. of Second Solvent, moles/l.	$k_1/k_3$	$k_1/k_2$	$k_2/k_3$
		$\text{CCl}_4$	0	4.5	6.1	0.74
0.8633	0.0245	$\text{CCl}_4\text{-CS}_2$	1.2	8.8	8.7	1.01
0.8657	0.0245	$\text{CCl}_4\text{-CS}_2$	2.2	11.4	10.2	1.11
0.8756	0.0245	$\text{CCl}_4\text{-CS}_2$	3.8	14.4	11.6	1.23
0.9144	0.0245	$\text{CCl}_4\text{-CS}_2$	6.3	19.7	13.6	1.45
0.9330	0.0245	$\text{CCl}_4\text{-CS}_2$	8.5	24.3	14.6	1.66
0.8743	0.0245	$\text{CCl}_4\text{-CS}_2$	9.2	24.3	14.8	1.64
0.8640	0.0241	$\text{CCl}_4\text{-CS}_2$	10.7	27.2	15.0	1.81
0.8687	0.0241	$\text{CS}_2$	12.5	29.1	15.3	1.90
0.8681	0.0245	$\text{CCl}_4\text{-C}_6\text{H}_6$	1.3	8.4	9.2	0.91
0.8712	0.0245	$\text{CCl}_4\text{-C}_6\text{H}_6$	2.5	11.2	10.6	1.06
0.8691	0.0245	$\text{CCl}_4\text{-C}_6\text{H}_6$	3.7	13.3	11.7	1.14
0.8736	0.0245	$\text{CCl}_4\text{-C}_6\text{H}_6$	5.0	15.7	12.5	1.26
0.8701	0.0245	$\text{CCl}_4\text{-C}_6\text{H}_6$	6.3	17.4	12.6	1.38
0.6431	0.0172	$\text{CCl}_4\text{-C}_6\text{H}_6$	7.4	19.6	a	a

a Not determined because of experimental difficulties.



chlorine atom in its reactions involving hydrogen abstraction from hydrocarbons. Thus the relative reactivity of tertiary to primary hydrogen in the photochlorination of 2,3-dimethylbutane at 25° is altered (113) from 4.2 in carbon tetrachloride to 225 in carbon disulfide (12M) and to 20 in benzene (4M). It is believed (112) that the increase of selectivity of chlorine atoms in aromatic solvents or in carbon disulfide is due to the formation of a charge transfer complex between the solvent and the chlorine atom, a phenomenon that lowers the reactivity of the chlorine atoms. Some workers (161) feel that solvation of the transition state in these reactions may contribute also to the observed solvent effects.

In contrast to the large solvent effects observed in the case of hydrocarbons, the reactivity of primary hydrogens of tert-butyl chloride relative to methyl hydrogens of 2,3-dimethylbutane changed (113) from 0.12 in carbon tetrachloride to 0.22 in carbon disulfide (12M). Only a small variation in relative reactivity was observed when trimethylchlorosilane and trimethylsilane were competitively photochlorinated in different solvents. These results led Russell (113) to suggest that in the case of hydrocarbons with electronegative substituents, the relative reactivities depend largely on the initial electron density of the carbon-hydrogen bonds being ruptured during chlorination and are not very sensitive to solvent changes. On the other hand, the reactivities which are determined mainly by the stabilities of the incipient radicals are quite sensitive to the nature of the solvent.

In the liquid-phase chlorination of n-butyl chloride at 68° (157), the solvent effect



4	3	2	1	
CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	Cl
1.00	2.52	1.25	0.4	no solvent
1.00	3.75	1.67	0.45	in benzene (7.5M)
1.00	4.82	1.91	0.59	in carbon disulfide (11.1M)

is greater for substitution of hydrogen atoms on carbon 3 than at the deactivated carbon 2. Similar results were obtained when n-hexanoyl chloride was chlorinated in the presence and absence of benzene (49).

CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	COCl
1.00	2.91	2.06	0.57	no solvent	
1.00	15.05	4.29	0.95	in benzene	

Smit and Hertog (137) studied the comparative chlorination of n-heptane and n-octanoyl chloride. It was found that solvent effects on carbons 1, 2, and 3 of n-heptane correspond in magnitude to those at carbons 8, 7 and 6 respectively of octanoyl chloride, indicating that the effect of resonance is identical at these positions.

The solvent effects observed in the chlorination of isobutyl chloride are much more significant than for any of the cases discussed above. It is, therefore, believed that for this chloride the resonance stability of the intermediate radicals determines the relative reactivities of the hydrogen atoms rather than the initial electron availability. The lower reactivity of the complexed chlorine atom results in greater stretching of the attacked carbon-hydrogen bond and hence the ionic character of the transition state becomes quite important. Although the transition state for the abstraction of tertiary hydrogen is stabilized by hyperconjugative resonance of the methyl hydrogens, the transition state involving the attack on a primary hydrogen receives



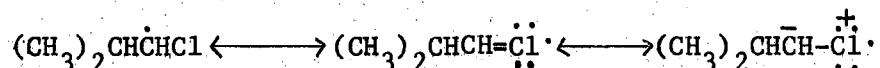
very little resonance contribution from the tertiary carbon-hydrogen bond. Thus the solvent effects support the conclusion earlier deduced from individual and competitive chlorinations of isobutane and isobutyl chloride in carbon tetrachloride.

An interesting feature of these experiments is the enhancement of the reactivity of the hydrogen atoms on the chlorine-bearing carbon of isobutyl chloride with respect to the reactivity of the hydrogen atoms on carbon 3 ( $k_2/k_3$  in Table XI) in the presence of "complexing" solvents; the ratios are 0.74 in carbon tetrachloride, 1.89 in carbon disulfide (12.5M) and 1.39 in benzene (6.3M). This trend is also seen in the chlorination of *n*-butyl chloride at 68° (157); the ratio of reactivities of hydrogen atoms on carbon 1 and 4 varied from 0.4 with no solvent to 0.59 in carbon disulfide (11.1M). Similar results have been reported (118) in the chlorination of chlorocyclopentane. Thus the reactivity of  $\alpha$  hydrogens relative to  $\beta$  or  $\gamma$  hydrogens increases appreciably when the solvent is altered from nitrobenzene to benzene to carbon disulfide. In the latter case, the  $\alpha$  hydrogens became more reactive than  $\beta$  hydrogen atoms.

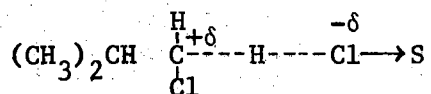
The relative reactivities of the primary hydrogen atoms of *tert*-butyl chloride and the primary hydrogen atoms on carbon 3 of isobutyl chloride (Table XII) change little when the solvent is varied from carbon tetrachloride to carbon disulfide or benzene. On the contrary, the reactivity of the hydrogen atoms on the chlorine-substituted carbon of

isobutyl chloride with respect to the methyl hydrogens of tert-butyl chloride steadily increases with the concentration of the complexing solvent. From these results it appears that the reactivity of the methyl hydrogen atoms in both compounds remains more or less the same whether the attack is by "free" or "complexed" chlorine atoms. One may conclude, therefore, that the apparent increase in rate of substitution of hydrogen atoms on carbons 1 and 2 of isobutyl chloride when the solvent is changed must be due to the preferred attack by complexed chlorine radicals at those sites which result in relatively more stable radicals (or transition states).

Thus in the presence of complexing solvents, the radical  $\text{CH}_3\text{CH}(\text{CH}_3)\dot{\text{C}}\text{HCl}$  seems to be favored over the radical  $\dot{\text{C}}\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$  although the contribution of hyperconjugative resonance is the same in both cases. This result may be rationalized in terms of the increased significance of the resonance of the form



The decreased reactivity of chlorine atom by complexation enhances the contribution to the transition state of the polar structure,



which would be relatively more stable in complexing solvents. Any dipole-induced dipole interaction of the polar structures with solvents having easily polarizable  $\pi$  electrons would also increase the stability of the chloroalkyl radicals. Polar solvents have been reported (161) to enhance the selectivity of alkoxy radicals.

tert-Butyl bromide was photochlorinated at 24° in carbon tetrachloride at an initial concentration of 0.3 g./ml. Gas chromatography analysis of the reaction mixture showed only one product peak which was identified as 1-bromo-2-chloro-2-methylpropane by comparing its retention time and nmr spectrum with those of the major product from chlorination of isobutyl bromide. 1-Bromo-2-chloro-2-methylpropane was the sole product reported by Skell (134) in the reaction of tert-butyl hypochlorite with tert-butyl bromide at -78°. Haag and Heiba (43), who repeated this reaction, found both normal and abnormal substitution products, however. The proportion of 1-chloro-2-bromo-2-methylpropane was found to increase with the concentration of tert-butyl hypochlorite.

Photochlorination of isobutyl bromide under the same conditions produced 1-bromo-2-chloro-2-methylpropane (59%), 1-bromo-3-chloro-2-methylpropane (33%) and 1-chloro-2-bromo-2-methylpropane (8%). In order to verify the structures, 1-chloro-2-bromo-2-methylpropane was prepared by ionic addition of hydrogen bromide to methallyl chloride whereas 1-chloro-3-bromo-2-methylpropane was made by peroxide-catalyzed addition of dry hydrogen bromide to methallyl chloride.

1,2-chlorobromo isomers could not be resolved completely although a satisfactory separation was achieved when the flow of the carrier gas was reduced to about 45-50 ml. per minute. These results differ considerably from those reported by Skell and associates (109) in the reaction of isobutyl bromide with tert-butyl hypochlorite at -78°. These workers obtained only two products, viz., 1-bromo-2-chloro-2-methylpropane (57%) and 1-bromo-1-chloro-2-methylpropane (20%). Neither 1-bromo-3-chloro-2-methylpropane nor any product from 1,2 migration of the bromine atom was found in this reaction.

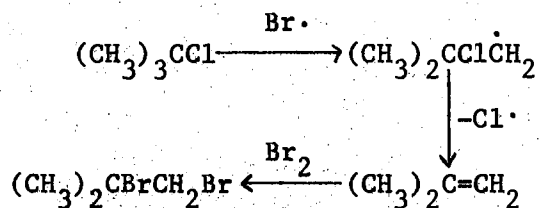
Exclusive formation of 1-bromo-2-chloro-2-methylpropane in the photochlorination of tert-butyl bromide can be rationalized most easily by assuming a non-classical bromine-bridged radical, the intermediate that has been proposed by other workers (134) to explain a 1,2 shift of bromine in the bromoalkyl radicals. If this is true, preferential attack by the chlorine molecule at the tertiary carbon would then lead to the observed product. If the classical radical  $(\text{CH}_3)_2\overset{\cdot}{\text{C}}\text{CH}_2\text{Br}$  underwent elimination of bromine atom to form isobutylene, the latter would most probably add a molecule of chlorine. Since no 1,2-dichloro product was detected, it seems reasonable to believe that the reaction did not follow the elimination and addition mechanism of Haag and Heiba (43).

1-Bromo-3-chloro-2-methylpropane observed in the photochlorination of isobutyl bromide arises evidently from the normal reaction of the radical  $\overset{\cdot}{\text{C}}\text{H}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$  with chlorine. Assuming that a bridged structure does intervene in the transition state, 1-bromo-2-chloro-2-methylpropane could have resulted from the attack of chlorine on the non-classical radical  $(\text{CH}_3)_2\overset{\cdot}{\text{C}}\begin{array}{c} \text{Br} \\ \triangle \\ \text{CH}_2 \end{array}$  or the open (localized) radical  $(\text{CH}_3)_2\overset{\cdot}{\text{C}}\text{CH}_2\text{Br}$ , or possibly both. Under normal conditions with a tertiary to primary reactivity ratio of approximately 4:1, one would expect 1-bromo-2-chloro-2-methylpropane and 1-bromo-3-chloro-2-methylpropane respectively in 60% and 40% proportions. The formation of 1-bromo-2-methylpropane in the greatest relative amount indicates that the bromine substituent in some manner enhances the rate of substitution of the tertiary hydrogen of isobutyl bromide.

The origin of the small but significant amount of 1-chloro-2-bromo-2-methylpropane, formation of which involves a 1,2 migration of bromine, is uncertain. It could arise from an attack of chlorine on

the primary carbon of the three-center transition state  $(\text{CH}_3)_2\overset{\text{Br}}{\underset{\cdot}{\text{C}}}\text{CH}_2$  but if this were the case some of this compound should have been formed in the chlorination of tert-butyl bromide; and this is not so. Thus the products observed in the photochlorination of these two bromides do not fit a common bridged intermediate.

Photobromination of tert-butyl chloride with elemental bromine gives exclusively 1,2-dibromo-2-methylpropane, the identity of which has been confirmed through comparison of its vpc analysis (on two different columns) and nmr spectrum with those of an authentic sample made by polar addition of bromine to isobutylene. Low reactivity of both the bromine atoms and the  $1^\circ$  hydrogens being abstracted render this reaction extremely slow. Decomposition of the intermediate chloroalkyl radical followed by bromine addition to the double bond appears to be the most plausible mechanism for this reaction. The nature of the last step

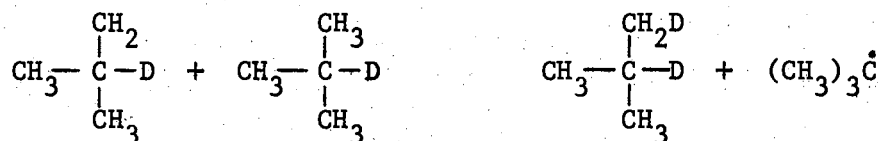


may be homolytic or heterolytic or both. Although the complete breakdown of chloroalkyl radicals at temperatures higher than  $300^\circ$  and the decomposition of bromoalkyl radicals at lower temperatures (26, 27) is known, no case involving chlorine atom elimination has been reported for chloroalkyl radicals at room temperature. No detection of bromo-chloro products and the slowness of the reaction are indicative of the lack of any anchimeric assistance of the substituent chlorine atom.

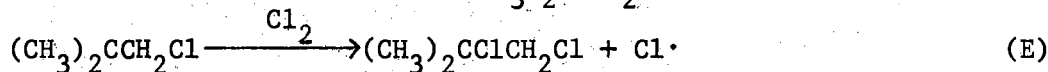
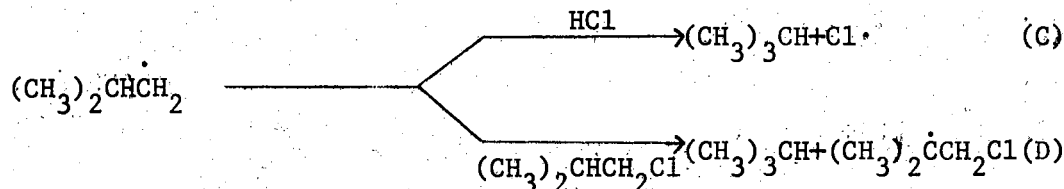
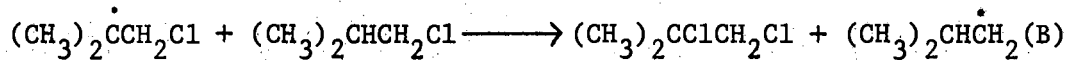
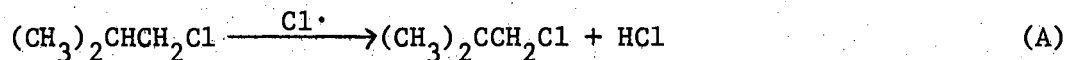
The reaction of bromine with isobutyl chloride at room temperature gives mainly 1-chloro-2-bromo-2-methylpropane, which is quite understandable since bromine is known to have high specificity for tertiary

hydrogen atoms (59, 22). 1-2-Dibromo-2-methylpropane (0.4%) detected in this reaction most probably arises by bromine addition to isobutylene which in turn is formed by the decomposition of  $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{Cl}$  radical.

Detectable amounts of isobutane are produced in the photochlorination of isobutyl chloride and isobutyl bromide. Brown and Russell (10) who investigated photochlorination of 2-methylpropane-2-d, ruled out any appreciable radical exchange of the type shown below.



The following sequence is tentatively suggested to produce the observed isobutane.



The tertiary radical  $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{Cl}$  formed in the slow step (A) may react with either a chlorine molecule (E) or an isobutyl chloride molecule (B) giving in each case 1,2-dichloro-2-methylpropane. Although the majority of the  $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{Cl}$  radicals would rupture the weaker Cl-Cl bond (bond energy = 58 kcal./gram bond) (40) rather than C-Cl bond of relatively greater bond strength (77 kcal./gram bond) (40), a few collisions of the type B can be envisioned since isobutyl chloride is present in large excess. In view of the recent developments (4, 166) which in-

indicate that alkyl radicals can abstract hydrogen from hydrogen chloride, reaction C may be quite important since the hydrogen chloride formed in these investigations was not permitted to escape during irradiation.

#### Tritium Isotope Effects in the Photochlorination of 2-Methylpropane-2-t

The final specific radioactivity of isobutane from the first set of experiments comprising one large-extent reaction (30-40 percent) and one low-extent reaction (~3%) is given in Table XIII.

The specific radioactivity of isobutyl chloride in E106A' could not be determined because of its low concentration in the sample. The specific radioactivity of isobutane and isobutyl chloride shown in Table XIV are for a run (E106C) in which the extent of chlorination was held in the 10-12% range.

It is seen from Tables XIII and XIV that the final specific radioactivity of isobutane both in E106B and E106C is lower than its initial specific radioactivity. On the basis of the normal primary isotope effect expected in radical reactions, these findings seem very unrealistic. For this reason, not much significance was attached to the specific radioactivity of isobutyl chloride found in the experiment E106C.

The lowering of specific radioactivity of isobutane may be ascribed to two possible factors. A highly reactive impurity may be present which has higher specific radioactivity than that of isobutane and is not separated from isobutane under vpc conditions, so that it enters the ion chamber along with the isobutane, (b) The reaction may be complicated by the presence of isobutyl and tert-butyl chloride, especially when the extent of chlorination is large.



TABLE XIII

## Final Specific Radioactivity of Isobutane

Expt. No.	Extent of Reaction	Specific Radioactivity, $\mu\text{c./mmole}$		Average Value
		Individual Assays		
E106A'	~ 3%	57.27	57.10	57.98 $\pm$ 0.70
		59.32	57.80	
		57.70	57.01	
		57.88	58.49	
		59.27		
E106B	30-40%	60.29	58.23	58.73 $\pm$ 0.92
		57.92	58.16	
		58.70	59.17	
		60.22	57.18	

TABLE XIV

## Final Specific Radioactivity of Isobutane and Isobutyl Chloride

Compound	Specific Radioactivity, $\mu\text{c./mmole}$		Ave. Value
	Individual	Assays	
Isobutane	57.62	58.28	57.18 $\pm$ 0.82
	57.69	55.60	
	56.69		
Isobutyl Chloride	51.78	50.86	51.02 $\pm$ 0.51
	50.14	54.39*	
	51.29		

\*Rejected

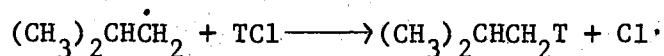
Gas chromatographic analyses of the tritiated isobutane showed only two contaminants, ethyl ether and isobutylene, both of which may be safely assumed to be non-radioactive. Isobutylene was removed even in the very low-extent reaction and the resulting 1,2-dichloro-2-methylpropane did not show any radioactivity. Furthermore it was noted that in E106E, 1,1-dichloro-2-methylpropane and 1,3-dichloro-2-methylpropane were radioactive whereas the 1,2-dichloro-2-methylpropane which was present in relatively the largest amount, did not show any activity. This appears to be a reasonable indication of the selective labeling of isobutane since otherwise the 1,2-dichloro isomer must have been radioactive.

Assuming once again the possibility of a "hotter" contaminant in the starting material, another experiment consisting of two parts was carried out. (I) Large-extent chlorination (25-30%) of isobutane-2-t (E106D) (II) Further chlorination of the isobutane in the reaction mixture from E106D without removing the substitution products (E106E).

Any reactive impurities present in isobutane should be removed in E106D and with the assumption of a normal primary isotope effect the final specific radioactivity of isobutane in E106E as compared to that in E106D should be higher. The final specific radioactivity of isobutane in E106D and E106E was respectively  $57.20 \pm 0.81$   $\mu\text{c./mmole}$  and  $47.82 \pm 0.14$   $\mu\text{c./mmole}$ .

Appreciable lowering of the specific radioactivity of isobutane in E106E leads to the belief that the presence of chloro derivatives complicates the photochlorination of isobutane. Injections of large amounts of the reaction mixture E106E showed the presence of slightly radioactive tert-butyl chloride and 1,2-dichloro-2-methylpropane although no

such activity was observed in E106D. Formation of 2-methylpropane-1-t by a reaction such as is represented below



appears very attractive, although in no way definite in the present case. Participation of hydrogen chloride and tritium chloride in free-radical reactions has been reported (4).

A carbon tetrachloride solution (8 ml.) of isobutane-2-t (containing ~ 90 mg./ml.) was photochlorinated using 0.15 ml. of liquified chlorine (run #E107A). A portion (5.5 ml.) of the reaction mixture from E107A (containing 54 mg. of isobutane per ml. of the solution) was degassed and the unreacted isobutane was recovered by fractionation on the vacuum line using cooling baths at  $-46^\circ$  and liquid nitrogen temperatures. After the final fractionation, about 1500 ml. of the vapor collected at  $25.5^\circ$  and 67 mm. pressure of mercury were transferred and thoroughly dissolved in 3.5 ml. of previously degassed carbon tetrachloride. Vpc analysis of this solution showed isobutane, isobutyl chloride and tert-butyl chloride in the concentrations of 36 mg./ml., 3.85 mg./ml. and 2.26 mg./ml. respectively. A portion (2 ml.) of this solution was reacted with 0.03 ml. of liquified chlorine (E107B). The final specific radioactivity of isobutane in E107A and E107B runs is summarized in Table XV.

The increase in the specific radioactivity of isobutane in E107B is encouraging but still not upto expectations. For instance, assuming a secondary isotope effect  $k_2/k_4 = 1.05$  and a primary isotope effect  $k_1/k_3 = 2.00$ , the specific radioactivity of isobutane after 20% reaction should be 1.16 times its initial specific radioactivity.

TABLE XV

## Final Specific Radioactivity of Isobutane

Expt. No.	Final Specific Radioactivity of Isobutane $\mu\text{c./mmole}$		
	Individual	Assays	Ave. Value
E107A	60.68	60.64	
	59.34	59.08	
	61.17	59.46	60.06 $\pm$ 0.77
E107B	62.58	64.12	
	61.72	63.39	
	63.44		63.05 $\pm$ 0.72

Another problem encountered in the large-extent reactions was the determination of the exact extent of chlorination. In all of the experiments carried out, the final concentration of isobutane was found to be much lower than expected on the basis of the amount of chlorine added. Even by using a blank for each run, reliable values for the true extent of reaction could not be obtained.

Two more runs (E108A, E108B), both involving low-extent chlorination (<3%), were conducted in order to obtain the value for secondary isotope effect. The final specific radioactivity of isobutane was found to be very nearly equal to its initial activity, thus satisfying the assumption made in deriving the equation IV. Unfortunately, the specific radioactivity of isobutyl chloride could not be determined satisfactorily, chiefly because of its very low concentration in the reaction mixtures.

The results of the experiments in which the hydrogen chloride and tritium chloride, formed from the chlorination of 2-methylpropane-2-t, were trapped as corresponding quinoline salts are described next. Three runs were made in carbon tetrachloride and two runs were made in a mixture of carbon tetrachloride and benzene (9.7M). The quantities of 2-methylpropane-2-t and chlorine used for these experiments are shown in Table XVI.

#### Primary Isotope Effect

Assay of quinoline hydrochloride gave very inconsistent data for the different runs as well as for the samples from a particular run. It was found that both the ethanol solutions as well as the solid salts lost radioactivity (indicated by the contents which had reached

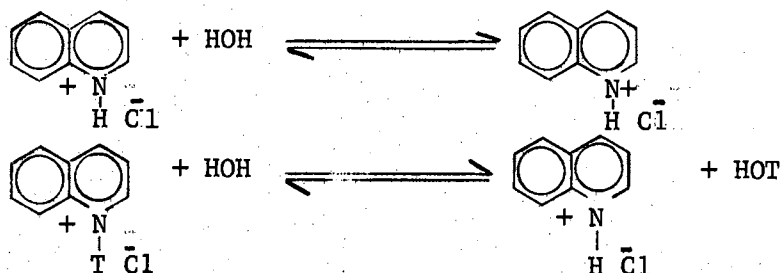
TABLE XVI

Reactants Used in the Chlorination of 2-Methylpropane-2-t

Expt. No.	Solvent System	Isobutane-t g.	Chlorine <sup>a</sup> g.
E109	CCl <sub>4</sub>	0.4410	0.0485
E110	CCl <sub>4</sub>	0.4096	0.0485
E113	CCl <sub>4</sub>	0.4645	0.0485
E111	CCl <sub>4</sub> -C <sub>6</sub> H <sub>6</sub>	0.4537	0.0485
E112	CCl <sub>4</sub> -C <sub>6</sub> H <sub>6</sub>	0.4410	0.0485

a. It includes the amount of chlorine necessary to react with isobutylene impurity

background level) after standing for about a week. The most plausible reason seems to be the exchange of tritium with atmospheric moisture in a irreversible or reversible manner.



It appears that this phenomenon may be avoided by employing a base that is considerably stronger than quinoline.

#### Secondary Isotope Effect

The final specific radioactivity of isobutane and isobutyl chloride from the first four runs (E109, E110, E113, and E111) determined by the flow method appears in Table XVII. Because of a very high selectivity for the chlorine attack on tertiary hydrogen atom in the two runs (E111, E112) involving benzene as the second solvent, the amount of isobutyl chloride produced in these experiments was too low to yield an accurate value for the specific radioactivity of isobutyl chloride. For instance the specific radioactivity of isobutyl chloride in the run E111 was found to be  $45.96 \pm 1.76$   $\mu\text{c./mmole}$ . which gives a secondary isotope effect ( $k_2/k_4$ ) of 1.304. This value is much higher than that obtained when the reaction is carried out in carbon tetrachloride. For this reason no attempt was made to analyze E112. The data on secondary isotope effect which appears in Table XVII has been derived only from the three runs in which carbon tetrachloride was the reaction medium.



TABLE XVII

## Assays of Isobutane and Isobutyl Chloride for Secondary Isotope Effect

Expt. No.	Compound	<u>Specific Radioactivity, c./mmole</u>			<u>Secondary Isotope Effect</u>
		Individual	Assays	Ave. Value <sup>a</sup>	$k_2/k_4^a$
E109	Isobutane	59.96	59.73	59.60±0.14	1.040±0.007
		59.01	59.87		
		59.46	59.56		
	Isobutyl Chloride	56.78	59.08	57.63±0.38	
		57.19	57.97		
		58.08	56.68		
E110	Isobutane	60.79	58.44	59.64±0.69	1.052±0.004
		61.77	57.58		
		60.78	58.47		
	Isobutyl Chloride	57.51	58.11	56.94±0.40	
		55.83	56.67		
		55.83	57.66		
E113	Isobutane	61.60	59.83	60.66±0.70	1.040±0.009
		61.55	63.13		
		59.20	58.65		
	Isobutyl Chloride	59.40	58.43	57.64±0.49	
		56.30	57.48		
		57.87	56.83		
Ave = 1.044±0.004					

<sup>a</sup>With standard deviations.

Although  $\beta$  deuterium isotope effect has been investigated in a number of carbonium ion reactions (127 to 130) not much work is known on isotope rate effects involving tritium atom either in ionic or in radical reactions. Very significant secondary deuterium effects observed in the solvolysis of polydeutero alkyl chlorides (127, 129) have been ascribed by Shiner (141) mainly to the hyperconjugative interactions similar explanation has been offered by Streitwieser and coworkers (141) for the  $\beta$ -deuterium effect observed in the acetolysis of tosylates of cyclopentanol-1d, cis- and trans-cyclopentanol-2d and cyclopentanol-2,2,5,5d<sub>4</sub> at 50°. The role of hyperconjugation has been stressed by Lewis and Boozer (81) to interpret the secondary deuterium isotope effect in carbonium ion reactions. The large isotope effect in carbonium ion reactions results from the extensive withdrawal of the bonding electrons on the  $\beta$ -carbon atom in order to lessen the electron deficiency of the positively charge carbon atom. Since the hyperconjugative delocalization of the unpaired electron in the  $(\text{CH}_3)_2\text{CTCH}_2$  or  $(\text{CH}_3)_2\text{CHCH}_2$  radical is not very extensive, relatively small  $\beta$ -tritium isotope effect in the radical chlorination of 2-methylpropane-2-t would be expected which is found to be so.

## BIBLIOGRAPHY

1. P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, 84, 916 (1962).
2. P. C. Anson, P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 918 (1959).
3. J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959).
4. H. L. Benson, Jr. and J. E. Willard, *J. Am. Chem. Soc.*, 83, 4672 (1961).
5. A. H. Blatt, "Organic Syntheses," Collective Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 144.
6. J. R. B. Boocock and W. J. Hickinbottom, *J. Chem. Soc.*, 1234 (1963).
7. C. E. Boozer, B. W. Ponder, J. C. Trisler and C. E. Wightman III, *J. Am. Chem. Soc.*, 78, 1506 (1956).
8. J. H. T. Brook, *Trans. Faraday Soc.*, 53, 327 (1957).
9. H. C. Brown, M. S. Kharasch and T. H. Chao, *J. Am. Chem. Soc.*, 62, 3435 (1940).
10. H. C. Brown and G. A. Russell, *J. Am. Chem. Soc.*, 74, 3995 (1952).
11. *Ibid.*, 77, 4578 (1955).
12. H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, 77, 4019 (1955).
13. *Ibid.*, *Rec. Chem. Progr.*, 9, 81 (1948).
14. A. Bruylants, M. Tits and R. Danby, *Bull. Soc. Chim. Belges.*, 58, 210 (1949).
15. A. Bruylants, M. Tits, C. Dieu and R. Gauthier., *Bull. Soc. Chim. Belges.*, 61, 266 (1952).
16. J. Burgin, G. Hearne and F. Rust, *Ind. Eng. Chem.*, 33, 385 (1941).
17. A. Butlerov, *Ann.*, 144, 15 (1867).
18. S. G. Cohen et al. (Ed.), "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, N. Y., 1963.

19. N. Colebourne and E. S. Stern, *J. Chem. Soc.*, 3599 (1965).
20. J. Dan's and J. Kautzsch, *J. Prak. Chem.*, 2, 80, 305 (1909).
21. R. T. Dillon and W. G. Young, *J. Am. Chem. Soc.*, 51, 2389 (1929).
22. B. H. Eckstein, H. A. Scheraga and E. R. Van Artsdalen, *J. Chem. Phys.*, 22, 28 (1954).
23. Rex L. Elmore, Ph.D. Thesis, Oklahoma State University, 1965.
24. M. Feld, A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, 84, 4451 (1962).
25. P. S. Fredricks and J. M. Tedder, *Chem. Ind.*, 490 (1959).
26. P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).
27. *Ibid.*, 3520 (1961).
28. R. Kh. Freidlina, M. Ya. Khorlina and A. N. Nesmeyanov, *Izvest. Akad. Nauk Otdel. Khim. Nauk.*, 658 (1960).
29. R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov, *Doklady Akad. Nauk SSSR*, 128, 316 (1959).
30. *Ibid.*, 137, 341 (1961).
31. R. Kh. Freidlina, A. B. Trentiev, R. G. Petrova and A. N. Nesmeyanov, *ibid.*, 138, 859 (1961).
32. A. E. Fuller and W. J. Hickinbottom, *J. Chem. Soc.*, 3228 (1965).
33. *Ibid.*, 3235 (1965).
34. I. Galiba, J. M. Tedder and J. C. Walton, *J. Chem. Soc.*, 604 (1966).
35. C. W. Gayler, and H. M. Waddle, *J. Am. Chem. Soc.*, 63, 3358 (1941).
36. H. L. Goering, P. I. Abell and B. F. Aycock, *J. Am. Chem. Soc.*, 74, 3588 (1952).
37. V. Gold (Ed.), "Advances in Physical Organic Chemistry," Vol. 2, Academic Press, N. Y., 1964, p. 1-91.
38. V. Gold (Ed.), "Advances in Physical Organic Chemistry," Vol. 2, Academic Press, N. Y., 1964, p. 163.
39. P. Goldfinger, M. Jeunehomme and G. Martens, *J. Chem. Phys.*, 29, 456 (1958).
40. E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt and Co., New York, N. Y., 1959, p. 37.

41. M. Gomberg, Ber. 33, 3150 (1900).
42. W. O. Haag and El. A. I. Heiba, Tetrahedron Letters, 41, 3679 (1965).
43. Ibid., 41, 3683 (1965).
44. H. B. Hass, E. T. McBee and Paul Weber, Ind. Eng. Chem., 27, 1190 (1935).
45. Ibid., 28, 333 (1936).
46. R. Van Helden and E. C. Kooyman, Rec. Trav. Chim., 73, 269 (1954).
47. D. G. Hendry and G. A. Russell, J. Am. Chem. Soc., 86, 2368 (1964).
48. A. L. Henne and F. B. Hinkamp, J. Am. Chem. Soc., 67, 1194, 1197 (1945).
49. H. J. Den Hertog and P. Smit, Proc. Chem. Soc. (Lond.), 132 (1959).
50. H. J. Den Hertog, B. De Vries, and J. Van Bragt, Rec. Trav. Chim., 74, 1561 (1955).
51. Ibid., 77, 73 (1958).
52. G. Herzberg, Proc. Roy. Soc. (Lond), 262A. 291 (1961).
53. G. Herzberg, Ann. Rev. Phys. Chem., 9, 327 (1958).
54. C. D. Hodgman (Ed.), "Handbook of Chemistry and Physics," 35th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953, p. 394.
55. V. L. Horner and L. Schläfer, Ann., 635, 31 (1960).
56. M. Karplus, J. Chem. Phys., 30, 15 (1959).
57. M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961)
58. B. A. Kazanski and M. Y. Lukina, Izvest. Akad. Nauk SSSR., Otdel. Khim. Nauk, 47 (1951); via CA; 46, 4491 (1952).
59. M. S. Kharasch, W. Hered and F. R. Mayo, J. Org. Chem., 6, 818 (1942).
60. M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).
61. M. S. Kharasch, P. C. White and F. R. Mayo, J. Am. Chem. Soc., 59, 1495 (1937).
62. M. S. Kharasch, P. C. White and F. R. Mayo, J. Org. Chem., 2, 574 (1938).

63. Ibid., 3, 33 (1938).
64. M. S. Kharasch, M. Z. Fineman and F. R. Mayo, J. Am. Chem. Soc., 61, 2139 (1939).
65. M. S. Kharasch and M. Z. Fineman, J. Am. Chem. Soc., 63, 2776 (1941).
66. M. S. Kharasch, W. Zimmt and W. Nudenberg, J. Chem. Phys., 20, 1659 (1952).
67. M. S. Kharasch, and H. C. Brown, J. Am. Chem. Soc., 62, 925 (1940).
68. M. S. Kharasch, W. S. Zimmt and W. Nudenberg, J. Org. Chem., 20, 1430 (1955).
69. M. S. Kharasch, Y. C. Liu and W. Nudenberg, J. Org. Chem., 19, 1150 (1954).
70. Ibid., 20, 680 (1955).
71. M. Ya. Khorlina and V. N. Kost, Doklady Akad. Nauk SSSR, 137, 1133 (1961).
72. J. H. Knox and R. L. Nelson, Trans. Faraday Soc., 55, 937 (1959).
73. E. C. Kooyman and G. C. Vegter, Tetrahedron, 4, 382 (1958).
74. E. C. Kooyman and A. Strang, Rec. Trav. Chim., 72, 329 (1953).
75. V. N. Kost, T. T. Vasilyeva and R. Kh. Friedlina, Izvest. Akad. Nauk, Otdel. Khim. Nauk, 1254 (1952).
76. V. N. Kost, T. T. Vasilyeva, L. Zakharkin and R. Kh. Freidlina ibid., 1992 (1963).
77. V. N. Kost, T. T. Sidorova, R. Kh. Freidlina and A. N. Nesmeyanov, Doklady Akad Nauk SSSR, 132, 606 (1960).
78. V. N. Kost, T. T. Vasilyeva and R. Kh. Freidlina, Doklady Akad. Nauk Belorus. SSR, 7, 614 (1963).
79. Ibid., 7, 538 (1963).
80. E. S. Lewis and C. E. Boozer, J. Am. Chem. Soc., 74, 6306 (1952).
81. Ibid., 76, 791 (1954).
82. W. F. Libby, Ind. Eng. Chem., Anal. Ed., 19, 2 (1947).
83. C. F. Mabery and E. J. Hudson, Am. Chem. J., 19, 243 (1897).
84. F. R. Mayo and W. B. Hardy, J. Am. Chem. Soc., 74, 911 (1952).

85. J. J. McBride and H. C. Beachell, *J. Am. Chem. Soc.*, 70, 2532 (1948).
86. L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, 1960.
87. I. E. Muskat and H. E. Northrup, *J. Am. Chem. Soc.*, 52, 4043 (1930).
88. A. N. Nesmeyanov, R. Kh. Freidlina and V. I. Firstov, *Izvest. Akad. Nauk, Otdel. Khim. Nauk*, 505 (1951).
89. A. N. Nesmeyanov, R. Kh. Freidlina and A. B. Belyavsky, *ibid.*, 1028 (1959).
90. A. N. Nesmeyanov, R. Kh. Freidlina and V. N. Kost, *ibid.*, 1205 (1958).
91. A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Doklady Akad. Nauk SSSR*, 81, 199 (1951).
92. A. N. Nesmeyanov, R. Kh. Freidlina and V. N. Kost, *ibid.*, 113, 828 (1947).
93. A. N. Nesmeyanov, R. Kh. Freidlina, R. G. Petrova and A. B. Terentiev, *ibid.*, 127, 575 (1959).
94. A. N. Nesmeyanov, R. Kh. Freidlina and V. N. Kost, *Tetrahedron*, 1, 241 (1957).
95. A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Quart. Rev.*, 10, 330 (1956).
96. W. A. Nevill, D. S. Frank and R. D. Trepka, *J. Org. Chem.*, 27, 422 (1962).
97. S. Oeconomides, *Bull. Soc. Chim. de France*, (2) 45, 497 (1881).
98. F. Paneth and W. Hofeditz, *Ber.*, 62, 1335 (1929).
99. J. D. Park, B. Striklin and J. R. Lacher, *J. Am. Chem. Soc.*, 76, 1387 (1954).
100. E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, 27, 4196 (1962).
101. R. N. Pease and F. Walz, *J. Am. Chem. Soc.*, 53, 3728 (1931).
102. G. Porter and K. J. Wright, *Discussions Faraday Soc.*, 14, 23 (1953).
103. H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.* 76, 1201 (1954).
104. *Ibid.*, 77, 2629 (1955).

105. W. A. Pryor, "Free Radicals," McGraw Hill Book Co., N. Y., 1966.
106. M. Ritchie and W. I. H. Winning, J. Chem. Soc. 3583 (1953).
107. S. D. Ross, M. Markarian and M. Nazzewski, J. Am. Chem. Soc., 69, 1914, 2468 (1947).
108. G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4025 (1955).
109. Ibid., 77, 4031 (1955).
110. Ibid., 77, 4578 (1955).
111. G. A. Russell, J. Am. Chem. Soc., 79, 2977 (1957).
112. Ibid., 80, 4987 (1958).
113. Ibid., 80, 4997 (1958).
114. Ibid., 80, 5002 (1958).
115. G. A. Russell, J. Org. Chem., 24, 300 (1959).
116. G. A. Russell, Tetrahedron, 8, 101 (1960).
117. G. A. Russell, A. Ito and D. G. Hendry, J. Am. Chem. Soc., 85, 2976 (1963).
118. G. A. Russell and A. Ito, J. Am. Chem. Soc., 85, 2983 (1963).
119. G. A. Russell and P. G. Haffley, J. Org. Chem., 31, 1869 (1966).
120. F. F. Rust and W. E. Vaughan, Ind. Eng. Chem., 41, 2595 (1949).
121. C. Schorlemmer, Proc. Roy. Soc. (Lond.), 17, 372 (1868).
122. H. J. Schumaker and K. L. Muller, Z. Physik. Chem., B37, 365 (1937).
123. H. J. Schumaker and W. A. Alexander, ibid., B44, 313 (1939).
124. H. J. Schumaker and W. Thurauffer, ibid., A189, 183 (1941).
125. R. P. W. Scott and D. W. Grant, Analyst, 89, 179 (1964).
126. W. V. Sherman and G. H. Williams, J. Chem. Soc., 1442 (1963).
127. V. J. Shiner, Jr., J. Am. Chem. Soc., 75, 2925 (1953).
128. Ibid., 76, 1603 (1954).
129. Ibid., 78, 2653 (1956).
130. V. J. Shiner, Jr., and C. J. Verbanic, ibid., 79, 373 (1957).



131. V. J. Shiner, Jr., *Tetrahedron*, 5, 243 (1959).
132. H. Singh and J. M. Tedder, *J. Chem. Soc.*, 608 (1966).
133. H. Singh and J. M. Tedder, *Chem. Commun.*, 5 (1965).
134. P. S. Skell, R. S. Allen and N. D. Gilmour, *J. Am. Chem. Soc.*, 83, 504 (1961).
135. P. S. Skell, D. L. Tuleen and P. D. Readio, *ibid.*, 85, 2849 (1963).
136. P. S. Skell and P. D. Readio, *ibid.*, 86, 3334 (1964).
137. P. Smit and H. J. Den Hertog, *Rec. Trav. Chim.*, 83, 891 (1964).
138. George Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," McMillan Co., N. Y., 1964.
139. H. M. Stanley and J. E. Youell, *U. S. Pat.*, 2,374,237 (1945).
140. E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publishing Corp., New York, 1954.
141. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, 80, 2326 (1958).
142. R. W. Taft and G. W. Stratton, *Ind. Engg. Chem.*, 40, 1485 (1948).
143. R. W. Taft and G. W. Stratton, *Trans. Kansas Acad. Sci.*, 48, 319 (1945).
144. H. S. Taylor, *Trans. Faraday Soc.*, 21 560 (1925).
145. J. M. Tedder, *Quart. Rev.*, 14, 336 (1960).
146. W. Thaler, *J. Am. Chem. Soc.*, 85, 2607 (1963).
147. D. V. Tischenko, *J. Gen. Chem. USSR*, 9, 1380 (1939); via *CA*, 34 1611 (1940).
148. A. F. Trotman-Dickenson, "Free Radicals, An Introduction," Methuen and Co. Ltd., London, 1959.
149. A. F. Trotman-Dickenson, *Quart. Rev.*, 7, 198 (1953).
150. W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, 74, 5822 (1952).
151. W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, 5, 449 (1940).
152. *Ibid.*, 6, 479 (1941).
153. C. Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, 1959.

154. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1959, p. 358.
155. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1959, p. 365.
156. C. Walling and B. Miller, J. Am. Chem. Soc., 79, 4181 (1957).
157. C. Walling and M. Mayahi, ibid., 81, 1485 (1959).
158. C. Walling and B. B. Jacknow, ibid., 82, 6108 (1960).
159. C. Walling and A. Padwa, ibid., 85, 1593 (1963).
160. C. Walling and P. Wagner, ibid., 85, 2333 (1963).
161. Ibid., 86, 3368 (1964).
162. W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1946.
163. R. C. Weast, S. M. Selby and C. D. Hodgman (Eds.), "Handbook of Chemistry and Physics," 45th ed., Chemical Rubber Co., Cleveland, Ohio, 1964, p. D-95.
164. F. C. Whitmore and D. E. Badertscher, J. Am. Chem. Soc., 55, 1559 (1933).
165. K. B. Wiberg and L. H. Slaugh, J. Am. Chem. Soc., 80, 3033 (1958).
166. R. H. Wiley, M. Miller, C. R. Jarboe, J. R. Harrell and D. J. Parish, Radiation Research, 13, 479 (1960).
167. G. H. Williams (Ed.), "Advances in Free Radical Chemistry," Vol. 1, Logos Press, London, 1965.
168. G. H. Williams (Ed.), "Advances in Free Radical Chemistry," Vol. 1, Logos Press, London, 1965, p. 101.
169. K. E. Wilzbach, L. Kaplan and W. G. Brown, Science, 118, 522 (1953).
170. K. E. Wilzbach, A. R. Van Dyken and L. Kaplan, Anal. Chem., 26, 880 (1954).
171. S. Yuster and L. H. Reyerson, J. Phys. Chem., 39, 859 (1935).
172. A. A. Zavistas and S. Seltzer, J. Am. Chem. Soc., 86, 3835 (1964).

VITA

Prem Sagar Juneja

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE LIQUID PHASE PHOTOCHEMICAL HALOGENATION  
OF ISOBUTANE AND ITS MONOHALO DERIVATIVES

Major Field: Organic Chemistry

Biographical:

Personal Data: Born in Ahmed-Pur-Syal, Panjab, India, on November, 3, 1940, the son of late Charanjive Lal and Sita Devi.

Education: Graduated from B.A.S.J.S. Khalsa High School Chamkaur Sahib, Panjab, India, in 1955; passed Intermediate Examination from S. A. Jain College, Ambala City, India, in 1957; received the Bachelor of Science degree from Panjab University, Chandigarh, Panjab, India, in 1959. Completed requirements for the Doctor of Philosophy degree in Organic Chemistry in May, 1967.

Professional experience: Instructor in Chemistry, S. A. Jain College, Ambala City, India, from May 1959 to April 1960; Trainee in the Atomic Energy Establishment, Training School, Trombay, July 1960 to July 1961; Scientific Officer in the Chemical Engineering Division of the Atomic Energy Establishment, Trombay, Bombay (India), August, 1961 to August, 1963; Research Assistant at Oklahoma State University from September, 1963 to August, 1965 and June, 1966 to August, 1966; Teaching Assistant at Oklahoma State University from September, 1965 to May, 1966 and September, 1966 to January, 1967.

Membership in Professional Societies: Member of Phi Lambda Upsilon. Associate member of Sigma Xi. Member of Phi Kappa Phi.