# ABSTRACT

## PART I

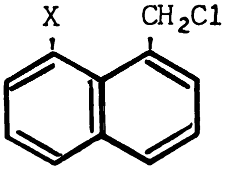
## THE EFFECT OF NON-BONDED INTERACTIONS IN SOLVOLYTIC DISPLACEMENT REACTIONS

## PART II

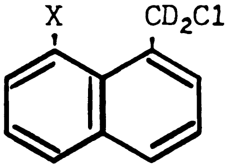
## SOME PROTON-$^{13}$C COUPLING CONSTANTS IN SUBSTITUTED ARYLCARBINYL COMPOUNDS

by Stuart Edward Scheppele

The rate retardation observed upon substitution of hydrogen by deuterium beta to the leaving group in $S_N1$ reactions has been principally attributed to the greater ability of hydrogen than deuterium to hyperconjugatively stabilize the transition state (1). Recently the concept of hyperconjugation has been questioned (2). Bartell (3) has attributed the beta deuterium isotope effect to the larger steric requirements of the proton than the deuteron. So far it has been impossible to assess the contribution of non-bonded interactions to isotope effects observed in solvolytic displacement reactions. Since hyperconjugative stabilization of the transition state is not possible, the rates of solvolysis of the following compounds were studied to ascertain the influence of non-bonded interactions on solvolytic deuterium isotope effects. The 8-methyl and 8-bromo isomers of I also offered



I



II

X = H, D, $CH_3$, $CD_3$, Br.

themselves as systems to investigate rate acceleration due to steric strain (4).

To insure $S_N1$ conditions the solvolyses were carried out in 0.32 m water-formic acid at 25.004°. The rates were followed by potentiometric titration of the liberated chloride. The rate constant observed for α-naphthylcarbinyl chloride was $4.49 \times 10^{-5}$ sec.$^{-1}$ with an average deviation of $\pm 0.11 \times 10^{-5}$ sec$^{-1}$. For X = H, $k^{I}_{H}/k^{II}_{H}$ was 1.35; for X = D, $k^{I}_{H}/k^{I}_{D}$ was 1.0. For X = Br, $k^{I}_{Br}/k^{I}_{H}$ was 1.37 and for X = $CH_3$, $k^{I}_{CH_3}/k^{I}_{H}$ was 85. Due to experimental difficulties the solvolysis rates of the remaining compounds could not be determined using the present method.

The failure to observe an isotope effect (greater than 4%) is attributed, to a first approximation, to compensatory effects in the ground and transition states.

The large increase for the 8-methyl compound is attributed to a partial release in the transition state of severe ground state steric strain. The rate factor is not a true measure of this effect due to complete loss of resonance stabilization of the incipient carbonium ion in the transition state. The small increase observed for the 8-bromo compound is attributed to an increased inductive stabilization of the ground state. Also the bromine atom, being polarizable, may be elongated and whittled down on the side facing the chloromethylene group, thus reducing steric strain.

The second part of this thesis was concerned with investigating some factors influencing $J_{^{13}C-H}$. The isomeric xylenes, halo-toluenes, methyl- and halobenzyl alcohols were included, along with a number of naphthalene derivatives.

The coupling constants were obtained at 60 Mc. from $^{13}C$ natural abundance using a Varian Associates Model A-60 spectrometer.

In the compounds studied non-bonded interactions have a negligible effect on the coupling. The small differences are reasonably ascribed to inductive effects.

## REFERENCES

(1) Halevi, E. A. in "Progress in Physical Organic Chemistry," edited by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Vol. 1, New York: Interscience, 1963.

(2) Dewar, M. J. S., "Hyperconjugation," New York: Ronald Press Co., 1962.

(3) Bartell, L. S., J. Am. Chem. Soc., 83, 3567 (1961).

(4) Brown, H. C. and I. Moritani, ibid., 77, 3623 (1955).

# PART I

# THE EFFECT OF NON-BONDED INTERACTIONS IN SOLVOLYTIC DISPLACEMENT REACTIONS

# PART II

# SOME PROTON-$^{13}C$ COUPLING CONSTANTS IN SUBSTITUTED ARYLCARBINYL COMPOUNDS

By

Stuart Edward Scheppele

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1964

# DEDICATION

This thesis is dedicated to my wife, Judith, for her patience and encouragement in completing the experimental work and for her invaluable assistance in perfecting this manuscript. It is also dedicated to my parents, not merely for their financial and moral support, but for their basic belief in the values of higher education.

# ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. G. J. Karabatsos for his inspiration and guidance not only during the course of this investigation but also in the many esoteric matters encountered by this author in the past four years.

Appreciation is extended to Dr. A. Timnick and Dr. K. G. Stone for their many helpful discussions concerning the analytical methods, and especially to Dr. Stone for use of the Karl Fischer reagents. Appreciation is extended to Dr. M. E. Russell for many stimulating discussions concerning kinetic problems and derivation of rate expressions.

Appreciation is extended to the National Science Foundation for financial support from September, 1961 to September, 1964.

TABLE OF CONTENTS

## PART I
## THE EFFECT OF NON-BONDED INTERACTIONS IN SOLVOLYTIC DISPLACEMENT REACTIONS

TABLE OF CONTENTS (Cont.)

TABLE OF CONTENTS (Cont.)

## PART II
## SOME PROTON-$^{13}$C COUPLING CONSTANTS IN SUBSTITUTED ARYLCARBINYL COMPOUNDS

# LIST OF TABLES

LIST OF TABLES (Cont.)

LIST OF TABLES (Cont.)

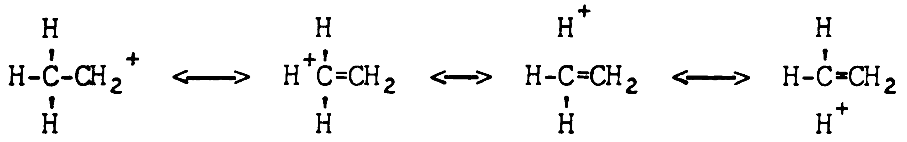
## LIST OF FIGURES

# PART I

# THE EFFECT OF NON-BONDED INTERACTIONS IN SOLVOLYTIC DISPLACEMENT REACTIONS

# INTRODUCTION

About a decade ago, Lewis and Boozer (1) and Shiner (2) reported that deuterium substitution beta to the leaving group in $S_N1$ reactions retarded the rate. To explain the results, hyperconjugative stabilization of the incipient carbonium ion in the transition state was invoked. It was postulated that such stabilization results from a reduction of the C-H and C-D bond vibrational frequencies in the transition state. Since the C-D bond lies deeper in the potential energy well than the C-H bond, the corresponding loss will be less. An equivalent representation is the no-bond structure, illustrated for the ethyl cation in Figure 1. Effectively in the transition state, the C-H bond is loosened more than the C-D bond and $k_H/k_D$ should be greater than unity.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}CH_2^{+}} \longleftrightarrow \mathrm{H^{+}\overset{H}{\underset{H}{C}}{=}CH_2} \longleftrightarrow \mathrm{H{-}\overset{H^{+}}{\underset{H}{C}}{=}CH_2} \longleftrightarrow \mathrm{H{-}\overset{H}{\underset{H^{+}}{C}}{=}CH_2}$$

Figure 1. Resonance structures representing hyperconjugative stabilization of the ethyl cation.

Secondary deuterium isotope effects are defined to be the effect on rate and equilibrium constants produced by replacement of hydrogen by deuterium in any part of the molecule, providing the bond to the isotopic atom is being neither broken nor formed. In the past decade a considerable amount of data, both experimental and theoretical, has been published (3).

Subsequent research on the beta deuterium isotope effect in $S_N1$ mechanisms has concerned itself with attempting to prove that hyperconjugation is the sole or dominant factor.

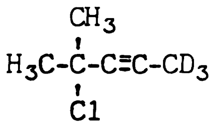
It has been shown that the beta isotope effect is small in $S_N2$ reactions (4).

Shiner (2,5) found that the effect of beta deuteration in $S_N1$ reactions is roughly additive, but that the magnitude of the effect increases with increased branching at the beta carbon atom.

The solvent and temperature dependence of the isotope effect is rather complicated (3). Usually changes in activation energies and/or enthalpies and entropies are compensatory.

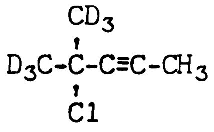
The effect of deuteration in the aromatic side chain has been investigated and found to be complicated (3). The magnitude of the isotope effect is strongly solvent and temperature dependent. Large differences in $\Delta\Delta E_a$ are counterbalanced by opposing entropy changes. However, the effect of deuteration of a p-methyl group is less than that of a β-methyl group.

The transmission of an isotope effect across a triple bond has been observed by Shiner(6) in the solvolysis of 4-chloro-4-methyl-2-pentyne and its deuterated analogs. The $k_H/k_D$ for Ia is 1.092 and



$H_3C-\overset{CH_3}{\underset{Cl}{C}}-C\equiv C-CD_3$

Ia



$D_3C-\overset{CD_3}{\underset{Cl}{C}}-C\equiv C-CH_3$

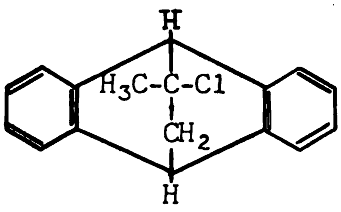
Ib

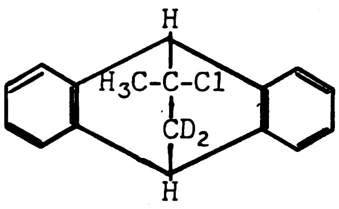
1.655 for Ib. The isotope effect is considerably reduced by the triple bond.

The importance of stereochemistry to hyperconjugation was first suggested by Shiner from solvolysis studies of 2,4,4-trimethyl-2-chloropentane and its deuterated analogs (7a).

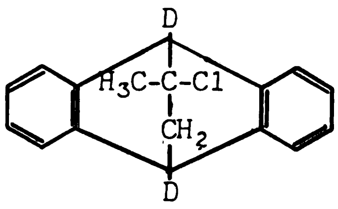
In comparison to the large reduction in the isotope effect produced by 3,3-dideuterio substitution in 2-chloro-2,4,4-trimethylpentane, the same isotope effect in the series 2-chloro-2-methylbutane, 2-chloro-2-methylpentane was large and approximately constant (7b).

It was suggested that maximum hyperconjugative stabilization of the incipient carbonium ion would be attained only when the C-H bond was parallel to the developing $\pi$ orbital. This hypothesis has been tested by Shiner and co-workers. They found that the solvolysis rate retardations caused by substitution of 1, 2, and 3 deuterium atoms in one methyl group of t-butyl chloride were not quite cumulative but increased as the extent of deuteration increased (8). These differences were quantitatively treated assuming conformation dependence. Further support was obtained from solvolysis studies of compounds IIa, IIb, and IIc(9).


IIa


IIb

$k_H/k_D = 1.14$


IIc

$k_H/k_D = 0.986$

The observed rate ratios are as expected, since in IIb the C-D bond is almost parallel to the vacant $\pi$ orbital developing in the transition state, whereas in IIc the C-D bond is almost perpendicular. The small rate retardation in IIc is attributed to the inductive effect.

The most striking effect was observed in the rates of solvolysis of cis-4-t-butylcyclohexyl brosylate-trans-2-d and cis-4-t-butylcyclohexyl brosylate-cis-2-d (10). The axial $\beta$-deuterium (-trans-2-d) exhibits a rate retardation of 1.436, whereas the equatorial β-deuterium (-cis-2-d) slows the rate by only 1.096.

Hyperconjugation in both ground and transition states has become an area of profound disagreement (11). An alternate explanation for ground state effects in terms of hybridization has been advanced (12). The origin of the Baker-Nathan effect has been the subject of much discussion (3,12). The claim that the existence of beta deuterium isotope effects is evidence for hyperconjugation has been criticized by Dewar (12). Hybridization has been invoked to explain the alpha deuterium isotope effect (13).

Bartell has proposed a theory of non-bonded interactions. The theory was first applied to molecular phenomena and then extended to secondary deuterium isotope effects (14). Bartell has suggested an approximate equality of non-bonded interactions for atoms bonded to the same carbon (14a). This approximate equality of C··C, C··H, and H··H non-bonded interactions no longer applies for atoms bonded to adjacent carbon atoms. On this basis he was able to account for the regular decrease in the C-C bond length as the number of adjacent atoms is decreased (14a, 14b). This model also accounts for the small changes in C-H bond lengths as the hybridization is changed from $sp^3$ to $sp^2$ to sp (14a, 14b). Using non-bonded potential functions, Bartell was able to successfully calculate the strain energy in cyclobutane (14a).

The extension of the theory to secondary isotope effects is based on the principle that the amplitudes of vibration of hydrogen atoms are larger than the amplitudes of the heavier deuterium atoms by a predictable amount. Therefore, non-bonded repulsions, averaged over the atomic vibrations, are greater for hydrogen atoms than for deuterium atoms. Moreover, there are more and stronger non-bonded repulsions in the crowded tetrahedral reactant than in the trigonal carbonium ion. Thus the relief of non-bonded repulsions at the transition state is greater for the protio compound than for the deuterio compound. The effect of deuterium substitution on the activation energy of *t*-butyl chloride is calculated to be 22 cal./D (14d).

Bartell has calculated the effect of deuterium substitution on the gas phase equilibrium (14d).

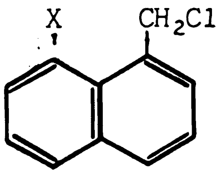
$$Me_3B{:}NMe_3 = Me_3B + {:}NMe_3$$

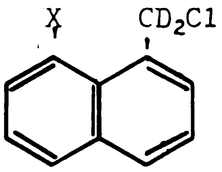
The experimentally observed value of $\Delta\Delta E_a$ is 22 cal./D. The best calculated value is 20 cal./D but the result is sensitive to the model assumed for the complex.

Bartell concludes (14b):

> that numerical computations show the effect is entirely reasonable in magnitude, but the numerical values depend so strongly upon assumed bond angles and lengths (which are at present largely conjectural) that a definite conclusion cannot yet be made. The best estimate suggests that some hyperconjugative delocalization occurs but that this has the effect, in turn, of enhancing the non-bonded effect.

In the $S_N1$ reactions so far reported, it has been impossible to separate effects due to hyperconjugation and non-bonded interactions or to decide on the relative magnitudes of each. Therefore to assess the role of non-bonded interactions in solvolytic displacement reactions, it is necessary to find a system in which the possibility for hyperconjugation has been eliminated. The following naphthalene derivatives offered themselves as attractive possibilities.

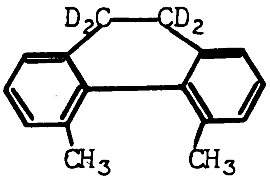




X = H, D, $CH_3$, $CD_3$, Br

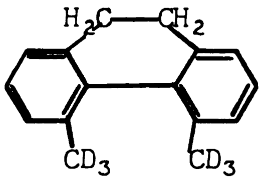
For these compounds it is impossible for groups in the 8 position to resonately stabilize the incipient carbonium ion in the transition state. Thus rate differences between the protio and corresponding deuterio compounds would only be due to non-bonded interactions. Therefore, the study of the solvolysis of these compounds was undertaken.

During the course of these investigations several instances of "steric" isotope effects have been reported. Melander and Carter (15) obtained a $k_D/k_H$ value of 1.19 from studies of the rates of racemization of 2,2'-dibromo-4,4'-dicarboxybiphenyl and its 6,6'-dideuterio derivative at -19.8°. Mislow and co-workers (16) studied the effects of deuterium substitution on the rate of racemization of 9,10-dihydro-4,5-dimethyl phenanthrene.



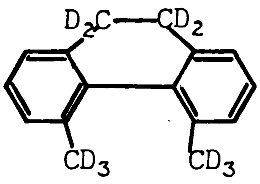
Va

$k_D/k_H = 1.05$



Vb

$k_D/k_H = 1.13$

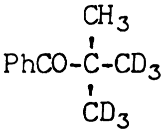


Vc

$k_D/k_H = 1.18$

The effect in Vc is additive. The authors conclude that the 5% effect in Va may be either a "steric" isotope effect or a result of a change in the potential energy barrier to torsion around the 9,10-bond. They conclude that the 13% effect observed in Vb and Vc is steric in origin.

Raaen and co-workers (17) report a steric isotope effect for the formation at 0° of 2,4-dinitrophenylhydrazones. The deuterium containing ketones whose isotope effects were determined with respect to the undeuterated species are shown in structures VI-IX along with the corresponding $k_H/k_D$ values.

| | | | |
|---|---|---|---|
| $PhCOCD_3$ |  $PhCO\text{-}\overset{CH_3}{\underset{CD_3}{C}}\text{-}CD_3$ | $PhCOCD_2CH_3$ | $PhCOCH_2CD_3$ |
| 1.119 ± 0.005<br>1.104 ± 0.002 | 1.046 | 1.124 | 0.9952 |
| VI | VII | VIII | IX |

The authors feel that these observations are explicable only on the basis of steric effects and are in agreement with the mechanism proposed for 2,4-dinitrophenylhydrazone formation.

Examination of Fisher-Herschfelder models reveals that 8-methyl- and 8-bromo-α-naphthylcarbinyl chlorides are severely strained. The existence of strain in some naphthalene compounds has been demonstrated by X-ray diffraction (18). Octamethylnaphthalene (19) has been shown to be severely distorted. A completely planar molecule would require the α-methyl groups to be 2.4 Å apart, a distance well below the sum of the appropriate van der Waals' radii. As a result, the α-methyl groups are bent out of the plane by about 28°. The β-methyl groups are displaced in the opposite directions by a smaller amount. This is probably a consequence of a slightly sideways displacement (0.06 Å) of the α-methyl groups.

Therefore it was felt that a comparison of the rates of the 8-methyl- and 8-bromo-α-naphthylcarbinyl chlorides with α-naphthylcarbinyl chloride might yield additional insight into the effects of ground state steric strains on solvolysis reactions.

Steric strain acceleration in solvolysis reactions of alkyl halides, due to relief of ground state non-bonded repulsions in the trigonal transition state, is not a new concept (20). For example, Brown and Moritani (20a) claim that the observed relative solvolysis rates of the series $MeCMe_2Cl$, $EtCMe_2Cl$, i$PrCMe_2Cl$, t$BuCMe_2Cl$, t$AmCMe_2Cl$, of 1.0, 1.67, 0.88, 1.21, and 5.67 can only be explained on this basis. However, it should be mentioned that such an explanation has been questioned (21).

The existence of steric acceleration in solvolysis reactions has been convincingly demonstrated by Moritani and co-workers (22) from their studies of the acetolysis of trans-1- and 2-decalyl p-toluenesulfonates. The observed rate sequence was 1 equatorial < 2 equatorial < 3 axial << 2 axial. The relative rates were 0.5, 1.0, 3.1, and 27.6.

Similar results were obtained by Nishida (23) from a study of the acetolysis rates of the isomeric p-toluenesulfonates of chlolestan-2α, 2β, 3α, 3β, and 6α-ol. The observed sequence of rates was $3\beta \cong 6\alpha < 2\alpha < 3\alpha \ll 2\beta$. The relative rate sequence was 1.0, 0.9, 3.1, 6.1, and 31. Winstein and Holness (24) ascribed the rate increase factor of 3.58 observed in the formolysis of cis-4-t-butylcyclohexyl p-toluenesulfonate over the corresponding trans isomer to steric acceleration.

Brown and co-workers (25) have found conformation of these steric effects from the rough correlation observed between the rates of ketone reduction with sodium borohydride and the rates of solvolysis of the corresponding alkyl halides and aryl sulfonates. It was observed that a rough linear free energy relationship existed between the rate of reduction of five to ten membered cycloalkanones with sodium borohydride and the acetolysis of cyclic tosylates (25a,c).

# RESULTS AND DISCUSSION

## I. Synthesis

A. *α-Naphthylcarbinol*. α-Naphthylcarbinol and its various deuterated analogs were prepared from the appropriate 1-naphthoic acids by reduction with lithium aluminum hydride or deuteride. The identity of the compounds was established by infrared and nuclear magnetic resonance spectra.

B. *8-Methyl-α-Naphthylcarbinol*. 8-Methyl-α-naphthylcarbinol was prepared by reduction of 8-methyl-1-naphthoic acid with lithium aluminum hydride (26).

C. *8-Bromo-α-Naphthylcarbinol*. 8-Bromo-α-naphthylcarbinol was prepared by lithium aluminum hydride reduction of 8-bromo-1-naphthoyl chloride (26).

D. *α-Naphthylcarbinyl p-Toluenesulfonate*. The tosylate ester of α-naphthylcarbinol was synthesized from the corresponding sodium salt of the alcohol and *p*-toluenesulfonyl chloride. It decomposes at 55.5°. It decomposes rapidly in the crystalline state under dry nitrogen or argon. The ester appears to be stable in anhydrous ether, but readily decomposes on recrystallization in solvents other than pentane. Similar instability was noted for the tosylate of β-naphthylcarbinol by Jacobs and Singer (27). They observed decomposition of the crystalline compound to a green tar at 61.5°. The tosylate esters, therefore, were considered unsuitable for kinetic study.

E. α-Naphthylcarbinyl 3,5-Dinitrobenzoate. Attempted preparation of α-naphthylcarbinyl 3,5-dinitrobenzoate from sodium α-naphthylmethylate and 3,5-dinitrobenzoyl chloride gave an amorphous yellow material that was insoluble in common organic solvents. The infrared spectrum indicated that it was a mixture. The material softened and coalesced at 150-160° turning to a viscous oil at 190°.

α-Naphthylcarbinyl 3,5-dinitrobenzoate was prepared by dissolving α-naphthylcarbinol and 3,5-dinitrobenzoyl chloride in ether containing pyridine. The infrared spectrum was consistent with the proposed structure and the principal absorptions are given in Table I.

Table I. Infrared data of α-naphthylcarbinyl 3,5-dinitrobenzoate[a]

| Group | Absorption (microns) |
|---|---|
| C=O | 5.80, 7.85, 8.55 |
| $NO_2$ | 6.5, 7.45 |
| aromatic | 3.25, 6.15, 6.28 |
| aliphatic | 3.5 |

[a] KBr pellet.

F. α-Naphthylcarbinyl p-Nitrobenzoate. The ester was prepared from α-naphthylcarbinol and p-nitrobenzoyl chloride in ether containing pyridine. The infrared data were consistent with its structure. Principal absorptions are given in Table II.

Table II. Infrared data of α-naphthylcarbinyl p-nitrobenzoate[a]

| Group | Absorption (microns) |
|---|---|
| C=O | 5.80, 7.90, 8.55 |
| $NO_2$ | 6.55, 7.45 |
| aromatic | 3.25, 6.15, 6.25 |
| aliphatic | 3.5 |

[a] KBr pellet.

G. Arylcarbinyl Chlorides. The arylcarbinyl chlorides were synthesized from the appropriate alcohol and thionyl chloride. Each arylcarbinyl chloride was prepared immediately before a series of kinetic runs and stored under dry petroleum ether at approximately 0°. Before a kinetic run an appropriate amount of compound was removed, placed in a weighing bottle, and gently ground with a spatula until a fine powder was obtained. The bottle and its contents were then placed in a desiccator and kept under high vacuum for 10 to 12 hours to remove all solvent.

The nuclear magnetic resonance and infrared spectra of the chlorides were in accord with their structures.

## II. Product Studies

A. Methanolysis of α-Naphthylcarbinyl p-Nitrobenzoate and α-Naphthylcarbinyl 3,5-Dinitrobenzoate. The methanolysis of these esters was studied to ascertain whether they would be suitable derivatives for kinetic studies. Thus it was essential that during methanolysis they suffer alkyl oxygen rather than acyl oxygen fission.

α-Naphthylcarbinyl 3,5-dinitrobenzoate was unsuitable because of its limited solubility in anhydrous methanol. Chromatographic studies showed only the formation of α-naphthylcarbinol.

Chromatographic analysis of the mixture from the methanolysis of α-naphthylcarbinyl p-nitrobenzoate yielded only α-naphthylcarbinol and methyl p-nitrobenzoate as established by infrared and m.p.

These results and the failure to detect any α-naphthylcarbinyl methyl ether indicate that these esters undergo only acyl oxygen fission during methanolysis. Therefore no further consideration was given to these derivatives.

B. Insoluble Products Formed During Solvolysis of α-Naphthylcarbinyl Chloride. Due to the complex nature of the insoluble products formed during the solvolysis of α-naphthylcarbinyl chloride, only preliminary results are reported.

In order to approximate kinetic conditions, a 0.014 M solution of α-naphthylcarbinyl chloride in 97% formic acid was prepared. After 3.5 days the precipitated material was collected, dissolved in ether, and the formic acid removed.

The nuclear magnetic resonance spectrum of the product mixture exhibits two principal absorptions: one, a broad series of unresolved peaks characteristic of aromatic protons centered around $\tau = 2.5$; and second, broad peaks at $\tau = 5.2$, 4.4. The peaks at $\tau = 5.2$, 4.4 are characteristic of the methylene protons of arylcarbinyl derivatives, i.e., methylene protons of α-naphthylcarbinyl chloride, α-naphthylcarbinol, and benzyl formate appear at $\tau = 5.15$, $\tau = 5.13$, and $\tau = 4.8$ respectively.

The infrared spectrum exhibits, in addition to aromatic and aliphatic bonds, a carbonyl absorption at 1720 cm.$^{-1}$. The spectrum reveals the absence of a hydroxyl group. Furthermore it is impossible to verify the presence of chemically bound chlorine.

A positive silver nitrate test indicated the presence of chemically bound chlorine in the mixture. This was further substantiated by the infrared spectrum of the recovered material which exhibited a weak band at 3500 cm.$^{-1}$.

The mixture was chromatographed on silica gel. Thin layer chromatography was then utilized to determine the extent of separation and the number of products. Figure 2 is a reproduction of the thin layer chromatogram. It suggests that the mixture contains at least 5 different products. This may well be a minimum as spots 20 and 21 do not show much movement and the small amount of material eluted by methanol was not spotted. Those fractions which had approximately the same rf values were combined before infrared and nuclear magnetic resonance spectra were taken. The salient features of the spectral data are: The spectrum of each fraction bears no simple relationship to those of the pure chloride or alcohol; all fractions except No. 1-9 exhibit a carbonyl absorption at 1720 cm.$^{-1}$ in the infrared; after fraction 12 a band at 1690 cm.$^{-1}$ appears; the infrared data reveal no evidence which would indicate the presence of a hydroxyl group; the nuclear magnetic resonance spectra of every fraction have peaks characteristic of protons of an aromatic methylene group containing a functional entity but no absorption characteristic of aromatic methyl protons; and absorptions in the aromatic regions are broad and apparently unresolved.

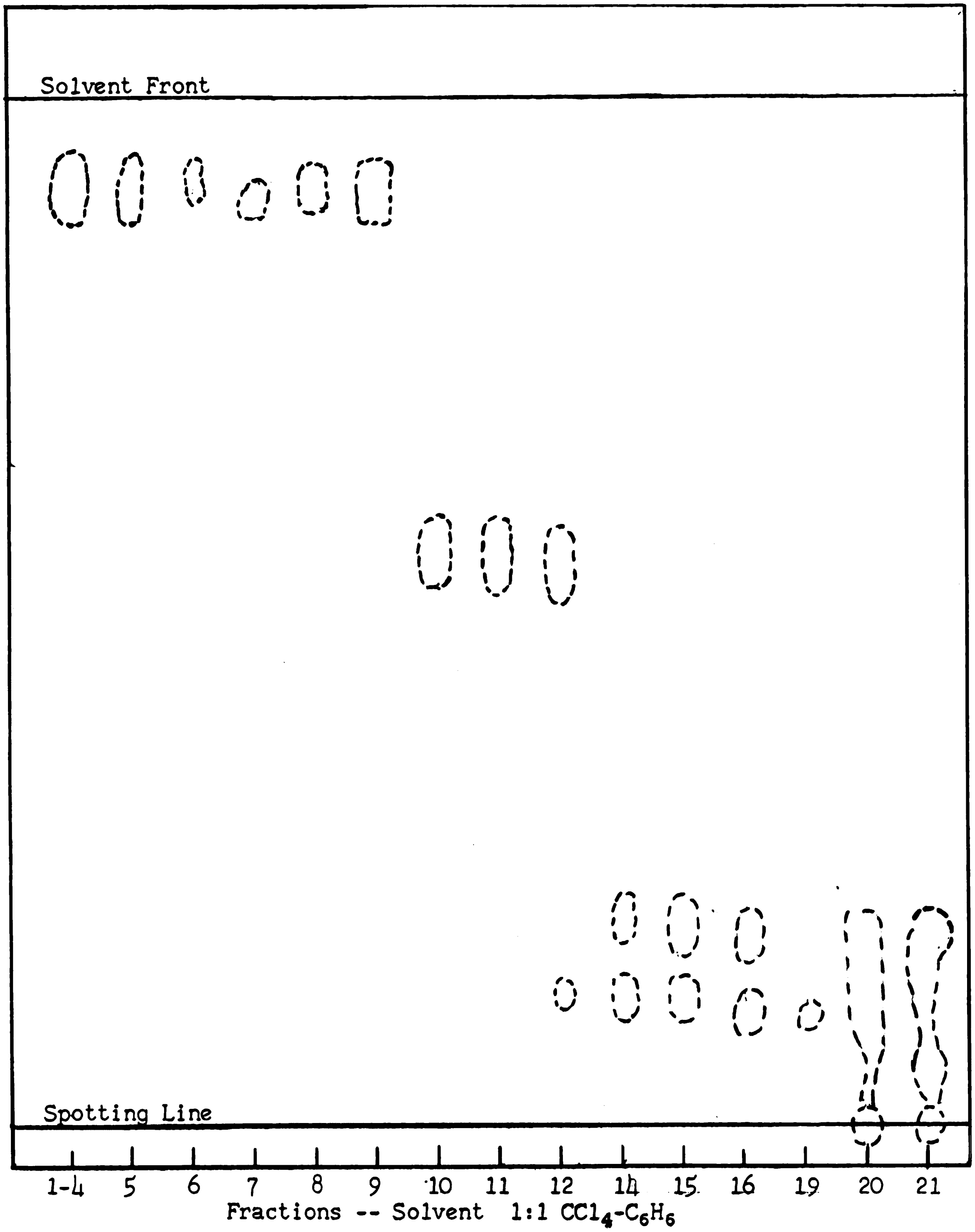
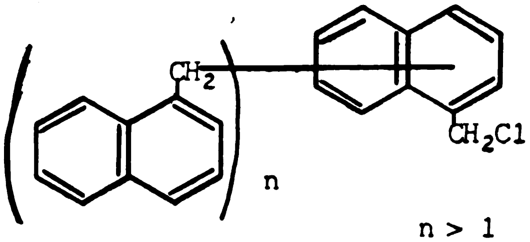


Figure 2. Thin layer chromatogram of various fractions from chromatographic separation of solvolysis products of α-naphthylcarbinyl chloride. Fractions and eluting solvents: 1-5, $CCl_4$; 6,7 5:1 $CCl_4$-$C_6H_6$; 8,9 1:1 $CCl_4$-$C_6H_6$; 10-14 1:3 $CCl_4$-$C_6H_6$; 15-18 $C_6H_6$; 19-21 1:1 C.H.-$Et_2O$; 22,23 $Et_2O$; 24 $CH_3OH$.

From these limited facts the following tentative conclusions are drawn concerning the nature of these insoluble products.

The first fraction (No. 1-9, Figure 2) may be multi-substituted arylcarbinyl chlorides of the following type:



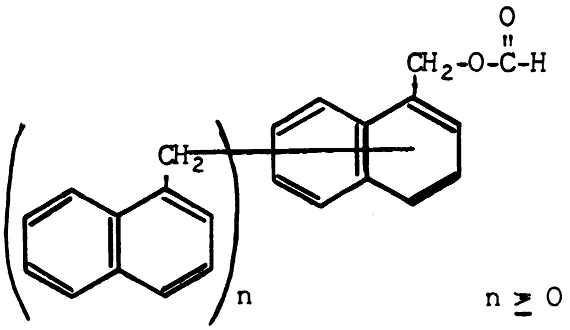
$n \geq 1$

The nuclear magnetic resonance spectrum of this fraction shows two peaks of unequal intensity at $\tau = 5.2$ and $\tau = 5.1$, possibly ascribable to magnetically non-equivalent methylene protons. Furthermore, the infrared spectrum exhibits an unusually strong band at 1245 $cm.^{-1}$ with a shoulder at 1280 $cm.^{-1}$, similar to the bands in the spectrum of α-naphthylcarbinyl chloride. These absorptions, due to usually weak carbon hydrogen deformations, may be strongly enhanced by the presence of electronegative elements (28).

The major amount of the material appeared to be contained in fractions 10 and 11 of Figure 2. The infrared shows, in addition to the usual aromatic and aliphatic absorptions, bands at 1720 $cm.^{-1}$ and 1160 $cm.^{-1}$. The nuclear magnetic resonance spectrum shows peaks at $\tau = 5.3$, 4.5, and a broad aromatic absorption centered around $\tau = 2.5$. Benzyl formate has a carbonyl absorption at 1720 $cm.^{-1}$ in the infrared. Its nuclear magnetic resonance spectrum exhibits a peak at $\tau = 4.8$ for the methylene protons, with the formyl proton appearing at $\tau = 1.9$. From these results, it is suggested that this material is a formate ester.

The remaining products appear to be of higher molecular weight. They all appear to exhibit the same general spectral features as previously noted with one important exception. The infrared spectra of fractions above 13 in Figure 2 show a band at 1690 cm.$^{-1}$. This band appears to grow in intensity relative to the band at 1720 cm.$^{-1}$. In the original mixture it appears as a very small peak at the base of the 1720 cm.$^{-1}$ band. Considering the limited amount of data, it appears impossible to suggest what structural unit this absorption represents.

The spectral data indicate that the principal remaining products are formate esters. The following general structure is suggested:



The formation of these products is visualized as an electrophilic attack of the carbonium ion formed during the solvolysis of α-naphthylcarbinyl chloride on either the arylcarbinyl chloride, arylcarbinol, or arylcarbinyl formate.

C. <u>Insoluble Products Formed During Solvolysis of 8-Methyl-α-Naphthylcarbinyl Chloride</u>. The precipitate obtained from solubility studies of 8-methyl-α-naphthylcarbinyl chloride was dissolved in ether and washed free of formic acid.

The presence of at least five components in the mixture was indicated by thin layer chromatography. Since some of the material showed only slight movement for the eluting solvents pentane, carbon disulfide, and benzene, the actual number of components in the mixture may be larger.

The principal infrared and nuclear magnetic resonance absorption peaks of the mixture are listed in Table III. Tables IV and V contain respectively infrared and nuclear magnetic resonance absorption peaks of some naphthalene derivatives. Comparison of the nuclear magnetic resonance data in Tables III and IV suggests that the mixture contains peaks characteristic of magnetically non-equivalent aromatic methyl protons, protons of magnetically non-equivalent methylene carbons containing a functional group, and peaks characteristic of aromatic protons. Due to the range over which these absorption peaks occur, the aromatic region appears anomalous. The peaks in this region can be divided into three main groups: the largest concentration of protons appears to be centered at $\tau = 2.52$, a broad peak characteristic of formyl protons occurs at $\tau = 1.97$, and a series of peaks is centered at $\tau = 3.17$.

The infrared data of Table III do not suggest the presence of a hydroxyl group. The band at 1720 cm.$^{-1}$ is ascribed to the carbonyl of a formate ester. The appearance of a band at 1250 cm.$^{-1}$, its presence in the parent chloride, and its absence in the parent alcohol suggests, as in the previous section, the presence of a chloromethylene group. From these data and the results of the previous section, it is suggested that the mixture contains multi-substituted arylcarbinyl chlorides and formates.

Interestingly, on the basis of the nuclear magnetic resonance data, the following reaction producing acenaphthene does not appear to occur.

Table III. Spectral data of the insoluble mixture formed during the solvolysis of 8-methyl-α-naphthylcarbinyl chloride

| I.R. Absorptions ($cm.^{-1}$) | N.M.R. Absorptions ($\tau$) |
|---|---|
| 2904 | 7.37 |
| 1916 | 7.33 |
| 1852 | 7.17 |
| 1720 | 7.00 |
| 1595 | 5.03 |
| 1450 | 4.92 |
| 1250 | 4.90 |
| 1156 | 4.30 |
| 1097 | 3.5 - 1.67 |
| 1042 | |

Table IV. Nuclear magnetic resonance spectral data of some substituted naphthalenes.

| Compound | Absorption ($\tau$) | | |
|---|---|---|---|
| | $CH_3$ | $CH_2$ | Aromatic |
| 8-Methyl-α-naphthylcarbinyl chloride | 7.00 | 4.95 | 2.17-2.83 |
| 1-Bromo-8-methyl naphthalene | 6.92 | | 2.20-3.08 |
| α-Methylnaphthalene | 7.75 | | 2.33-3.25 |
| Acenaphthene | | 6.8 | 2.33-3.08 |
| 8-Methyl-α-naphthylcarbinol | 7.15 | 5.10 | 2.25-3.00 |

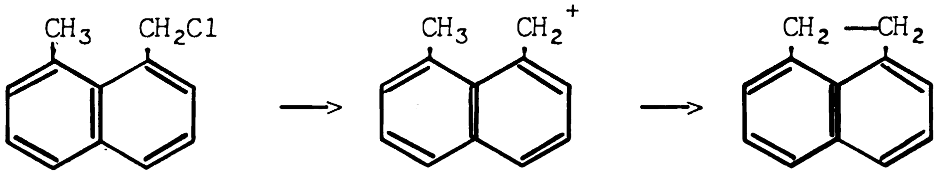


Table V. Infrared spectral data of some substituted naphthalenes.

| Compound | Absorptions (cm.$^{-1}$) |
|---|---|
| 8-Methyl-α-naphthylcarbinol | 3600, 3000, 1920-1600, 1510, 1460, 1390, 1170, 1000 |
| 8-Methyl-α-naphthylcarbinyl chloride | 3000, 1920-1600, 1510, 1480, 1460, 1390, 1250 |

## III. Analytical Methods for the Determination of Chloride

A. Volumetric Determination of Chloride by the Volhard Method. The experimental procedures were adapted from Blaedel and Meloche (29), Koltoff and Sandell (30), and Swift (31).

The reproducibility of rate constants is sensitive to the accuracy and precision of the analytical method used to follow the appearance of one of the products in a reaction. Fainberg and Winstein (32) report rate constants to 1% using this analytical method, but give no details of the accuracy of the Volhard method when titrating samples containing less than 0.2 meq. of chloride. Numerous other authors have used this analytical method, but details of its accuracy are rather scarce. Therefore, the following experimental work was performed to determine both the accuracy and precision for samples containing chloride concentrations similar to those which were expected during kinetic runs, i.e., 0.1 to 1 meq.

Silver nitrate solutions were standardized against primary standard sodium chloride solutions. Potassium thiocyanate solutions were titrated against the silver nitrate solutions. Micro-burets (10 and 5 ml.) calibrated in 0.02 and 0.01 ml. intervals respectively were used. Samples containing 2.5 to 5 meq. of chloride were analyzed to within the 0.1% level.

Table VI lists the results obtained from the standardization of silver nitrate against 0.1011 M sodium chloride using both the micro- and 50 ml. burets. The percentage difference is only 0.089% and a high level of precision is indicated.

Table VI. Comparison of results for Volhard titrations using 50 ml.- and micro-burets.

| Buret | $AgNO_3$ ml. | KSCN ml. | $\frac{AgNO_3}{KSCN}$ | NaCl ml. | $AgNO_3$ M | Avg. Ratio | % Dev. |
|---|---|---|---|---|---|---|---|
| 50 ml. | 35.09 | 38.88 | 0.9025 | | | 0.9023 | |
| 50 ml. | 35.00 | 38.80 | 0.9021 | | | | |
| 50 ml. | 36.00 | 39.90 | 0.9023 | | | | |
| 50 ml. | 24.11 | 1.82[a] | | 25.00[b] | 0.1125 | 0.1125 | 0.000 |
| 50 ml. | 23.70 | 1.35[a] | | 25.00[b] | 0.1124 | | -0.089 |
| 50 ml. | 23.00 | 0.62[a] | | 25.00[b] | 0.1126 | | 0.089 |
| 50 ml. | 22.99 | 0.59[a] | | 25.00[b] | 0.1125 | | 0.000 |
| Micro- | 9.160 | 0.212 | 0.9023 | 10.00[b] | 0.1127 | 0.1126 | 0.098 |
| Micro- | 9.125 | 0.155 | 0.9023 | 10.00[b] | 0.1125 | | -0.089 |
| Micro- | 9.165 | 0.219 | 0.9023 | 10.00[b] | 0.1127 | | 0.089 |

[a] 10 ml. buret used.

[b] 0.1011 M NaCl solution.

Volhard procedure 1 used for 50 ml. burets.

Volhard procedure 2 used for micro-buret.

Since samples were to be quenched during kinetic runs by extracting the aliquot of the reaction mixture with carbon tetrachloride, it was imperative to know the resulting chloride loss. Fainberg and Winstein (32) and Bateman and Hughes (33) indicate that at least 99.8% of chloride is recovered after extraction. This problem was reinvestigated. Table VII lists the results obtained for samples containing 31 to 38 meq. of chloride. For these data 2 ml. of 0.33 $\underline{M}$ ferric nitrate indicator was used.

Before analyzing these results, a discussion of the sources and magnitudes of possible error in the titration of solutions less than $10^{-2}$ $\underline{M}$ in chloride is necessary. A serious source of error at these concentrations is the appearance of a false end point early in a titration (29). This is caused by the reversible formation of the colored $(FeSCN)^{+2}$ complex before the number of meq. of added thiocyanate equal to the excess meq. of silver ion has been added. This false end-point which faded upon stirring for about one minute introduced an error of approximately 1%.

At these concentrations another problem was the non-abrupt color change of the indicator in the region of the end point. Using 2 ml. of 0.33 $\underline{M}$ indicator, the color of the solution changed from essentially clear to intense orange over an interval of about 0.1 ml. of thiocyanate. Therefore, titration to a constant color change was found to be very difficult and in some instances many titrations had to be performed and discarded. The resulting color change was reproducible to about 0.01 ml. of thiocyanate resulting in deviations of about ± 0.3%. This problem introduced two other possible sources of error: one, the reproducibility to the same color change over an extended period

Table VII. Titration of hydrogen chloride in formic acid by the Volhard method before and after extraction[a]

| Soln. No. | U.E.[b] | E.[c] | Mg. Cl | Avg. | A | B | C |
|---|---|---|---|---|---|---|---|
| 1 | - | | 31.26 | 31.20 | 0.192 | 0.000 | |
| 1 | - | | 31.15 | | -0.160 | | |
| 1 | - | | 31.18 | | -0.064 | | |
| 1 | | - | 31.22 | 31.20 | 0.064 | | 0.064 |
| 1 | | - | 31.19 | | -0.032 | | -0.032 |
| 1 | | - | 31.19 | | -0.032 | | -0.032 |
| 2 | - | | 27.93 | 27.92 | 0.036 | 0.072 | |
| 2 | - | | 27.91 | | 0.036 | | |
| 2 | | - | 27.98 | 27.94 | 0.143 | | 0.215 |
| 2 | | - | 27.96 | | 0.072 | | 0.143 |
| 2 | | - | 27.88 | | -0.215 | | -0.143 |
| 3 | - | | 24.48 | 24.48 | 0.000 | -0.531 | |
| 3 | - | | 24.47 | | -0.041 | | |
| 3 | | - | 24.35 | 24.35 | 0.000 | | -0.531 |
| 3 | | - | 24.35 | | 0.000 | | -0.531 |
| 4 | - | | 21.05 | 21.06 | -0.048 | -0.522 | |
| 4 | - | | 21.09 | | 0.142 | | |
| 4 | - | | 21.05 | | -0.048 | | |
| 4 | | - | 20.98 | 20.95 | 0.143 | | -0.380 |
| 4 | | - | 21.00 | | 0.239 | | -0.285 |
| 4 | | - | 20.88 | | -0.334 | | -0.855 |
| stock | - | | 37.91 | 37.90 | 0.026 | -0.106 | |
| stock | - | | 37.89 | | -0.026 | | |
| stock | | - | 37.86 | 37.86 | 0.000 | | -0.106 |

[a] Volhard procedure 2, 10 ml. aliquots.

[b] U.E. is unextracted sample.

[c] E. is extracted sample.

A = % deviation of each sample in a group from average of that group.

B = % deviation of average of E. samples from U.E. average.

C = % deviation of each E. sample in a group from average value of U.E. for each group.

of time; and two, the non-equivalence of the observed end point with the equivalence point. Over a two day period the molarity of a silver nitrate solution decreased by 0.007 which seems excessive considering the caution exercised in handling the silver nitrate solutions. Swift (31) has calculated the amount of indicator necessary to produce simultaneous occurrence of the end point and the equivalence point when titrating under equilibrium conditions. In the present method the silver chloride was removed by shaking it with nitrobenzene, i.e., non-equilibrium condition. Therefore, the problem of calculating the end point error is reduced to a calculation of the excess thiocyanate ion concentration over silver ion concentration at the end point as a function of indicator concentration. Implicit is the assumption that the precipitated silver chloride is no longer in equilibrium with the solution. The validity of this assumption was demonstrated by the stability of the color change over long periods of time. Using the equations as outlined by Blaedel and Meloche (29) it can be shown that the end point is past the equivalence point by a volume of 0.1 M potassium thiocyanate equal to 0.009 ml. of 0.1 M potassium thiocyanate using 5 ml. of 0.33 M ferric nitrate indicator and approximately 100 ml. total titrating volume. For macroscopic samples the error so introduced is less than 0.1%. Using these equations, various concentrations of 0.33 M indicator, and various total titration volumes, the approximate error has been calculated. The results are given in Table VIII. The errors are calculated for varying amounts of chloride requiring different volumes of a given silver nitrate concentration. In these calculations, the ratio of silver nitrate to potassium thiocyanate was assumed to be unity. The results are valid because experimentally the ratio deviated insignificantly from unity. The calculations reveal that for a given molarity of silver nitrate and a given indicator concentration, a decrease in the required volume of silver nitrate leads, as expected, to an increase in the error. The error grows considerably as both the molarity and the required volume of silver nitrate decrease. Increasing the amount of indicator reduces the error. The error ranges from approximately 0.1 to 1% for 5 ml. of indicator and from approximately 0.2 to 2% for 2 ml. Swift suggests using 2 M indicator. Table IX systematically lists the calculated error in the required volumes of silver nitrate for indicator concentrations of 2 and 4 ml. These calculations indicate that better accuracy would be obtained by using the higher indicator concentration and by reducing the total titrating volume. Furthermore, the calculations indicate that chloride concentrations down to 0.1 meq. should be analyzable to within 1%.

Table VIII. Calculation of end point error in chloride determinations by the Volhard method.

| Tit. Vol. | M $Fe(NO_3)_3$ | Ml. $Fe(NO_3)_3$ | M KSCN | Ml.[a] KSCN | M $AgNO_3$ | Ml. $AgNO_3$ | %Error[b] |
|---|---|---|---|---|---|---|---|
| 100-110 | 0.33 | 2 | 0.1 | 0.015 | 0.1 | 10.000 | 0.15-.165 |
| 100-110 | 0.33 | 2 | 0.1 | 0.015 | 0.1 | 5.000 | 0.30-.33 |
| 100-110 | 0.33 | 2 | 0.05 | 0.031 | 0.05 | 10.000 | 0.31 |
| 100-110 | 0.33 | 2 | 0.05 | 0.031 | 0.05 | 5.000 | 0.62 |
| 100-110 | 0.33 | 2 | 0.05 | 0.031 | 0.05 | 2.000 | 1.55 |
| 100-110 | 0.33 | 5 | 0.1 | 0.009 | 0.1 | 10.000 | 0.09-.1 |
| 100-110 | 0.33 | 5 | 0.1 | 0.009 | 0.1 | 5.000 | 0.18-.2 |
| 100 | 0.33 | 5 | 0.05 | 0.018 | 0.05 | 10.000 | 0.18 |
| 100 | 0.33 | 5 | 0.05 | 0.018 | 0.05 | 5.000 | 0.36 |
| 100 | 0.33 | 5 | 0.05 | 0.018 | 0.05 | 2.000 | 0.90 |

[a] Calculated excess at end point.

[b] % Error is the error in vol. of $AgNO_3$ assuming $AgNO_3/KSCN$ ratio = 1.

Table IX. Calculation of end point error in chloride determination by the Volhard method

| Tit. Vol. | Ml. $Fe(NO_3)_3$ | M $Fe(NO_3)_3$ | M KSCN | Ml. KSCN | M $AgNO_3$ | Ml. $AgNO_3$ | % Error[a] |
|---|---|---|---|---|---|---|---|
| 70 | 2 | 2 | 0.1 | 0.004 | 0.1 | 10.000 | 0.04 |
| 70 | 2 | 2 | 0.1 | 0.004 | 0.1 | 5.000 | 0.08 |
| 100 | 2 | 2 | 0.1 | 0.007 | 0.1 | 10.000 | 0.07 |
| 100 | 2 | 2 | 0.1 | 0.007 | 0.1 | 5.000 | 0.14 |
| 70 | 2 | 2 | 0.05 | 0.008 | 0.05 | 10.000 | 0.08 |
| 70 | 2 | 2 | 0.05 | 0.008 | 0.05 | 5.000 | 0.16 |
| 70 | 2 | 2 | 0.05 | 0.008 | 0.05 | 2.000 | 0.4 |
| 100 | 2 | 2 | 0.05 | 0.013 | 0.05 | 10.000 | 0.13 |
| 100 | 2 | 2 | 0.05 | 0.013 | 0.05 | 5.000 | 0.26 |
| 100 | 2 | 2 | 0.05 | 0.013 | 0.05 | 2.000 | 0.65 |
| b | | | | | | | |
| 70 | 4 | 2 | 0.1 | 0.003 | 0.1 | 10.000 | 0.03 |
| 70 | 4 | 2 | 0.1 | 0.003 | 0.1 | 5.000 | 0.06 |
| 100 | 4 | 2 | 0.1 | 0.005 | 0.1 | 10.000 | 0.05 |
| 100 | 4 | 2 | 0.1 | 0.005 | 0.1 | 5.000 | 0.1 |
| 70 | 4 | 2 | 0.05 | 0.006 | 0.05 | 10.000 | 0.06 |
| 70 | 4 | 2 | 0.05 | 0.006 | 0.05 | 5.000 | 0.12 |
| 70 | 4 | 2 | 0.05 | 0.006 | 0.05 | 2.000 | 0.3 |
| 100 | 4 | 2 | 0.05 | 0.010 | 0.05 | 10.000 | 0.1 |
| 100 | 4 | 2 | 0.05 | 0.010 | 0.05 | 5.000 | 0.2 |
| 100 | 4 | 2 | 0.05 | 0.010 | 0.05 | 3.000 | 0.5 |

[a] % error is the error in vol. of $AgNO_3$ assuming $AgNO_3$/KSCN ratio = 1.

Tables X and XI give the results obtained from titrating known amounts of chloride using 2 ml. of 2 M indicator. From the data in Tables IX, X, and XI it is apparent that the observed error agrees, within the accuracy of the calculations, with the expected error. Comparison of the results from Tables IX, X, and XI with the results of Table VII reveals a significant improvement in the accuracy using the increased indicator concentrations and decreased titrating volumes. Furthermore, a sharper and more reproducible color change was obtained. Finally, from Table X the ratio of silver nitrate to potassium thiocyanate is slightly greater than unity, whereas using less indicator the ratio was slightly less than unity. The results are in agreement with theory.

Table XII lists data obtained from the titration of extracted and unextracted samples of 0.05 and 0.04 M hydrogen chloride in formic acid. An exact analysis of the loss of chloride during extraction is difficult in view of the previous discussion. Solutions 3 and 4 of Table VII show large percentage deviations of the average values of the extracted samples from the unextracted. The data in Tables VII and XII, which show positive values for this percentage, indicate that the average loss of chloride is less than the reproducibility of the analytical method. Percentage deviations within a group from their average further support this conclusion. If for the previous reasons the results of Table XII are more significant than those in Table VII, a reasonable level of precision is ± 0.15% with an average apparent loss of chloride of - 0.12%. Thus it is concluded that the average loss of chloride during extraction is of the same order of magnitude as the precision of the analytical method.

Table X. Standardization of silver nitrate by the Volhard method increasing indicator concentration[a]

| $\underline{M}$ NaCl x $10^2$ | Ml. $AgNO_3$ | Ml. KSCN | $\frac{AgNO_3}{KSCN}$ | Ml. NaCl | $\underline{M}$ $AgNO_3$ x $10^2$ | % Dev. |
|---|---|---|---|---|---|---|
| - | 4.000 | 3.980 | 1.005 | - | | |
| - | 4.000 | 3.975 | 1.006 | - | | |
| - | 4.500 | 4.470 | 1.007 | - | | |
| - | 5.000 | 4.970 | 1.006 | - | | |
| 5.069 | 9.900 | 0.102 | 1.006 | 10.00 | 5.173 | -0.019 |
| | 9.940 | 0.140 | 1.006 | 10.00 | 5.172 | -0.038 |
| | 9.980 | 0.190 | 1.006 | 10.00 | 5.178 | 0.077 |
| Av. | | | | | 5.174 | |

[a] Volhard procedure 3.

Table XI. Titration of chloride by the Volhard method increasing indicator concentration[a]

| $\underline{M}$ NaCl x $10^2$ | Mg. Cl taken | Mg. Cl found | Avg. | % Error | % Dev. from avg. |
|---|---|---|---|---|---|
| 5.114 | 18.13 | 18.11 | | -0.110 | 0.000 |
| | 18.13 | 18.11 | 18.11 | -0.110 | 0.000 |
| | 18.13 | 18.11 | | -0.110 | 0.000 |
| 5.166 | 18.32 | 18.31 | | -0.055 | 0.055 |
| | 18.32 | 18.29 | 18.30 | -0.164 | -0.055 |
| | 18.32 | 18.30 | | -0.109 | 0.000 |

[a] Volhard procedure 3.

Table XII. Titration of hydrogen chloride in formic acid by the Volhard method before and after extraction - increased indicator concentration[a]

| Soln. No. | U.E.[b] | E.[c] | Mg. Cl | Avg. | A | B | C |
|---|---|---|---|---|---|---|---|
| 5 | - | | 17.25 | | 0.000 | | |
| 5 | - | | 17.25 | 17.25 | 0.000 | | |
| 5 | - | | 17.25 | | 0.000 | | |
| 5 | | - | 17.22 | | 0.000 | -0.174 | -0.174 |
| 5 | | - | 17.22 | 17.22 | 0.000 | | -0.174 |
| 5 | | - | 17.22 | | 0.000 | | -0.174 |
| 6 | - | | 13.85 | | -0.144 | | |
| 6 | - | | 13.88 | 13.87 | 0.072 | | |
| 6 | - | | 13.89 | | 0.144 | | |
| 6 | | - | 13.87 | | -0.072 | 0.072 | 0.000 |
| 6 | | - | 13.88 | 13.88 | 0.000 | | 0.072 |
| 6 | | - | 13.88 | | 0.000 | | 0.072 |

[a] Volhard procedure 3, 10 ml. aliquots.

[b] U.E. is unextracted sample.

[c] E. is extracted sample.

A = % deviation of each sample from average.

B = % deviation of average of E. samples from U.E. average.

C = % deviation of each E. sample in a group from average value of U.E. for each group.

B. Determination of Chloride by Potentiometric Titration. Due to the difficulties and limitations found with the Volhard method, a more accurate method for titrating chloride was needed. Shiner (34) has reported that in acetic acid - sodium acetate buffer, chloride concentrations greater than 0.1 meq. can be accurately determined by potentiometric titration.

Experiments were performed to ascertain the limitations of the procedure in aqueous formic acid and to reinvestigate the loss of chloride during extraction.

Volumetric glassware except the micro-burets was calibrated. The precision of the calibrations was within 0.1%. The corrected volumes of the 1 l. volumetric flasks were negligible and thus usually neglected. It was found necessary to perform the experimental work in an air conditioned room maintained at approximately 23 ± 2°.

For solutions greater than $10^{-3}$ $\underline{M}$ in chloride end points were obtained by two methods: the derivative technique and graphical analysis (35,36).

The end point using the derivative technique was taken as the midpoint of that increment of titrant at which the rate of potential change was greatest, i.e., $\Delta E/\Delta C$ was a maximum. In a titration the increments of titrant added near the equivalence point were adjusted so as not to give a disproportionate weight to the normal error in measurement.

Graphical analysis consisted of plotting ml. of titrant against the corresponding potentials. The end point was taken as the midpoint of the straight line segment of the titration curve. This method, which is inconvenient to use, was employed primarily to obtain the end point potential and to verify the results of the previous method.

Table XIII reveals the precision obtained by potentiometric titration. Of the twenty determinations only four show deviations from their predicted end points, and of the four only two (numbers 15 and 16) appear to deviate significantly. This conclusion is supported by the end points obtained by the graphical method. Omitting the four questionable samples the derivative end point is 7.735 ± 0.015 ml. Including

Table XIII. Precision of potentiometric titration of chloride[a]

| Sample Number | A | B | C | Emf | M $AgNO_3$[b] |
|---|---|---|---|---|---|
| 1 | 7.74 | 7.74 | 7.735 | 270.5 | 0.02611 |
| 2 | 7.72 | 7.74 | 7.740 | 269.0 | 0.02617 |
| 3 | 7.74 | 7.74 | 7.740 | 263.0 | 0.02611 |
| 10 | 7.74 | 7.74 | 7.730 | 264.5 | 0.02611 |
| 11 | 7.74 | 7.74 | 7.740 | 268.0 | 0.02611 |
| 12 | 7.74 | 7.74 | 7.740 | 265.5 | 0.02611 |
| 4 | 7.72 | 7.72 | 7.735 | 263.0 | 0.02617 |
| 5 | 7.76 | 7.72 | 7.735 | 259.5 | 0.02604 |
| 6 | 7.72 | 7.72 | 7.730 | 263.0 | 0.02617 |
| 7 | 7.72 | 7.72 | 7.725 | 268.3 | 0.02617 |
| 8 | 7.72 | 7.72 | 7.720 | 264.5 | 0.02617 |
| 9 | 7.72 | 7.72 | 7.730 | 265.4 | 0.02617 |
| 20 | 7.72 | 7.72 | 7.735 | 263.5 | 0.02617 |
| 13 | 7.75 | 7.75 | 7.727 | 264.2 | 0.02607 |
| 14 | 7.75 | 7.75 | 7.737 | 262.5 | 0.02607 |
| 15 | 7.71 | 7.75 | 7.737 | 264.5 | 0.02621 |
| 16 | 7.77 | 7.75 | 7.772 | 266.4 | 0.02600 |
| 17 | 7.73 | 7.73 | 7.720 | 262.5 | 0.02614 |
| 18 | 7.73 | 7.73 | 7.730 | 262.3 | 0.02614 |
| 19 | 7.73 | 7.73 | 7.730 | 262.0 | 0.02614 |

[a] M NaCl = 0.04052; 5 cc. of HCOOH; pipet volume (pip. vol.) = 4.986 ml.

[b] M calculated from data in column A.

A = end point by derivative.

B = expected derivative end point.

C = end point by graph.

all samples the value is 7.74 ± 0.030 ml. The results indicate that the observed deviations are random.

Table XIV reveals the accuracy obtained for a representative number of determinations. The results indicate that in aqueous formic acid, potentiometric titration is accurate and reproducible. For solutions down to $10^{-3}$ $\underline{M}$ in chloride the error is within the 0.1% level with a maximum error of approximately ± 0.3% for any one determination. To obtain these results meticulous attention was paid to analytical techniques. Only by allowing the system to reach equilibrium after the addition of each increment of titrant could smooth changes in the derivative be obtained. For solutions 4, and 5 in Table XIV, the calomel half cell had been thermostatted. This resulted in a further stabilization of potentials during a titration. Allowing the electrode system to stabilize itself prior to titration by stirring for several minutes in the solution to be titrated was helpful.

A reinvestigation of the loss of chloride accompanying extraction was undertaken. Since a clean separation of the two phases could not be effected, carbon tetrachloride was always present in the aqueous solution to be titrated. Its presence interfered with the potentiometric titration. In the course of titrating chloride with silver, the chloride ions are strongly adsorbed on the silver chloride precipitate(37). Therefore, a reasonable rationale for this behavior is that carbon tetrachloride coats the forming precipitate and thus effectively removes it from solution. This destroys the dynamic equilibrium between the chloride ion adsorbed on the precipitate and free chloride ions in the solution. Furthermore, the carbon tetrachloride appeared to coat the silver electrode.

Table XIV. Accuracy of potentiometric titration of chloride

| $\underline{M}$ NaCl | Sample | Solution | E.P. ml. | $\underline{M}$ $AgNO_3$ | Meq. Cl taken | Meq. Cl found | % Error |
|---|---|---|---|---|---|---|---|
| 0.04107[a,c] | 1 | 1 | 7.84 | 0.02612 | 0.2047 | 0.2048 | 0.0488 |
| | 2 | | 7.82 | | | 0.2043 | -0.1954 |
| | 3 | | 7.82 | | | 0.2043 | -0.1954 |
| | 4 | | 7.83 | | | 0.2045 | -0.0977 |
| | average | | 7.83 | | | 0.2045 | -0.0977 |
| 0.04095[b,c] | 1 | 2 | 7.84 | 0.02612 | 0.2044 | 0.2048 | 0.1957 |
| | 2 | | 7.82 | | | 0.2043 | -0.0488 |
| | 3 | | 7.83 | | | 0.2045 | 0.0488 |
| | average | | 7.83 | | | 0.2045 | 0.0488 |
| 0.02486[a,c] | 1 | 3 | 4.74 | 0.02610 | 0.1239 | 0.1237 | -0.1614 |
| | 2 | | 4.76 | | | 0.1242 | 0.2421 |
| | average | | 4.75 | | | 0.1240 | 0.0871 |
| 0.1003[d,f] | 1 | 4 | 13.37 | 0.02988 | 0.3997 | 0.3995 | -0.0500 |
| | 2 | | 13.37 | | | 0.3995 | -0.0500 |
| | 3 | | 13.40 | | | 0.4004 | 0.1751 |
| | average | | 13.38 | | | 0.3998 | 0.0250 |
| 0.1004[e,f] | 1 | 5 | 10.10 | 0.02988 | 0.3010 | 0.3018 | 0.2658 |
| | 2 | | 10.08 | | | 0.3012 | 0.0644 |
| | 3 | | 10.07 | | | 0.3013 | 0.0996 |
| | average | | 10.08 | | | 0.3013 | 0.0996 |

[a] pipet volume = 4.984 ml.

[b] pipet volume = 4.992 ml.

[c] 5 cc. of HCOOH.

[d] pipet volume = 3.985 ml.

[e] pipet volume = 2.998 ml.

[f] 10 cc. of HCOOH, calomel temp. = 23.00 ± 0.05°.

Removal of the carbon tetrachloride was accomplished by either of two methods: removing it from the bottom of the titration beaker with an eyedropper or re-extracting each aqueous layer with a small portion of petroleum ether. For kinetic runs the latter method was used. The insolubility in hydrocarbon solvents of the compounds to be studied kinetically precluded them as replacements for carbon tetrachloride. Due to its instability chloroform was not considered. Methylene chloride separated cleanly, but an approximate 0.5% chloride loss was observed. Therefore, it was considered unsatifactory.

Milliequivalents of chloride titrated after sample extraction are listed in Table XV. The meq. of chloride are calculated by both methods for obtaining the end point. The data reveal that the meq. of chloride recovered are randomly distributed about the meq. taken. This conclusion is supported by the following: the percentage deviations using the graphically determined end points are small and random, and the same end point distribution was obtained for un-extracted samples. Therefore, the loss of chloride occurring during sample extraction must be insignificant, well within the 0.1% level. This conclusion is further supported by data to be presented later.

The average end point potential obtained for 56 unextracted samples was 265.13 mv. while the corresponding value for 21 extracted samples was 264.03 mv. Only 5 samples showed deviations greater than ± 3 mv., and only 16 samples showed deviations greater than ± 2 mv. These fluctuations can be reduced by thermostatting the calomel half cell and keeping approximately constant the volumes of solutions to be titrated. Nevertheless, either of these average end point potentials agrees well with the theoretical value for the equivalence potential of 266 mv. (34).

Table XV.[a] Titration of chloride after sample extraction

| Sample | A | B | Emf | Meq. Found A | Meq. Found B | % Error A | % Error B |
|---|---|---|---|---|---|---|---|
| 1 | 7.76 | 7.772 | 264.0 | 0.2025 | 0.2028 | 0.2475 | 0.3960 |
| 2 | 7.76 | 7.740 | 263.5 | 0.2025 | 0.2020 | 0.2475 | 0.0000 |
| 3 | 7.76 | 7.745 | 265.5 | 0.2025 | 0.2021 | 0.2475 | 0.0500 |
| 4 | 7.74 | 7.740 | 260.0 | 0.2020 | 0.2020 | 0.0000 | 0.0000 |
| 5 | 7.74 | 7.760 | 264.0 | 0.2020 | 0.2025 | 0.0000 | 0.2475 |
| 6 | 7.74 | 7.740 | 264.3 | 0.2020 | 0.2020 | 0.0000 | 0.0000 |
| 7 | 7.75 | 7.742 | 264.0 | 0.2023 | 0.2021 | 0.1485 | 0.0500 |
| 8 | 7.73 | 7.735 | 264.5 | 0.2018 | 0.2019 | -0.0990 | -0.0500 |
| 9 | 7.75 | 7.736 | 264.5 | 0.2023 | 0.2019 | 0.1485 | -0.0500 |
| 10 | 7.76 | 7.738 | 265.3 | 0.2025 | 0.2020 | 0.2475 | 0.0000 |
| 11 | 7.74 | 7.728 | 265.3 | 0.2020 | 0.2017 | 0.0000 | -0.1485 |
| 12 | 7.75 | 7.740 | 268.3 | 0.2023 | 0.2020 | 0.1485 | 0.0000 |

[a] Meq. Cl taken = 0.2020; M NaCl = 0.04052; pipet volume = 4.984 ml.; M $AgNO_3$ = 0.02610 ± 0.00002.

A = end point by derivative.

B = end point from graph.

It became necessary to accurately titrate solutions down to $10^{-4}$ M in chloride. Precise titration of solutions less than $10^{-3}$ M in chloride is difficult. As the chloride concentration decreases, titration curves become progressively flatter and exhibit less "break" in the region of the equivalence point (35,36). The rise or fall in the potential in the neighborhood of the equivalence point is dependent upon the concentration of the solutions to be titrated and upon the solubility product of the precipitate (35, 36). At these concentrations the influence of the solubility of silver chloride upon the total ion concentration near the equivalence point may not be neglected, and, therefore, the silver ion concentration shows no sudden increase near the equivalence point resulting in the slow rate of potential change in this region (35,36).

For solutions varying from $5 \times 10^{-4}$ to $1 \times 10^{-3}$ M in chloride, two methods of obtaining the end point were attempted: graphical analysis and titration to a preset potential.

Using the second method, it has been reported (37) that chloride concentrations of $10^{-4}$ M and $10^{-5}$ M can be determined with an error of 1 and 10% respectively. Shiner (34) has reported the accuracy of the method to be well within the 1% level for solutions down to $10^{-4}$ M. One set of data in the paper reveal the average error in the titration of a $10^{-4}$M solution to be 0.1% with a precision of ± 0.3%.

Since the equivalence potential is temperature dependent, it is necessary to thermostat the calomel half cell and maintain a reasonably constant room temperature. It is necessary to reproduce or eliminate junction potentials.

Results obtained by graphical analysis of titration data for solutions $1.5 \times 10^{-3}$ to $2 \times 10^{-4}$ M in chloride are listed in Table XVI. For solutions containing 0.08 to 0.1 meq. of chloride end points were estimated by the derivative technique. This was done by taking the mid point of that increment of titrant giving the largest value of $\Delta E/\Delta C$ around 265 mv. The reliability of this method is at best questionable. The uncertainty in location of the end point by graphical analysis increases as the chloride concentration decreases. This results from the necessity of compressing the axes due to increasing linearity. This method appears to be accurate to about 0.4% in this concentration range. Titration curves obtained from data for chloride solutions ranging from $5 \times 10^{-5}$ to $1 \times 10^{-4}$ M begin to approximate straight lines. The following

Table XVI. Titration of dilute chloride solutions

| $\underline{M}$ NaCl | Sample | A | B | C x $10^2$ | D x $10^2$ | E x $10^2$ | F | G | U.E. | E. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.501 x $10^{-2}$ b,e,h | 1 | 14.97 | 14.98 | 15.00 | 14.98 | 14.99 | -0.133 | -0.067 | - | |
| | 2 | 14.99 | 14.98 | | 15.00 | 14.99 | 0.000 | -0.067 | - | |
| | 3 | 15.00$^d$ | - | | 15.02 | - | 0.133 | - | - | |
| | average | | | | 15.00 | 14.99 | 0.000 | -0.067 | - | |
| | 1 | 15.02 | 15.01 | | 15.04 | 15.02 | 0.267 | 0.133 | | - |
| | 2 | 15.02 | 15.01 | | 15.04 | 15.02 | 0.267 | 0.133 | | - |
| | 3 | 15.04 | 14.95 | | 15.06 | 14.96 | 0.400 | -0.267 | | - |
| | average | | | | 15.05 | 15.00 | 0.333 | 0.000 | | - |
| 2.000 x $10^{-2}$ a,e,i | 1 | 10.00 | 9.938 | 9.972 | 10.01 | 9.948 | 0.381 | -0.241 | - | |
| | 2 | 10.00 | 9.977 | | 10.01 | 9.987 | 0.381 | 0.150 | - | |
| | 3 | 9.986 | 9.965 | | 9.996 | 9.975 | 0.241 | 0.030 | - | |
| | average | | | | 10.00 | 9.970 | 0.281 | -0.020 | - | |
| 9.998 x $10^{-2}$ b,e,j | 1 | 10.02$^d$ | - | 10.00 | 10.03 | - | 0.300 | - | - | |
| | 2 | 10.02 | 10.01 | | 10.03 | 10.02 | 0.300 | 0.200 | - | |
| | 3 | 10.00 | - | | 10.01 | - | 0.100 | - | - | |
| | average | | | | 10.02 | 10.02 | 0.200 | 0.200 | - | |
| | 1 | 9.97 | 9.990 | | 9.980 | 10.00 | -0.200 | 0.000 | | - |
| | 2 | 9.99 | 9.985 | | 10.00 | 9.995 | 0.000 | -0.050 | | - |
| | 3 | 10.01 | 10.02 | | 10.02 | 10.03 | 0.200 | 0.300 | | - |
| | average | | | | 10.00 | 10.01 | 0.000 | 0.100 | | - |
| 8.011 x $10^{-3}$ b,e,k | 1 | 7.95 | 8.007 | 8.011 | 7.958 | 8.015 | -0.662 | 0.050 | - | |
| | 2 | 8.005 | 7.998 | | 8.013 | 7.996 | 0.025 | -0.187 | - | |
| | 3 | 7.975 | 7.991 | | 7.983 | 7.999 | -0.350 | -0.150 | - | |
| | average | | | | 7.984 | 8.003 | -0.337 | -0.062 | - | |
| | 1 | 8.02 | 7.998 | | 8.028 | 8.006 | 0.212 | -0.062 | | - |
| | 2 | 8.00 | 8.015 | | 8.008 | 8.023 | -0.037 | 0.015 | | - |
| | 3 | 8.01 | 7.994 | | 8.018 | 8.002 | 0.087 | -0.112 | | - |
| | average | | | | 8.018 | 8.010 | 0.087 | -0.012 | | - |

Table XVI. (Continued).

| $\underline{M}$ NaCl | Sample | A | B | C x $10^2$ | D x $10^2$ | E x $10^2$ | F | G | U.E. | E. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.023 x $10^{-3}$ [c,f,1] | 1 | | 5.08 | 2.045 | | 2.042 | | -0.147 | - | |
| | 2 | | 5.095 | | | 2.048 | | 0.147 | - | |
| | 3 | | 5.09 | | | 2.046 | | 0.049 | - | |
| | average | | | | | 2.045 | | 0.000 | - | |
| 2.045 x $10^{-3}$ [c.f.m] | 1 | | 10.20 | 4.086 | | 4.101 | | 0.367 | - | |
| | 2 | | 10.20 | | | 4.101 | | 0.367 | - | |
| | 3 | | 10.17 | | | 4.088 | | 0.049 | - | |
| | average | | | | | 4.096 | | 0.245 | - | |

A. = end point ΔE/ΔC.

B = end point, graphical.

C = meq. of chloride taken.

D = meq. of chloride calc. from A.

E = meq. of chloride calc. from B.

F = % error in D.

G = % error in E.

[a] 5 cc. sample.

[b] 10 cc. sample.

[c] 20 cc. sample.

[d] titrated to preset emf.

[e] $\underline{M}$ $AgNO_3$ = 1.001 x $10^{-2}$.

[f] $\underline{M}$ $AgNO_3$ = 4.020 x $10^{-2}$.

[g] 5 cc. of formic acid added.

[h] pip. vol. = 9.993 ml.

[i] pip. vol. = 4.986 ml.

[j] pip. vol. = 10.006 ml.

[k] pip. vol. = 10.000 ml.

[l] pip. vol. = 19.99 ml.

[m] pip. vol. = 19.98 ml.

procedure was used in an an attempt to obtain end points from these curves providing they were not straight lines.

1) At any point on the curve before the end point a tangent to the curve was constructed.

2) At any point on the curve after the end point, a tangent to the curve parallel to the first was drawn.

3) At an assumed end point a tangent was constructed to the curve and projected until it intersected those of 1 and 2.

4) The end point was taken as the mid point of the projection of these intersections on the X- axis.

The data in Table XVII indicate that this method is accurate to about 1% for solutions $10^{-4}$ $\underline{M}$ in chloride. For the $5 \times 10^{-5}$ $\underline{M}$ solution only one out of four curves could be analyzed. Neither of these methods appeared adequate because of the error and the large amount of time required for a given determination. Table XVI reveals that the degree of accuracy observed for those samples titrated to a preset potential is comparable to these graphical methods. This was further substantiated by experimental results obtained prior to thermostatting the calomel half cell.

Comparing the percentage deviations of the extracted and unextracted samples, Table XVI further supports the previous conclusions concerning the extraction procedure.

When titrating samples to a preset potential the calomel half cell was thermostatted and the initial volume of solutions to be titrated was 100 ± 5 ml. Table XVIII lists the results of a representative number of titrations. It can be seen that the end point potential is approximately constant with deviations of approximately ± 0.5 mv. Some of the potentials were obtained after the correct volume of titrant had been added. A large number of the potentials were obtained by balancing the potentiometer after titration to 265 mv. From the data it would appear that these potential fluctuations are serious for only four samples. These results indicate that chloride solutions down to $10^{-4}$ $\underline{M}$ can be titrated with an average error of approximately 0.2%. Solutions to be titrated were prepared by adding 10 ml. of formic acid to 80 ml. of water and pipetting in a 10 ml. aliquot of standard sodium chloride solution.

Table XVII. Titration of dilute chloride solutions[a]

| Sample | U.E. | E. | End Point (ml.) | Meq. Cl taken x $10^3$ | Meq. Cl found x $10^3$ | % Error |
|---|---|---|---|---|---|---|
| 1 | - | | 9.95 | 9.993 | 9.95 | -0.400 |
| 2 | - | | 9.93 | | 9.93 | -0.601 |
| 3 | - | | 9.94 | | 9.94 | -0.500 |
| 4 | | - | 10.21 | | 10.21 | 2.20 |
| 5 | | - | 10.54 | | 10.54 | 5.47 |
| 6 | | - | 10.05 | | 10.05 | 0.601 |

[a] $\underline{M}$ $AgNO_3$ = $1.000 \times 10^{-3}$; $\underline{M}$ NaCl = $9.997 \times 10^{-4}$; pip. vol. = 9.996 ml.

Table XIX reveals that the equivalence point potential is dependent upon the formic acid concentration. Doubling the formic acid content of the titration solution reduced this potential by approximately 5 mv. This change in the equivalence point potential was measured after the addition of approximately the correct volumes of silver nitrate to solutions containing 10 ml. of formic acid.

Table XVIII. Titration of limiting chloride concentrations to preset potential[a]

| $\underline{M}$ NaCl | Sample | E.P. ml. | Meq. Cl taken x $10^2$ | Meq. Cl found x $10^2$ | % Error | Emf |
|---|---|---|---|---|---|---|
| 1.023 x $10^{-3}$ [b] | 1 | 2.565 | 1.022 | 1.023 | 0.0978 | 265.00 |
| | 2 | 2.561 | | 1.022 | 0.0000 | 264.90 |
| | 3 | 2.540 | | 1.013 | -0.8806 | 265.50 |
| | 4 | 2.550 | | 1.017 | -0.4892 | 265.90 |
| | 5 | 2.580 | | 1.029 | 0.6849 | 265.20 |
| | average | 2.559 | | 1.021 | -0.0978 | |
| 2.045 x $10^{-3}$ [b] | 1 | 5.130 | 2.044 | 2.047 | 0.1467 | 265.00 |
| | 2 | 5.115 | | 2.041 | -0.1467 | 265.60 |
| | 3 | 5.122 | | 2.044 | 0.0000 | 265.13 |
| | 4 | 5.120 | | 2.043 | -0.0489 | 265.13 |
| | 5 | 5.120 | | 2.043 | -0.0489 | 265.13 |
| | average | 5.121 | | 2.043 | -0.0489 | |
| 3.054 x $10^{-3}$ [c] | 1 | 7.645 | 3.053 | 3.050 | -0.0983 | 265.14 |
| | 2 | 7.670 | | 3.060 | 0.2293 | 265.17 |
| | 3 | 7.660 | | 3.056 | 0.0983 | 265.20 |
| | 4 | 7.67 | | 3.060 | 0.2293 | 265.27 |
| | 5 | 7.68 | | 3.064 | 0.4258 | 265.00 |
| | 6 | 7.66 | | 3.056 | 0.2293 | 264.00 |
| | 7 | 7.66 | | 3.056 | 0.2293 | 263.00 |
| | 8 | 7.655 | | 3.054 | 0.0328 | 264.80 |
| | 9 | 7.680 | | 3.064 | 0.4258 | 264.05 |
| | 10 | 7.660 | | 3.056 | 0.0983 | 263.00 |
| | 11 | 7.650 | | 3.052 | -0.0328 | 263.00 |
| | 12 | 7.655 | | 3.054 | 0.0328 | 262.60 |
| | 13 | 7.63 | | 3.044 | -0.2948 | 264.53 |
| | average | 7.66 | | 3.056 | 0.0983 | |
| 1.018 x $10^{-3}$ [c] | 1 | 2.540 | 1.018 | 1.013 | -0.4912 | 265.00 |
| | 2 | 2.555 | | 1.019 | 0.0982 | 265.00 |
| | 3 | 2.555 | | 1.019 | 0.0982 | 265.38 |
| | average | 2.550 | | 1.017 | -0.0982 | |
| 2.036 x $10^{-3}$ [c] | 1 | 5.090 | 2.035 | 2.031 | -0.1966 | 265.00 |
| | 2 | 5.100 | | 2.035 | 0.0000 | 266.00 |
| | 3 | 5.102 | | 2.036 | 0.0491 | 265.10 |
| | average | 5.097 | | 2.034 | 0.0491 | |

[a] N.B.S. volumetrics used, 10 cc. sample, tit. vol. 100 ± 5 ml., room temp. 23 ± 1°, calomel cell temp. 23.30 ± 0.05°, $\underline{M}$ $AgNO_3$ = 3.990 x $10^{-3}$.

[b] Pip. vol. = 9.996 ml.

[c] Pip. vol. = 9.997 ml.

Table XIX. Dependence of end point potential upon formic acid concentration[a]

| $\underline{M}$ NaCl | Sample | Ml. HCOOH | Ml. $AgNO_3$ | Emf | Avg. Emf | Meq. Cl taken | Meq. Cl found |
|---|---|---|---|---|---|---|---|
| $2.005_3 \times 10^{-3}$ [b] | 1 | 5 | 7.882 | 265.15 | | | |
| | 2 | 5 | 7.885 | 265.50 | 265.55 | | |
| | 3 | 5 | 7.900 | 266.00 | | | |
| | 4 | 10 | 7.890 | 260.00 | | | |
| | 5 | 10 | 7.895 | 262.00 | | | |
| | 6 | 10 | 7.890 | 260.62 | | | |
| | 7 | 10 | 7.895 | 260.40 | | | |
| | 8 | 10 | 7.900 | 259.50 | 260.15 | | |
| | 9 | 10 | 7.895 | 259.30 | | | |
| | 10 | 10 | 7.895 | 259.80 | | | |
| | 11 | 10 | 7.890 | 259.80 | | | |
| | 12 | 10 | 7.870 | 260.00 | | | |
| 0.1003[c] | 1 | 10 | 7.972 | 262.80 | | 0.5001 | 0.5004 |
| | 2 | 10 | 7.976 | 260.50 | | | 0.5007 |
| | 3 | 10 | 7.975 | 262.50 | 261.18 | | 0.5006 |
| | 4 | 10 | 7.972 | 262.00 | | | 0.5004 |
| | 5 | 10 | 7.970 | 258.00 | | | 0.5003 |
| | average | | | | | | 0.5004 |

[a] Tit. vol. = 100 ± 5 ml.

[b] Pip. vol. = 19.98, $\underline{M}$ $AgNO_3$ = $5.076 \times 10^{-3}$, calc. vol. $AgNO_3$ = 7.892.

[c] Pip. vol. = 4.986, $\underline{M}$ $AgNO_3$ = $6.277 \times 10^{-2}$.

The last major problem encountered was the occasional shift in the equivalence point potential observed upon introduction of a new salt bridge. Such shifts were recognizable from the analytical results. Errors were reproducible for any given chloride concentration. However, the relative error changed as the chloride ion concentration was varied. This result is not unreasonable, since titration curves are not identical at these limiting concentrations. The value of the equivalence potential was checked by adding the calculated volume of standard silver nitrate to standard sodium chloride, or by titrating solutions containing at least 0.2 meq. of chloride. It is strongly advised that such periodic checks be made when using this procedure. During kinetic runs many such titrations were performed. The previous results are representative, and by no means the best obtained; in some instances end point potentials were reproducible to within ± 0.2 mv.

In summary, the error in potentiometric titration of solutions containing more than 0.1 meq. of chloride is at the 0.1% level. By stringently observing the necessary precautions, solutions down to 0.01 meq. can be accurately titrated to a preset potential. In the present work, the resulting average error was usually less than 0.2%.

The accuracy attainable by the Volhard method is dependent on indicator concentration. For chloride concentrations ranging from 0.1 to 1.0 meq., the accuracy might reasonably be expected to vary from 1% to 0.1%. In the opinion of the author, lower chloride concentration cannot be titrated with any reasonable degree of accuracy.

Because of its precision, accuracy, and simplicity, the potentiometric method is clearly preferable to the Volhard method.

By taking the necessary precautions, the recovery of chloride after extraction is nearly quantitative.

If the proper choice of extraction solvents is made, potentiometry can be used to follow kinetics in other solvent systems (38).

## IV. Kinetics

In the present studies, it was imperative that the solvolysis proceed by the $S_N1$ mechanism. Therefore the choice of solvent was critical. The mechanistic dichotomies accompanying the solvolysis of arylmethyl halides and, in particular, benzylhalides, are well known and have been reviewed by Streitwieser (39). These compounds present a low steric hindrance to nucleophilic attack, but have a carbonium ion stability somewhat greater than that of secondary alkyl systems. As solvent nucleophilicity is increased, the relative rates of benzyl systems increase with respect to the corresponding secondary systems, but decrease with respect to the primary systems. Conversely, because of the greater role played by nucleophilic character in benzyl systems, the sensitivity of rate to solvent ionizing power is less than for secondary systems. In attempting to correlate displacement reactions and solvolyses using the Hammett equation, Swain and Langsdorf (40) obtained non-linear relations. They concluded that the mechanism was neither $S_N1$ nor $S_N2$ but rather a termolecular or "push-pull" mechanism. Bensley and Kohnstam (41) in a detailed study of benzyl chloride solvolysis concluded that in partly aqueous solvents, 50% aqueous acetone and 50% aqueous ethanol, the mechanism is in the borderline region which marks the transition from $S_N2$ to $S_N1$. Dewar and Sampson (42) correlated the rates of solvolysis of several arylmethylchlorides in different solvents with delocalization energies. From these correlations the authors obtained values for the effective overlap integral, $\beta_{eff.}$. As anticipated, $\beta_{eff.}$ decreased with increasing nucleophilicity of the solvent. The effective overlap integral had a maximum value of 33 kcal. in either 0.38 M or 1.2 M water-formic acid, decreased to 20 kcal. in the ternary solvent 54% formic acid, 6.1% water, 39.8% dioxane, and fell to a value of 9 to 5 kcal. in 80% aqueous ethanol. In the fully nucleophilic displacement by potassium iodide, the value was 5 kcal.

From these results, Dewar and Sampson concluded that the solvolysis was most limiting, $S_N1$, in moist formic acid. Therefore, the solvent chosen was 0.32 m water-formic acid. For expediency, solvents were prepared on a molal rather than a molar basis. From approximate densities (43) 0.32 m water-formic acid is approximately equivalent to 0.38 M water-formic acid.

Dewar and Sampson (42) observed that the limiting solvolysis of arylcarbinyl chlorides in moist formic acid was adequately represented by equation 1.

$$ArCH_2Cl \xrightleftharpoons{H_2O} ArCH_2OH + HCl \qquad (1)$$

Since a measurable equilibrium was established during solvolysis of the more reactive compounds, the unimolecular rate constant, $k_1$, was obtained from the integrated equation for a reaction which is first order forward and second order backward.

$$k_1 t = \left(\frac{x_e}{2A_0 - x_e}\right) \ln \left(\frac{A_0 x_e + x(A_0 - x_e)}{A_0(x_e - x)}\right) \qquad (2)$$

where $A_0$ is the initial concentration of $ArCH_2Cl$
$x$ is the concentration of HCl at time t
$x_e$ is the concentration of HCl at infinite time.

Usually 8, 9 or 10 samples over a time period of 10 to 12 hours were taken during kinetic runs of α-naphthylcarbinyl chloride and its deuterated analogs. Due to the appearance of turbidity, infinity titres were obtained after 22 to 28 hours. At this time solvolysis had proceeded through approximately six half-lives. Except for run 13a (Table XX) some turbidity was always present. The infinity samples for run 13b taken after 51-52 hours had just begun to show the presence of

Table XX. Rate and equilibrium constants for solvolysis of α-naphthylcarbinyl chloride[a]

| Run | $A_0 \times 10^3$ | $[x]_{eq.} \times 10^3$ | $k \times 10^5$ sec.$^{-1}$ | % rx. | $K_{eq.} \times 10^2$ |
|---|---|---|---|---|---|
| 1 | 8.964 | 7.265 | 4.63 | 81.0 | 3.11 |
| 1a | 8.964 | 7.271 | 4.62 | 81.1 | 3.12 |
| 1b | 8.964 | 7.253 | 4.65 | 80.9 | 3.11 |
| 2 | 8.613 | 7.112 | 4.55 | 82.6 | 3.39 |
| 3 | 8.718 | 7.163 | 4.62 | 82.2 | 3.30 |
| 4 | 8.573 | 6.927 | 4.57 | 80.8 | 2.92 |
| 4a | 8.573 | 6.948 | 4.52 | 81.0 | 2.97 |
| 4b | 8.573 | 6.914 | 4.61 | 80.6 | 2.88 |
| 4c | 8.573 | 6.919 | 4.59 | 80.7 | 2.89 |
| 4d[b] | 8.573 | 6.927 | 4.62 | 80.8 | 2.92 |
| 8 | 9.382 | 7.411 | 4.40 | 79.0 | 2.79 |
| 12 | 9.615 | 7.600 | 4.35 | 79.0 | 2.87 |
| 12a | 9.615 | 7.633 | 4.31 | 79.4 | 2.94 |
| 12b | 9.615 | 7.609 | 4.34 | 79.1 | 2.89 |
| 12c | 9.615 | 7.563 | 4.40 | 78.7 | 2.79 |
| 12d | 9.615 | 7.594 | 4.36 | 79.0 | 2.85 |
| 12e | 9.592 | 7.600 | 4.37 | 79.2 | 2.90 |
| 13a | 4.981 | 4.489 | 4.43 | 90.1 | 4.10 |
| 13b[c] | 4.981 | 4.559 | 4.32 | 91.5 | 4.92 |
| average least squares | | | 4.49 | | |

[a] Sub-runs calculated for changes in x, $x_{eq.}$, or $A_0$.

[b] Each value of x increased by 0.2%.

[c] Used as the rate constant for run 13.

turbidity. Usually infinity titres were obtained for three samples. The maximum deviation of the individual values of $x_{eq.}$ from their average in any run was usually within 0.5% and only for run 12 did this value rise to 1%. Rate constants were obtained by linear least squares analysis. Equation 2 and the linear least squares equation were programmed, using Fortran notation, and the raw data were processed on a Control Data 3600 computer. Tables XX, XXI, and XXII list the unimolecular rate constants for α-naphthylcarbinyl chloride, α-naphthylcarbinyl chloride -8-d, and α-naphthylcarbinyl chloride-α,α- $d_2$. The average least squares rate constant for α-naphthylcarbinyl chloride is $4.49 \times 10^{-5}$ sec.$^{-1}$. The maximum deviation is ± $0.17 \times 10^{-5}$ sec.$^{-1}$ and the average deviation is ± $0.11 \times 10^{-5}$ sec.$^{-1}$. The present value compares favorably with the value $4.4 \times 10^{-5}$ sec.$^{-1}$ reported by Dewar and Sampson. An estimate of the influence of changes in x, $x_{eq.}$, and $A_0$ on the rate constant can be seen from the sub-runs in Table XX. Run 4d reveals that increasing each value of x by 0.2% increases k by 1%. Reduction of $A_0$ by 0.2% reduces k by 0.5% (run 12e). Comparing 1a and 1b reveals that decreasing $x_e$ by 0.25% increases k by 0.65%. Increasing $x_{eq.}$ by 0.92% decreases k by 2% (runs 12a and 12c).

Taking the activation energy as 25 kcal./mole (44), it can be shown that temperature control should be ± 0.1° for a 2% error in k. Since temperature control was better than ± 0.01°, contributions to the error due to temperature fluctuations were negligible. The estimated error in k due to error in time measurements is less than 2%. As predicted (45) and verified by the above data, the largest source of error is related to the analytical precision. It is not known whether the observed precision in k is the best that can be obtained with the present analytical method or whether other problems contribute measurably. Shiner (38b) has reported rate constant precision of ± 4% using potentiometric titration to follow the appearance of halide ion, with initial organic halide concentration of approximately 0.05 M. Part of this error may have been caused by a small mass law effect which prevented the reaction from strictly obeying the first order kinetic rate expression.

Table XXI. Rate and equilibrium constants for solvolysis of α-naphthylcarbinyl chloride-8-d.

| Run | $A_0 \times 10^3$ | $[x]_{eq.} \times 10^3$ | $k \times 10^5$ sec.$^{-1}$ | % rx. | $K_{eq.} \times 10^2$ |
|---|---|---|---|---|---|
| 5 | 8.561 | 6.949 | 4.54 | 81.2 | 2.97 |
| 6 | 9.105 | 7.290 | 4.53 | 80.1 | 2.93 |
| 7 | 9.215 | 7.453 | 4.45 | 80.1 | 3.15 |
| average least squares | | | 4.51 | | |

Table XXII. Rate and equilibrium constants for solvolysis of α-naphthylcarbinyl chloride-α,α-$d_2$.

| Run | $A_0 \times 10^3$ | $[x]_{eq.} \times 10^3$ | $k \times 10^5$ sec.$^{-1}$ | % rx. | $K_{eq.} \times 10^2$ |
|---|---|---|---|---|---|
| 9 | 9.815 | 7.754 | 3.31 | 79.0 | 2.92 |
| 10 | 10.39 | 8.046 | 3.29 | 77.4 | 2.77 |
| 11 | 9.972 | 7.717 | 3.35 | 77.4 | 2.64 |
| average least squares | | | 3.32 | | |

Due to the difficult solubility of 8-bromo-α-naphthylcarbinyl chloride and its increased rate of solvolysis, a thorough kinetic study was not made. Since a measurable equilibrium appeared to be established, the rate constants were calculated using Equation 2. The accuracy of the rate constants may be less than the results indicate (Table XXIII).

Table XXIII. Rate constants for solvolysis of 8-bromo-α-naphthylcarbinyl chloride and 8-methyl-α-naphthylcarbinyl chloride.

| Compound | $A_0 \times 10^3$ | $[x]_{eq.} \times 10^3$ | $k \times 10^5$ sec.$^{-1}$ | % rx. |
|---|---|---|---|---|
| 8-bromo | 5.225 | 4.888 | 6.15 | 93.6 |
| 8-bromo | 5.022 | 4.736 | 6.11 | 94.3 |
| 8-methyl | 5.18 | 4.83 | $3.8 \times 10^2$ | 88-93 |

The very fast rate of solvolysis of 8-methyl-α-naphthylcarbinyl chloride, combined with its low rate of solubility, prohibited accurate rate studies. The rate was obtained by estimating the half-life.

To a first approximation, the equilibrium constant and percentage reaction should be the same for α-naphthylcarbinyl chloride and its deuterated analogs. Obviously, neither of these terms should be concentration dependent. However, Tables XX, XXI, and XXII reveal that both the equilibrium constant and percentage reaction vary with initial concentration, and a systematic trend is exhibited. Decreasing the initial concentration of organic chloride from $1.039 \times 10^{-2}$ $\underline{M}$ to $4.981 \times 10^{-3}$ $\underline{M}$ increases the percentage reaction from 77.4% to 91.5% and the equilibrium constant from $2.77 \times 10^{-2}$ to $4.92 \times 10^{-2}$. However, Table XX reveals no such systematic trend in the rate constant.

Therefore it is necessary to examine the assumptions made in deriving equation 2, the mechanistic implications of equation 1, and the effects of turbidity.

Let us first assume that equation 1 is valid and consider the assumptions implicit in equation 2. Let equation 3 be a general reaction scheme representing 1.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C \qquad (3)$$

The general differential rate expression is

$$\frac{dx}{dt} = k_1 [A_0 - x] - \frac{k_1}{K} [B_0 + x]^2 \qquad (4)$$

where

$$K = k_1/k_2 = \frac{[B_0 + x_e][C_0 + x_e]}{[A_0 - x_e]}$$

assuming $[H_2O]$ to be constant and $B_0 = C_0$.

For the completely general case, $B_0$ and $C_0$ are not necessarily equal to zero.

Equation 4 is easily reduced to equation 5 which is in standard form.

$$\int_{v=v_1}^{v=v_2} \frac{dv}{a^2-v^2} = \frac{k_1}{K} \int_{T=0}^{T=T_2} dt \qquad (5)$$

where

$$a = \left\{ KA_0 - B_0{}^2 + \left(\frac{K + 2B_0}{2}\right)^2 \right\}^{1/2}$$

$$v = [x] + \frac{(K + 2B_0)}{2}$$

$$v^2 < a^2.$$

Equation 2 is easily derivable from equation 5 by assuming that $B_0$ and $C_0$ are identically zero. Therefore, for equation 2 to be rigorously correct, there must be no initial concentration gradient. Since α-naphthylcarbinyl chloride and its deuterated analogs were not readily soluble, one source of error is immediately introduced. The time required to dissolve the compound, 4 to 9 minutes, varied both with the amount of material and its crystalline form. Since vigorous shaking was required, the volumetric flask could be filled to only about 60% capacity, introducing other sources of error. Initially concentration gradients existed and the rate of solvolysis was not uniform. Due to the extremely vigorous agitation required, the loss of a small amount of solution from the tightly stoppered volumetric flask was occasionally noted. A non-uniform rate of solvolysis resulted from the decrease in the temperature over the time required to prepare the solution and fill and seal the ampoules. This time varied from 15 to 17 minutes. The first samples were taken after approximately 60 minutes, which corresponded to about 15-20% solvolysis. Thus these effects may be partly obscured by the long half-life. However, the rate constants calculated by equation 2 will undoubtedly reflect some of these effects.

The magnitude of this effect is undoubtedly increased for 8-bromo-α-naphthylcarbinyl chloride due to its increased rate of solvolysis and its low rate of solution; Twenty-two to twenty-five minutes were required to prepare a $5 \times 10^{-3}$ <u>M</u> solution. The time required to dissolve 8-methyl-α-naphthylcarbinyl chloride was longer than its half-life.

The general condition $B_0 = C_0 \neq 0$ yields equation 6.

$$\ln\left\{\frac{\theta^{1/2} + (x + \phi)}{\theta^{1/2} - (x + \phi)}\right\} = \frac{2\theta^{1/2}k_1t}{K} + \ln\left(\frac{\theta^{1/2} + \phi}{\theta^{1/2} - \phi}\right)$$

where

$$\theta = K[A_0] - [B_0]^2 + \left(\frac{K + 2[B_0]}{2}\right)^2 \qquad (6)$$

$$\phi = \frac{K + 2[B_0]}{2}$$

$$K = \frac{([B_0] + [x]_{eq.})^2}{[A_0'] - [x]_{eq.}}$$

$$[A_0'] = [A_0] - [x_{t=t_1}] \text{ and } [B_0] = [x_{t=t_1}].$$

The rate constant is influenced in a complex manner by initial concentration and temperature gradients, which effectively make $B_0$ and $C_0$ not zero at T = 25.004°. In principle, this error could be eliminated by use of equation 6. This was not attempted because of the uncertainty in the analytical results for chloride concentrations below $10^{-4}$ M and the variance in the equilibrium constant.

We now consider whether the solvolysis reaction is adequately represented by equation 1. Assuming no turbidity, we write the following mechanism:

$$\begin{aligned}
&ArCH_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH_2^+ + Cl^- && (7a)\\
&ArCH_2^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArCH_2OH + H^+ && (7b)\\
&ArCH_2^+ + HCOOH \xrightarrow{k_3} ArCH_2OOCH + H^+ && (7c)\\
&ArCH_2OH + HCOOH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} ArCH_2OOCH + H_2O && (7d)
\end{aligned} \qquad (7)$$

The equilibrium constant for the solvolysis reaction is given by:

$$K = K_{7a} \times K_{7b} = \frac{[ArCH_2OH][H^+][Cl^-]}{[ArCH_2Cl][H_2O]} \qquad (8)$$

Equation 8 is the same equilibrium equation as that obtained from equation 1, providing $[H^+]$ is constant. Clearly $[x]_{eq.}$ is really $[Cl^-]_{eq.}$, not $[HCl]_{eq.}$.

Let us examine the effect of formate on the equilibrium constant. The correct stoichiometry would then be

$$[\mathrm{ArCH_2OH}] + [\mathrm{ArCH_2OOCH}] = [\mathrm{Cl^-}] \qquad (9)$$

Assuming that at equilibrium $[\mathrm{Cl^-}] = [\mathrm{ArCH_2OH}]$, equation 9 suggests that the equilibrium constant would change with initial concentration of organic halide if esterification occurs. We write

$$K_{7d} = \frac{[\mathrm{ester}][\mathrm{H_2O}]}{[\mathrm{alcohol}]} \qquad (10)$$

Rearranging equation 10 in terms of [ester] and substituting in equation 9, we obtain

$$[\mathrm{ArCH_2OH}]_{eq.} = \frac{[\mathrm{Cl^-}]_{eq.}}{(1 + K_{7d}[\mathrm{H_2O}]^{-1})} \qquad (11)$$

Substituting equation 11 into equation 8 gives

$$K = \frac{[\mathrm{Cl^-}]^2_{eq.}}{[\mathrm{ArCH_2Cl}]_{eq.}([\mathrm{H_2O}] + K_{7d})} \qquad (12)$$

Making the reasonable assumption that $[\mathrm{H_2O}]$ is constant, equation 12 reveals that the formate ester has no effect on the calculated equilibrium constant at a given water concentration. However, as the water content of the solvent is changed, K should change unless $[\mathrm{H_2O}] \ll K_{7d}$ or $[\mathrm{H_2O}] \gg K_{7d}$.

Dewar and Sampson (42) found that for the more reactive compounds equilibrium appeared to be reached whether the alcohol and gaseous hydrogen chloride, or the arylmethyl chloride, was dissolved in formic acid. The equilibrium constant was approximately constant over a threefold variation in water content (0.38 M - 1.2 M). Therefore, they concluded that the reactions producing formate ester were relatively slow, or that the alcohol-formate equilibrium strongly favored the alcohol. The problem needs to be reinvestigated, since these authors reported their equilibrium constants accurate to ± 10%. For half of the compounds for which an equilibrium constant was reported, changing the water concentration from 1.2 $\underline{M}$ to 0.38 $\underline{M}$ increases the equilibrium constant in accord with equation 12. However, the change is in the opposite direction for the remaining compounds.

Neglecting equations 7c and 7d, we consider the differential rate law derived, assuming the solvolysis mechanism is described by equations 7a and 7b. We write

$$-\frac{d[ArCH_2Cl]}{dt} = k_1\,[ArCH_2Cl] - k_{-1}[ArCH_2^+][Cl^-] \qquad (13)$$

and

$$\frac{d[ArCH_2^+]}{dt} = k_1\,[ArCH_2Cl] - k_{-1}[ArCH_2^+][Cl^-] \qquad (14)$$
$$-k_2[ArCH_2^+][H_2O] + k_{-2}[ArCH_2OH][H^+]$$

Applying the steady state assumption, solving for $[ArCH_2^+]$, and substituting into equation 13, we obtain

$$\frac{-d[ArCH_2Cl]}{dt} = k_1[ArCH_2Cl] - k_{-1}[Cl^-]\left(\frac{k_1[ArCH_2Cl] + k_{-2}[ArCH_2OH][H^+]}{k_{-1}[Cl^-] + k_2[H_2O]}\right) \qquad (15)$$

Assuming that $k_{-2}\,[ArCH_2OH][H^+] > k_1[ArCH_2Cl]$ and $k_2[H_2O] > k_{-1}[Cl^-]$ and noting that $k_{-2}/k_2 = 1/K_{7b}$, $K_{7b} = K_{7a}/K$, and $K_{7a} = k_1/k_{-1}$ we obtain

$$\frac{-d[ArCH_2Cl]}{dt} = k_1[ArCH_2Cl] - \frac{k_1[ArCH_2OH][H^+][Cl^-]}{K[H_2O]}. \qquad (16)$$

Equation 16 is equivalent to equation 4 on the condition that both $[H^+]$ and $[H_2O]$ remain constant. Furthermore, equation 16 predicts that the rate of solvolysis should increase with increasing water content of the solvent. Such an increase was observed by Dewar and Sampson (42). The previous assumptions require that $k_{-1}$ be the rate determining step for the reverse reaction with equation 7b a pre-equilibrium step. It is easily shown, assuming equilibrium conditions, that the inverse assumption leads to a different rate law. The experimental results therefore support the validity of the present assumption. We can conclude on this basis that equation 1 is a valid representation of the solvolysis.

We now examine the rate expression including equation 7c. Applying the steady state approximation and the previous assumptions we obtain

$$\frac{-d[ArCH_2Cl]}{dt} = k_1\,[ArCH_2Cl] - \frac{k_1[ArCH_2OH][H^+][Cl^-]}{K([H_2O] + k_3'/k_2)} \qquad (17)$$

where $k_3' = k_3\,[HCOOH]$.

Equation 17 shows that the rate of solvolysis is actually affected by the rate of esterification. Since $k_3'$ will remain essentially constant over various water concentrations, its neglect will introduce a constant error in the rate constant ($k_1$). It is also apparent that unless the equilibrium between formate ester and alcohol strongly favors the alcohol, or that $k_3' << k_2$, an error is introduced due to erroneously assumed stoichiometry. Equation 9 reveals that even if a finite equilibrium is immediately established, an error is introduced, the magnitude of which, however, decreases as the solvolysis proceeds. Since it is reasonable to expect esterification to occur (equation 7d), the rate constant obtained will differ from the rate constant for solvolysis based on equation 1, and equation 7d should introduce some deviation in k within a run.

We now consider the influence of turbidity on the equilibrium constant, percentage reaction, and rate constant. From limited results of studies of the insoluble products formed in the solvolysis of α-naphthylcarbinyl chloride, the following equations are postulated.

$$ArCH_2^+ + ArCH_2OOCH \xrightarrow{k_{18}} \underline{ArCH_2ArCH_2OOCH} \qquad (18)$$

$$\begin{aligned} ArCH_2^+ + ArCH_2OH &\xrightarrow{k_{19}} ArCH_2ArCH_2OH + HCOOH \\ &\xrightarrow{k'_{19}} \underline{ArCH_2ArCH_2OOCH} \end{aligned} \qquad (19)$$

$$ArCH_2^+ + ArCH_2Cl \xrightarrow{k_{20}} \underline{ArCH_2ArCH_2Cl} \qquad (20)$$

Dewar and Sampson, using initial arylcarbinyl chloride concentrations below 4 x $10^{-3}$ $\underline{M}$, observed no turbidity for 15 to 20 half-lives. They concluded that solvolysis could be studied without interference from this source. The effect of equations 18, 19, and 20 is not obvious. Let us re-examine $d[ArCH_2^+]/dt$, including equations 18 through 20.

$$\begin{aligned} \frac{d[ArCH_2^+]}{dt} &= k_1[ArCH_2Cl] - [ArCH_2^+]\,(k_{-1}[Cl^-] - k_2[H_2O] - k_3) + \\ &k_{-2}[ArCH_2OH][H^+] - [ArCH_2^+] \sum_i k_i([ArCH_2OOCH] + [ArCH_2OH] + [ArCH_2Cl]) \end{aligned} \qquad (21)$$

In deriving equation 21 the following assumptions were made: (1) The solubility of the monomeric formate has not been exceeded. (2) It is entirely reasonable to expect the carbonium ion to attack the alcohol. Since the product studies indicated the absence of multi-substituted alcohols in the precipitate, these must have remained in solution until they were esterified. This is reasonable in view of the high solubility of α-naphthylcarbinol. (3) The ionization of any substituted α-naphthylcarbinyl chlorides remaining in solution has been neglected. (4) The rate constants $k_{18}$, $k_{19}$, and $k_{20}$ are to a first approximation equal. (5) Equations 18, 19, and 20 are actually a composite of reactions leading to different positional isomers and thus are better represented by summations.

Clearly, if all $k_i$'s are small, equation 21 requires that the appearance of turbidity should be sensitive to the initial concentration of α-naphthylcarbinyl chloride. The results of Table XXIV confirm this hypothesis. The data show an extremely strong dependence between the time for appearance of turbidity and initial concentration. At low concentrations of α-naphthylcarbinyl chloride and early in the solvolysis equation 17 should be obeyed, the effect of equations 18 through 20 becoming significant only with additional time. As the initial concentration of α-naphthylcarbinyl chloride increases, the effect of these reactions should appear earlier. This observation was qualitatively confirmed since the amount of turbidity present when infinity titres were taken appeared to increase with increasing concentration of the halide. In the present studies, percentage reaction was defined as

$$\%\ \text{Rx.} = \frac{[\text{Cl}^-]_{\text{eq.}}}{[\text{ArCH}_2\text{Cl}]_{\text{initial}}} \tag{22}$$

and the equilibrium constant as

$$K' = K([H_2O] + K_{7d}) = \frac{[x]_{\text{eq.}}^2}{[A_0]-[x]_{\text{eq.}}} \tag{23}$$

The observed trend in these terms is now obvious. At "equilibrium" equations 18 and 19 have the effect of producing more ionization.

However, equation 20 both reduces the concentration of solvolyzable chloride in solution and the [Cl$^-$]. Therefore, the amount of unsolvolyzed halide is less than the stoichiometric value based on equation 7. From a statistical viewpoint the effect of equation 20 increases with increasing concentration of the organic halide. Thus the percentage reaction and the equilibrium constant should decrease with increasing initial concentration of organic halide.

Table XXIV. Study of time for appearance of turbidity as a function of initial concentration of α-naphthylcarbinyl chloride.

| Concentration (moles/l.) | Solvent[a] | Time (hours) |
|---|---|---|
| 0.12 | 0.25 <u>m</u> | 1 |
| 0.095 | 0.4 <u>M</u> | 1.2 |
| 0.054 | 0.28 <u>M</u> | 0 - 13.5 |
| 0.031 | 0.43 <u>M</u> | 19 |
| 0.016 | 0.43 <u>M</u> | 20 |
| 0.012 | 0.32 <u>m</u> | 22 - 28 |
| $9.5 \times 10^{-3}$ | 0.43 <u>M</u> | 34 - 44 |
| $9.8 \times 10^{-3}$ | 0.28 <u>M</u> | 27 - 30 |
| $5.3 \times 10^{-3}$ | 0.43 <u>M</u> | 72 |
| $4.8 \times 10^{-3}$ | 0.28 <u>M</u> | 72 |
| $4.981 \times 10^{-3}$ | 0.32 <u>m</u> | 51 |

[a] Estimated to be minimum water content.

It is easily shown that equations 18 through 20 affect the rate constant. The rate of reaction, neglecting the backward reaction, is given by

$$\frac{\Delta[\mathrm{Cl}^-]}{\Delta t} = k_1\ [\mathrm{ArCH_2Cl}] \tag{24}$$

The left side of equation 24 is experimentally determined. The concentration of arylmethyl chloride at time t is calculated from the relation

$$[ArCH_2Cl]_{t=t} = [ArCH_2Cl]_{initial} - [Cl^-]_{t=t} \qquad (25)$$

However, the stoichiometry is no longer correct because of equation 20. The correct relation is

$$[ArCH_2Cl]_{t=t} = [ArCH_2Cl]_{initial} - [ArCH_2ArCH_2Cl]_{t=t} - [Cl^-]_{t=t} \quad (26)$$

Equation 26 shows that k must change to compensate for the effect of neglecting equation 20.

Equation 21 reveals that equations 18 through 20 would affect the bimolecular ($k_{-2}$) term, by reducing its contribution to the rate of solvolysis.

Before visible turbidity develops, equations such as 18, 19, and 20 may occur. This would also introduce errors in the rate constant.

Table XXV lists the calculated values of $k_H/k_D$. Since the difference in rate constants between α-naphthylcarbinyl chloride and α-naphthylcarbinyl chloride-8-d is less than either the maximum or average deviation of the former, the isotope effect is insignificant. Considering the uncertainty in the rate constants, the α-deuterium isotope effect must be considered as normal.

Dewar and Sampson (42) observed that the solvolysis rate of α-naphthylcarbinyl chloride was 17 times greater than that of the β-isomer. From correlation of rate with delocalization energy, they concluded that the rate of the α-isomer was actually retarded. They argue that maximum resonance stabilization of the incipient carbonium ion in the transition state requires the hydrogens of the exocyclic $-CH_2^+$ group to be approximately co-planar with the ring, as shown in Figure 3.

Such an effect would require an abnormally close approach between one of the methylene hydrogens and the peri hydrogen, resulting in an increase in $\sigma$ bond energy in the transition state. The resulting strain energy was estimated to be 2.5 kcal.

Table XXV. Relative rate ratios of deuterated and substituted α-naphthylcarbinyl chlorides.

| Compound | $k_H/k_D$ | $k_8/k_H$ |
|---|---|---|
| 8-d | 0.996 ± 0.05 | |
| α,α-$d_2$ | 1.35 | |
| 8-bromo | | 1.37 |
| 8-methyl | | 85 |

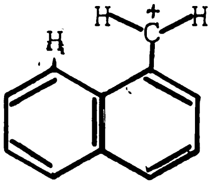


Figure 3. Carbonium ion representing the transition state for the solvolysis of α-naphthyl carbinyl chloride.

From Dreiding models the H··H non-bonded distance is estimated to be 1.9 Å., which is well within the sum of the van der Waals' radii for two hydrogen atoms, 2.4 Å. It appears reasonable to suggest that such a compression would effectively decrease the out-of-plane bending vibration of at least one of the α-hydrogens in the trigonal transition state. Such a reduction should decrease the magnitude of the α-deuterium isotope effect (13). Furthermore, substitution of deuterium in the 8 position might be expected to result in an inverse isotope effect. On this basis, and in view of the isotope effects reported by Melander (15) and Mislow (16) in related systems, an inverse isotope effect and a low α-deuterium isotope effect would have been expected.

An important consideration, neglected by Dewar in this particular paper, is that overlap is a cosine function (46). Rotating the exocyclic $-CH_2^+$ group out of the naphthalene plane by 60° reduces the overlap only 50%. Thus the increase in steric compression in the transition state can be partly compensated by rotation of the methylene group, with a small loss in resonance energy. Therefore any rate retardation might reasonably be expected to be small. On this basis, it appears reasonable to conclude that resonance stabilization of the transition state should be slightly increased for either of the deuterium analogs. Consequently, the magnitude of the isotopic rate ratios, $k_H/k_D$, should decrease.

Steric strain may exist in the ground state of α-naphthylcarbinyl chloride. Figure 4 shows the preferred molecular conformation of α-naphthylcarbinyl chloride, based on examination of Dreiding models.

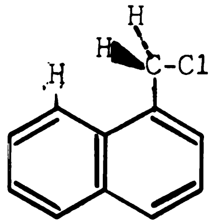


Figure 4. Preferred molecular conformation of α-naphthylcarbinyl chloride.

Free rotation of the chloromethylene group is impossible. Since the maximum H··H non-bonded distance is estimated to be 2.4 Å., which is just equal to the sum of the van der Waals' radii for hydrogen, oscillation of the chloromethylene group must result in an energy increase. Such increase may be partly compensated by an opening of the $C_9$-$C_1$-$C_\alpha$ angle. Deuterium substitutions in either the α-position or the 8-position should decrease this energy. Therefore a normal isotope effect would be predicted. Fortuitously, the ground state and transition state effects might cancel.

The results of X-ray, chemical, and micro-wave studies support the existence of steric interaction between alpha substituents and the peri hydrogen. 1,5-Dinitronaphthalene is planar, but this is accomplished only by bending the nitro groups away from the peri hydrogen; the $C_9C_1N$ and $C_{10}C_5N$ angles are opened to 125° (47). 1,4-Dibromo- and 1,3-dichloronaphthalene have been studied by Trotter (48). The data indicate, but by no means prove, that the alpha halogen atoms deviate by about 0.4 Å. and 0.28 Å., respectively, from the naphthalene planes. X-ray analysis of 1-naphthoic acid (49) reveals that the carboxyl group is rotated about 11° out of the plane. In addition, there is a significant in-plane displacement of the C (aromatic) - C (carboxyl) bond away from the peri position, and the $C_9C_1C_\alpha$ angle is 128°.

Hall and co-workers (50) were able to isolate an optically active form of 1-(2-carboxyphenyl) naphthalene.

Grubb and Smyth (51) attribute the restriction of internal rotation of α-methoxy- and α-ethoxynaphthalene over the corresponding β-isomers, observed in micro-wave studies, to steric hindrance by the peri hydrogen. If such steric strain exists in the ground state, then the rate of solvolysis of α-naphthylcarbinyl chloride might actually be accelerated.

In their treatment, Dewar and Sampson have neglected solvation effects. Harrison, Kebarle, and Lossing (52) observed that the effect of substituents upon the stability of the benzyl cation in the gas phase was greater than the substituent effect observed for the $S_N1$ solvolysis of t-cumyl chlorides studies by Brown (53). Rho in the gas phase was approximately -20, compared to -4.54 in solution. These authors concluded that the large difference was due not only to incomplete charge formation in the transition state but also to solvation effects. Within experimental error, an excellent linear correlation was observed between the energies of ion-pair formation in the gas phase and $\sum_r q_r^2$, where $q_r$ is the fraction of positive charge at atom r. The fact that the α-naphthylcarbinyl cation did not deviate significantly indicates that the loss in resonance stabilization of the ion by steric interaction with the peri hydrogen must be small.

Mason (54) has shown that serious error can result by correlating rates of solvolysis with only delocalization energies. Accounting for solvation effects, he was able to obtain good linear correlation for solvolysis of arylmethyl compounds in a number of solvents. An interesting theoretical conclusion is that the free energy of solvation should decrease with increasing charge dispersal. This would tend to increase the solvolysis rate of β-naphthylcarbinyl chloride, as compared to that of the α-isomer. Also, the $S_N2$ reaction with potassium iodide in acetone showed no evidence for steric retardation in the "peri" compounds.

Dewar and Sampson (55) studied the rates of ethanolysis of α- and β-naphthyldimethylcarbinyl chlorides. The relative rate factor was 0.6. They concluded that this rate inversion was due to increased steric inhibition of resonance, and the α-isomer suffers a 17/0.6 or an additional 27 fold rate retardation. It is well known that comparison of solvolysis rates obtained in different solvents can be misleading. For example, Okamoto and Brown (56) studied the rates of solvolysis of α- and β-naphthyldimethylcarbinyl chlorides in 90% aqueous acetone. The α-isomer was 1.02 times as reactive as the β-isomer. The relative rate for the corresponding monomethyl compounds in 80% aqueous acetone was 2.56. These results suggest that both steric inhibition of resonance and solvent effects are important. However, steric effects are characterized by a rapid increase in magnitude with increasing bulk (20a). For the previous compounds, steric effects should increase in the order no methyl < monomethyl << dimethyl. The loss of resonance energy should increase in the same order, but its effect should be decreased by the increasing intrinsic stability of the transition state. From studies of the rates of solvolysis of o-, m-, and p-substituted t-cumyl chlorides and related compounds, Brown and co-workers (57) concluded that steric inhibition of resonance in the transition state could not be neglected, but that inductive and solvation effects were important. The relative rate decrease, $k_o/k_p$, in the series methyl, ethyl, and isopropyl t-cumyl chloride was 0.14, 0.094, and 0.045, respectively. These were ascribed to increasing steric inhibition of resonance (57a). Later, Brown and Inukai (57e) concluded that the difference in the relative rate acceleration factor of 26 for p-methyl t-cumyl chloride, as compared to only 3.63 for the o-methyl compound, could not be solely due to steric inhibition of resonance. They concluded that the influence of the o-alkyl substituents in hindering solvation of the incipient carbonium ion was also important.

Baddeley and co-workers (58) have studied the solvolysis rates of monoalkylphenylcarbinyl chlorides and the basicities of the corresponding amines. The order of reactivity decreased along the series: R = Me, Et, i-Pr, t-Bu, corresponding to the order of increasing basicity. The authors concluded that the results are in accord with increasing steric interaction of the side chain with the ring.

The complexity of steric inhibition of solvation is evident from the results of Chapman and co-workers (59), obtained from studies of the basic hydrolysis of o-substituted methyl benzoates. The entropy of activation is influenced by two effects, the "bulk effect" and steric inhibition of solvation. In the series Me, Et, Pr, and t-Bu steric inhibition of solvation increases, tending to make $\Delta S^{\neq}$ more positive. The "bulk effect", which increases in the same order, has the opposite effect on $\Delta S^{\neq}$. The two effects are clearly discernible but the relative dominance of either is solvent dependent.

From this discussion, the conclusions reached by Dewar and Sampson concerning a rate retardation due to large strain energy in the transition state in the solvolysis of α-naphthylcarbinyl chloride are probably oversimplifications. Thus if the rate is actually retarded, part of the effect may well be due to steric hindrance to solvation (54,60). Also, steric strain in the ground state may compensate transition state effects. Furthermore, as the solvolysis reaction assumed more $S_N2$ character the strain energy steadily decreased and finally disappeared in the $S_N2$ displacement by iodide ion in acetone (42). Thus the previous conclusions concerning the compensatory effects of isotopic substitutions are not necessarily negated. Alternately, the substitution of deuterium for hydrogen may not produce an observable steric isotope effect in the compounds so far studied. The results of precise conductometric rate measurements must be obtained before any definite conclusions can be drawn.

Table XXV reveals that substitution of a methyl group in the 8 position of α-naphthylcarbinyl chloride increases the rate of solvolysis by a factor of approximately 85, whereas the rate increase for bromine substitution is only 1.37. The large rate increase for 8-methyl-α-naphthylcarbinyl chloride is attributed to steric strain in the ground state. The severe strain is probably compensated by bending the groups out of the naphthalene plane and away from each other. Figure 5 reveals that a considerable part, but not all, of this strain can be eliminated in the transition state. The H··H non-bonded distance is estimated from Dreiding models to be 2 Å. Thus complete relief of strain has probably not been achieved, and the observed rate increase is less than expected for complete relief of non-bonded interactions. Furthermore, it is not unreasonable to assume complete steric inhibition of resonance in the transition state. This would increase the energy of the transition state relative to that of α-naphthylcarbinyl chloride and thus mask the rate acceleration due to relief of ground state steric strain.

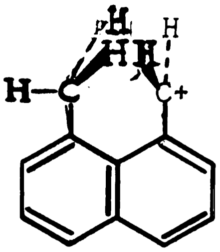


Figure 5. Carbonium ion representing the transition state for the solvolysis of 8-methyl-α-naphthylcarbinyl chloride.

The relatively small rate enhancement noted for 8-bromo-α-naphthylcarbinyl chloride can be ascribed to several factors. First, Dreiding models indicate, because of the increased C-Br bond length, that the non-bonded repulsions should be slightly less than that of the 8-methyl isomer. Second, the bromine atom, being more polarizable, may be "elongated" and "whittled down" on the side facing the chloromethylene group, thus reducing steric strain. Third, the ground state of the bromo isomer may be considerably better solvated. Fourth, the close proximity of the bromine atom to the chloromethylene group may result in a strong inductive stabilization of the ground state. Brown and co-workers (57b) concluded from their studies of the rates of solvolysis of the *o*-, *m*-, and *p*- halogen *t*-cumyl chlorides that the increased rate reduction observed for the *o*-halogens was not only due to steric inhibition of resonance, but also to an enhanced inductive effect.

For the previously discussed reasons, comparison of the 8-bromo isomer with α-naphthylcarbinyl chloride does not yield in a true measure the rate enhancement due to relief of steric strain in the ground state.

An alternate explanation, based upon non-classical structures, can be visualized (Figure 6.). These are considered unlikely; if methyl participation were important, the product might contain large amounts of acenaphthene. Also, participation by the bromine would be expected to be larger than that by the methyl group.

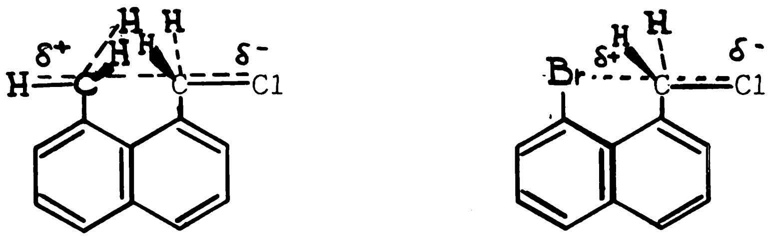


Figure 6. Transition states for solvolysis of 8-methyl-α-naphthylcarbinyl chloride and 8-bromo-α-naphthylcarbinyl chloride showing participation by the methyl group and the bromine atom.

# EXPERIMENTAL

## I. Synthesis

A. Preparation of α-Naphthylcarbinol. To a 2 l., three-necked, round bottom flask fitted with a Tru-bore stirrer, dropping funnel, and a reflux condenser was added 1 l. of anhydrous ether and 12 g. (0.317 moles) of lithium aluminum hydride. A solution of 30 g. (0.174 moles) of 1-naphthoic acid in 650 ml. of anhydrous ether was added to the stirred suspension over a period of two hours. After addition was complete, the mixture was refluxed for six hours. The reaction mixture was then cooled in an ice bath, hydrolyzed with water (2 ml./g. of hydride), and the precipitated alkoxides dissolved by adding 5% sulfuric acid. The aqueous layer was separated and extracted with several portions of ether. The ether extracts were combined, washed with 10% sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and the ether was evaporated. Recrystallization of the crude alcohol three times from a mixture of benzene and cyclohexane gave 23 g. (88%) of α-naphthylcarbinol, m.p. 60.5-61.5° (lit. 59.5-61°).

B. Preparation of α-Naphthylcarbinol-α,α-$d_2$. 1-Naphthoic acid was reduced by the previous procedure with lithium aluminum deuteride.

C. Preparation of α-Naphthylcarbinol-8-d. 1-Naphthoic acid-8-d was reduced by the previous procedure with lithium aluminum hydride.

D. Preparation of α-Naphthylcarbinyl p-Toluenesulfonate. This compound was prepared by the method of Kochi and Hammond (61).

To a 200 ml., three-necked, round bottom flask equipped with a Tru-bore stirrer, reflux condenser, and a dropping funnel was added 35 ml. of anhydrous ether, 2 g. (0.013 moles) of α-naphthylcarbinol, and 0.31 g. (0.013 moles) of sodium hydride. After the mixture had been stirred and refluxed for twelve hours, it was cooled with a dry ice-acetone bath to -20° and a solution of 2.41 g. (0.013 moles) of purified p-toluenesulfonyl chloride dissolved in 35 to 40 ml. of anhydrous ether was added dropwise to the suspension. After addition was complete, the reaction mixture was stirred for two hours at -10° and then at room temperature for an additional hour. In all operations care was taken to exclude moist air from the system. The reaction mixture was then filtered repeatedly with a minimum exposure to the air, using a medium grade sintered glass funnel until a clear suspension was obtained. The clear solution was then cooled in a dry ice-acetone bath until a copious precipitate of fine white needles was obtained. These crystals were collected on a Büchner funnel and stored in a stoppered Erlenmeyer flask. Attempted recrystallization from 2,4-dimethylpentane (b.p. 79.8°) resulted in decomposition. Recrystallization from pentane produced a white crystalline compound decomposing at 55-56°. Due to the compound's insolubility some decomposition occurred during recrystallization. Therefore, the material was recrystallized by adding it to 300 ml. of boiling pentane and adding anhydrous ether until solution was complete. The recovered material decomposed at 55.5°.

E. Preparation of α-Naphthylcarbinyl p-Nitrobenzoate. Five grams (0.032 moles) of α-naphthylcarbinol, 5.9 g. (0.032 moles) of p-nitrobenzoyl chloride, 3.0 g. (0.038 moles) of pyridine, and 400 ml. of anhydrous ether were added to a 2 l., single-necked, round bottom flask fitted with a reflux condenser. The reaction mixture was refluxed for twenty-four hours, 600-800 ml. of ether was then added, and the mixture was poured into a beaker containing 5% hydrochloric acid and ice. The aqueous and ether layers were separated and the ether layer washed with 10% soidum bicarbonate, distilled water, dried over anhydrous magnesium sulfate, filtered and the ether was evaporated. Recrystallization of the crude product three times from a 4:1 cyclohexane-benzene mixture gave 5 g. (53%) of α-naphthylcarbinyl p-nitrobenzoate, m.p. 126-127°.

F. Preparation of α-Naphthylcarbinyl 3,5-Dinitrobenzoate. Five grams (0.032 moles) of α-naphthylcarbinol, 7.3 g. (0.032 moles) of freshly prepared 3,5-dinitrobenzoyl chloride, and 2.5 g. (0.032 moles) of pyridine were added to a 2 l., single-necked, round bottom flask containing 900 ml. of anhydrous ether and fitted with a reflux condenser. The reaction mixture was allowed to stand at room temperature for twenty-four hours. The precipitate was collected on a Büchner funnel and repeatedly extracted with a boiling 4:1 mixture of cyclohexane-benzene until no further precipitate dissolved. The boiling extracts were filtered, cooled, and the crude product collected on a Büchner funnel. n-Heptane was added to the original ether solution which was then cooled in a dry ice-acetone bath, and the precipitate was collected. Recrystallization of the combined products three times from a 4:1 cyclohexane-benzene mixture gave 6.5 g. (58%) of α-naphthylcarbinyl 3,5-dinitrobenzoate, m.p. 162.5-163.5°

G. Preparation of 1-Bromonaphthalene-8-d. Previous to use all glassware was thoroughly cleaned in sulfuric acid, liberally rinsed with distilled water, and oven-dried.

A 500 ml., three-necked, round bottom flask was fitted with a Tru-bore stirrer, a pressure equilibrated dropping funnel containing an outlet tube, and a reflux condenser. A second 500 ml., three-necked, round bottom flask containing a ground glass stopper and an inlet tube was joined to the first flask by a u-tube fitted to the top of its reflux condenser. With dry argon passing, the entire system was flamed out. In all subsequent operations dry argon was passed through the system. After cooling, ether and lithium aluminum hydride were added to the second flask and approximately 200 ml. of dry ether was distilled over into the reaction vessel. With the argon flow increased, 1.82 g. (0.075 moles) of high purity magnesium which had been oven-dried and cooled in a desiccator, 25 g. (0.076 moles) of 8-iodo-1-bromonaphthalene, and several drops of ethylene dibromide were added to the reaction vessel. The flow of argon was reduced and reversed, and the ether suspension warmed to initiate the reaction. A gentle rate of reaction was maintained for two hours, after which time the mixture was refluxed for an additional two hours. The reaction mixture was then cooled in an ice bath and 10 ml. of deuterium oxide was added dropwise from the dropping funnel. After addition was complete, the mixture was stirred for an additional thirty minutes. The ice bath was then removed and stirring was continued for eight hours at room temperature. With the argon flow discontinued and a calcium chloride drying tube inserted into the top of the condenser, the reaction mixture was stirred overnight.

The ether layer was then separated and the aqueous phase was extracted with two 100 ml. portions of ether. The combined ether portions were washed, dried over anhydrous magnesium sulfate, filtered, and the ether was evaporated. Two successive preparations were combined and vacuum distilled; b.p. 82-84° at 0.5 mm. and 110-112° at 1 to 2 mm. Percentage yields varied from 70 to 83%.

H. Preparation of 1-Naphthoic Acid-8-d. The basic procedure used was that of Gilman and co-workers (62).

The same type of apparatus as described in the preparation of 1-bromonaphthalene-8-d was used. The following describes the steps involved in a typical preparation. Approximately 250 ml. of dry ether was distilled into the reaction vessel containing 2.95 g. (0.121 moles) of dry purified magnesium. Using a pipet 50 ml. of the ether was quickly withdrawn and added to 24.65 g. (0.118 moles) of 1-bromonaphthalene-8-d. The resulting solution was added to the dropping funnel. Several drops of ethylene dibromide and a small aliquot of the 1-bromonaphthalene-8-d solution was added to the reaction vessel which was then placed in a warm water bath to initiate the reaction. Stirring was then commenced and the remaining 1-bromonaphthalene-8-d solution was added at such a rate as to maintain a vigorous but not violent reaction. After addition of the 1-bromonaphthalene-8-d solution was complete, the reaction mixture was refluxed for one hour. Dry benzene, 50 ml., was added to dissolve the Grignard reagent and the reaction vessel was immersed in a dry ice-acetone bath. The temperature was adjusted to -7 to -10°, argon-flow was discontinued, and the dropping funnel was replaced by an entry tube, 10 mm. in diameter, which was adjusted so that its end was about 50 mm. above the surface of the reaction mixture. The temperature was measured by suspending a thermometer through the condenser which was fitted with a calcium chloride drying tube. The reaction mixture was stirred and dry carbon dioxide was admitted through the entry tube. The rate of carbon dioxide flow was controlled so that the temperature did not rise above -2°. When the reaction temperature started to fall the flow of carbon dioxide was increased and maintained for about thirty minutes. The reaction flask was then placed in an ice bath and 25% sulfuric acid was slowly added with stirring until reaction had ceased and all excess magnesium had dissolved. The oily layer was separated and the aqueous layer was extracted with two 50 ml. portions of ether. These were combined with the original ether-benzene fraction, and the resulting solution was filtered if it was not clear. The combined ether-benzene fractions were then extracted with three 35 ml. portions of 25% sodium hydroxide. Each alkaline layer was successively extracted with a 25 ml. portion of ether and the combined alkaline extracts were heated to 90° to drive off the volatile components. The solution was then cooled and strongly acidified with 50% sulfuric acid. The crude 1-naphthoic acid-8-d was collected on a Büchner funnel, washed free of sulfate, and dried. Recrystallization from 3:1 heptane-toluene yielded 14 g. (81%) of 1-naphthoic acid-8-d, m.p. 163-163.5°. (Lit. 160°)

I. Preparation of α-Naphthylcarbinyl Chloride. Five grams (0.032 moles) of α-naphthylcarbinol was added to a 50 ml., round bottom flask fitted with a reflux condenser. Six grams (0.050 moles) of thionyl chloride was slowly added from the top of the condenser and the mixture was refluxed for approximately one hour. The reaction mixture was then transferred to a 10 ml. flask, the excess thionyl chloride stripped off, and the crude α-naphthylcarbinyl chloride vacuum distilled. The distilled chloride was then recrystallized from purified petroleum ether (b.p. 40-60°) and stored under dry petroleum ether (m.p. 31-31.5°).

J. Preparation of α-Naphthylcarbinyl Chloride-8-d. α-Naphthylcarbinyl chloride-8-d was prepared by the procedure described for α-naphthylcarbinyl chloride.

K. Preparation of α-Naphthylcarbinyl Chloride $\alpha,\alpha$-$d_2$. α-Naphthylcarbinyl chloride-$\alpha,\alpha$-$d_2$ was prepared by the procedure described for α-naphthylcarbinyl chloride.

L. Preparation of 8-Bromo-α-Naphthylcarbinyl Chloride. 8-Bromo-α-naphthylcarbinyl chloride was prepared by the procedure described for α-naphthylcarbinyl chloride.

M. Preparation of 8-Methyl-α-Naphthylcarbinyl Chloride. 8-Methyl-α-naphthylcarbinyl chloride was prepared by the procedure described for α-naphthylcarbinyl chloride except that several drops of pyridine were added to the reaction mixture after refluxing for forty-five minutes.

## II. Product Studies

A. Methanolysis of α-Naphthylcarbinyl *p*-Nitrobenzoate. To a 100 ml., single necked, round bottom flask fitted with a reflux condenser and a calcium chloride drying tube was added 1 g. ($3.25 \times 10^{-3}$ moles) of α-naphthylcarbinyl *p*-nitrobenzoate and 75 ml. of purified anhydrous methanol. After refluxing for one week the methanol was removed by a Rinco rotary evaporator and the precipitate placed under vacuum for one hour to remove any traces of methanol. The crude material was dissolved in 6 ml. of carbon tetrachloride and 3 ml. was chromatographed on 25 g. of alumina using carbon tetrachloride, benzene, and ether as eluting solvents. The carbon tetrachloride elutable material yielded methyl p-nitrobenzoate, identified by its infrared spectrum and m.p. The benzene fraction yielded essentially no material. The ether elutable material yielded α-naphthylcarbinol, identified by its infrared spectrum and m.p. No α-naphthylcarbinyl methyl ether was recovered. The yield of α-naphthylcarbinol was over 100% based on one-half of the solvolysis mixture.

B. Methanolysis of α-Naphthylcarbinyl 3,5-Dinitrobenzoate. To a 100 ml., single necked, round bottom flask fitted with a reflux condenser and a calcium chloride drying tube was added 1 g. ($2.83 \times 10^{-3}$ moles) of α-naphthylcarbinyl 3,5-dinitrobenzoate and 75 ml. of purified anhydrous methanol. After refluxing the reaction mixture for one week, the ester had not completely dissolved. Therefore, an additional 25 ml. of methanol was added and the mixture was refluxed for an additional five days. After cooling the reaction mixture was filtered to remove the small amount of precipitate, presumably unsolvolyzed ester, and the methanol was removed using a Rinco rotary evaporator. The crude product was placed under vacuum for one hour to remove any traces of methanol. The crude product was dissolved in 6 ml. of carbon tetrachloride and 3 ml. was chromatographed on 25 g. of alumina using petroleum ether (b.p. 40-60°), carbon tetrachloride, cyclohexane, benzene, ether, and ethylene dichloride as eluting solvents. The petroleum ether, carbon tetrachloride, and cyclohexane fractions yielded no material. The benzene fraction contained a trace of material tentatively identified as α-naphthylcarbinol by its infrared spectrum. The ether elutable material was shown to be α-naphthylcarbinol by infrared spectra and m.p. No α-naphthylcarbinyl methyl ether, 3,5-dinitrobenzoic acid or methyl 3,5-dinitrobenzoate was recovered from the column. Within experimental error the yield of recovered alcohol was quantitative.

C. Insoluble Products Formed During Solvolysis of α-Naphthylcarbinyl Chloride in Aqueous Formic Acid. α-Naphthylcarbinyl chloride (4.926 g., 0.0279 moles) was dissolved in 2 l. of 97-100% formic acid. After standing for eighty-four hours at room temperature, the solution was filtered and the precipitate collected on a Büchner funnel. The precipitate was dissolved in boiling ether, filtered, and repeatedly washed with saturated sodium bicarbonate. The aqueous washings were re-extracted with ether and the combined ether fractions were washed with a small portion of saturated sodium bicarbonate, water, dried over anhydrous magnesium sulfate, and filtered. The aqueous fraction, after acidification with nitric acid, gave a negative chloride test with silver nitrate.

A small portion of the ether solution was evaporated to dryness. The nuclear magnetic resonance spectrum ($CCl_4$) shows absorption peaks at $\tau$ = 5.2, 4.4, and 3.3 to 1.8 with relative areas roughly 1:6:28. The infrared spectrum ($CS_2$) shows bands at 3050-3100 cm.$^{-1}$, 2950 cm.$^{-1}$, 1720 cm.$^{-1}$, 1600 cm.$^{-1}$, 1400 cm.$^{-1}$, and 1160 cm.$^{-1}$.

A small portion of the ether solution was evaporated to dryness and dissolved in acetone. Addition of aqueous silver nitrate produced a white precipitate indicating formation of silver chloride. The resulting suspension was repeatedly filtered until a clear solution was obtained. Water was then added and the resulting suspension extracted with several portions of ether. The ether fractions were combined, washed, and dried over anhydrous magnesium sulfate. The nuclear magnetic resonance spectrum ($CCl_4$) shows absorption peaks at $\tau$ = 5.2, 4.4, and 3.3 to 1.7. The infrared spectrum ($CS_2$) shows bands at 3500 cm.$^{-1}$ (weak), 3000 cm.$^{-1}$, 1720 cm.$^{-1}$, 1100 cm.$^{-1}$, 1020 cm $^{-1}$.

It had been previously shown that under the same conditions α-naphthylcarbinyl chloride is converted to α-naphthylcarbinol.

The remaining ether solution was evaporated to dryness and the crude mixture chromatographed on silica gel. Carbon tetrachloride ; 5:1, 1:1 and 1:3 mixtures of carbon tetrachloride-benzene, benzene, 1:1 mixture of benzene-ether, ether, and methanol were used as eluting solvents. Thin layer chromatography, using a 1:1 mixture of carbon tetrachloride and benzene as the eluting solvent, was utilized to determine the extent of separation and the number of products. The appropriate fractions were then combined for infrared and nuclear magnetic resonance spectra. The principal absorptions of the various fractions are given in Table XXVI. Only a trace material was obtained in the methanol fraction.

D. Insoluble Products Formed During Solvolysis of 8-Methyl-α-Naphthylcarbinyl Chloride in Aqueous Formic Acid. The precipitate formed during solubility studies of 8-methyl-α-naphthylcarbinyl chloride was collected on a Büchner funnel, dissolved in ether, washed repeatedly with saturated sodium bicarbonate, water, dried over anhydrous magnesium sulfate, and filtered. After evaporation of the ether, nuclear magnetic resonance and infrared spectra were obtained.

Table XXVI. Infrared and nuclear magnetic resonance spectral data of fractions from chromatographic studies of the insoluble products from the solvolysis of α-naphthylcarbinyl chloride.

| Fraction | I.R.(cm.$^{-1}$) | N.M.R. ($\tau$) |
|---|---|---|
| 1- 9 | 3050, 2950, 1700-1950, 1600, 1520, 1450, 1430, 1400, 1280, 1245, 1100, 1030 | 5.2, 5.1, 3.17-1.7 |
| 10-11 | 3100, 2950, 1720, 1600, 1520, 1470, 1450, 1430, 1400, 1160 | 5.3, 4.5, 3.3-1.7 |
| 12 | ---- | 5.3, 4.5, 3.3-1.7 |
| 13-18 | 3100, 2950, 2850, 1720 1690, 1600, 1520, 1470, 1400, 1260, 1160 | 5.3, 5.1, 3.3-1.7 |
| 19 | ---- | 5.1, 3.3-1.7 |
| 20-21 | 3000, 1720, 1690, 1600, 1520, 1470, 1400, 1170 | 5.2, 3.3-1.7 |

## III. Analytic Procedures

### A. Preparation of Reagents and Standard Solutions

Purification of Carbon Tetrachloride. Carbon tetrachloride was purified by the method given by Vogel (63). It was distilled from phosphorus pentoxide.

Purification of Petroleum Ether. Petroleum ether was purified by the method given by Vogel (63) except that it was dried over magnesium sulfate and distilled from calcium hydride. The fraction boiling in the range 37-57$^{0}$ at atmospheric pressure was collected.

Preparation of 1 M Potassium Chloride. Oven-dried "Baker Analyzed" reagent grade potassium chloride, 18.6390 g., was quantitatively transferred to a 250 ml. volumetric flask and diluted to the mark with distilled water.

Preparation of Potassium Thiocyanate. Solutions were prepared by taking the approximate quantity of potassium thiocyanate and diluting in a given volumetric flask. These solutions were stored in brown stoppered bottles.

Preparation of Silver Nitrate Solutions. Silver nitrate solutions of approximate molarities were prepared by adding the approximate quantity of silver nitrate to a volumetric flask. After diluting, these solutions were stored in brown bottles.

Preparation of Indicator Solutions. Ferric nitrate indicator solutions, 0.33 M and 2 M, were prepared from Baker and Adamson reagent grade ferric nitrate by adding the approximate amount of reagent to the approximate volume of water.

Preparation of Primary Standard Sodium Chloride Solutions. Primary standard sodium chloride solutions were prepared from "Baker Analyzed" reagent grade sodium chloride by the usual procedures (29).

During potentiometric titration these solutions were prepared with temperature equilibrated water.

Solutions less than $10^{-3}$ $\underline{M}$ were prepared from the appropriate aliquots of stock solution and the appropriate calibrated National Bureau of Standards volumetric flasks.

### Preparation of Primary Standard Silver Nitrate Solutions.

Primary standard silver nitrate solutions were prepared from "Baker and Adamson" reagent grade silver nitrate by the usual method.

For potentiometric titration of solutions less than $10^{-3}$ $\underline{M}$ in chloride standard solutions were prepared by using National Bureau of Standards calibrated volumetric flasks.

### Preparation of Sodium Chloride Solutions in Formic Acid.

Matheson formic acid (97-100%) exhibited a negative chloride test and was used without further purification. Solutions were prepared from the appropriate quantities of oven-dried "Baker Analyzed" reagent grade sodium chloride.

### Preparation of Solutions of Hydrogen Chloride in Formic Acid.

Matheson formic acid (97-100%) was used without further purification. Dry hydrogen chloride (Matheson) was bubbled directly into approximately 2 l. of formic acid contained in a clean dry 2 l. Erlenmeyer flask. Periodically samples were withdrawn and the chloride concentration determined by Volhard titration. When the chloride concentration approximately reached 0.1 $\underline{M}$, it was accuratedly determined and the solution stored in a ground glass stoppered flask.

Dilute solutions were prepared by buretting volumes of this stock solution into clean, dry 100 ml. volumetric flasks and diluting to the mark with formic acid.

General Techniques. Accurate weighings were performed using Mettler balances.

Distilled water was used in all analytical procedures.

Silver nitrate and potassium thiocyanate solutions were stored in 1 l. brown bottles. Each bottle was fitted by means of 24/40 ground glass joints with a liquid outlet and air inlet tube. Using clean tygon tubing the outlet was connected to the bottom of the automatic filling micro-buret and the inlet to a rubber squeeze bulb. The tubing and exposed glass fitting were wrapped with black tape. When not in use, the solution was protected against the atmosphere by closing the tubing with pinch clamps.

B. Calibration of Glassware. Pipets and volumetric flasks were calibrated by established methods (30). Weighings were performed using a Mettler balance except for 500 ml. and 1 l. volumetric flasks, which were weighed to the nearest 0.01 g. on a large free swinging balance. Correction factors were obtained from Blaedel and Meloche (29). The micro-burets were not calibrated.

Kimax National Bureau of Standards calibrated 1 l. and 2 l. volumetric flasks were also used.

C. Volhard Titrations.

Procedure 1. Macroscopic samples were analyzed by the usual procedure (29).

Procedure 2. The basic procedure using micro-burets was adapted from Blaedel and Meloche (29) and Kolthoff and Sandell (30).

A given aliquot of sodium chloride solution was delivered to a 300 ml. Erlenmeyer flask; 5 ml. of 1:1 concentrated nitric acid-water solution (boiled for several minutes) was added, and a measured excess of silver nitrate was added while the solution was magnetically stirred. The excess volume of silver nitrate was kept as small as possible. Nitrobenzene (3-3.5 ml.) was then added, the flask stoppered with a clean rubber stopper and vigorously shaken until a clear point was obtained. Indicator (2 ml. of 0.33 M $Fe(NO_3)_3$) was added and the excess silver ion back-titrated with potassium thiocyanate. Silver nitrate solution was standardized by titration against primary standard sodium chloride solutions.

Potassium thiocyanate was standardized against silver nitrate by the procedure described above.

Procedure 3. This procedure was modified from that of Swift et., al. (31). Seven to eight milliliters of a 1:1 mixture of concentrated nitric acid and water, 1 ml. of nitrobenzene and, depending upon the total titrating volume, 2 or 4 ml. of 2 M indicator were used. Samples were diluted with 35 to 40 ml. of water.

D. Potentiometric Titration.

Apparatus. The indicator electrode was a Beckmann (No. 30784) silver billet electrode that dipped into the titration beaker. A salt bridge connected the titration beaker to a small jacketed flask containing 1 M potassium chloride and a Beckmann (No. 39170) saturated calomel electrode. The reference half cell was connected to a constant temperature bath maintained at 23.00 ± 0.05°, although such thermostatting is not necessary unless determinations of concentrations less than $10^{-3}$ M are being made. The titration beaker was surrounded by a black cloth bag to keep out light, and its contents were stirred rapidly during titration with a magnetic stirrer. The potential between the silver and calomel electrodes was measured with a Leeds and Northrup Type K potentiometer and a PYE Scalamp galvanometer. During titration galvonometer sensitivity was switched to the x1 position. An Eppley standard cell (serial number 764043) was used. Power was supplied from four 1.5 volt dry cell batteries producing 6 volts.

Preparation of Silver Electrode. The silver electrode was soaked in a 1:1 solution of concentrated nitric acid and water, to which a little sodium nitrite had been added, until the surface was bright. It was then rinsed liberally with distilled water and polished with a fine grade of emery cloth. For continued stability the electrode was polished from time to time or whenever the surface became darkened.

Preparation of Salt Bridges. The salt bridge was a U-shaped glass tube 10 mm. in diameter, 15 cm. high, and 12 cm. wide. It was inverted and filled with a hot liquid 3% solution of agar-agar in 1 M potassium nitrate. After cooling to room temperature this solution formed a thick gel and solidified. Care was taken to exclude air bubbles and to ensure that the solidified gel completely filled the tube. A number of these salt bridges were prepared at the same time and stored in a desiccator with their ends immersed in 1 M potassium nitrate.

The 3% agar-agar in 1 M potassium nitrate was prepared by the following method. Oven-dried Baker reagent grade potassium nitrate (50.5538 g.) was weighed into a tared 50 ml. beaker and quantitatively transferred to an uncalibrated 500 ml. volumetric flask. A 200 ml. aliquot of this solution was pipetted into a clean 300 ml. Erlenmeyer flask and 6.000 g. of agar-agar was added. The suspension was then placed into a beaker of boiling water and heating continued until the solution became clear.

General Titration Procedures: (a) Solutions greater than $10^{-3}$ M in chloride: A given volume of halide solution was delivered into a 150 ml. beaker containing approximately 75 ml. water and an appropriate volume of formic acid. The entire titration beaker was covered with a black cloth bag and the sample titrated by adding aliquots of silver nitrate, rinsing the buret tip, and reading the corresponding potential.

Silver nitrate solutions not prepared as primary standard reagents were standardized by titration against primary standard sodium chloride.

(b) Solutions less than $10^{-3}$ M in chloride: A given volume of halide solution was delivered into a 150 ml. beaker containing a given amount of formic acid and enough water to bring the final volume to 100 ± 5 ml. The entire titration beaker was covered with a black cloth bag. Standard silver nitrate solution was delivered into the beaker from a 10 ml. microburet, graduated in 0.02 ml. intervals, while the solution was efficiently stirred. Initially, the potentiometer was set about 15 mv. less than the previously determined equivalence point potential and silver nitrate delivered until a null reading on the galvanometer was obtained. The titration was then stopped, the external balance of the potentiometer was checked, and the potentiometer was set at the determined equivalence point potential. Silver nitrate was then added slowly until a null reading on the galvanometer was obtained.

## IV. Extraction Procedures

A. Procedure 1. A 10 ml. aliquot of hydrogen chloride in formic acid was delivered to a 125 ml. separatory funnel containing 50 ml. of carbon tetrachloride and 20 ml. of distilled water. The mixture was then extracted, the carbon tetrachloride layer run into a second separatory funnel containing 15 ml. of distilled water, and the extraction repeated. The extractions were standardized at 40 and 30 shakes, respectively. The water layers were then quantitatively transferred to a 300 ml. Erlenmeyer flask and the chloride content determined by Volhard titration.

B. Procedure 2. To a 125 ml. separatory funnel containing 50 ml. of carbon tetrachloride and 25 ml. of distilled water was pipetted a given volume of solution, allowing 15 seconds drainage time. The mixture was then vigorously extracted, the carbon tetrachloride layer run into a second separatory funnel containing 15 ml. of distilled water and the extraction repeated. The extractions were standardized at 50 and 30 shakes, respectively. Each aqueous phase was then extracted with a small portion of purified petroleum ether and then quantitatively transferred to a 150 ml. beaker. The chloride content was then determined by potentiometric titration.

For aqueous sodium chloride solutions either a 5 or 10 ml. aliquot of formic acid was added.

## V. Determination of Appearance of Turbidity in the Solvolysis of α-Naphthylcarbinyl Chloride as a Function of Concentration

Formic acid freshly distilled from boric anhydride was used without determination of its water content. Assuming 0% water in the formic acid, 0.43 M and 0.28 M solvents were prepared by adding a given weight of water to the appropriate volumetric flask and diluting to the mark with formic acid. Assuming 0.15% water in the formic acid, 0.25 m solvent was prepared by adding a given weight of water to a weighed quantity of formic acid.

Various molar concentrations of α-naphthylcarbinyl chloride were prepared in each solvent. An appropriate amount of compound was weighed into a glass stoppered Erlenmeyer flask and a given volume of solvent added. The flask was then stoppered, shaken until solution was complete and allowed to stand at room temperature. Periodically the flasks were examined for the appearance of turbidity.

## VI. Preparation of Aqueous Formic Acid—Solvent for Kinetic Runs

A. Purification of Formic Acid. The method used was that of Winstein and Marshall (64).

To a 5 l. round bottom flask which was fitted with a 20 inch fractionating column and a distillation head was added 4 l. (approximately 4800 g.) of Matheson 97-100% formic acid. The low boiling components were distilled off and heating continued until the head temperature reached 99°. The formic acid was allowed to cool and 775 g. of boric anhydride was added. This amount of boric anhydride was calculated assuming the water content of the formic acid to be 4%. Four grams of boric anhydride was used per gram of calculated water. After standing for 3 days the formic acid was decanted into a clean dry 5 l. round bottom flask, and 150 g. of fresh boric anhydride was added. The fraction boiling in the range 27 to $33^{o}$ at 50 ± 10 mm. was collected, transferred to a brown bottle, and stored at $5^{o}$.

B. Determination of the Water Content in Formic Acid. The small water content of the formic acid purified by the above procedure was determined by Karl Fischer titration using the two solution technique (65).

The small water content of the blank was determined by titrating 25.00 ml. of the methanol solution which had been buretted into a clean, dry 125 ml. Erlenmeyer flask. A weighed amount of water was then added and titrated. A clean, dry, stoppered 125 ml. Erlenmeyer flask was weighed. A sample of formic acid to be titrated was introduced from a clean, dry pipet, the flask stoppered, and re-weighed. The stoppered flask and its contents were placed in an ice bath and 25.00 ml. of the methanol solvent added. The resulting solution was then titrated. In calculating the water content of the formic acid, the volume of reagent required to titrate the blank was subtracted from the total reagent volume. Results were reproducible to ± 0.02%.

C. Preparation of 0.32 m Water in Formic Acid. A clean, dry 2 l. volumetric flask was weighed to the nearest 0.01 g. The anhydrous formic acid was transferred to the volumetric flask. From the results of the Karl Fischer titration, the amount of additional water required to prepare a 0.32 m solution was calculated and added from a weight buret. The solution was thoroughly mixed, transferred to a clean, dry brown bottle, and stored in a cold room when not being used.

## VII. Rate Determination

An amount of compound was accurately weighed into either a 100 ml. or 200 ml. volumetric flask. Temperature equilibrated solvent was then added to about 80% capacity. The volumetric flask was then stoppered and vigorously shaken until solution of the material was complete. The solution was then diluted to the mark, the flask inverted several times to effect complete mixing, and the contents transferred to a clean, dry polyethylene squeeze bottle from which 5.5 ml. or 10.5 ml. ampoules were filled. Initial time of mixing was called zero time. At definite time intervals an ampoule was withdrawn, broken open, and a 5 ml. or 10 ml. aliquot withdrawn. The reaction was quenched by extracting the sample using extraction procedure 2. Time was recorded at the end of the first extraction. The average sampling time was approximately 2 minutes ± 10 sec. The volume of the resulting solution was adjusted to 100 ml. and its chloride content determined by potentiometric titration. For 5 ml. aliquots an additional 5 ml. of 97% formic acid was pipetted into the beaker before titration.

During kinetic studies on 8-methyl-α-naphthylcarbinyl chloride and 8-bromo-α-naphthylcarbinyl chloride, the sealed ampoule technique was not used.

During kinetic studies on 8-methyl-α-naphthylcarbinyl chloride the second extraction was not performed until the end of the run.

In most cases the average of three samples was taken for the infinity titre.

Bath temperature was $25.004 \pm < 0.01^{\circ}$.

# PART II

# SOME PROTON-$^{13}$C COUPLING CONSTANTS IN SUBSTITUTED ARYLCARBINYL COMPOUNDS

# PART II

## INTRODUCTION

It is generally agreed that the major contribution to the short range proton-$^{13}$C coupling, $J_{^{13}C-H}$, is the Fermi contact term (66).

The elucidation of factors affecting long range proton $^{13}$C coupling has been less extensively investigated. Karabatsos and co-workers (67) were able to conclude that the contact term dominates $J_{^{13}C-C-H}$ when $^{13}$C-C-H angle is tetrahedral. However, three bond coupling showed no simple dependence on the contact term.

Karabatsos and Orzech (68) have postulated, from studies of $^{13}$C labeled neo-pentyl derivatives, that spin-dipole and electron-orbital effects contribute to both $J_{^{13}C-H}$ and $J_{^{13}C-C-C-H}$ since no simple relationship between electronegativities and coupling was observed. Furthermore, some of the variations of $J_{^{13}C-C-C-H}$ could only be qualitatively explained by assuming bond bending as a result of steric repulsions (69). Qualitatively, the magnitude of J should decrease as the bond is bent, since the overlap is being reduced. The availability of a number of 1,8-disubstituted naphthalene derivatives suggested themselves as systems to test these effects on the magnitude of $J_{^{13}C-H}$. The values of $J_{^{13}C-H}$ were obtained for the isomeric halo and methyl toluenes and benzyl alcohols.

# RESULTS

Summarized in Tables XXVII, XXVIII, and XXIX are the $J_{^{13}C-H}$ for the various naphthalene compounds, isomeric toluenes, and isomeric benzyl halides, respectively. The coupling constants were obtained from $^{13}C$ natural abundance.

Table XXVII. Proton-$^{13}C$ couplings calculated from substituted naphthalenes.

| Compound | $J_{^{13}C-H}(CH_3)$ | $J_{^{13}C-H}(CH_2)$ | Solvent |
|---|---|---|---|
| β-methylnaphthalene | 125.5 | | $CCl_4$ |
| α-methylnaphthalene | 126.0 | | neat |
| 8-bromo-1-methylnaphthalene | 127.2 | | $CCl_4$ |
| 8-methyl-α-naphthylcarbinol | 125.2 | 142.0 | acetone[a] |
| 8-bromo-α-naphthylcarbinol | | 144.0 | acetone[a] |
| α-naphthylcarbinol | | 141.0 | acetone |

[a] 5% HCl added.

Table XXVIII. Proton-$^{13}$C couplings calculated from isomeric toluenes.

| Compound | $J_{^{13}C-H}$ ($CH_3$) | Solvent |
|---|---|---|
| parent | 125.5 | neat |
| *o*-F | 127.1 | neat |
| *o*-Cl | 127.0 | neat |
| *o*-Br | 127.0 | neat |
| *o*-I | 126.8 | neat |
| *o*-Me | 125.0 | neat |
| *m*-F | 126.0 | neat |
| *m*-Cl | 126.0 | neat |
| *m*-Br | 126.0 | neat |
| *m*-I | 125.8 | neat |
| *m*-Me | 125.0 | neat |
| *p*-F | 125.6 | neat |
| *p*-Cl | 125.6 | neat |
| *p*-Br | 125.7 | neat |
| *p*-I | 125.6 | $CCl_4$ |
| *p*-Me | 125.7 | neat |

Table XXIX. Proton-$^{13}$C couplings calculated from isomeric benzyl alcohols.

| Compound | $J_{^{13}C-H}$ ($CH_2$) | $J_{^{13}C-H}$ ($CH_3$) | Solvent |
|---|---|---|---|
| parent | 141.0 | | neat[a] |
| o-F | 143.4 | | neat[a] |
| o-Cl | 142.5 | | acetone |
| o-Br | 142.5 | | acetone[a] |
| o-Me | 140.4 | 125.5 | neat |
| m-F | 142.1 | | neat[a] |
| m-Cl | 141.8 | | neat[a] |
| m-Br | 141.3 | | neat |
| m-I | 141.8[b] | | neat[a] |
| m-Me | 141.4 | 125.8[b] | neat |
| p-F | 141.4 | | neat[a] |
| p-Cl | 141.5 | | $CCl_4$ |
| p-Br | 140.8 | | acetone |
| p-I | 141.3[b] | | neat |
| p-Me | 140.7 | 125.4 | $CCl_4$ |
| p-MeO | 140.6 | | neat |

[a] 5% HCl added.

[b] Increased uncertainty.

# DISCUSSION

Examination of the results reveals that differences in $J_{^{13}C\text{-}H}$ are very small.

For halotoluenes (Table XXVIII) differences within the ortho, meta, and para isomers are negligible. Small differences exist between the ortho, meta, and para positions. These differences are in qualitative agreement with expectations based on the influence of electronegativity on $J_{^{13}C\text{-}H}$. The order $J_{^{13}C\text{-}H}(p) < J_{^{13}C\text{-}H}(m) < J_{^{13}C\text{-}H}(o)$ is in agreement with the increasing inductive effect. That only insignificant differences are observed within each series must mean that only gross electronegativity effects are important and that small electronegativity differences among the halogens produce changes of no greater than several hundredths of a cps in $J_{^{13}C\text{-}H}$. Whether the relative increase observed for the ortho halogens is due entirely to the increased inductive effect or also represents contributions from spin-dipole and electron-orbital terms is difficult to assess. The somewhat anomalous behavior of iodine is well documented and reflected by its $\sigma$ and $\sigma^+$ values (70).

Table XXIX reveals that the same trends in $J_{^{13}C\text{-}H}$ are observed for the benzyl alcohols. Due to the increased uncertainty of $J_{^{13}C\text{-}H}$ values, the small differences within each positional isomer must be treated with scepticism.

Table XXVII reveals that the largest changes in $J_{^{13}C\text{-}H}$ are observed for 8-bromo-α-methylnaphthalene and 8-bromo-α-naphthylcarbinol. The differences for the remaining naphthalene compounds are small.

Steric strain is probably present in the 1,8-disubstituted compounds. This strain is probably relieved by in-plane splaying-out of the $C_\alpha$-$C_8$-$C_9$ and $C_\alpha$-$C_1$-$C_9$ bonds and also possibly by bending the groups out of the naphthalene plane. Comparison of the coupling constant of 8-methyl-α-naphthylcarbinol with those of α- and β-methyl naphthalene and α-naphthylcarbinol reveals that the effect of these steric interactions on $J_{^{13}C\text{-}H}$ is probably small. Previously it has been postulated that part of the slow rate of solvolysis of 8-bromo-α-naphthylcarbinyl chloride was due to the enhanced inductive effect because of the close proximity of the bromine. The increase observed in the $J_{^{13}C\text{-}H}$ in the 8-bromo compounds is in agreement with this hypothesis. However, part of the observed increase may be due to contributions from spin-dipole and/or electron-orbital terms.

# EXPERIMENTAL

A. Substituted Benzyl Alcohols. Commercially available benzyl alcohol and p-methoxybenzyl alcohol were used without further purification. The remaining alcohols were prepared by reduction of the corresponding acids with lithium aluminum hydride.

o-Fluoro- and m-fluorobenzyl alcohols were prepared by lithium aluminum hydride reduction of the corresponding aldehydes.

B. Substituted Toluenes. Commercially available compounds were used without purification. The N.M.R. spectra were in accord with the structures.

C. Substituted Naphthalenes. Either commercially available compounds or compounds previously prepared were used.

All N.M.R. spectra were determined at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), at a temperature of about 36°. The coupling constants, determined at sweep width of 250 cps., are the averages of at least three determinations with an estimated precision of ± 0.2 cps.

# BIBLIOGRAPHY

(1) Lewis, E. S. and C. E. Boozer, J. Am. Chem. Soc., 74, 6306 (1952).

(2) Shiner, V. J., Jr., ibid., 75, 2925 (1953).

(3) For a recent review see E. A. Halevi in "Progress in Physical Organic Chemistry," Vol. 1, edited by S. G. Cohen, A. Streitwieser, Jr. and R. W. Taft, New York: Interscience, 1963.

(4) a) Shiner, V. J., Jr., J. Am. Chem. Soc., 74, 5285 (1952);
b) Lewis, E. S., Tetrahedron, 5, 143 (1959).

(5) a) Shiner, V. J., Jr., J. Am. Chem. Soc., 76, 1603 (1954);
b) Shiner, V. J., Jr. and S. Cross, ibid., 79, 3599 (1957).

(6) Shiner, V. J., Jr. and G. S. Kriz, Jr., ibid., 86, 2643 (1964).

(7) a) Shiner, V. J., Jr., ibid., 78, 2653 (1956); b) ibid., 83, 240 (1961).

(8) Shiner, V. J., Jr., B. L. Murr, and G. Heinemann, ibid., 85, 2413 (1963).

(9) Shiner, V. J., Jr. and J. S. Humphrey, Jr., ibid., 85, 2416 (1963).

(10) Shiner, V. J., Jr. and J. G. Jewett, ibid., 86, 945 (1964).

(11) For a discussion, see "Indiana University Conference on Hyperconjugation," V. J. Shiner, Jr. and E. Campaigne, co-chairmen, Tetrahedron, 5, 105-274 (1959).

(12) Dewar, M. J. S., "Hyperconjugation," New York: Ronald Press Co., 1962.

(13) Streitwieser, A., Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Am. Chem. Soc., 80, 2326 (1958).

(14) a) Bartell, L. S., J. Chem. Phys., 32, 827 (1960); b) Tetrahedron, 17, 177 (1962); c) Tetrahedron Letters, No. 6, 13 (1960); d) J. Am. Chem. Soc., 83, 3567 (1961).

(15) Melander, L. and R. E. Carter, ibid., 86, 295 (1964).

(16) a) Mislow, K., R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., ibid., 85, 1199 (1963); b) ibid., 86, 1733 (1964).

(17) Raaen, V. F., T. K. Dunham, D. D. Thompson, and C. J. Collins, ibid., 85, 3497 (1963).

(18) Ferguson, G. and J. M. Robertson in "Advances in Physical Organic Chemistry," Vol. 1, edited by V. Gold, New York: Academic Press, 1963.

(19) Donaldson, D. M. and J. M. Robertson, J. Chem. Soc., 17 (1953).

(20) For leading references see H. C. Brown and I. Moritani, J. Am. Chem. Soc., 77, 3623 (1955); b) Brown, H. C., J. Chem. Soc., 1248 (1956); c) Science 103, 385 (1946) and references cited therein.

(21) Banthorpe, D. V., E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 4054 (1960) and references cited therein.

(22) Moritani, I., S. Nishida, and M. Murakami, J. Am. Chem. Soc., 81, 3420 (1959).

(23) Nishida, S., ibid., 82, 4290 (1960).

(24) Winstein, S. and N. J. Holness, ibid., 77, 5562 (1955).

(25) a) Brown, H. C., and K. Ichikawa, Tetrahedron, 1, 221 (1957); b) Brown, H. C., O. H. Wheeler, and K. Ichikawa, ibid., 1, 214 (1957); c) Brown, H. C. and K. Ichikawa, J. Am. Chem. Soc., 84, 373 (1962).

(26) Shone, R. L., Ph.D. thesis, Michigan State University, 1964.

(27) Jacobs, T. L. and S. Singer, J. Org. Chem., 475 (1952).

(28) Nakanishi, K., "Practical Infrared Absorption Spectroscopy," San Francisco: Holden Day, Inc., 1962, p. 22.

(29) Blaedel, W. J. and V. W. Meloche, "Elementary Quantitative Analysis," White Plains, N.Y.: Row, Peterson, and Co., 1957.

(30) Kolthoff, I. M. and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," New York: MacMillan Co., 3rd edition, 1952.

(31) Swift, E. H., G. M. Arcand, R. Lutwack, and D. J. Meies, Anal. Chem., 22, 306 (1950).

(32) Fainberg, A. H. and S. Winstein, J. Am. Chem. Soc., 78, 2770 (1956).

(33) Bateman, L. C. and E. D. Hughes, J. Chem. Soc., 1187 (1937).

(34) Shiner, V. J., Jr. and M. L. Smith, Anal. Chem., 28, 1043 (1956).

(35) Kolthoff, I. M. and H. H. Furman, "Potentiometric Titrations," New York: John Wiley and Sons, 1926.

(36) Meires, L. and H. C. Thomas, "Advanced Analytical Chemistry," New York: McGraw-Hill Book Co., Inc., 1958, Chapter 3.

(37) Armstrong, G. W., H. H. Gill, and R. F. Rolf in "Treatise on Analytical Chemistry," edited by I. M. Kolthoff, P. S. Elving, and E. B. Sandell, Part II, Vol. 7, New York: Interscience, 1961, pp. 364-377.

(38) a) Shiner, V. J., Jr. and J. W. Wilson, J. Am. Chem. Soc., 84, 2402 (1962); b) Shiner, V. J., Jr., G. Heinemann, J. W. Wilson, and N. Solliday, ibid., 84, 2408 (1962).

(39) Streitwieser, A., Jr., "Solvolytic Displacement Reactions," New York: McGraw-Hill Book Co., Inc., 1962.

(40) Swain, C. G. and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951).

(41) Bensley, B. and G. Kohnstam, J. Chem. Soc., 4747 (1957).

(42) a) Dewar, M. J. S. and R. J. Sampson, ibid., 2789 (1956); b) ibid., 2946 (1957).

(43) Handbook of Chemistry and Physics, 39th edition, Cleveland, Ohio: Chemical Rubber Publishing Co., 1957, pp. 1869-1870.

(44) Fierens, P. J. C., H. Hannaert, J. Van Rysselberge, and R. H. Martin, Helv. Chim. Acta., 238, 2009 (1955).

(45) Benson, S. W., "The Foundations of Chemical Kinetics," New York: McGraw-Hill Book Co., Inc., 1960, p. 86.

(46) Streitwieser, A., Jr., "Molecular Orbital Theory for Organic Chemists," New York: John Wiley and Sons, Inc., 1961, p. 105.

(47) Sevast'yenov, N. G., G. S. Zhdanov, and M. M. Umanski from B. M. Webster in "Progress in Stereochemistry," edited by W. Klyne and P. B. D. de la Mare, Vol. 2, New York: Academic Press, 1958.

(48) Trotter, J., Can. J. Chem., 39, 1574, 1964 (1961).

(49) Trotter, J., Acta. Cryst., 13, 732 (1960).

(50) Hall, D. M., S. Ridgewell, and E. E. Turner, J. Chem. Soc., 2498 (1954).

(51) Grubb, E. L. and C. P. Smyth, J. Am. Chem. Soc., 83, 4873 (1961).

(52) Harrison, A. G., P. Kebarle, and F. P. Lossing, ibid., 83, 777 (1961).

(53) Brown, H. C. and Y. Okamoto, ibid., 80, 4979 (1958).

(54) Mason, S. F., J. Chem. Soc., 808 (1958).

(55) Dewar, M. J. S. and R. J. Sampson, ibid., 2952 (1957).

(56) Okamoto, Y. and H. C. Brown, J. Am. Chem. Soc., 79, 1903 (1957).

(57) a) Brown, H. C., J. D. Brady, M. Grayson, and W. H. Bonner, ibid., 79, 1897 (1957); b) Brown, H. C., Y. Okamoto, and G. Ham, ibid., 79, 1906 (1957); c) Okamoto, Y. and H. C. Brown, ibid., 79, 1909 (1957); d) Brown, H. C., Y. Okamoto, and T. Inukai, ibid., 80, 4964 (1958); e) Brown, H. C. and T. Inukai, ibid., 83, 4825 (1961).

(58) Baddeley, C., J. Chadwick, and H. T. Taylor, J. Chem. Soc., 2405 (1954).

(59) Chapman, N. B., J. Shorter, and J. H. P. Utley, ibid., 1291 (1963).

(60) Verbit, L. and E. Berliner, J. Am. Chem. Soc., 86, 3307 (1964).

(61) Kochi, J. K. and G. S. Hammond, ibid., 75, 3443 (1953).

(62) Organic Syntheses, collective vol. II, p. 425.

(63) Vogel, A. I., "Textbook of Practical Organic Chemistry," London: Spottis Woode, Ballantyne and Co., Ltd., 3rd edition, 1961.

(64) Winstein, S. and H. Marshall, J. Am. Chem. Soc., 74, 1120 (1952).

(65) Stone, K. G., "Determination of Organic Compounds," New York: McGraw-Hill Book Co., Inc., 1956, Chapter 1.

(66) a) Shoolery, J. N., J. Chem. Phys., 31, 1427 (1959); b) Muller, C. N. and D. E. Pritchard, ibid., 31, 768, 1471 (1959); c) Gutowsky, H. S. and C. S. Juan, ibid., 84, 307 (1962).

(67) Karabatsos, G. J., J. D. Graham, and F. M. Vane, J. Phys. Chem., 65, 1657 (1961).

(68) Karabatsos, G. J. and C. E. Orzech, Jr., in press.

(69) Karabatsos, G. J. and C. E. Orzech, Jr., private communication.

(70) Leffler, J. E. and E. Grunwald, "Rates and Equilibria of Organic Reactions," New York: John Wiley and Sons, Inc., 1963.

# APPENDIX

# APPENDIX

## Data Obtained from the Solvolysis Rate Measurements

The following tables contain the data obtained from the rate measurements.

w = weight (g.) of arylcarbinyl chloride.

V = corrected volume (ml.) of the volumetric flask used in each run.

$A_0$ = the initial concentration of arylcarbinyl chloride.

$\underline{M}$ $AgNO_3$ = the molarity of silver nitrate used in a run.

Pip.Vol.= the calibrated volume (ml.) of each pipet.

Titre = volume of standard silver nitrate required to titrate chloride in an extracted kinetic sample.

[X] = the concentration of chloride at time t.

t = time in minutes.

$X_{eq.av.}$ =the average value of the chloride content at equilibrium, $\underline{M}$.

k = rate constant obtained by least squares analysis.

The molecular weights of the arylcarbinyl chlorides used to calculate $A_0$ were:

α-naphthylcarbinyl chloride = 176.53

α-naphthylcarbinyl chloride-8-d = 177.54

α-naphthylcarbinyl chloride-α,α-$d_2$ = 178.54

8-bromo-α-naphthylcarbinyl chloride = 255.44

8-methyl-α-naphthylcarbinyl chloride = 190.54

Table XXX. Solvolysis of α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 1.

w = 0.3163 g.; V = 199.88 ml.; $A_0$ = 8.964 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.282 | 5.076 | 1.155 | 51.31 |
| 9.996 | 4.400 | | 2.234 | 108.51 |
| 10.01 | 6.575 | | 3.334 | 174.23 |
| 9.997 | 8.030 | | 4.077 | 233.96 |
| 9.998 | 9.235 | | 4.689 | 291.63 |
| 9.982 | 10.24 | | 5.207 | 347.93 |
| 10.00 | 6.470 | 9.046 | 5.853 | 442.53 |
| 9.991 | 6.985 | | 6.324 | 543.28 |
| 9.988 | 7.340 | | 6.648 | 645.00 |
| 9.990 | 8.030 | | 7.271 | equilibrium |
| 9.990 | 8.010 | | 7.253 | equilibrium |
| 9.990 | 8.030 | | 7.271 | equilibrium |

$X_{eq.av.}$ = 7.265 x $10^{-3}$; k = 4.63 x $10^{-5}$ sec.$^{-1}$.

Table XXXI. Solvolysis of α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 2.

w = 0.3039 g.; V = 199.88 ml.; $A_0$ = 8.613 x $10^{-3}$ M

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.130 | 5.076 | 1.078 | 51.79 |
| 9.996 | 4.302 | | 2.184 | 110.80 |
| 10.01 | 6.338 | | 3.214 | 180.65 |
| 9.997 | 7.880 | | 4.001 | 242.36 |
| 9.998 | 9.125 | | 4.633 | 301.32 |
| 9.982 | 10.25 | | 5.212 | 367.79 |
| 10.00 | 10.99 | | 5.579 | 428.93 |
| 9.991 | 6.878 | 9.046 | 6.227 | 561.86 |
| 9.989 | 7.182 | | 6.504 | 667.91 |
| 10.02 | 7.400 | | 6.681 | 777.88 |
| 9.999 | 7.870 | | 7.120 | equilibrium |
| 9.999 | 7.862 | | 7.113 | equilibrium |
| 9.999 | 7.850 | | 7.102 | equilibrium |

$X_{eq.av.}$ = 7.112 x $10^{-3}$; k = 4.55 x $10^{-5}$ sec.$^{-1}$.

Table XXXII. Solvolysis of α-naphthylcarbinyl chloride in 0.32 $\underline{m}$ water-formic acid. Run 3.

$w = 0.3075$ g.; $V = 199.80$ ml.; $A_0 = 8.718 \times 10^{-3}$ $\underline{M}$.

| Pip. Vol. (ml.) | Titre (ml.) | $\underline{M}$ AgNO$_3$ x 10$^3$ | [X] x 10$^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.575 | 5.076 | 1.303 | 58.77 |
| 9.996 | 4.785 | | 2.430 | 121.02 |
| 10.01 | 6.958 | | 3.528 | 193.82 |
| 9.997 | 8.390 | | 4.260 | 256.81 |
| 9.998 | 9.575 | | 4.861 | 317.10 |
| 9.982 | 10.78 | | 5.482 | 381.92 |
| 10.00 | 6.580 | 9.046 | 5.952 | 486.06 |
| 9.991 | 6.910 | | 6.256 | 549.91 |
| 9.988 | 7.275 | | 6.589 | 666.42 |
| 9.993 | 7.410 | | 6.708 | 741.52 |
| 9.990 | 7.895 | | 7.149 | equilibrium |
| 9.990 | 7.930 | | 7.181 | equilibrium |
| 9.990 | 7.905 | | 7.158 | equilibrium |

$X_{eq.av.} = 7.163 \times 10^{-3}$; $k = 4.62 \times 10^{-5}$ sec.$^{-1}$.

Table XXXIII. Solvolysis of α-naphthylcarbinyl chloride in 0.32 $\underline{m}$ water-formic acid. Run 4.

$w = 0.3025$ g.; $V = 199.88$ ml.; $A_0 = 8.573 \times 10^{-3}$ $\underline{M}$.

| Pip. Vol. (ml.) | Titre (ml.) | $\underline{M}$ AgNO$_3$ x 10$^3$ | [X] x 10$^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.365 | 5.053 | 1.191 | 57.37 |
| 9.996 | 4.400 | | 2.224 | 116.66 |
| 10.01 | 6.290 | | 3.175 | 181.13 |
| 9.997 | 8.000 | | 4.044 | 254.55 |
| 9.998 | 9.125 | | 4.612 | 316.84 |
| 9.982 | 10.10 | | 5.113 | 376.01 |
| 10.00 | 5.400 | 10.06 | 5.432 | 444.02 |
| 9.991 | 6.040 | | 6.082 | 573.44 |
| 9.988 | 6.348 | | 6.394 | 673.16 |
| 9.993 | 6.485 | | 6.528 | 750.98 |
| 9.989 | 6.899 | | 6.948 | equilibrium |
| 9.989 | 6.865 | | 6.914 | equilibrium |
| 9.989 | 6.870 | | 6.919 | equilibrium |

$X_{eq.av.} = 6.927 \times 10^{-3}$; $k = 4.57 \times 10^{-5}$ sec.$^{-1}$.

Table XXXIV. Solvolysis of α-naphthylcarbinyl chloride-8-d in 0.32 $\underline{m}$ water-formic acid. Run 5.

$w = 0.3038$ g.; $V = 199.88$ ml.; $A_0 = 8.561 \times 10^{-3}$ $\underline{M}$.

| Pip. Vol. (ml.) | Titre (ml.) | $\underline{M}$ $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.630 | 5.053 | 1.325 | 61.63 |
| 9.996 | 4.440 | | 2.244 | 116.80 |
| 10.01 | 6.280 | | 3.170 | 179.76 |
| 9.997 | 7.695 | | 3.889 | 239.65 |
| 9.998 | 8.995 | | 4.546 | 302.89 |
| 9.982 | 9.960 | | 5.042 | 365.15 |
| 10.00 | 5.560 | 10.06 | 5.593 | 452.74 |
| 9.991 | 6.080 | | 6.122 | 584.15 |
| 9.988 | 6.382 | | 6.428 | 686.57 |
| 9.993 | 6.490 | | 6.533 | 753.62 |
| 9.989 | 6.885 | | 6.934 | equilibrium |
| 9.989 | 6.910 | | 6.959 | equilibrium |
| 9.989 | 6.905 | | 6.954 | equilibrium |

$X_{eq.av.} = 6.949 \times 10^{-3}$; $k = 4.54 \times 10^{-5}$ sec.$^{-1}$.

Table XXXV. Solvolysis of α-naphthylcarbinyl chloride-8-d in 0.32 $\underline{m}$ water-formic acid. Run 6.

$w = 0.3231$ g.; $V = 199.88$ ml.; $A_0 = 9.105 \times 10^{-3}$ $\underline{M}$.

| Pip. Vol. (ml.) | Titre (ml.) | $\underline{M}$ $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.680 | 5.053 | 1.350 | 57.10 |
| 9.996 | 4.825 | | 2.439 | 116.83 |
| 10.01 | 6.760 | | 3.412 | 179.61 |
| 9.997 | 8.225 | | 4.157 | 237.01 |
| 9.998 | 9.482 | | 4.792 | 297.05 |
| 9.982 | 10.56 | | 5.346 | 357.77 |
| 10.00 | 11.42 | | 5.770 | 420.85 |
| 9.991 | 6.162 | 10.06 | 6.204 | 503.01 |
| 9.988 | 6.570 | | 6.617 | 613.09 |
| 9.993 | 6.795 | | 6.840 | 737.68 |
| 9.989 | 7.245 | | 7.296 | equilibrium |
| 9.989 | 7.228 | | 7.279 | equilibrium |
| 9.989 | 7.240 | | 7.291 | equilibrium |
| 9.989 | 7.245 | | 7.296 | equilibrium |

$X_{eq.av.} = 7.290 \times 10^{-3}$; $k = 4.53 \times 10^{-5}$ sec.$^{-1}$.

Table XXXVI. Solvolysis of α-naphthylcarbinyl chloride-8-d in 0.32 m water-formic acid. Run 7.

w = 0.1634 g.; V = 99.865 ml.; $A_0$ = 9.215 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M AgNO$_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 3.005 | 5.053 | 1.514 | 65.15 |
| 9.996 | 5.590 | | 2.826 | 138.79 |
| 10.01 | 8.040 | | 4.059 | 230.05 |
| 10.00 | 10.10 | | 5.104 | 325.62 |
| 9.998 | 5.800 | 10.11 | 5.865 | 426.50 |
| 9.989 | 14.73 | 5.053 | 7.451 | equilibrium |
| 9.989 | 14.74 | | 7.456 | equilibrium |

$X_{eq.av.}$ = 7.453 x $10^{-3}$; k = 4.45 x $10^{-5}$ sec.$^{-1}$.

Table XXXVI. Solvoysis of α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 8.

w = 0.1654 g.; V = 99.865 ml.; $A_0$ = 9.382 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M AgNO$_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 10.03 | 2.665 | 5.053 | 1.343 | 60.13 |
| 9.990 | 4.942 | | 2.500 | 120.32 |
| 9.993 | 6.820 | | 3.448 | 180.47 |
| 9.982 | 8.462 | | 4.284 | 242.46 |
| 10.00 | 9.925 | | 5.015 | 310.87 |
| 4.986 | 5.505 | | 5.579 | 380.23 |
| 4.992 | 5.902 | | 5.974 | 459.46 |
| 4.986 | 6.550 | | 6.638 | 604.58 |
| 4.992 | 6.842 | | 6.926 | 714.84 |
| 3.985 | 5.820 | | 7.380 | equilibrium |
| 4.986 | 7.310 | | 7.408 | equilibrium |
| 4.986 | 7.345 | | 7.444 | equilibrium |

$X_{eq.av.}$ = 7.411 x $10^{-3}$; k = 4.40 x $10^{-5}$ sec.$^{-1}$.

Table XXXVIII. Solvolysis of α-naphthylcarbinyl chloride-α,α-$d_2$ in 0.32 m water-formic acid. Run 9.

$w = 0.1750$ g.; $V = 99.865$ ml.; $A_0 = 9.815 \times 10^{-3}$ M

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 9.991 | 2.100 | 5.053 | 1.062 | 60.33 |
| 9.988 | 4.007 | | 2.027 | 120.56 |
| 9.998 | 5.660 | | 2.856 | 180.90 |
| 10.02 | 7.265 | | 3.664 | 246.07 |
| 10.03 | 4.285 | | 2.159 | 312.63 |
| 4.986 | 5.340 | | 5.412 | 449.86 |
| 4.992 | 6.178 | | 6.253 | 593.00 |
| 4.986 | 6.670 | | 6.760 | 742.38 |
| 4.992 | 7.630 | | 7.723 | equilibrium |
| 4.992 | 7.680 | | 7.774 | equilibrium |
| 4.992 | 7.670 | | 7.764 | equilibrium |

$X_{eq.av.} = 7.754 \times 10^{-3}$; $k = 3.31 \times 10^{-5}$ sec.$^{-1}$.

Table XXXIX. Solvolysis of α-naphthylcarbinyl chloride-α,α-$d_2$ in 0.32 m water-formic acid. Run 10.

$w = 0.1853$ g.; $V = 99.857$ ml.; $A_0 = 1.039 \times 10^{-2}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 9.991 | 2.250 | 5.053 | 1.138 | 60.09 |
| 9.988 | 4.290 | | 2.170 | 121.26 |
| 9.996 | 6.022 | | 3.044 | 182.08 |
| 10.01 | 7.560 | | 3.816 | 241.48 |
| 9.989 | 8.998 | | 4.552 | 303.46 |
| 4.986 | 5.070 | | 5.139 | 371.63 |
| 4.992 | 5.665 | | 5.734 | 434.25 |
| 4.986 | 6.412 | | 6.498 | 576.63 |
| 4.986 | 6.862 | | 6.954 | 706.49 |
| 4.986 | 7.920 | | 8.026 | equilibrium |
| 4.984 | 7.990 | | 8.097 | equilibrium |
| 3.985 | 6.320 | | 8.014 | equilibrium |

$X_{eq.av.} = 8.046 \times 10^{-3}$; $k = 3.29 \times 10^{-5}$ sec.$^{-1}$.

Table XL. Solvolysis of α-naphthylcarbinyl chloride-α,α-$d_2$ in 0.32 m water-formic acid. Run 11.

w = 0.1778 g., V = 99.865 ml.; $A_0$ = 9.972 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 10.02 | 2.225 | 5.053 | 1.122 | 59.95 |
| 9.998 | 4.085 | | 2.065 | 120.11 |
| 9.982 | 5.755 | | 2.913 | 180.19 |
| 10.00 | 7.245 | | 3.661 | 241.38 |
| 9.993 | 8.610 | | 4.354 | 306.95 |
| 4.986 | 4.840 | | 4.905 | 375.17 |
| 4.986 | 5.395 | | 5.468 | 447.11 |
| 4.984 | 6.200 | | 6.286 | 589.42 |
| 4.984 | 6.740 | | 6.833 | 736.45 |
| 4.986 | 7.655 | | 7.758 | equilibrium |
| 3.985 | 6.080 | | 7.709 | equilibrium |
| 3.985 | 6.060 | | 7.684 | equilibrium |

$X_{eq.av.}$ = 7.717 x $10^{-3}$; k = 3.35 x $10^{-5}$ sec.$^{-1}$.

Table XLI. Solvolysis of α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 12.

w = 0.1695 g.; V = 99.865 ml.; $A_0$ = 9.615 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 9.996 | 2.882 | 5.053 | 1.457 | 61.42 |
| 9.998 | 5.335 | | 2.696 | 125.17 |
| 10.00 | 7.140 | | 3.608 | 184.55 |
| 10.01 | 8.880 | | 4.483 | 251.46 |
| 4.984 | 5.165 | | 5.236 | 325.97 |
| 4.986 | 5.742 | | 5.819 | 401.87 |
| 4.984 | 6.210 | | 6.296 | 476.35 |
| 4.986 | 6.710 | | 6.800 | 605.73 |
| 4.984 | 7.505 | | 7.609 | equilibrium |
| 4.984 | 7.460 | | 7.563 | equilibrium |
| 4.984 | 7.490 | | 7.594 | equilibrium |
| 9.989 | 15.09 | | 7.633 | equilibrium |

$X_{eq.av.}$ = 7.600 x $10^{-3}$; k = 4.35 x $10^{-5}$ sec.$^{-1}$.

Table XLII. Solvolysis of α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 13.

$w = 0.1757$ g.; $V = 199.80$ ml.; $A_0 = 4.981 \times 10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 9.998 | 1.535 | 5.053 | 0.7758 | 64.42 |
| 9.996 | 2.818 | | 1.424 | 126.90 |
| 10.01 | 4.630 | | 2.337 | 249.68 |
| 9.982 | 5.482 | | 2.775 | 323.91 |
| 10.02 | 6.320 | | 3.187 | 408.70 |
| 9.988 | 7.022 | | 3.552 | 511.66 |
| 9.990 | 7.765 | | 3.928 | 665.47 |
| 9.989 | 8.865 | | 4.484 | equilibrium$^a$ |
| 9.989 | 8.875 | | 4.489 | equilibrium$^a$ |
| 9.989 | 8.885 | | 4.495 | equilibrium$^a$ |
| 9.989 | 9.000 | | 4.553 | equilibrium$^b$ |
| 9.989 | 9.015 | | 4.560 | equilibrium$^b$ |
| 9.989 | 9.020 | | 4.563 | equilibrium$^b$ |

$X^{a}_{eq.av.} = 4.489 \times 10^{-3}$ at 27.5 hours; $k = 4.43 \times 10^{-5}$ sec.$^{-1}$.

$X^{b}_{eq.av.} = 4.559 \times 10^{-3}$ at 51-52 hours; $k = 4.32 \times 10^{-5}$ sec.$^{-1}$.

Table XLIII. Solvolysis of 8-bromo-α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 14.

$w = 0.1333$ g.; $V = 99.865$ ml.; $A_0 = 5.225 \times 10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3 \times 10^3$ | $[X] \times 10^3$ | t (min.) |
|---|---|---|---|---|
| 9.998 | 1.090 | 5.053 | 0.5509 | 24.99 |
| 9.998 | 1.220 | | 0.6166 | 28.18 |
| 9.998 | 1.340 | | 0.6772 | 31.90 |
| 9.998 | 1.640 | | 0.8289 | 40.41 |
| 9.998 | 2.320 | | 1.173 | 63.45 |
| 9.998 | 4.040 | | 2.042 | 129.42 |
| 9.998 | 6.020 | | 3.043 | 235.55 |
| 9.991 | 9.680 | | 4.896 | equilibrium |
| 9.991 | 9.650 | | 4.880 | equilibrium |

$X_{eq.av.} = 4.888 \times 10^{-3}$; $k = 6.15 \times 10^{-5}$ sec.$^{-1}$.

Table XLIV. Solvolysis of 8-bromo-α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 15.

w = 0.1281 g.; V = 99.857 ml.; $A_0$ = 5.022 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 9.996 | 1.680 | 5.053 | 0.8492 | 47.96 |
| 9.996 | 2.795 | | 1.413 | 87.80 |
| 9.996 | 3.862 | | 1.952 | 132.74 |
| 9.989 | 5.150 | | 2.605 | 198.94 |
| 9.988 | 6.520 | | 3.299 | 295.07 |
| 10.01 | 7.260 | | 3.665 | 368.84 |
| 9.990 | 8.065 | | 4.079 | 491.18 |
| 9.982 | 9.360 | | 4.738 | equilibrium |
| 9.982 | 9.350 | | 4.733 | equilibrium |

$X_{eq.av.}$ = 4.736 x $10^{-3}$; k = 6.11 x $10^{-5}$ sec.$^{-1}$.

Table XLV. Solvolysis of 8-methyl-α-naphthylcarbinyl chloride in 0.32 m water-formic acid. Run 16.

w = 0.0987 g.; V = 100 ml.; $A_0$ = 5.18 x $10^{-3}$ M.

| Pip. Vol. (ml.) | Titre (ml.) | M $AgNO_3$ x $10^3$ | [X] x $10^3$ | t (min.) |
|---|---|---|---|---|
| 9.991 | 9.030 | 5.053 | 4.567 | 8.90 |
| 9.982 | 9.500 | | 4.809 | 16.12 |
| 9.990 | 9.540 | | 4.825 | 19.89[b] |
| 9.990 | 9.565 | | 4.838 | equilibrium |
| 9.996 | 9.545 | | 4.825 | equilibrium |
| 9.996 | 9.565 | | 4.835 | equilibrium |

$X_{eq.av.}$ = 4.831 x $10^{-3}$; k[a] = 3.8 x $10^{-3}$ sec.$^{-1}$

[a] Rate constant obtained from estimation of half-life treating data as simple FIRST ORDER REACTION.

[b] Taken as infinity titre.