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A MECHANISTIC STUDY OF SOME REACTIONS OF 2-ARYL-2-PROPYL CHLORIDES

by

© LOIS B. GREEN

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "A Mechanistic Study of Some Reactions of 2-Aryl-2-propyl Chlorides" submitted by Lois B. Green in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

David Dawson
Supervisor

External Examiner

Date 27 August 1969

THIS WORK IS DEDICATED

TO

A GOOD CHEMIST AND LOVING HUSBAND:

ROBERT

Without your unfailing support and constant encouragement this volume had not been written

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ABSTRACT

The ethanolysis of 2-phenyl-2-propyl chloride (RCl) proceeds through ionic intermediates. The addition of tetrabutylammonium azide causes diversion of some of the starting material from products of ethanolysis to 2-phenyl-2-propyl azide. Three schemes have been considered for the reaction: (a) nucleophilic displacement on the substrate by azide ion; (b) the formation of organic azide and ethanolysis products from the same intermediate(s); (c) a pathway involving two or more intermediates, one of which is capable of reacting to give solvolysis products but not of capture by azide ion.

A kinetic analysis of each of the three schemes shows that the reaction pathway for the ethanolysis of RCl is best represented by scheme (c). In contrast, the results of kinetic and product studies for the reaction of p-methoxybenzyl chloride in the presence of azide ion are best explained within the context of scheme (a).

Product studies for 2-p-methoxyphenyl-2-propyl chloride and 2-p-tolyl-2-propyl chloride give results that are consistent with a reaction scheme similar to that for 2-phenyl-2-propyl chloride.

The reaction of 2-p-nitrophenyl-2-propyl chloride does

not proceed in the same manner as the reaction of the unsubstituted compound. It is suggested that the former reacts in a manner analogous to the reaction of 2-p-nitrophenyl-2-propyl chloride with sodium thiophenoxide, which has been investigated by Kornblum and coworkers.

An investigation of the reaction for 2-p-acetylphenyl-2-propyl chloride shows the reaction pathway to be (a) or (b) rather than (c).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Chemists have long been fascinated by the mechanisms by which reactions occur. The devising of methods of studying reactions in order to glean information about possible intermediates and reaction pathways has occupied

a very large proportion of their time during the last half-century. A great deal of effort has been directed towards the elucidation of substitution type, or displacement reactions at saturated carbon atoms. Some of the first detailed kinetic studies were carried out by Hughes, Ingold, and coworkers.

They found the base catalyzed hydrolysis of methyl bromide in 90% aqueous acetone to be predominantly second order, dependent upon the concentration of starting material, and upon hydroxide ion concentration(1). When the substrate was changed to ethyl bromide, i.e. a methyl group was substituted for one of the hydrogens of the substrate, a decrease in second-order rate constant relative to methyl bromide was observed. On substitution of a second hydrogen by a methyl group to give isopropyl bromide, a further decrease in the second-order rate constant was observed. However, when all of the hydrogens of methyl bromide were substituted by methyl groups to give tert-butyl bromide, the reaction rate was observed to increase sharply and to become independent of hydroxide ion concentration.

The results were interpreted in terms of the now familiar S_N1 and S_N2 displacement reactions. It was suggested that the methyl, ethyl and isopropyl bromides

were undergoing a second-order displacement reaction, while the reaction of tert-butyl bromide was occurring by a two-step process involving an ionic intermediate, the first ionization step being slow and rate-determining.

$$RBr \underset{\text{slow}}{\rightleftharpoons} R^+ + Br^- \xrightarrow[\text{fast}]{H_2O} ROH + HBr \qquad [1]$$

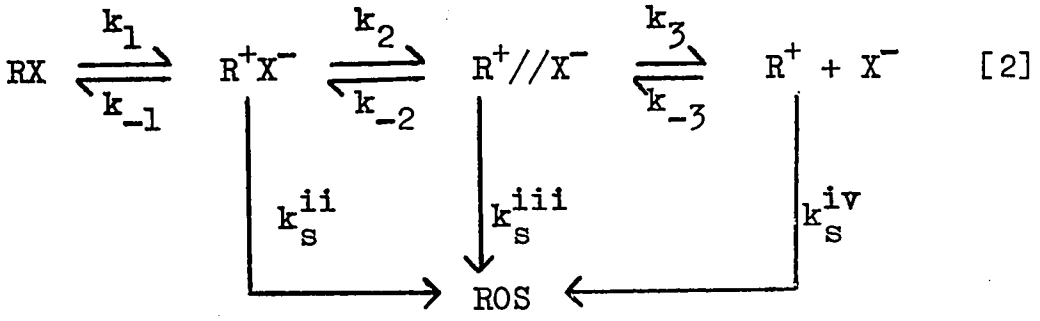
An immediate consequence of a reaction of this type is that the addition of a common ion salt should slow the reaction by causing return to starting material. Ingold, Hughes, et al.(2) found evidence for such a mass law effect on studying the kinetics and effects of salts on p,p'-dimethylbenzhydryl chloride in aqueous acetone. Since that time, the observation of the mass law effect has been widely employed as a tool in the study of ionic intermediates.

A second consequence of a reaction scheme of type [1] is that, since it predicts that a carbonium ion, which is a planar species, will be formed as an intermediate, an optically active starting material should yield racemic products. The use of optically active materials, then, should be another tool in the study of reaction mechanisms. In fact, when this study was carried out by Hughes et al. for 2-bromooctane(3) in

60% ethanol, the products formed were found to be only 30% racemized and 70% inverted. Similarly for 2-methyl-2-chlorooctane(4) in 60% aqueous ethanol, the products were found to be 80% racemized and 20% inverted. Hammett suggested that the lack of complete racemization could be explained by the intervention of ion pairs(5). In the early 1950's, this suggestion was substantiated.

Winstein, Young and Goering studied the acetolysis of α,α-dimethylallyl chloride(6). They found that, as the reaction proceeded, the first-order rate constant drifted downwards for the first 30% of the reaction, then remained constant. Investigation showed that the α,α-dimethylallyl chloride was rearranging to γ,γ-dimethylallyl chloride. By the time that 30% of the solvolysis reaction was completed, only the γ,γ compound was isolable, and the rate of the reaction was the same as that found for the rate of reaction of an authentic sample of γ,γ-dimethylallyl chloride. The rearrangement from α,α to γ,γ-dimethylallyl chloride must be proceeding <u>via</u> an ionic intermediate, but there was no evidence for mass law effect. Therefore, the intermediate could not be a free carbonium ion. Instead, the authors interpreted the results as arising from "internal return" from an ion pair intermediate.

It thus became necessary to elaborate the kinetic scheme of Ingold to include an ion pair form as well as the dissociated form of the carbonium ion. The observations of Winstein's group led them to consider the necessity of incorporating more than one ion pair in the reaction sequence. They proposed an overall mechanism for reactions of this type as: (7)



[2]

In this scheme, k_1 is the rate constant for ionization, R^+X^- is an intimate ion pair, two ions of opposite charge in contact with no solvent molecules separating them, $R^+//X^-$ is a solvent-separated ion pair, the two ions being separated by a small number of solvent molecules, and R^+ and X^- represent dissociated ions.

The furthest stage of ionization-dissociation reached in any reaction involving ionization of RX may vary. Solvolysis products might arise from more than one of the varieties of carbonium ions.

The suggestion of more than one intervening ion pair was the result of the study of the effect of salts on solvolysis reactions that yield carbonium ions with bridged structures. One of the best examples is the acetolysis of optically active threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate(7). For this compound, the rate constant for ionization is measured by the polarimetric rate constant k_α. It was found that k_α was four times as large as k_t, the solvolysis rate constant. The addition of lithium perchlorate to the reaction mixture caused an increase in k_α, which was linear with salt concentration; this was described by the authors as a "normal" salt effect. The effect of the salt on the solvolysis rate constant, k_t, was quite different. The addition of lithium perchlorate caused an initial steep rise in rate constant, a "special" salt effect, then at higher salt concentrations, a linear dependence on salt concentration, of the same magnitude as found for k_α. The results of the study are portrayed graphically in Figure 1.

Observation of the special salt effect on k_t only must be due to the interaction of the salt with an intermediate rather than with the substrate. Extrapolation of the normal salt effect portion of the curve for k_t gives an intercept k^o_{ext}, the difference between k^o_t and k^o_{ext} being a rate acceleration due to the special

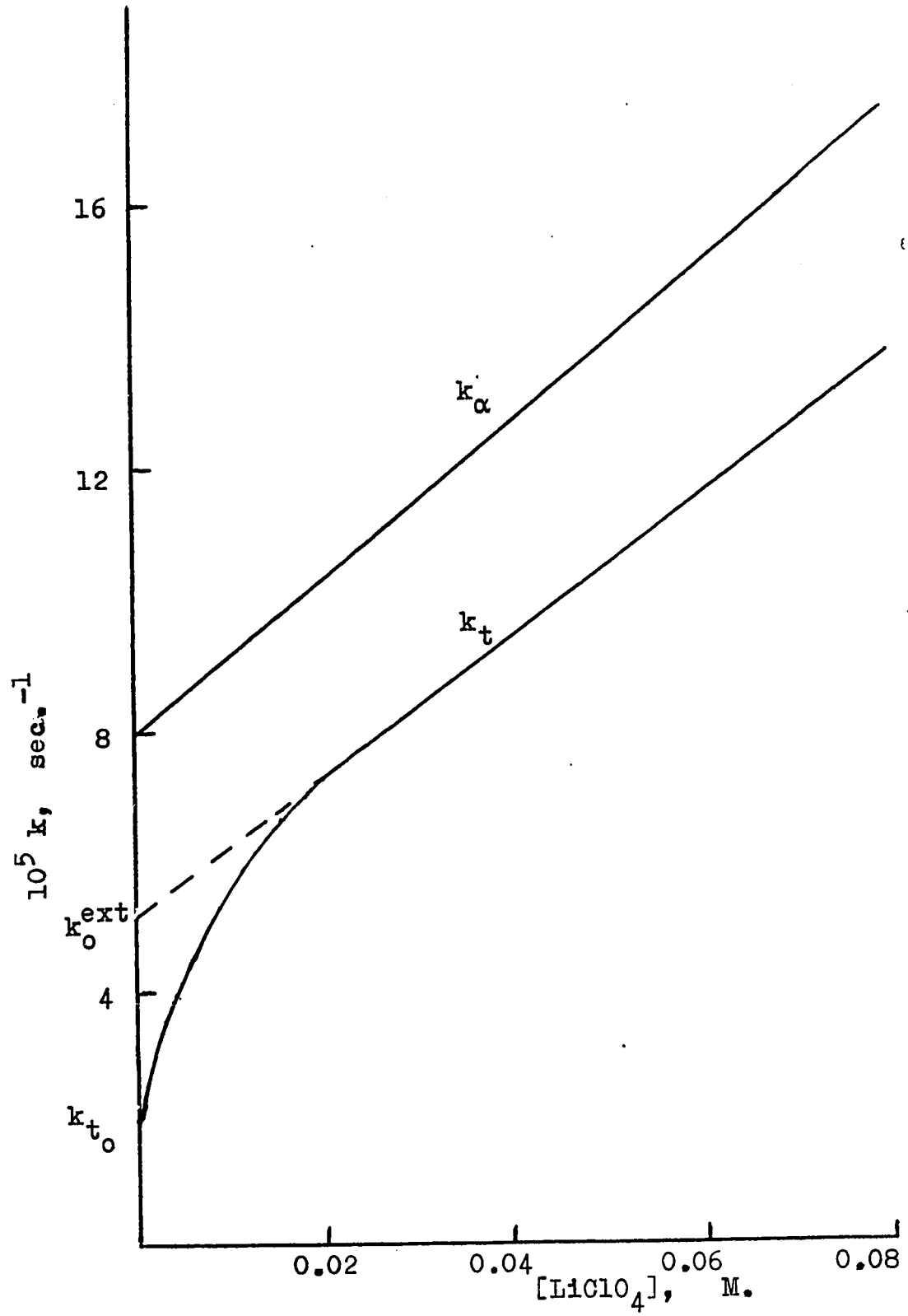


Figure 1. Effect of Lithium Perchlorate on Acetolysis of threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25°C.

salt effect. If the effect of the salt were to prevent the return of all ion pairs to substrate, then it would be expected that k^{o}_{ext} should equal k_{α}. As can be seen from Figure 1, this was not observed. Therefore, the salt must be acting to prevent only part of the ion-pair return. Hence, it was necessary to invoke at least two intermediates. Since it had been shown previously that dissociated ions were not involved in the solvolysis of threo-3-p-anisyl-2-butyl arenesulfonates, it became necessary to invoke two ion pairs to explain the results.

Observation of the special salt effect also required at least two ion-pair intermediates in the solvolysis of cholesteryl tosylate(8) and 2-anisyl-1-propyl tosylate(9).

Elucidation of the reaction mechanism for the solvolysis of these systems is dependent on two necessary conditions: an independent measure of the ionization rate constant k_1, and a difference in the effect of salt on k_1 and the solvolysis rate constant, k_t. For compounds such as 2-p-anisyl-2-butyl arenesulfonates, which yield bridged intermediates on ionization, k_1 equals the polarimetric rate constant k_{α}. Many compounds, however, do not necessarily racemize on ionization, in which case return to starting material without loss of optical activity may occur; then k_{α} can be only an estimate of a lower limit of k_1.

Furthermore, lithium perchlorate fails to induce a special salt effect in some solvents. There was, for example, no evidence of a special salt effect on the ethanolysis of threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate in the presence of the salt, even though ethanol, being similar in ionizing power to acetic acid, could be expected to support similar intermediates.

In the study of systems where conditions are such that the special salt effect might not be observed, other means of detecting intermediates must be devised. One such method is the use of radioactive labelling techniques. This method was used successfully by Winstein et al. in the study of the benzhydryl system. The rate of loss of optical activity of optically active p-chlorobenzhydryl chloride(11) in 80% aqueous acetone was found to be 2.5 times as fast as its rate of solvolysis, and two times as fast as the sum of the rate constants for solvolysis plus exchange with radioactive chloride ion. The exchange rate must be a measure of the maximum amount of return to starting material from dissociated ions; most of the racemization must occur without the formation of free ions, and must involve ion-pair return.

The use of oxygen-18 labelling has also been useful in detecting intermediates. For benzhydryl p-nitrobenzoate carbonyl-^{18}O in 90% aqueous acetone, scrambling

of the labelled oxygen was found to be faster than solvolysis by a factor of three.(12) The oxygen-18 equilibration must be due to return to starting material from ion pairs. The question of whether this return involved one or more ion pairs was later answered by another experiment of Goering and Levy(13). In the study of solvolysis of optically active p-chlorobenzhydryl p-nitrobenzoate in 90% aqueous acetone, the rate constant for oxygen-18 equilibration was found to exceed that for loss of optical activity by 2.6, indicating that return occurred with predominant retention of configuration. On the addition of sodium azide, however, oxygen-18 equilibration continued to occur, while the rate constant for racemization of the starting material fell to zero. Clearly, the azide ion is intercepting an intermediate that would otherwise return with loss of configuration, while failing to intercept some other intermediate that returns with retention of configuration, but with scrambling of the acyl and ether oxygens of the benzoate moiety. Since it was shown that dissociated ions are not involved in the reaction, both intermediates must be ion pairs.

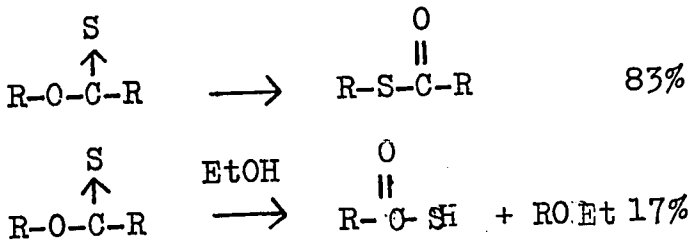
Another method of detecting intermediates in solvolytic reactions is to study isomerization reactions of the substrate. There are several types of compounds

for which recombination of the ions produced may lead to stable products isomeric with the starting material. For example, it has been shown(14) that benzhydryl thiocyanate rearranges to benzhydryl isothiocyanate in several solvents.

$$RSCN \longrightarrow RNCS$$

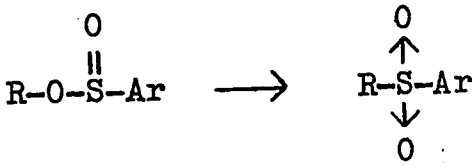
The kinetic order, salt and substituent effects of the reaction indicate that it is proceeding by way of a rate-determining ionization. On the addition of ^{35}S-labelled NaSCN to the reaction, some isotopic exchange occurred; however, the rate of isomerization was substantially faster than the rate of the exchange reaction. The authors calculated the upper limit of product formation from exchange to be 31%, assuming all the activity incorporated to have entered <u>via</u> ionization. Thus, it was concluded that a minimum of 70% of the reaction proceeded through ion pair formation.

A similar experiment has been performed for the isomerization of benzhydryl thionbenzoate(15). In ethanol, 83% thiol benzoate and 17% ether are produced.

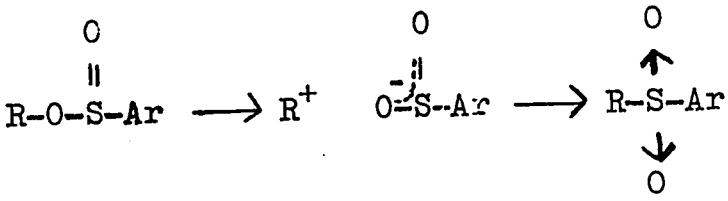


Substituent effects indicate that the reaction proceeds *via* an ionic pathway. However, there is no exchange found on the addition of p-methoxythiobenzoate anion. The results are consistent with ion pair return.

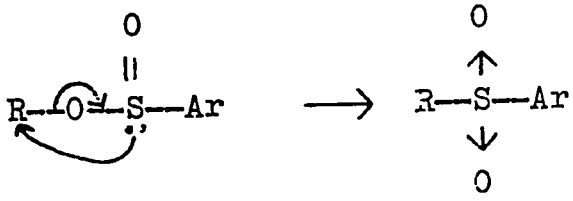
Arenesulfinate esters are potentially useful for isomerization studies, since they are often capable of isomerization to sulfones that are stable under the



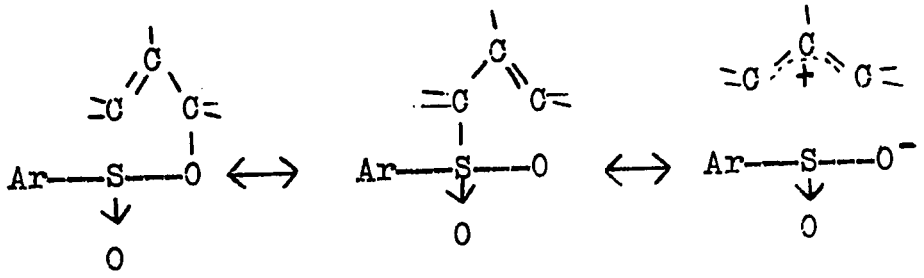
reaction conditions. Considerable work on such systems has been carried out in these laboratories as well as by other workers. Isomerization to sulfone could occur either by an ionic pathway



or by a cyclic rearrangement mechanism.



Braverman and Darwish, on examination of several allylic systems(16), found that the results were best interpreted by a transition state which may be pictured as a resonance hybrid:



the importance of the ionic structure was dependent upon the substituents on the allyl group and on the reaction conditions.

In non-allylic systems, the evidence indicates that rearrangement to sulfone may proceed <u>via</u> an ionic pathway. The studies by Preston of the rearrangement of trityl arenesulfinates(17), by Mermelstein of 2-aryl-2-propyl benzenesulfinates(18), and by Grover of benzhydryl 2,6-dimethylbenzenesulfinate(19), are all consistent with isomerization occurring <u>via</u> an ionic pathway.

Winstein's mechanistic scheme (Equation [2]), involving as it does various intermediates, allows for the formation of products by several different pathways. Products might be formed from the intimate ion pair, the solvent separated ion pair, the dissociated ion; or it might arise from two or all three of these species,

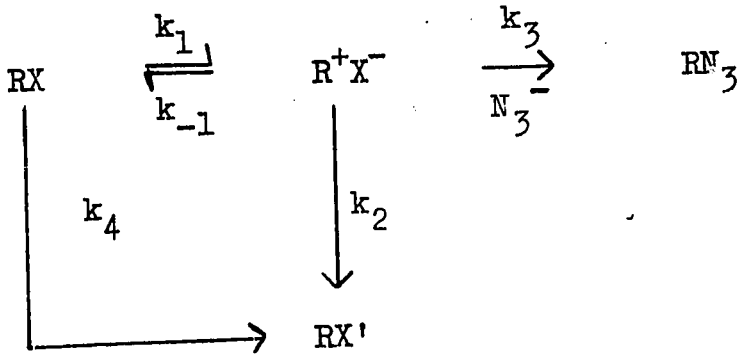
depending on the stability of the intermediates formed. Winstein *et al.* have suggested that the solvolysis reactions of tert-butyl chloride(20) and α,α-dimethylallyl chloride(6) occur exclusively by way of the intimate ion pair intermediate.

For very stable systems, it would be expected that the other end of the scale should be approached. Compared to other systems that undergo reaction *via* carbonium ion intermediates, the trityl system should be a structural extreme in stability and as such provide a calibration point with which to compare the others. As such, it has been the subject of considerable study.

Winstein and Appel have recently carried out an extensive study of trityl benzoate in acetone(21, 22). They found that the rate constant for oxygen-18 equilibration greatly exceeded the rate constant for exchange with carbon-14-labelled benzoate (k_{14_C}), which equalled the rate constant for consumption of azide ion (k_{N_3}). Both k_{14_C} and k_{N_3} were found to be independent of the concentration of azide salt. The addition of azide salt suppressed exchange, but not oxygen-18 equilibration. The results are best explained by at least two intermediates, one of which is not capable of diversion to exchange products.

Preston and Darwish(17) studied the trityl system in

a slightly different manner, the rearrangement of trityl 2-methylbenzenesulfinate in several non-hydroxylic solvents yielding most interesting results. When this compound was allowed to react with azide ion in chloroform, there was observed concurrent rearrangement to sulfone and formation of trityl azide. With increased azide ion concentration, the fraction of azide formed increased while the fraction of sulfone decreased. The possibility of a direct displacement reaction by azide ion was ruled out experimentally. The evidence presented was best explained by a reaction scheme of the type

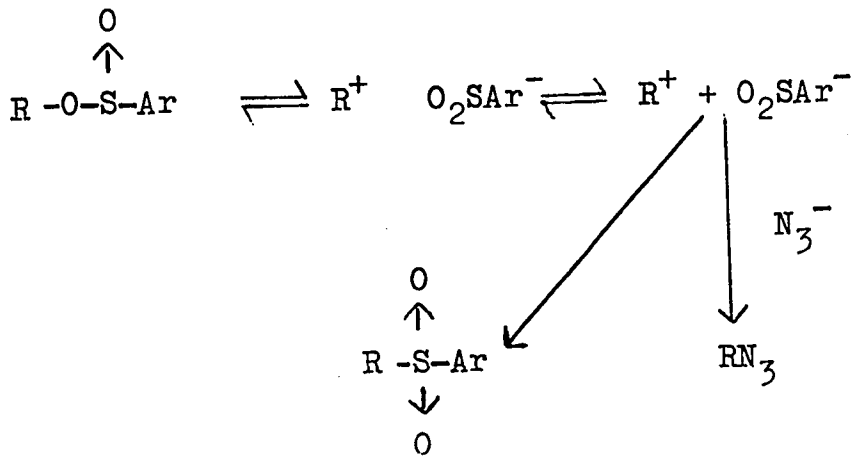


where k_4 represents sulfone formation by all paths other than those capable of being trapped by nucleophiles. A kinetic analysis of this scheme yields the expression

$$\frac{1}{F_{azide}} = \frac{k_4/k_1\ (k_{-1} + k_2) + k_2}{k_3\ [N_3^-]} + \left(\frac{k_4}{k_1} + 1\right). \quad [3]$$

A plot of $1/F_{azide}$ *vs.* $1/[N_3^-]$ should give a straight line with an intercept of $(k_4/k_1 + 1)$. When such a plot was made, the intercept was found to be unity, indicating that $k_4 = 0$, and that all the sulfone and azide must be arising from a common intermediate.

Persad and Darwish(23) subsequently showed that the reaction of trityl 2,6-dimethylbenzenesulfinate in acetonitrile was subject to common ion rate depression, and concluded that, assuming the 2-substituted and 2,6-disubstituted esters undergo the same type of reactions, the trappable species is the free trityl ion; the mechanism proposed for the reaction was



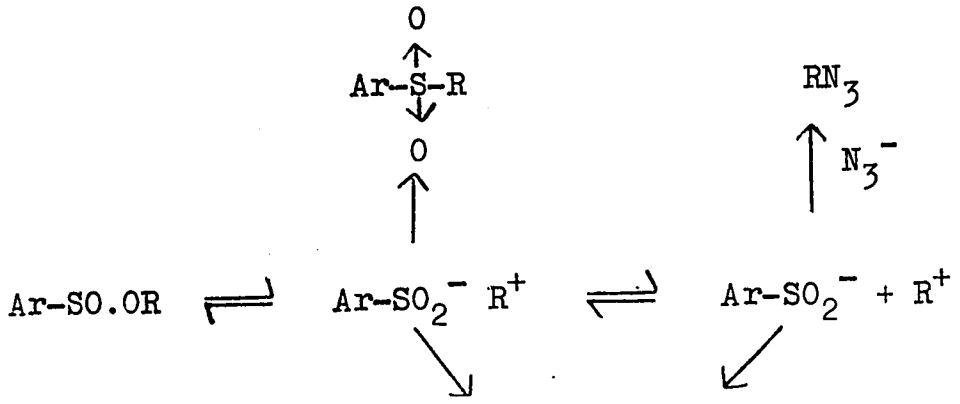
In the study of this limiting system, a new tool for deriving information about intermediates had presented itself, the use of a nucleophile such as azide ion to distinguish between two types of intermediates,

those trappable and those not capable of capture by nucleophile, as determined by the (k_4/k_1) ratio obtained from plots of $(1/F_{azide})$ *vs.* $(1/[N_3^-])$.

Although no non-capturable species was found for the trityl system, it was borne in mind that this is a limiting case, and it was thought that in a less structurally extreme system, two types of ions might be able to be identified. Mermelstein(18) initiated the study of the solvolysis and rearrangement of 2-aryl-2-propyl benzenesulfinates in several solvents. The relative rates of ionization and isomerization in acetic acid, ethanol and 60% aqueous ethanol were consistent with an ionic process. On addition of 2,6-dimethylbenzenesulfinate, no common-ion rate depression was observed for 2-phenyl-2-propyl or 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate. The reaction of the esters in the presence of 4-methylbenzenesulfinate anion yielded no exchange product. All these results are consistent with formation of the sulfone rearrangement product *via* ion-pair return.

The effect of added azide ion on the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate was studied extensively. In anhydrous ethanol, on increasing the azide ion concentration from 0 to 0.28M, the fraction of solvolysis decreased from 0.9 to 0.6, the fraction of

rearrangement changed from 0.095 to 0.071, and the fraction of 2-phenyl-2-propyl azide increased from 0 to 0.25. A plot of the results in the form of $(1/F_{azide})$ *vs.* $(1/[N_3^-])$ gave an intercept of 2.4. Examination of these results within the context of the reaction scheme proposed by Preston gives a value of (k_4/k_1) of 1.4. Since k_4 represents sulfone formation by a pathway not capable of capture by nucleophile, the results require at least two intermediates and are best explained by a minimum kinetic scheme of the type



where $Ar\text{-}SO_2^- + R^+$ may be a solvent-separated ion pair, or dissociated ions, or both.

The kinetic expression in Equation [3] was used in this case to determine the reaction pathway of a system wherein the existence of ion pair intermediates was

demonstrable by some other means, in this case by isomerization of the starting sulfinate to sulfone. It was desirable to demonstrate its use for a system not easily analyzed by some other means. Accordingly, we wished in this study to make use of this kinetic scheme to elucidate the reaction pathway of some simpler system. We chose to study the effect of a nucleophile, azide ion, on the ethanolysis of the 2-aryl-2-propyl chloride system. We proposed to determine the pathway of the reaction and simultaneously to test the assumptions made in the derivation of the kinetic expression we were to use.

ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE

CHAPTER 1

INTRODUCTION

In this chapter, the preparation of 2-phenyl-2-propyl chloride and the products of its ethanolysis are described. The rate constants for ethanolysis of

2-phenyl-2-propyl chloride under a variety of conditions were measured and the products of reactions determined. The effects of several addends on reaction rate and on product formation were evaluated.

RESULTS

Preparation of 2-Phenyl-2-propyl Chloride

2-Phenyl-2-propyl chloride was prepared from 2-phenyl-2-propanol, 2-phenylpropene, or a mixture of the two by the method of H. C. Brown(24). The nmr spectrum of each sample synthesized had a small peak at τ 8.0, indicative of the presence of 2-phenylpropene as an impurity. Analysis of the material by g.c. using a commercial column Q at 150° on a Vapour Refractometer Model 154D gave two peaks of relative intensity 97:3. The smaller peak had the same retention time as an authentic sample of 2-phenylpropene. On solvolysis of the material, 96 ± 1 % of theoretical acid was released. Hence, the starting material used in this study was considered to be 96% 2-phenyl-2-propyl chloride and 4% 2-phenylpropene.

Preparation of Anhydrous Ethanol for Rates

When anhydrous ethanol was prepared from 95% ethanol by drying over lump calcium oxide followed by treatment with magnesium ethoxide according to the method of Lund and Bjerrum(25), the material showed a large peak blocking the ultraviolet region below 300 nm. Ethanol so prepared turned yellow on standing. Upon treatment with 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone of acetone precipitated and was positively identified by nmr, infrared analysis, and mixed melting point determination. Investigation showed that acetone was not present in the starting 95% ethanol. After treatment with calcium oxide, however, the acetone was found. It was assumed to be formed by basic oxidation of some impurity in the starting material.

Anhydrous ethanol prepared by the reaction of distilled "98" ethanol with magnesium ethoxide was found not to absorb in the ultraviolet above 210 nm and to contain less than 0.01% water, as determined by Karl Fischer titration.

Preparation of Solvolysis Products

The expected products of ethanolysis of 2-phenyl-2-propyl chloride under the reaction conditions employed

were 2-phenylpropene, 2-phenyl-2-propyl ethyl ether, and 2-phenyl-2-propyl azide. They were obtained as described below.

Commercial 2-phenylpropene was used after distillation.

2-Phenyl-2-propyl ethyl ether was prepared according to the general method of Wallis and Bowman(26). The reaction of 2-phenyl-2-propanol and excess anhydrous ethanol in the presence of concentrated sulfuric acid gave the desired product.

The reaction of 2-phenyl-2-propyl chloride with sodium azide in aqueous acetone, followed by chromatography over alumina gave the desired 2-phenyl-2-propyl azide.

Preparation and Analysis of Tetrabutylammonium Azide

Tetrabutylammonium azide was prepared by the addition of hydrazoic acid to an aqueous solution of tetrabutylammonium hydroxide, which was prepared from tetrabutylammonium bromide. The salt was found to be extremely hygroscopic. This salt had not been previously characterized satisfactorily. Several methods of analysis were attempted. Analysis by infrared or by ultraviolet spectroscopy were not successful. Analysis for azide ion by the method of van de Meulen(27) could not be used

because of interference by the tetrabutylammonium cation. A satisfactory carbon and hydrogen analysis was obtained indirectly as described on page 243. A melting range for the compound was obtained using a dry box technique.

Kinetic Runs

Titrimetric kinetic runs were carried out in volumetric flasks at 25.00 $\pm$0.03°, using Titrimetric Procedure A, B, or C (page 246), depending on which was appropriate for the reaction mixture. The concentration of starting material in most cases was 0.02-0.03 M. Usually the reactions were followed to 80-90% completion. The first-order rate constants were calculated from the experimental infinity values, obtained after 10 and/or 20 half-lives of the reaction. Thus, the rate constant is a measure of the total reaction rate. The acid titre for these reactions was found to remain constant for at least 50 half-lives of reaction.

Kinetic runs measured by ultraviolet spectroscopy were carried out in cleaned quartz cells at 25.10 $\pm$0.03° in the thermostated cell compartment of a Beckman DU spectrophotometer, by following the appearance of a band at 242 nm due to the formation of 2-phenylpropene (page 252). The concentration of starting material used

in the runs was 4-6 x 10^{-4} M. The first order constants were calculated from the experimental absorbance values using the equation

$$k = \frac{2.303}{t} \log \frac{A_\infty - A_o}{A_\infty - A}$$

where A is the absorbance at time t, A_o the absorbance at zero time, and A_∞ the absorbance after 10 or more half lives. A_∞ was found to be constant for at least 100 half-lives.

For a few of the runs in which tetrabutylammonium azide was added, the reaction rate was followed by the appearance of the infrared band at 4.76 μm which was due to the formation of 2-phenyl-2-propyl azide (page 247). The first order rate constant was calculated from the experimental values of azide formed using the equation

$$k = \frac{2.303}{t} \log \frac{[RN_3]_\infty - [RN_3]_o}{[RN_3]_\infty - [RN_3]}$$

where $[RN_3]$ is the concentration of 2-phenyl-2-propyl azide formed at time t, $[RN_3]_o$, the concentration of the azide at zero reaction time, $[RN_3]_\infty$, the concentration after 10 half lives.

Calibration Curve for Azide Analysis

In order to determine the relationship between absorbance and concentration of 2-phenyl-2-propyl azide and to check on the efficiency of the extraction procedure, aliquots of solution containing accurately known quantities of the azide were carried through a standard extraction procedure (page 253). Then the sample was dissolved in a known volume of carbon tetrachloride. The transmittance, I, was measured between 4.4 and 5.1 μm. From the transmittance at 4.76 μm, the absorbance, $\log I_o/I$, was calculated and plotted against the concentration of 2-phenyl-2-propyl azide, $[RN_3]$; see Table I and Figure 2. The plot is linear, but does not pass through the origin. Two separate determinations, made several months apart, gave results which were identical within experimental error.

Reaction in Anhydrous Ethanol in the Presence and Absence of Lithium Ethoxide

The reaction of 2-phenyl-2-propyl chloride in 100% ethanol with no added base was studied by Titrimetric Procedure A (page 247) and by Ultraviolet Spectroscopy (page 252). The results are presented in Table II; 97% of the theoretical infinity was found in the titrimetric studies.

TABLE I

THE RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION OF 2-PHENYL-2-PROPYL AZIDE (RN_3) AT 4.76 μm.

4.907 ml. aliquot residue dissolved in 2.056 ml. CCl_4

Sample No.*	10^3 [RN_3] M	log I_0/I
I-277-a	11.21	0.490, 0.514
I-277-b	8.39	0.379, 0.366
I-277-c	5.61	0.228, 0.222
II-212-a	5.32	0.221, 0.210
II-212-c	4.60	0.198, 0.201
I-277-d	4.19	0.146, 0.149
II-212-b	2.66	0.111, 0.108
I-277-e	2.10	0.065, 0.061
I-277-f	1.12	0.026, 0.025
II-212-d	1.04	0.014, 0.013
II-212-e	0.904	0.015, 0.016

*Sample numbers quoted in this work refer to the number of the research notebook and the page number in it. For example, I-277 means the work is recorded on page 277 of the first notebook.

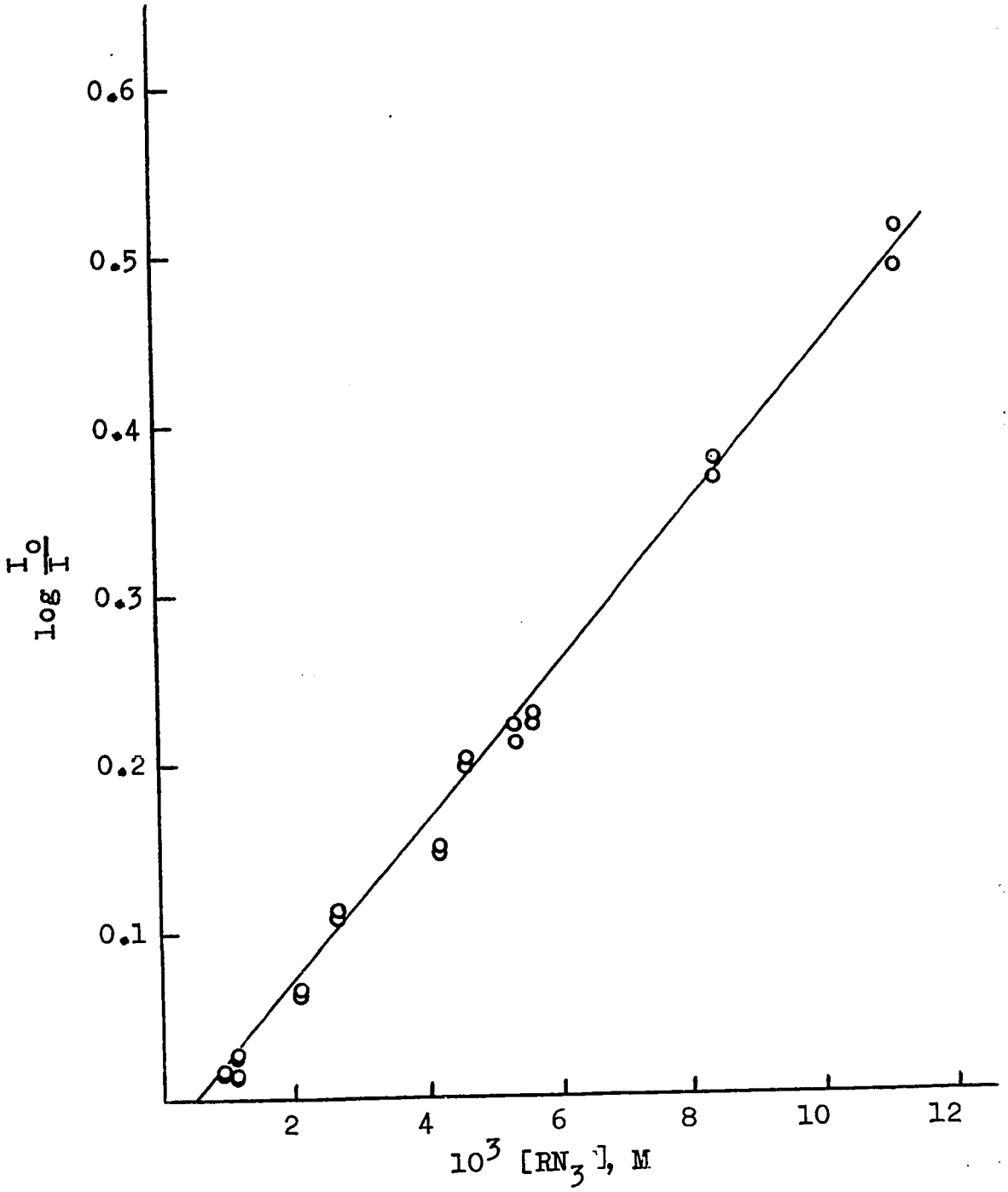


Figure 2. Relationship between Absorbance and Concentration for 2-Phenyl-2-propyl Azide.

TABLE II

RATE OF ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE (RCl) IN 100% ETHANOL AT 25.00°

Run No.	[RCl] M	Procedure	$10^4 k_1$ (sec^{-1})
I-103	0.03457	Titr. A	3.66 ±0.05
I-105	0.02718	Titr. A	3.71 ±0.05
II-142	4.790×10^{-4}	Ultraviolet	3.88 ±0.13
II-153	4.711×10^{-4}	Ultraviolet	3.78 ±0.07

In each case, good first-order rate constants were obtained. The average observed rate constant, 3.8×10^{-4} sec^{-1}, is in reasonable agreement with that reported by Brown(24) for the same conditions, 3.9×10^{-4} sec^{-1}.

When lithium ethoxide was added, the reaction was studied using Titrimetric Procedure C (page 248) and ultraviolet spectroscopy. The precision of rates studied using Procedure C was low due to the inherent difficulties in exact duplication of each point when using such an extraction procedure. Much more precise results were obtained from study of rates using the ultraviolet method. The results for both methods are presented in Table III and Figure 3.

The rate constants obtained from the two methods are within experimental error of each other. The addition of 0.1 M lithium ethoxide appears to have no effect on the rate of ethanolysis of 2-phenyl-2-propyl chloride.

The Effect of Added Salts on the Rate of Ethanolysis of 2-Phenyl-2-propyl Chloride

The rate of ethanolysis at 25° of 2-phenyl-2-propyl chloride was studied in the presence of several added salts in both the presence and absence of lithium ethoxide.

TABLE III

EFFECT OF LITHIUM ETHOXIDE ON THE RATE OF ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25°

Run No.	[RCl] M	[EtOLi] M	$10^4 k_1$ (sec^{-1})
a) Titrimetric Procedure			
I-103	0.03457	0	3.66 ±0.05
II- 67	0.02372	0.04003	3.60 ±0.13
II- 65	0.02645	0.07020	3.95 ±0.58
II- 73	0.02635	0.07142	3.86 ±0.41
b) By Ultraviolet Spectroscopy			
II-153	4.790×10^{-4}	0	3.78 ±0.07
II-145	4.715×10^{-4}	0.02862	3.70 ±0.07
II-147	4.872×10^{-4}	0.1037	3.78 ±0.19

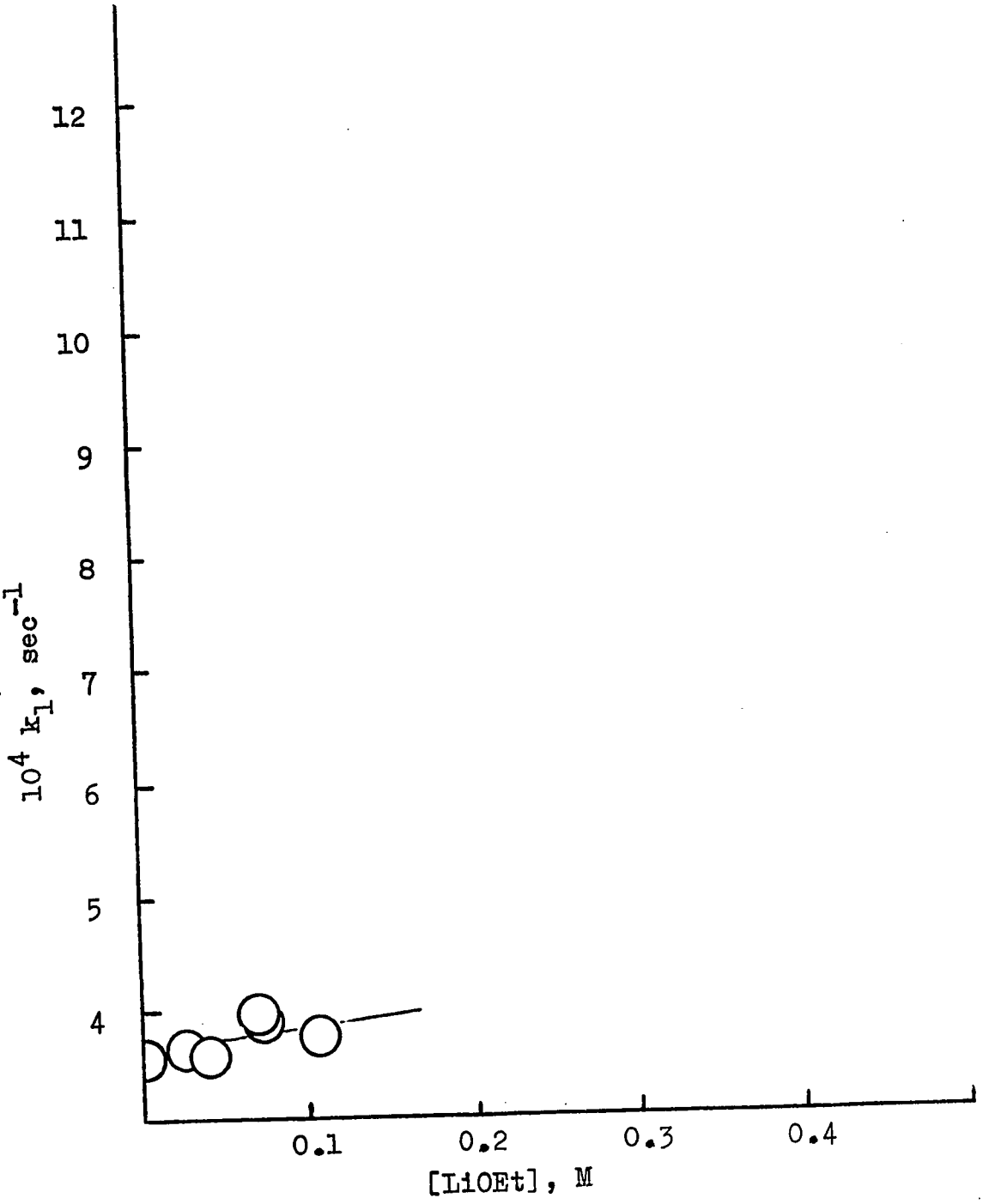


Figure 3. The Effect of Lithium Ethoxide on the Rate of Ethanolysis of 2-Phenyl-2-propyl Chloride.

The effect of tetrabutylammonium perchlorate was studied titrimetrically and using ultraviolet spectroscopy. When lithium ethoxide was present, the precision in measurement of the rate by titrimetry was very low. The titrimetric rate constant determined in the absence of base was also subject to large error. Study of this system by ultraviolet methods was much more satisfactory. The results are recorded in Table IV and plotted in Figure 4.

A small linear increase in rate constant with increasing salt concentration was observed. The addition of lithium ethoxide had no discernable effect on the results obtained.

The effect of addition of lithium perchlorate on the ethanolysis rate of 2-phenyl-2-propyl chloride was studied at 25° by ultraviolet spectroscopy. No base was added. The results are recorded in Table V and Figure 5. The increase in rate with increasing salt concentration was found to be linear. The results of a study of the effect of lithium chloride under the same conditions are also recorded in Table V and Figure 5. The limit of solubility of the salt, 0.1 M, curtailed the study. Up to this concentration, however, the salt appears to have only a slight effect on the rate constant of the reaction.

TABLE IV

EFFECT OF TETRABUTYLAMMONIUM PERCHLORATE (Bu_4NClO_4) ON THE RATE OF ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25° IN THE ABSENCE AND PRESENCE OF LITHIUM ETHOXIDE

Run No.	[RCl] M	[Bu_4NClO_4] M	[EtOLi] M	$10^4 k_1$, sec^{-1}
a) Titrimetric Procedure B				
I-103	0.03457	0	0	3.66 ±0.05
II- 91	0.02615	0.05165	0	4.13 ±0.21
II-105	0.02839	0.1495	0	4.18 ±0.21
II-117	0.02487	0.1536	0	4.53 ±0.23
II- 95	0.02747	0.2478	0	4.75 ±0.23
II- 99	0.02644	0.4035	0	5.16 ±0.50
b) Titrimetric Procedure C				
II- 65	0.02645	0	0.0400	3.66 ±0.13
II-119	0.02476	0.07451	0.0280	4.76 ±0.26
II-121	0.02464	0.1515	0.0630	5.51 ±0.42
II-123	0.02540	0.3416	0.0514	4.7 ±0.7
II-125	0.02599	0.1670	0.0330	4.82 ±0.31

TABLE IV (Continued)

Run No.	[RCl] M	[Bu_4NClO_4] M	[EtOLi] M	$10^4 k_1$, sec^{-1}
c) Ultraviolet Procedure				
II-153	4.711×10^{-4}	0	0	3.78 ± 0.07
III- 27	7.331×10^{-4}	0.0198	0	3.78 ± 0.09
II-236	3.027×10^{-4}	0.06547	0	4.45 ± 0.14
II-226	3.146×10^{-4}	0.1232	0	4.66 ± 0.25
II-196	4.985×10^{-4}	0.1967	0	5.22 ± 0.17
II-145	4.790×10^{-4}	0.0	0.0286	3.70 ± 0.07
II-155	5.354×10^{-4}	0.05866	0.0384	4.22 ± 0.09
II-177	4.211×10^{-4}	0.06046	0.0300	4.34 ± 0.18
II-172	5.473×10^{-4}	0.1597	0.0239	4.91 ± 0.14
II-161	4.613×10^{-4}	0.1628	0.0239	4.32 ± 0.13
II-167	4.011×10^{-4}	0.1682	0.0279	5.01 ± 0.17
II-163	4.723×10^{-4}	0.3194	0.0285	5.29 ± 0.14
II-185	3.846×10^{-4}	0.3242	0.0300	5.24 ± 0.17

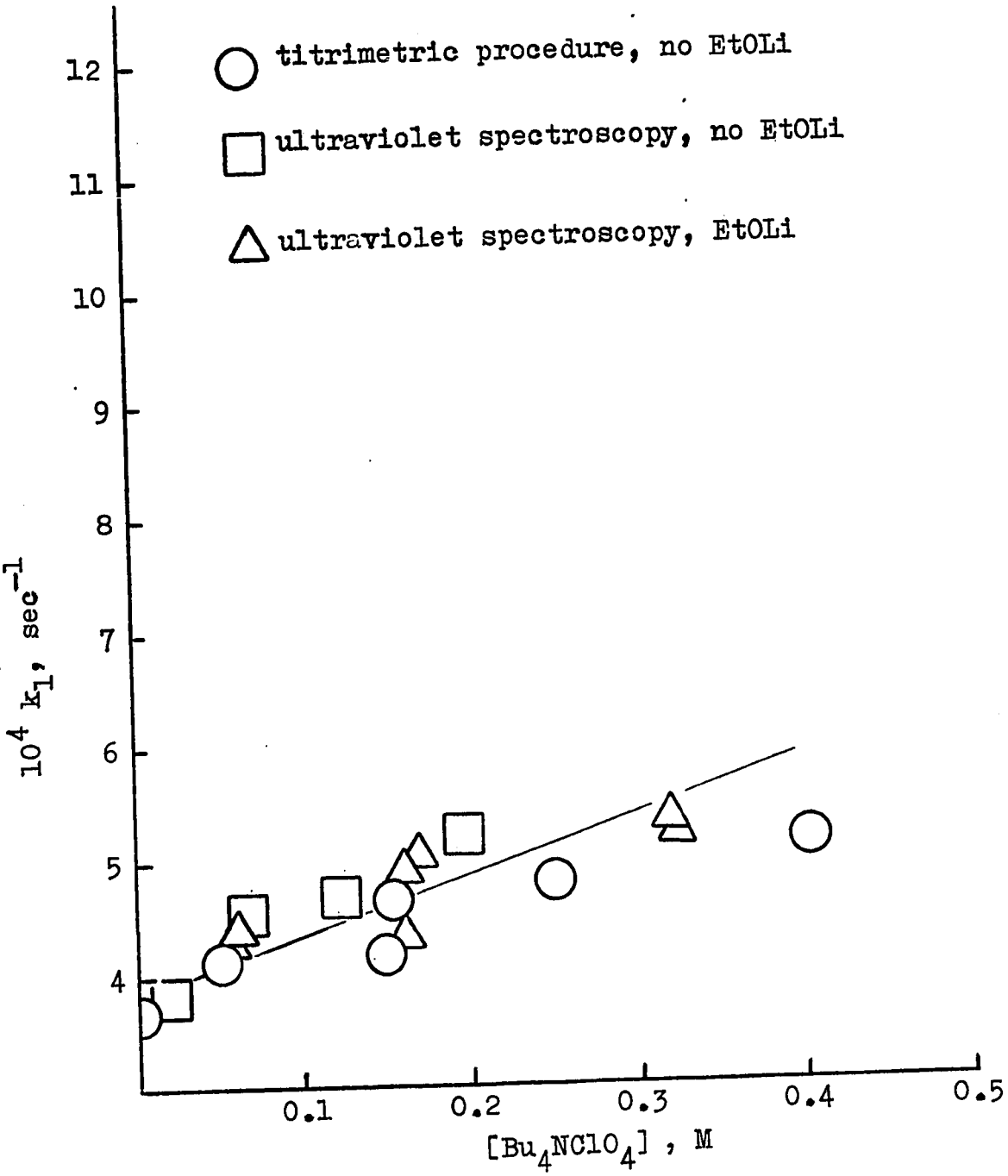


Figure 4. The Effect of Tetrabutylammonium Perchlorate on the Rate of Ethanolysis of 2-Phenyl-2-propyl Chloride.

TABLE V

THE EFFECT OF LITHIUM PERCHLORATE AND OF LITHIUM CHLORIDE ON THE RATE OF ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25.10° AS STUDIED BY ULTRAVIOLET SPECTROSCOPY

Run No.	10^4 [RCl] M	[salt] M	$10^4 k_1$, sec^{-1}
a) $LiClO_4$			
II-153	4.711	0	3.78 ±0.07
II-277	2.658	0.03477	4.42 ±0.17
III- 6	3.398	0.04492	4.53 ±0.18
II-289	3.784	0.05365	5.59 ±0.23
II-281	2.962	0.07128	5.71 ±0.23
II-267	2.657	0.07523	6.48 ±0.26
II-263	3.610	0.1732	8.14 ±0.33
II-297	2.847	0.2120	9.6 ±0.5
II-233	3.081	0.4085	12.6 ±0.9
b) LiCl			
III- 17	6.426	0.00886	3.82 ±0.09
III- 11	4.446	0.04793	3.90 ±0.13
III- 9	5.039	0.1008	4.20 ±0.17

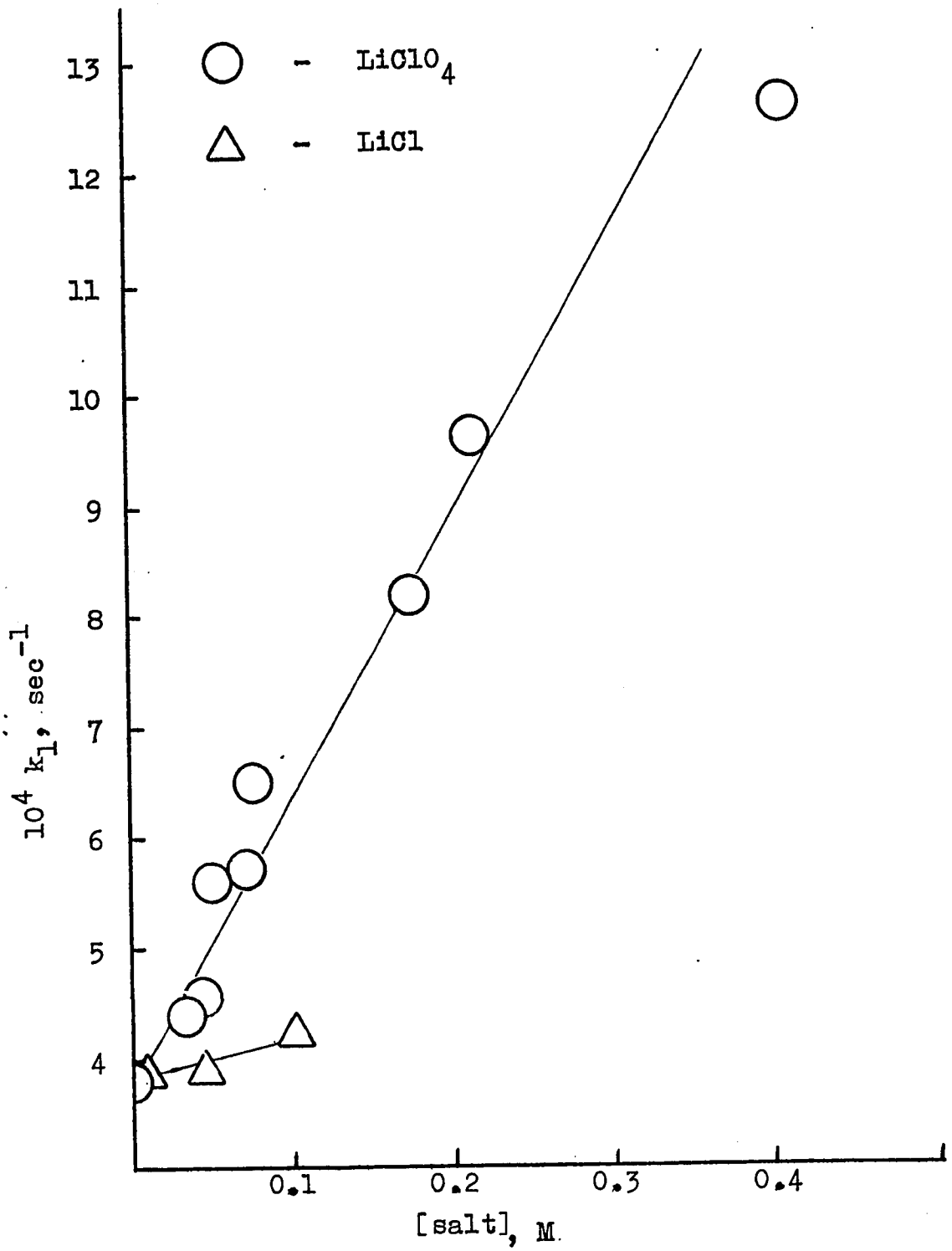


Figure 5. The Effect of Lithium Perchlorate and Lithium Chloride on the Rate of Ethanolysis of 2-Phenyl-2-propyl Chloride.

Effect of Tetrabutylammonium Azide on the Rate and Products of Ethanolysis of 2-Phenyl-2-propyl Chloride at 25°

The addition of tetrabutylammonium azide to the reaction mixture resulted in the diversion of some of the solvolysis products to 2-phenyl-2-propyl azide, with a consequent lowering of the infinity acid titre for the reaction.

As can be seen from the reaction sequence below, reaction with solvent results in the formation of acid, HCl, while reaction with salt, $M^+N_3^-$, results in formation of M^+Cl^- rather than HCl:

$$RCl + SOH \longrightarrow ROS + HCl$$
$$RCl + M^+N_3^- \longrightarrow RN_3 + M^+Cl^-$$

The decrease in acid titre should be a measure of azide formation. The amount of RN_3 could also be determined directly by measurement of the infrared band at 4.76 μm and comparison of the result to the plot of absorbance vs. concentration for 2-phenyl-2-propyl azide (Figure 2). The total rate of reaction may be determined by following the formation of HCl or formation of RN_3, as long as the experimental infinity value of the appropriate species is used in the calculation of the rate constant.

In most cases, the reaction rate was studied titrimetrically using Procedure B in the absence of base, and Procedure C (page 248) when base was present. As mentioned earlier, the precision obtained by these methods is poor. Attempts were made to circumvent the difficulties inherent in the use of these methods by quenching the reaction mixture in cold acetone and titrating directly (Procedure A, page 247); however, when the amount of salt exceeded 0.1 M, the end-point of the titration was effectively masked, so for the most part this method was not very useful. Neither could the rate be followed by ultraviolet spectroscopy since the salt effectively blanked out the 200-280 nm range. A few rates were followed by the infrared method (page 251); the precision of these rates was very low. The results obtained, however, were within experimental error of the titrimetrically determined rate constants for the same runs. The results are presented in Table VI and Figure 6.

Although tetrabutylammonium azide has only a small effect on the ethanolysis rate constants, its effect on product distribution is marked. When this salt is present, some of the products of ethanolysis are diverted to 2-phenyl-2-propyl azide. The change in product

TABLE VI

THE EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE RATE OF ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25.00° IN THE ABSENCE AND PRESENCE OF LITHIUM ETHOXIDE

Run No.	[RCl] M	[Bu_4NN_3] M	[EtOLi] M	$10^4 k_1$, sec^{-1}
a) Titrimetric Results				
I-103	0.03457	0	0	3.66 ±0.05
I-246	0.02443	0.02868	0	3.74 ±0.28
I-165*	0.01873	0.04971	0	3.84 ±0.22
I-171*	0.02043	0.04989	0	3.83 ±0.17
I-221	0.02264	0.05356	0	3.88 ±0.17
I-175*	0.01842	0.1023	0	3.95 ±0.40
I-217	0.01883	0.1047	0	4.32 ±0.08
I-291	0.02787	0.1113	0	4.07 ±0.25
I-177*	0.02040	0.1542	0	4.72 ±0.37
I-223	0.02398	0.1623	0	4.82 ±0.23
I-237	0.02361	0.2045	0	5.0 ±0.5
II- 85	0.02378	0.02627	0.0323	3.99 ±0.34
II- 75	0.02547	0.05596	0.0232	4.38 ±0.16
II- 79	0.02473	0.1174	0.0371	4.60 ±0.32
II- 87	0.02429	0.2147	0.0388	5.74 ±0.27

TABLE VI (Continued)

Run No.	[RCl]	[Bu_4NN_3]	[EtOLi]	$10^4 k_1$, sec^{-1}
b) Infrared Results				
I-291	0.02429	0.1113	0	4.6 $\pm$0.5
II- 86	0.02429	0.2147	0.0388	5.9 $\pm$0.8

*These rate points were quenched in cold acetone. All other titrimetric rates were determined by Procedure B or C (page 247)

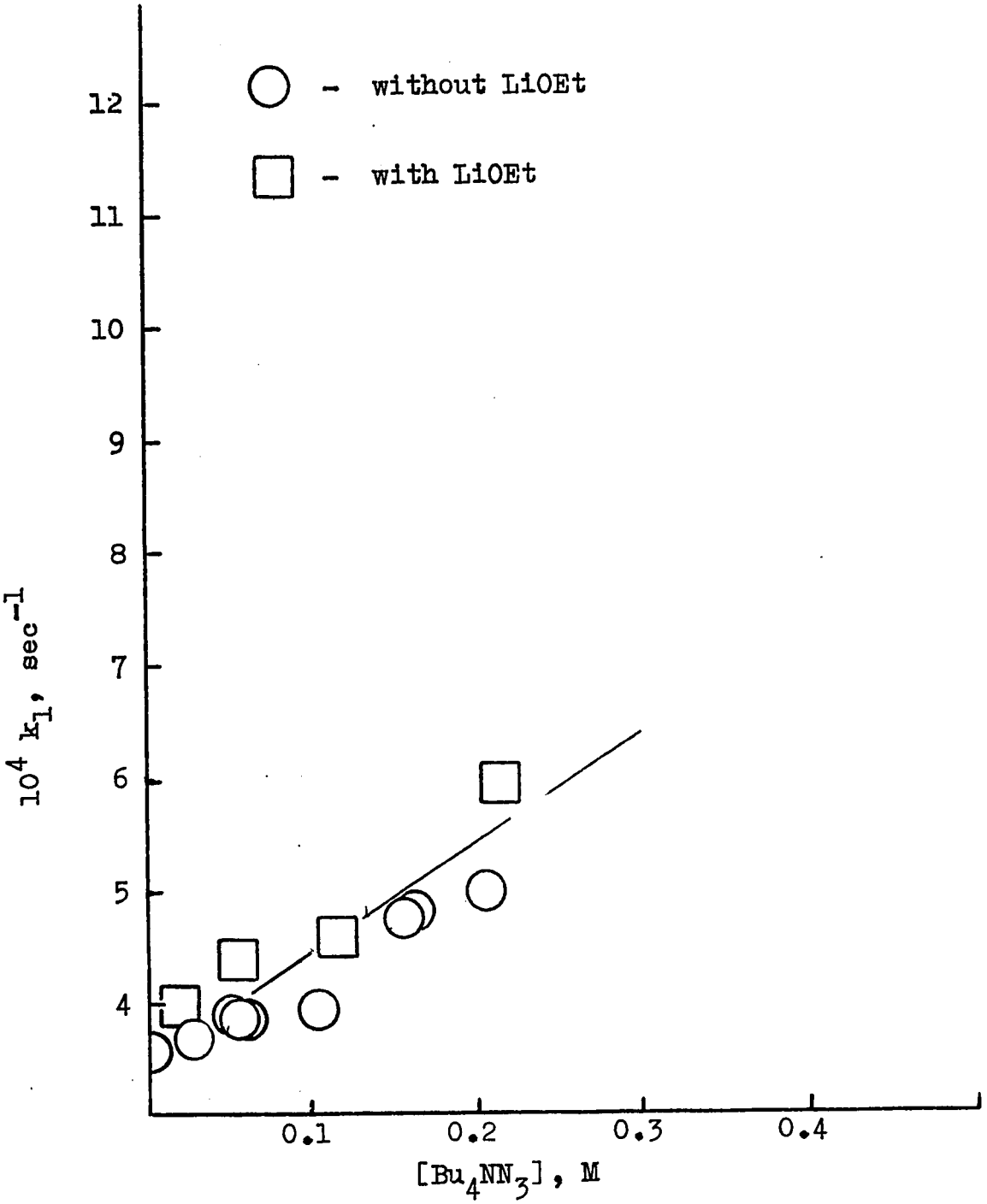


Figure 6. Effect of Tetrabutylammonium Azide on the Rate of Ethanolysis of 2-Phenyl-2-propyl Chloride

distribution was studied for several salt concentrations between 0 and 0.4 M, and the results shown in Table VII. In the presence of 0.4 M salt, 27% of the solvolysis products have been diverted to the organic azide.

The infrared results in Table VII were obtained by comparison of the absorbance of the sample at 4.76 μm to the standard curve, Figure 2. Duplicates of each run were made; both results are recorded in order to demonstrate the magnitude of error inherent in the results. The titrimetric values were obtained by difference of the infinity acid titre in the presence and absence of salt. The titrimetric results represent the average of duplicate determinations. In almost every case, the duplicate titres agreed to within 0.04 ml, 2%. It is assumed that only 96% of the starting material is 2-phenyl-2-propyl chloride, since 96% of the theoretical amount of acid was found when no salt was present. The molarity of 2-phenyl-2-propyl chloride reported in Table VII has been corrected accordingly.

Comparison of the two methods may be made directly in runs II-5, II-6, II-103, and I-295. In every case the results agree to within 2% absolute. The values of duplicate runs measured by either infrared spectroscopy or titrimetry show the same magnitude of error (i.e. 2%

TABLE VII

THE EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE DISTRIBUTION OF PRODUCTS FOR THE ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25.00°

Run No.	[RCl] M	$[Bu_4NN_3]$ M	% RN_3	$\frac{1}{[N_3^-]}$	$\frac{1}{F_{RN_3}}$	$\frac{[N_3^-]}{F_{RN_3}}$
a) Titrimetric Results						
I-241	0.02443	0.02868	4.8	34.8	20.8	0.596
II- 5	0.02640	0.06484	11.1	15.4	9.0	0.587
I-242	0.02030	0.09846	9.9	10.2	10.1	0.99
I-244	0.02284	0.1077	16.8	9.30	5.95	0.64
I-250	0.02962	0.1122	12.1	8.91	8.46	0.925
I-251	0.02605	0.1454	14.8	6.89	6.76	0.973
II- 6	0.02640	0.1515	18.1	6.60	5.43	0.835
I-243	0.02288	0.1761	14.0	6.40	7.14	1.11
I-253	0.02999	0.2159	19.5	4.64	5.14	1.11
I-252	0.02997	0.2179	18.0	4.60	5.56	1.21
I-295	0.02577	0.3960	27.6	2.53	3.62	1.43
I-255	0.03246	0.4082	25.2	2.45	3.97	1.62
I-256	0.02665	0.4067	25.6	2.46	3.92	1.59
II-103	0.02562	0.4810	33.6	2.08	2.97	1.46

TABLE VII (Continued)

Run No.	[RCl] M	[Bu_4NN_3] M	% RN_3	$\frac{1}{[N_3^-]}$	$\frac{1}{F_{RN_3}}$	$\frac{[N_3^-]}{F_{RN_3}}$
b) Infrared Results						
I-287	0.02539	0.05275	7.3	19.0	13.7	0.721
			7.3	19.0	13.7	0.721
I-286	0.02630	0.05389	7.3	18.6	13.7	0.740
			6.7	18.6	14.9	0.804
II- 5	0.02640	0.06484	10.5	15.5	9.54	0.615
			9.7	15.5	10.3	0.668
II-199	0.02588	0.09752	12.1	10.2	8.26	0.807
			12.2	10.2	8.20	0.800
I-200	0.02501	0.09857	12.5	10.15	8.00	0.789
			11.5	10.15	8.70	0.856
I-293	0.02661	0.1113	12.5	8.85	8.00	0.904
			12.5	8.85	8.00	0.904
II- 6	0.02526	0.1515	17.6	6.60	5.68	0.863
			16.6	6.60	6.03	0.912
I-288	0.02563	0.1644	16.6	6.09	6.03	1.03
			17.9	6.09	5.59	0.916
II-201	0.02497	0.2078	18.7	4.82	5.35	1.11
			19.1	4.82	5.24	1.09
I-289	0.02465	0.2123	23.2	4.71	4.42	0.916
			18.4	4.71	5.35	1.15
II-198	0.02588	0.05020	7.9	19.9	12.7	0.635
			7.2	19.9	13.9	0.697

TABLE VII (Continued)

Run No.	[RCl] M	$[Bu_4NN_3]$ M	% RN_3	$\frac{1}{[N_3^-]}$	$\frac{1}{F_{RN_3}}$	$\frac{[N_3^-]}{F_{RN_3}}$
II-222	0.02681	0.2770	23.3	3.62	4.29	1.19
			21.7	3.62	4.60	1.28
I-295	0.02577	0.3960	28.6	2.52	3.50	1.38
			29.2	2.52	3.42	1.36
II-223	0.02742	0.4128	24.8	2.42	4.04	1.67
			28.2	2.42	3.54	1.46
II-103	0.02562	0.4810	30.4	2.08	3.29	1.58
			29.4	2.08	3.40	1.63

absolute). The error within any one run as measured by the infrared method is somewhat smaller, usually ±1% absolute.

The significance of the results will be dealt with in detail in the discussion.

The effect of tetrabutylammonium azide on product distribution was also studied under conditions of constant ionic strength. Tetrabutylammonium perchlorate was used as the inert salt. The analyses were carried out using infrared spectroscopy. They are presented in Table VIII.

The effect of tetrabutylammonium azide on the product distribution in the presence of lithium ethoxide was found to differ somewhat from the effect in the absence of base. The results of this study are presented in Table IX.

Lastly, the effect of this salt on product distribution was studied at constant ionic strength in the presence of base by infrared spectroscopy, and the results reported in Table X.

Product Studies

STANDARDS: The expected products of ethanolysis of 2-phenyl-2-propyl chloride under the conditions of

TABLE VIII

THE EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE PRODUCT DISTRIBUTION OF THE ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25° AT CONSTANT IONIC STRENGTH BY INFRARED SPECTROSCOPY AT 4.76 um

Run No.	[RCl] M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	% RN_3	$1/[N_3^-]$	$1/F_{RN_3}$	$[N_3^-]/F_{RN_3}$
II-113	0.02487	0.05425	0.309	4.5, 5.5	18.4	22.2, 18.8	1.21, 0.984
II-100	0.02527	0.05686	0.296	4.3, 3.6	17.6	23.3, 27.8	1.32, 1.58
II-115	0.02675	0.06046	0.304	6.1, 5.5	16.6	16.4, 18.2	0.988, 1.10
II-101	0.02512	0.1078	0.234	9.7, 10.9	9.20	10.3, 9.18	1.11, 0.988
II-114	0.02487	0.1748	0.197	15.4, 14.4	5.73	6.49, 6.94	1.13, 1.21
II-102	0.02657	0.2248	0.156	19.2, 18.8	4.45	5.21, 5.32	1.17, 1.19
I-295	0.02577	0.3960	0	28.6, 29.2	2.52	3.50, 3.42	1.38, 1.36
II-223	0.02742	0.4180	0	24.8, 28.2	2.42	4.04, 3.54	1.67, 1.46

TABLE IX

EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE PRODUCT DISTRIBUTION OF THE ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25° IN THE PRESENCE OF LITHIUM ETHOXIDE BY INFRARED SPECTROSCOPY

Run No.	[RCl] M	[EtOLi] M	[Bu_4NN_3] M	% RN_3	$1/[N_3^-]$	$1/F_{RN_3}$	$[N_3^-]/F_{RN_3}$
II-81	0.02398	0.0333	0.02585	5.1	39.8	19.6	0.509
				5.1	39.8	19.6	0.509
II-85	0.02378	0.0323	0.02627	5.7	39.0	17.6	0.465
				5.5	39.0	18.2	0.466
II-88	0.02563	0.0388	0.02673	5.5	37.4	18.2	0.466
II-75	0.02547	0.0232	0.05596	9.3	17.9	10.8	0.601
				9.5	17.9	10.5	0.588
II-89	0.02473	0.0371	0.1174	14.5	8.52	6.89	0.809
				15.6	8.52	6.46	0.753
II-87	0.02429	0.0388	0.2147	22.7	4.66	4.32	0.905
				22.0	4.66	4.54	0.931

TABLE X

THE EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE PRODUCT DISTRIBUTION OF THE ETHANOLYSIS OF 2-PHENYL-2-PROPYL CHLORIDE AT 25° AT CONSTANT IONIC STRENGTH IN THE PRESENCE OF LITHIUM ETHOXIDE BY INFRARED SPECTROSCOPY

Run No.	[RCl] M	[EtOLi] M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	% RN_3	$1/[N_3^-]$	$1/F_{RN_3}$	$[N_3^-]/F_{RN_3}$
II-134	0.02881	0.0396	0.02621	0.311	4.4	38.1	22.8	0.598
					4.6	38.1	21.7	0.571
II-135	0.02514	0.0396	0.04842	0.281	5.2	20.7	19.2	0.930
					6.4	20.7	15.7	0.756
II-136	0.02923	0.0396	0.1002	0.234	10.8	10.0	9.27	0.931
					10.9	10.0	9.18	0.920
II-137	0.02574	0.0396	0.1534	0.212	14.3	6.52	7.00	1.07
					15.0	6.52	6.67	1.02
II-138	0.02662	0.0396	0.2090	0.139	18.9	4.79	5.29	1.11
					18.9	4.79	5.29	1.11

reaction used, were 2-phenylpropene, 2-phenyl-2-propyl ethyl ether, and, when tetrabutylammonium azide was present, 2-phenyl-2-propyl azide. Experiment showed that these products could be cleanly separated on a 2 m by $\frac{1}{4}$ in commercial column K (Carbowax 1500) at 150°. Naphthalene was shown to be a satisfactory internal standard.

Mixtures of the expected products were prepared and treated in the manner described in the experimental section (page 255).

Let us define the following terms. "RA" shall represent the ratio of the area of the g.c. peak of a particular compound to that of the g.c. peak of the internal standard, all multiplied by the number of moles of internal standard. For example, for 2-phenylpropene:

$$RA = \frac{\text{area (olefin)}}{\text{area (standard)}} \times \text{no. of moles of standard}.$$

"Moles" shall represent the number of moles of each material present in the sample.

A plot of RA vs. moles was made for each of the expected products. The results are shown for 2-phenylpropene in Table XI and Figure 7; for 2-phenyl-2-propyl ethyl ether in Table XII and Figure 8; for 2-phenyl-2-propyl azide in Table XIII and Figure 9.

TABLE XI

THE RELATIONSHIP BETWEEN RA AND MOLES FOR 2-PHENYLPROPENE

Run No.	10^4 moles	10^4 RA
II-186	0.857	0.882 + 0.022
II-187	0.429	0.448 ± 0.012
II-188	0.356	0.348 ± 0.018
II-178	0.355	0.311 + 0.020
II-192	0.301	0.266 ± 0.014
II-179	0.194	0.158 ± 0.006
II-189	0.178	0.161 ± 0.012
II-180	0.037	0.035 ± 0.002

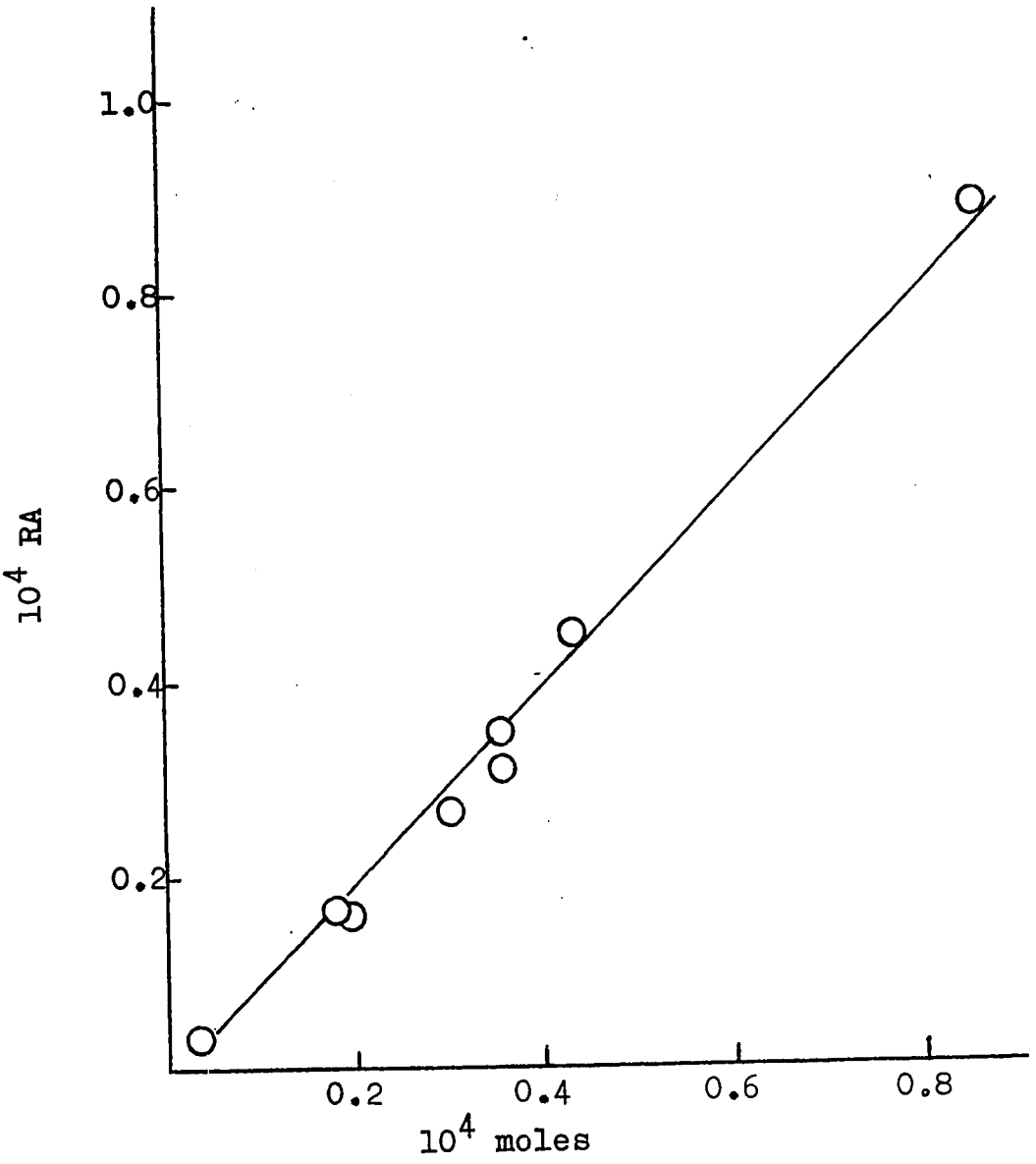


Figure 7. The Relationship Between RA and Moles for 2-Phenylpropene.

TABLE XII

THE RELATIONSHIP BETWEEN MOLES AND RA FOR 2-PHENYL-2-PROPYL ETHYL ETHER

Run No.	10^4 moles	10^4 RA
II-179	1.525	2.23 ± 0.05
II-158	1.408	1.76 ± 0.02
II-186	1.295	1.67 ± 0.04
II-189	0.917	1.16 ± 0.04
II-180	0.611	0.77 ± 0.01
II-188	0.608	0.78 ± 0.01

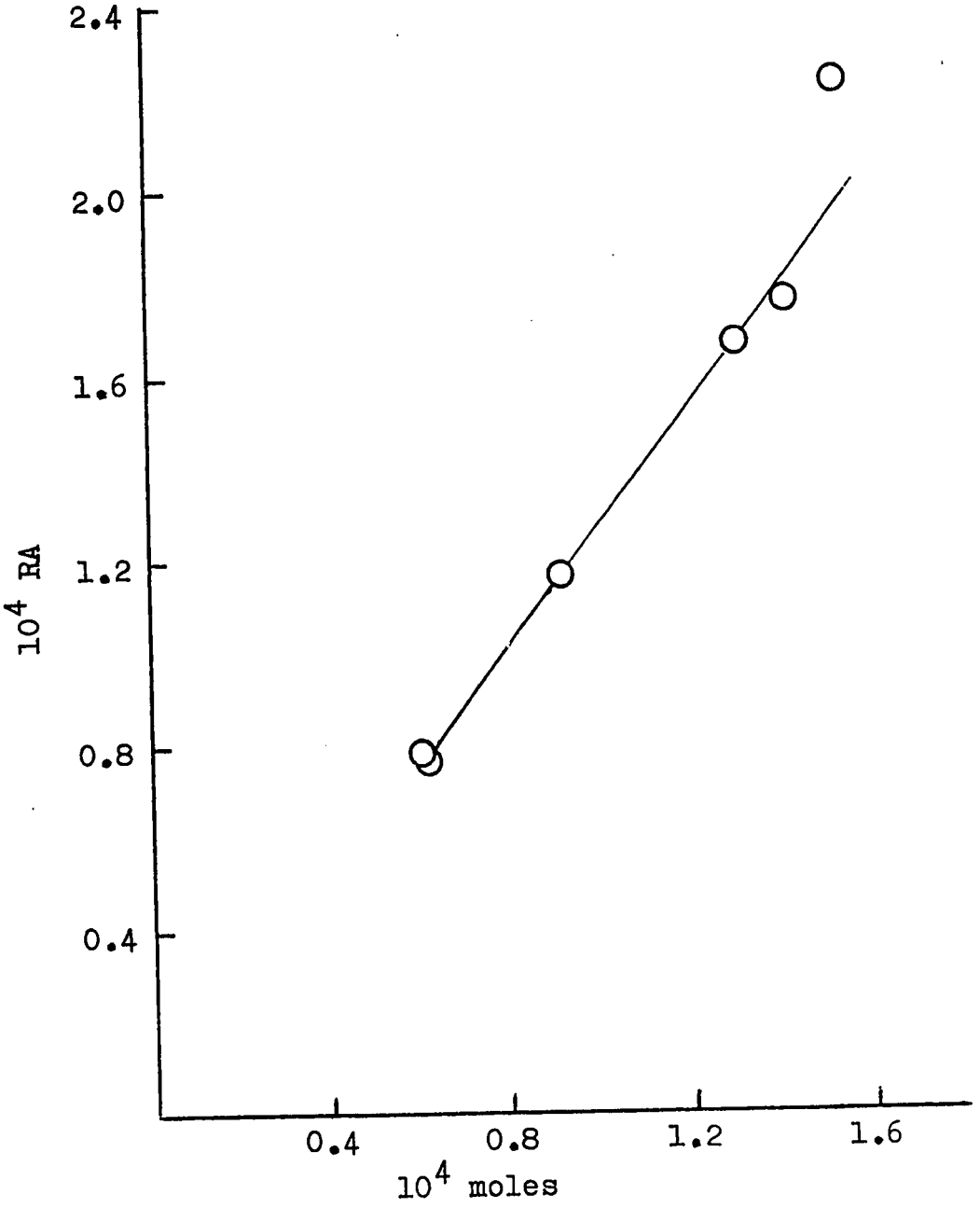


Figure 8. The Relationship Between RA and moles for 2-Phenyl-2-propyl Ethyl Ether.

TABLE XIII

THE RELATIONSHIP BETWEEN MOLES AND RA FOR 2-PHENYL-2-PROPYL AZIDE

Run No.	10^4 moles	10^4 RA
II-187	0.695	0.840 ± 0.018
II-189	0.566	0.693 ± 0.009
II-214-1	0.461	0.540 ± 0.004
II-215-1	0.371	0.404 ± 0.006
II-186	0.347	0.413 ± 0.019
II-188	0.283	0.340 ± 0.015
II-214-2	0.231	0.263 ± 0.004
II-215-2	0.186	0.202 ± 0.002
II-180	0.167	0.204 ± 0.006
II-193	0.125	0.095 ± 0.004
II-214-3	0.097	0.109 ± 0.003
II-215-3	0.078	0.084 ± 0.005
II-192	0.050	0.061 ± 0.002

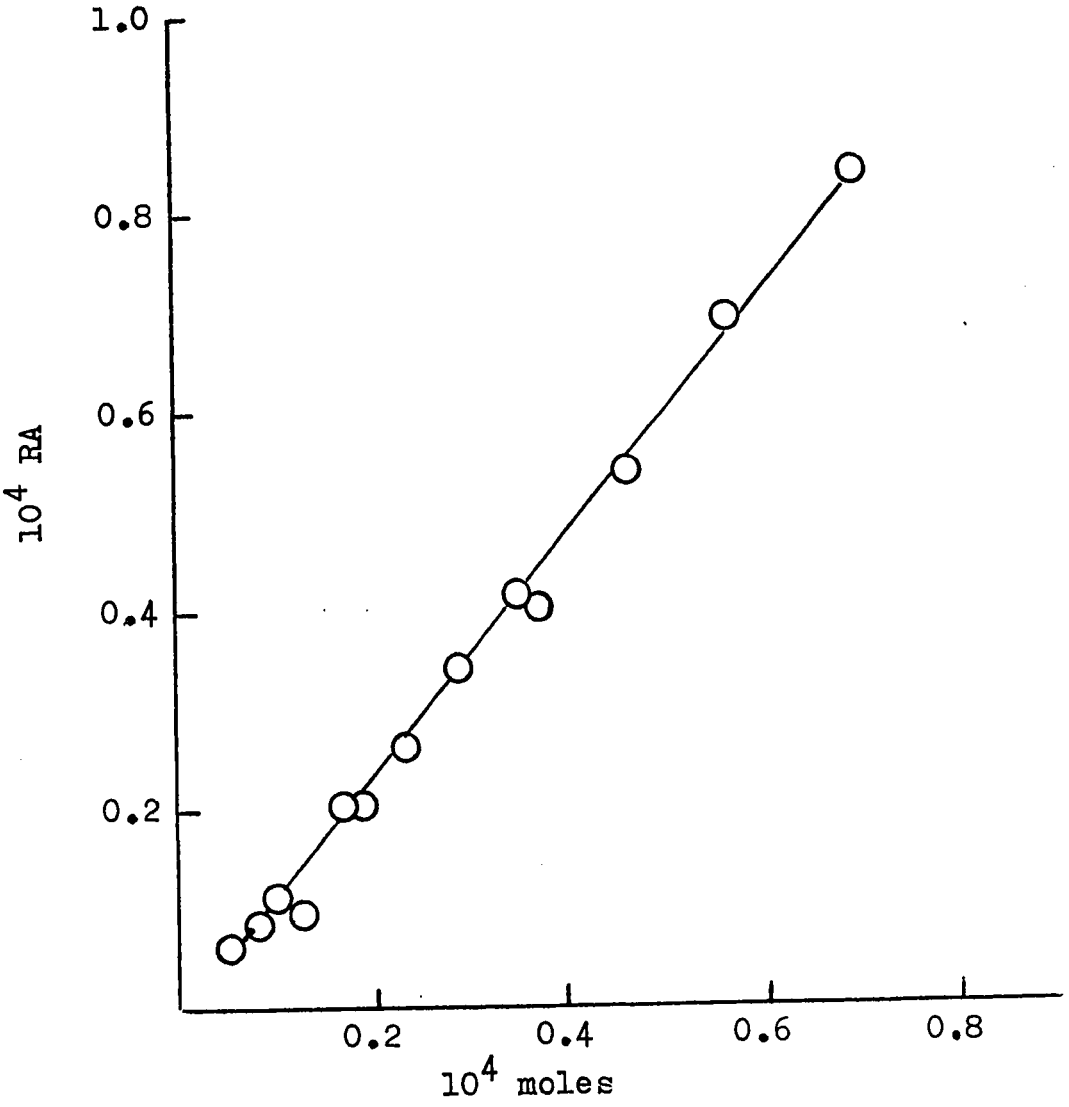


Figure 9. The Relationship Between RA and Moles for 2-Phenyl-2-propyl Azide.

In each case, the relationship between RA and moles appears to be linear.

The best fit straight line for each Figure was obtained using a weighted least mean squares fit of the data. This was done on an IBM 360/67 computer using the programme LSEFIT kindly supplied by Dr J. S. Martin. The results obtained by this method are presented in Table XIV.

PRODUCT ANALYSES: 2-Phenyl-2-propyl chloride was allowed to react for 10 half-lives in anhydrous ethanol at 25° and then the mixture analyzed for solvolysis products using the procedure described in the experimental section (page 255). The results obtained are summarized in Table XV.

Besides the expected products 2-phenylpropene and 2-phenyl-2-propyl ethyl ether, a third product was found in very small amounts. This material was characterized as acetophenone.

The acetophenone was also shown to be present in the alcohol from which the starting material was synthesized. The alcohol was synthesized by a Grignard reaction with acetophenone. Thus it is easy to account for its presence in the 2-phenyl-2-propanol.

The relationship between RA and moles (see page 52) was not determined for acetophenone; it was assumed to

TABLE XIV

RESULTS OF LEAST-MEAN-SQUARES ANALYSIS OF FIGURES 7, 8, AND 9 BY LSEFIT COMPUTER ANALYSIS

Figure Number	Slope	σ *	E*	Intercept	σ *	E*
7	0.999	0.027	0.034	-0.009	0.008	0.009
8	1.261	0.011	0.021	-0.003	0.007	0.014
9	1.116	0.029	0.031	0.006	0.006	0.007

* σ = Standard deviation

E = Standard Error (see page 85)

TABLE XV

SUMMARY OF PRODUCT ANALYSIS RUNS FOR 2-PHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25°

Run No.	[RCl] M	% olefin	% ether	% acetophenone	% products
II-194	0.04699	9.8 ±1.1	84.5 ±2.1	1	95.3
II-195	0.02594	10.0 ±0.6	82.2 ±1.6	1	93.2
II-220	0.02491	11.9 ±1.7	85.8 ±3.3	0	97.7
II-221	0.01876	8.5 ±1.2	83.7 ±3.7	0	92.2

be unity. Although this is not likely to be correct, the error introduced in calculating the fraction of acetophenone present should be small, since the relative amount of the material is small.

When 2-phenyl-2-propanol was synthesized again, using longer reaction times and a greater excess of magnesium methyl iodide, the alcohol still contained undesired acetophenone. It was finally removed by chromatography of the alcohol over alumina. Product runs II-220 and II-221 were carried out using 2-phenyl-2-propyl chloride made from alcohol free of acetophenone. There was no acetophenone found in these product runs.

2-Phenyl-2-propyl chloride was allowed to react for 10 half-lives in anhydrous ethanol at 25° in the presence of 2,6-lutidine. The results of these runs are presented in Table XVI. For these two runs, the work-up procedure used was Extraction Procedure III rather than Procedure I. This is probably the reason for the very large errors found in the numbers, since it is not strictly correct to compare the RA's of these runs with those of the standards which were prepared in a different manner.

Product analysis by g.c. was also carried out for some runs in which 2-phenyl-2-propyl chloride was allowed to solvolyze for 10 half-lives at 25° in the presence of tetrabutylammonium azide. The results are presented in

TABLE XVI

SUMMARY OF PRODUCT ANALYSIS RUNS FOR 2-PHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25°IN THE PRESENCE OF 0.03281 M 2,6-LUTIDINE

Run No.	[RCl] M	% olefin	% ether	% acetophenone	% product
II-203	0.02974	11.2 ±0.8	91.1 ±7.0	1	103.3
II-204	0.03412	10.4 ±1.0	86.3 ±4.0	1	97.7

Table XVII.

The fraction of 2-phenylpropene reported for these product analyses includes the olefin in the starting material, approximately 4%, as well as the olefin formed on solvolysis.

Each error reported in Tables XV-XVII is composed of the relative error found in the standard curve for the material (Table XIV) plus the average deviation found in the analysis of the material; the number was converted to an absolute value. The error in the standard curve was considered to be represented by the standard deviation of the slope of the curve, neglecting the error in the intercept. Thus, the relative error in the curve was calculated to be:

for olefin, $0.027/0.999 \times 100 = 2.7\%$

for ether, $0.011/1.261 \times 100 = 0.9\%$

for azide, $0.029/1.116 \times 100 = 2.5\%$.

The following is an example of the error calculations for run II-205:

	RA	% error in RA	10^4 moles	calculated error	% product found
olefin	$0.126 \pm .004$	3.1	0.135	5.8%	9.8 ± 0.5
ether	$1.16 \pm .02$	1.7	0.922	2.6%	66.7 ± 1.9
azide	$0.239 \pm .005$	2.1	0.210	4.6%	15.2 ± 0.6

TABLE XVII

SUMMARY OF PRCDUCT ANALYSIS RUNS FOR 2-PHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25° IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE; g.c. RESULTS

Run No.	[RCl] M	$[Bu_4NN_3]$ M	% olefin	% ether	% azide	% acetophenone	% products
II-198	0.02588	0.0502	9.8 ±0.7	76.8 ±2.6	5.7 ±0.7	1	93.3
II-199	0.02535	0.0975	8.9 ±1.5	73.5 ±2.6	10.1 ±0.4	1	93.5
II-200	0.02501	0.0986	10.4 ±1.0	71.6 ±3.1	10.0 ±0.5	1	93.0
II-201	0.02497	0.2078	9.3 ±0.8	65.2 ±2.7	16.9 ±0.5	1	92.4
II-205	0.02698	0.2241	9.8 ±0.5	66.7 ±1.9	15.2 ±0.6	1	92.7
II-222	0.02822	0.2325	9.7 ±0.6	66.9 ±2.9	18.0 ±0.5	0	94.6
II-223	0.02770	0.4128	8.7 ±0.6	61.0 ±4.1	23.4 ±1.2	0	93.1

If the error in the intercept of the standard curve were taken into account, the total relative error would appear to be somewhat larger.

For run II-205, for example, the relative error due to the uncertainty in the intercept of the standard curve may be calculated

for olefin,	0.006/0.126 x 100	=	5.0%
for ether,	0.006/1.16 x 100	=	0.5%
for azide,	0.005/0.239 x 100	=	2.1%

by making the assumption that the error in the intercept is measured by the standard deviation in the intercept.

Consequently, the errors given in the tables are conservative and must be treated as such.

In these product studies, the amount of starting material accounted for always appears to be less than 100%. In the runs where no salts are present, (Table IV), 95-97% of products were found, within experimental error of 100%. But, as the numbers are always low, the error appears to be systematic rather than random. The 2-phenyl-2-propyl chloride used in the study is only 96% pure, and the impurity is assumed to be 2-phenyl-propene. If the assumption is correct, then about 101% of the starting material should be found.

The impurity, however, may not be only 2-phenylpropene. Certainly some of it is the olefin, since every sample of 2-phenyl-2-propyl chloride used exhibited a small nmr peak at τ 8.0, indicative of the methyl group of 2-phenylpropene. But part of the impurity might be polymer. Quite large amounts of polymer were formed when the more reactive 2-aryl-2-propyl chlorides were synthesized by the method of Brown(24). It would not be reasonable to assume that none would be formed in this system. Any polymeric material in the starting material would condense on the inlet of the instrument and not be found by g.c. analysis. In fact, some tar was found in the inlet tube when the analysis was carried out.

In principle, the concentration of olefin in both the starting material and products should be measurable independently by ultraviolet spectroscopy. The $n \rightarrow \pi^*$ transition (ϵ = 13,000) occurs at 242 nm.

In actual practice, the method is not feasible.

The starting material in most of the runs contained about 1% acetophenone impurity (ϵ =14,500 at 245 nm), thus making the measurement of olefin impossible for the runs. Even when the acetophenone is removed, the problems are not solved. Tetrabutylammonium azide,

when present, effectively blanks out the ultraviolet range between 200 and 280 nm. Measurement of olefin by ultraviolet spectroscopy in runs where the salt is present would require a lengthy work-up procedure similar to that used for g.c. analysis. The precision of the results would be no better than that of those obtained by g.c. Even when both salt and acetophenone are absent, the absorbance at 242 nm cannot be related directly to olefin concentration. 2-Phenyl-2-propyl ethyl ether has a low intensity absorbance band at 250 nm ($\epsilon = 300$) which has residual absorbance at 242 nm. It is expected that 2-phenyl-2-propyl chloride would exhibit the same type of behaviour, although it is not possible to measure the extinction coefficient, since all samples of this material contain olefin. Even though the absorbance due to these materials is small, since they are present in tenfold excess over the olefin, correction must be made for them. In view of all these complications, the analysis of olefin by ultraviolet spectroscopy is experimentally impractical.

DISCUSSION

An extensive study of the solvolysis of 2-aryl-2-propyl chlorides in the solvent 90% aqueous acetone has been carried out by Brown(24). The effects of substituents on the rates of solvolysis clearly indicate that in this solvent the reaction is proceeding by an ionic pathway.

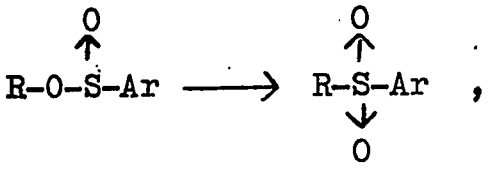
Winstein, Grunwald and Jones(28) have examined the effect of change of solvent on rates of reaction and have suggested that the "ionizing power" of a solvent, Y, be defined by the equation

$$\log k/k_o = m\,Y$$

where k and k_o are the solvolysis rate constants of a given compound in the solvent and in 80% ethanol, respectively; m is characteristic of compound.

Using this correlation, the Y value for 90% acetone is -1.86, while Y for 100% ethanol is -2.30; i.e., the ionizing power of the two solvents is quite similar. Therefore, if the reaction of 2-aryl-2-propyl chloride in 90% acetone is ionic in nature, the reaction of the same compound in 100% ethanol must also be considered to be ionic in character.

Furthermore, extensive studies of 2-aryl-2-propyl 2,6-dimethylbenzenesulfinates have been carried out by Mermelstein and Darwish(18) in these laboratories. Both rearrangement to sulfone,



and solvolysis of these sulfinate systems were shown to be of ionic character in several solvents, including anhydrous ethanol. The arenesulfinate ion is a much poorer leaving group than is chloride ion. For example, for 2-phenyl-2-propyl chloride, k_1 at 25° in ethanol is 3.8×10^{-4} sec^{-1}; k_1 at 90° is 2×10^{-4} sec^{-1} for 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. Hence, if the reaction of the 2,6-dimethylbenzenesulfinate is proceeding by an ionic pathway, then so must be the reaction of the chloride. Thus, from both considerations, we may conclude that the reaction of 2-phenyl-2-propyl chloride is proceeding <u>via</u> an ionic pathway.

Winstein and coworkers(7) have proposed reaction scheme [2], outlined in detail on page 5 of this work, for reactions proceeding through ionic intermediates. The results obtained for 2-phenyl-2-propyl chloride in anhydrous ethanol may be examined within the context of

this scheme.

The effect of inert salts on ionic reactions has been examined extensively by Fainberg and Winstein(29), who have suggested that the salt effects on such reactions be correlated by the empirical equation

$$k/k_o = 1 + b\,[\text{salt}]$$

where k is the rate constant observed in the presence of salt, k_o is the rate constant when no salt is present, and b is the percentage increase in rate constant per 1/100 M salt added.

Salts which obey this type of relationship are said to have a "normal" salt effect. Winstein found that different salts had different effects and the effect of any salt was dependent on the nature of the material solvolyzing, as well as on the temperature and the solvent.

Examination of the effect of salts on the rate of solvolysis of 2-phenyl-2-propyl chloride gave the following results:

for lithium perchlorate, $b = 6.9 \pm 1.2$ (Table V, Figure 5)

for tetrabutylammonium perchlorate, $b = 1.4 \pm 0.5$ (Table IV, Figure 4).

It is interesting to compare these results with those obtained for 2-phenyl-2-propyl 2,6-dimethylbenzene-

sulfinate in 100% ethanol(18):

$$b_{LiClO_4} = 7.5 \pm 0.4$$

$$b_{Bu_4NClO_4} = 1.0 \pm 0.1 \ .$$

With these two similar systems in the same solvent, the salt effects are very similar even at different reaction temperatures.

Examination of Winstein's reaction scheme shows the possibility of depressing the reaction by the addition of the common ion, X^-. A study of the effect of the common ion, chloride, on the ethanolysis rate of 2-phenyl-2-propyl chloride (Table V, Figure 5) shows that LiCl has little effect on the rate. On the addition of 0.1 M salt, the rate constant has increased by only 10%. There are two possible explanations of the result. Either the normal salt effect exhibited by lithium chloride is very small, "b" being of the order of 1, and there is no common ion effect, or the salt is inhibiting the reaction (common ion rate depression), the magnitude of the depression being of the same order as the increase in rate due to a normal salt effect, so that there is no net effect.

There are arguments in favour of both explanations. If there is no common ion rate depression occurring,

the effect of lithium chloride on the rate constant is abnormally low for a salt of the lithium cation. If there is common ion rate depression, one would expect to find a downward drift in the rate as the reaction proceeds and chloride ion is released. The reaction was followed to 90% completion both in the presence of base (Table XVIII) and in its absence (Table XIX). There was no observed drift in the rate constant. Considering the results of this study, then, the question of whether or not there is any common ion rate depression must remain unanswered. A study of the effect of tetrabutylammonium chloride on the reaction rate might help to resolve the ambiguity.

The possibility of acid catalysis on the ethanolysis of 2-phenyl-2-propyl chloride was considered. If acid catalysis were to occur, an upward rate drift might be expected as the reaction proceeds, since HCl is released. No upward drift was found. This might mean that there is no acid catalysis, or it may mean that catalysis by the acid released is counterbalanced by common ion rate depression due to the chloride released, so that the net effect is zero. If this were so, then a net downward rate drift would occur in the presence of base, providing that catalysis by the base is not occurring.

TABLE XVIII

THE RATE OF REACTION OF 2-PHENYL-2-PROPYL CHLORIDE (4.711×10^{-4} M) IN ANHYDROUS ETHANOL AT 25.10°, BY ULTRAVIOLET SPECTROSCOPY. Run No. II-153

Time (sec)	Absorbance	$10^4 k_1$, sec^{-1}	Time (sec)	Absorbance	$10^4 k_1$, sec^{-1}
0	0.369		1020	0.473	3.84
60	0.379	(5.26)	1080	0.479	3.88
120	0.382	3.44	1200	0.489	3.90
180	0.391	3.93	1320	0.498	3.89
300	0.403	3.73	1500	0.509	3.57
360	0.410	3.79	1560	0.513	3.82
420	0.414	3.60	1740	0.524	3.79
480	0.422	3.76	1800	0.528	3.80
540	0.428	3.76	2220	0.551	3.78
600	0.433	3.74	2340	0.556	3.73
660	0.440	3.79	2880	0.582	3.78
750	0.450	3.88	3000	0.588	3.82
840	0.458	3.86	3360	0.599	3.75
900	0.463	3.85	3480	0.605	3.82
			$13t_{\frac{1}{2}}$	0.690	

Average: $3.78 \pm .07$

TABLE XIX

RATE OF REACTION OF 2-PHENYL-2-PROPYL CHLORIDE (4.715×10^{-4} M) IN ANHYDROUS ETHANOL AT 25.10° IN THE PRESENCE OF LITHIUM ETHOXIDE (0.02862 M) BY ULTRAVIOLET SPECTROSCOPY. Run No. II-145

Time, sec.	Absorbance	$10^4 k_1$, sec^{-1}
0	0.376	
60	0.383	(3.04)
120	0.392	3.50
180	0.401	3.66
240	0.409	3.68
360	0.425	3.72
480	0.438	3.60
600	0.453	3.66
780	0.473	3.66
960	0.496	3.81
1260	0.522	3.71
1740	0.565	3.79
2220	0.596	3.73
5040	0.711	3.85
$11t_{\frac{1}{2}}$	0.764	
$50t_{\frac{1}{2}}$	0.767	

Average: 3.70 ± 0.07

The effect of lithium ethoxide on the rate was studied at several concentrations. The rate of reaction was unaffected at 0.1 M base concentration, thus ruling out the possibility of base catalysis. There is no evidence for a downward drift in rate at concentrations of lithium ethoxide (0.02 M) such that the acid formed is just neutralized. This argues against both acid catalysis and common ion rate depression. It is not, however, conclusive evidence for either case.

2,6-Lutidine is such a weak base (pK_b = 7.4 in water) that it would not be expected to have much effect as a basic catalyst even if such catalysis were to occur. It can, however, efficiently neutralize a strong acid such as HCl. The products of ethanolysis of 2-phenyl-2-propyl chloride were examined in the absence of any base (Table XV) and in the presence of 2,6-lutidine (Table XVI). The results were observed to be the same in both cases. Thus, on the basis of the results of the product studies, together with the results from the studies in the presence of base, acid catalysis can be tentatively ruled out.

The addition of tetrabutylammonium azide to the reaction mixture during the ethanolysis of 2-phenyl-2-propyl chloride was found to result in the diversion of some of the products from ethanolysis products to

2-phenyl-2-propyl azide. Two possible mechanisms may be considered for this process. Azide ion may be acting as a nucleophile to carry out a direct displacement reaction on the substrate. Alternatively, azide ion may be functioning as a trapping agent to divert one or more ionic intermediates from products of ethanolysis to the azide. The consequences of each possibility must be examined.

Considering the first mechanism, azide ion is known to be a good nucleophile, of the order of the reactivity of hydroxide ion(30). In fact, during these studies azide ion has been shown to carry out a displacement, S_N2 type, reaction on both benzyl chloride and p-methoxybenzyl chloride. The results of such a study are presented in detail in Chapter 2 of this work. 2-Phenyl-2-propyl chloride, however, is a tertiary alkyl halide; displacement on this compound would be expected to be difficult to carry out even for a nucleophile having the reactivity of azide ion. Also, the strong base lithium ethoxide has been shown to have no effect on the reaction, and ethoxide would be expected to be at least as good a nucleophile as hydroxide ion or azide ion. Further, the effect of tetrabutylammonium azide on the rate of reaction of 2-phenyl-2-propyl chloride is quite different from

the effect of the same salt on the benzyl systems where the reaction is shown to be one of displacement. In the benzyl systems, the rate increase is large and linearly dependent on the salt concentration. For the 2-phenyl-2-propyl chloride case, the rate increase with salt concentration is very small (Table VI). Even at 0.4 M salt concentration, where 30% of products formed are organic azide, the rate has increased by only 50%. The observed increase in rate, in fact, is of the same order of magnitude as that found for the "inert" salt tetrabutylammonium perchlorate (Table IV). The effect of tetrabutylammonium azide on the rate could well be explained by a normal salt effect, $b = 1.2 \pm 0.3$, in the same manner as the effect of tetrabutylammonium perchlorate is explained.

Although these considerations cast some doubt on the occurrence of a direct displacement reaction, the process cannot be definitely ruled out.

An unequivocal decision can be reached by considering the reaction scheme required for such a reaction:

$$RN_3 \xleftarrow[N_3^-]{k_2} RX \xrightarrow[HOS]{k_1} ROS + HX \qquad [3]$$

A mathematical analysis of scheme [3], applying the

steady state approximation, yields Equation [I]. The expression is derived in Appendix A.

$$1/F_{RN_3} = 1 + k_1/k_2[N_3^-] \qquad [I]$$

F_{RN_3} is defined as the fraction of the products that is alkyl azide; $[N_3^-]$ is defined as the concentration of the trapping species present. It can be seen from this relationship that if [3] does represent the reaction pathway, then a plot of $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ must have a slope of k_1/k_2 and an intercept of unity.

We can examine the second possibility within the context of Winstein's reaction scheme. There are three intermediates proposed: an intimate ion pair, a solvent-separated ion pair, and free ions. How many of these three intermediates must be invoked in order to explain the results found in the solvolysis of 2-phenyl-2-propyl chloride?

If there is only one intermediate, the reaction scheme becomes

$$RCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+Cl^- \xrightarrow[N_3^-]{k_3} RN_3 \qquad [4]$$

$$\downarrow k_2$$

$$ROS$$

Upon application of the steady state approximation, mathematical analysis of the system yields Equation [II]:

$$1/F_{RN_3} = 1 + k_2/k_3\,[N_3^-] \qquad [II]$$

If two intermediates are involved, only one of which gives the azide, the scheme becomes:

$$RCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B \xrightarrow[N_3^-]{k_5} RN_3 \qquad [5]$$

$$A \xrightarrow{k_6} \text{products} \qquad B \xrightarrow{k_7} \text{products}$$

Application of the steady state approximation to the analysis of this scheme yields:

$$\frac{1}{F_{RN_3}} = \left(1 + \frac{k_6}{k_3}\right) + \frac{k_3k_7 + k_4k_6 + k_6k_7}{k_3k_5}\,\frac{1}{[N_3^-]} \qquad [III]$$

The derivation of Equation [II] is found in Appendix B, that of Equation [III] in Appendix C. Again, F_{RN_3} is the fraction of organic azide formed; $[N_3^-]$ is the concentration of the trapping species present.

In scheme [4], the products of solvolysis and the alkyl azide are both formed from the same intermediate. Reaction scheme [5] differs from scheme [4] in that

besides assuming two intermediates, it also assumes that solvolysis products may arise from reaction of solvent with either of the intermediates, while only one of these intermediates may be diverted to the azide. For scheme [4], all of the solvolysis products would be diverted to azide if infinite concentration of the trapping agent were approached. If scheme [5] represents the reaction mechanism, some solvolysis products would still be formed even if the concentration of trapping species were to approach infinity.

In the limit where k_6 becomes much smaller than k_3, scheme [5] becomes indistinguishable from scheme [4].

A plot of $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ should give a straight line of intercept 1 if scheme [4] represents the reaction pathway. If scheme [5] represents the reaction sequence, then a plot of $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ would have an intercept of $(k_6/k_3 + 1)$.

A study of the effect of tetrabutylammonium azide on the product distribution for the ethanolysis of 2-phenyl-2-propyl chloride, then, should yield information about the mechanism of the reaction. Assuming that there is some means of measuring F_{RN_3} and $[N_3^-]$, a plot of their reciprocals should allow us to decide whether scheme [5] represents the reaction sequence or whether it is better represented by scheme [3] or [4]. It will not be

possible to decide between the latter two on the basis of this experiment; both predict the same result.

As a first approximation, it was assumed that the concentration of tetrabutylammonium azide, $[Bu_4NN_3]$, equalled the concentration of the trapping species, $[N_3^-]$. F_{RN_3}, the fraction of organic azide formed, was obtained by three independent methods.

In the first, the concentration of azide formed was determined directly by infrared spectroscopy (Table III). A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ for these results is shown in Figure 10. In the second method, the amount of azide formed was obtained indirectly by following the decrease in acid formed in the reaction (Table VII). A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ is shown in Figure 11. Since both of these methods should give equally reliable results, the difference in F_{RN_3} found at similar salt concentrations is a measure of the magnitude of the errors involved in the analysis.

In the third method of analysis, the azide formed was determined by g.c. (Table XVII). When this method was used, the apparent F_{RN_3} was found always to be lower than F_{RN_3} determined by the other two methods. The error appears to be constant, about 2% absolute, regardless of the amount of azide formed. While it is possible that the error is really random, it appears to be

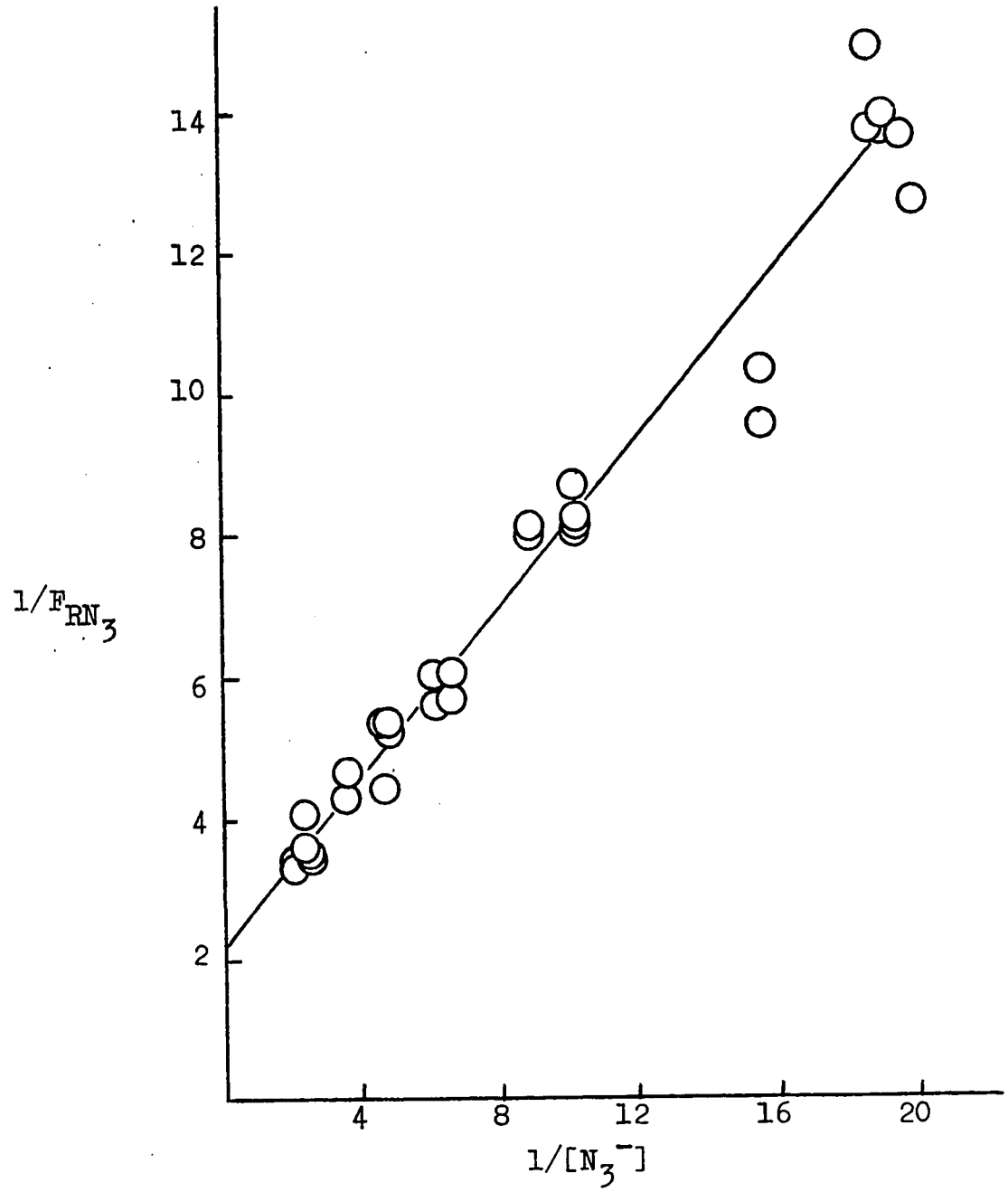


Figure 10. Relationship Between $1/F_{RN_3}$ and $1/[N_3^-]$, F_{RN_3} Determined by Infrared Spectroscopy.

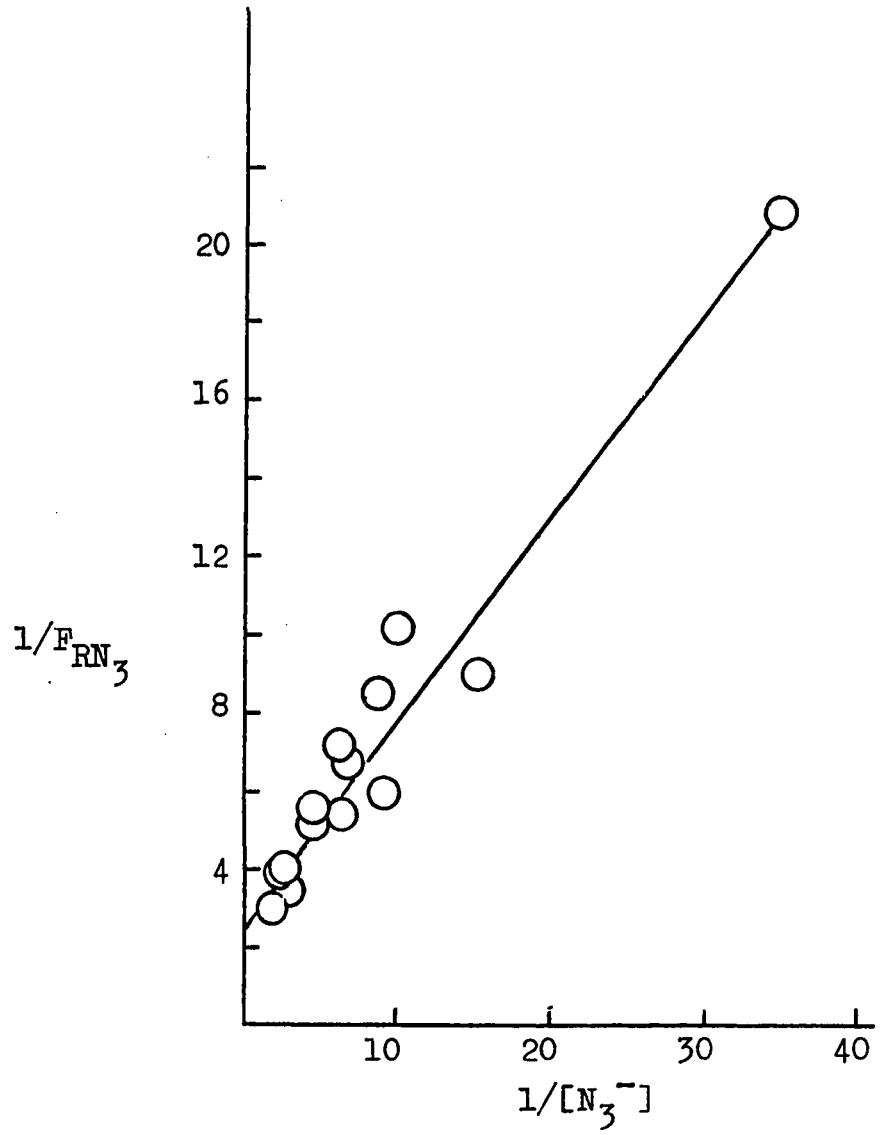


Figure 11. Relationship Between $1/F_{RN_3}$ and $1/[N_3^-]$, F_{RN_3} Determined by Titrimetry.

systematic. Checks on the standard plots prepared for the g.c. and the infrared analyses showed the discrepancy not to be due to an error in these plots. An attempt was made to isolate the material corresponding to the g.c. peak assigned to the azide. When a sample of the material causing this peak was isolated, it was found that the material was not 2-phenyl-2-propyl azide, but rather an unidentified nitrogen-containing material. The fact that this is a decomposition product rather than 2-phenyl-2-propyl azide probably accounts for the discrepancies observed. In further agreement with this explanation is the fact that the sum of materials accounted for in the product analysis appears to be about 2% less in the presence of the azide salt than in its absence (Tables XIV and XVI). These analyses were obtained by g.c.

Best fit straight lines for Figures 10 and 11 were obtained by using a least mean squares fit. The computer programme LSEFIT of J. S. Martin was used for the analysis. The LSEFIT programme may be used to calculate a least squares fit and the standard deviation, σ, while assigning the same limits of confidence to each point, or it may be used while taking into account the error associated with each individual point. If an absolute

error is assigned to each point, the programme will assign a weight to the point inversely proportional to the relative error associated with that point, then will calculate the best fit straight line, the standard deviation σ, and the standard error E, where

$$E^2 = \sum_{o}^{n} \frac{(\sigma_m^2 + E_m^2)}{n-1}$$

σ_m is the deviation from the line, and E_m the assigned error for the m'th point; n is the number of points in the analysis.

So long as a reasonable estimate of the error associated with each point is available, E should be an excellent measure of the limits of confidence of the results.

Both unweighted and weighted least-squares fits have been calculated for Figures 10 and 11. The results obtained are shown in Table XX.

In making the weighted plots, an absolute error of $\pm 1\%$ was assumed for each point. This value was arbitrarily assigned because it is about the average error found in the values of duplicate determinations of F_{RN_3} obtained by infrared spectroscopic analysis (Table VII). It was assumed that the errors in the titrimetric results would be similar since both sets of data were obtained using the same type of work-up procedure.

TABLE XX

RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 10 (TITRIMETRIC RESULTS) AND 11 (RESULTS BY INFRARED SPECTROSCOPY) BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
10	0.59	0.02	--	2.23	0.21	--
11	0.51	0.03	--	2.74	0.41	--
b) Weighted Results						
10	0.58	0.02	0.03	2.20	0.11	0.18
11	0.53	0.06	0.07	2.48	0.32	0.37

Comparison of the results of the titrimetric and infrared analyses shows them to be the same within experimental error. The weighted and unweighted results do not vary significantly. This is not surprising in view of the large number of points analysed. The intercept of the plots is certainly greater than 1. Extrapolation of the line to $1/[N_3^-] = 0$ shows that a maximum of 60% of the products formed would be 2-phenyl-2-propyl azide, even if the concentration of tetrabutylammonium azide were to approach infinity. Reaction schemes [3] and [4] are thus ruled out. Reaction scheme [5] would account for the results; the value of k_6/k_3 is 1.2.

There is a disadvantage to plotting data in the form of reciprocal plots, particularly in cases such as we have here, where the relative errors are largest when the values involved are smallest. The most accurate points become closely grouped together while the less accurate points spread across the graph and will be assigned an unfair weight in the determination of the slope and consequently of the intercept. Figure 11 provides a very good example of the problem. There are many points between $1/[N_3^-]$ values of 2 and 10, with one at a value of 35. The overall effect is almost that of defining the whole graph by a 2-point line, one point of which has a relative error of almost 20%. The problem

may be overcome to some extent by the weighting methods used in the LSEFIT programme. There is another simple and effective method of overcoming the whole problem. If Equation III is multiplied by $[N_3^-]$, Equation IV is obtained.

$$\frac{[N_3^-]}{F_{RN_3}} = \left(\frac{k_6}{k_3} + 1\right)[N_3^-] + \frac{k_3k_7 + k_4k_6 + k_6k_7}{k_3k_5} \quad [IV]$$

In this format, the points corresponding to low azide ion concentrations do not have unfair weight in determining the slope.

The roles of slope and intercept are reversed relative to Equation III. Such plots were made using the data in Table VII. The titrimetric results are shown in Figure 12. The values obtained by infrared analysis are plotted in Figure 13. The results of a least mean squares fit of the data are shown in Table XXI.

The results from Equation IV (Table XXI) lead to the same qualitative and quantitative conclusions as reached from the results from Equation IV (Table XX) except, as anticipated, the level of confidence is improved.

Several assumptions were made in arriving at the conclusion that scheme [5] represents the reaction

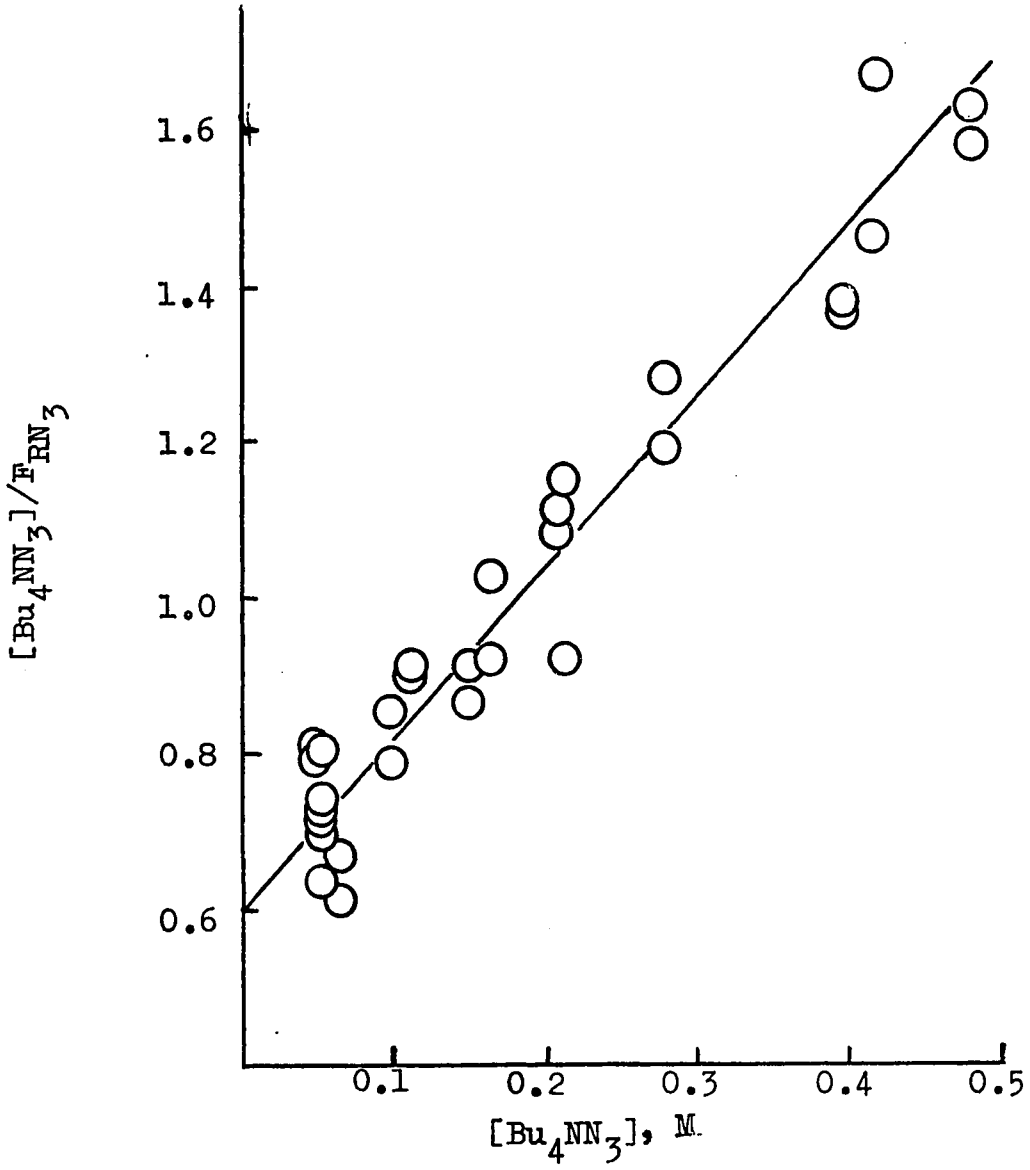


Figure 12. Relationship Between $[Bu_4NN_3]/F_{RN_3}$ and $[Bu_4NN_3]$ for 2-Phenyl-2-propyl Chloride. Titrimetric Results

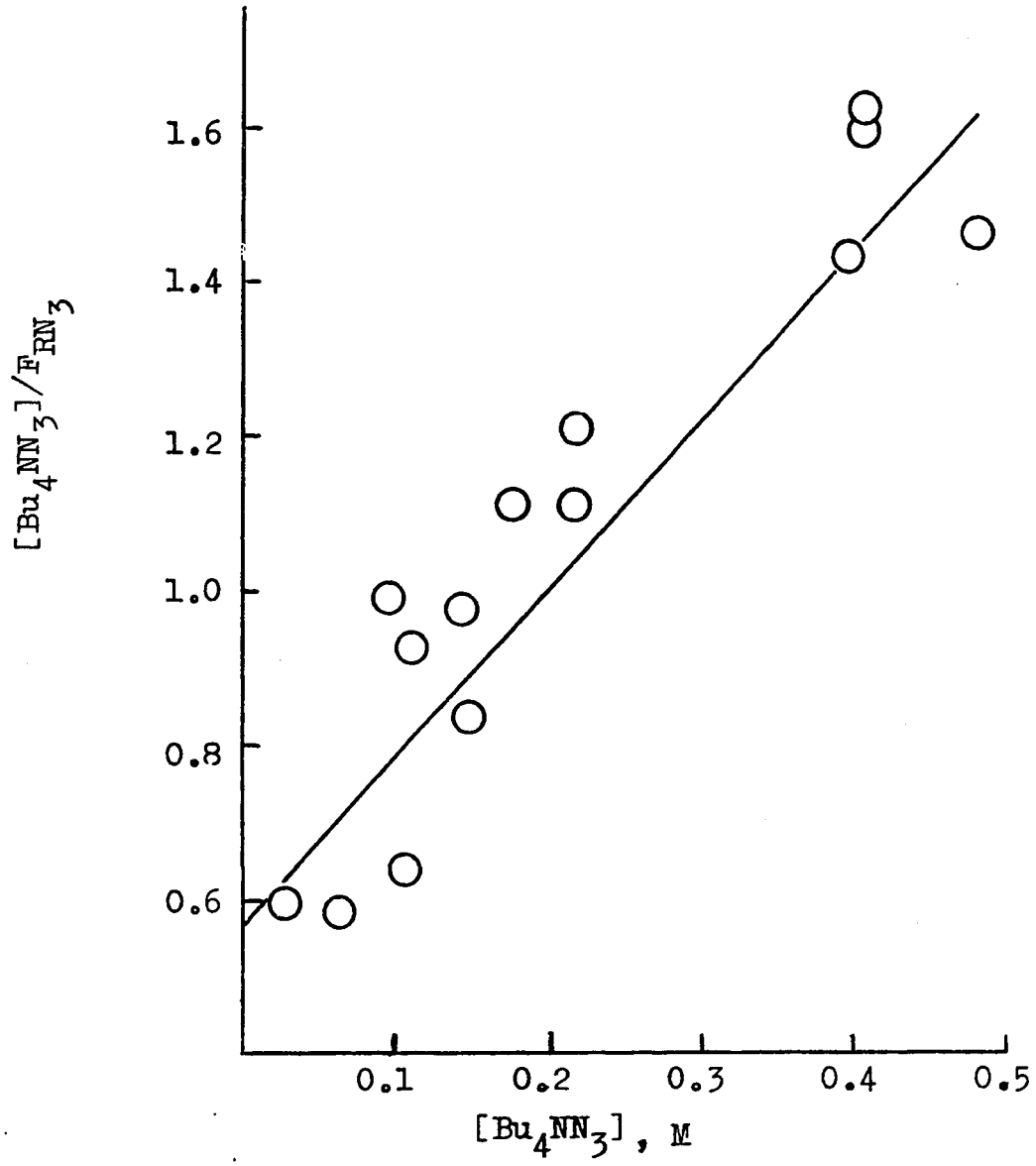


Figure 13. Relationship Between $[Bu_4NN_3]/F_{RN_3}$ and $[Bu_4NN_3]$ for 2-Phenyl-2-propyl Chloride. Determined by Infrared Spectroscopy

TABLE XXI

THE RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 12 (TITRIMETRIC RESULTS) AND 13 (RESULTS OF INFRARED SPECTROSCOPY), BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
12	2.15	0.10	--	0.60	0.02	--
13	2.23	0.25	--	0.60	0.06	--
b) Weighted Results						
12	2.14	0.10	0.13	0.60	0.02	0.03
13	2.24	0.26	0.29	0.57	0.07	0.08

pathway. They must be justified before the conclusion can be accepted as reasonable.

First, in the derivation of the mathematical formulation, it was assumed that azide ion concentration is constant throughout the reaction. Considering only the salt consumed in the reaction, the approximation holds well, even at the most dilute concentrations. For example, at 0.05 M tetrabutylammonium azide, about 6% azide was formed, so about 6% of 0.02 M salt, or 0.001 M, would be consumed. Even at complete reaction, the concentration of salt would be 0.0499 M. As the reaction proceeds, however, HCl is produced. This strong acid will react with azide ion to form undissociated hydrazoic acid. By the time the reaction has reached completion, about 0.02 M salt will have been consumed in this manner. At high salt concentration, the error introduced in ignoring this side reaction is quite small. It increases as the initial salt concentration decreases. Failure to correct for this when plotting $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ would lead to an intercept value, and predicted k_6/k_3, smaller than the real value.

By allowing the reaction to proceed in the presence of a strong base, the acid would be neutralized as it was formed and this source of error would be eliminated.

The results of such a study for 2-phenyl-2-propyl chloride with lithium ethoxide as added base are presented in Table IX.

A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ for these results is shown in Figure 14. For convenience, this type of plot will be referred to as an intercept plot, since values of k_6/k_3 are derived from the intercept of the plot. A plot of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$ is shown in Figure 15. This type of plot will henceforth be referred to as a slope plot. The result of a least mean squares analysis of the Figures is shown in Table XXII.

As expected, the fraction of azide formed at low salt concentrations is larger in the presence of base than in its absence, and the numbers converge as the salt concentration increases.

The results of this experiment, too, are consistent with scheme [5] rather than [3] or [4]. The best value of k_6/k_3 is 1.3, obtained from Figure 15, the "slope" plot. As was expected, this value is larger than that obtained when no base was present in the reaction mixture (k_6/k_3 = 1.2, Table XXI). The standard error, E, reported in Table XXII is larger than that found in Table XXI because there are fewer points on the graphs.

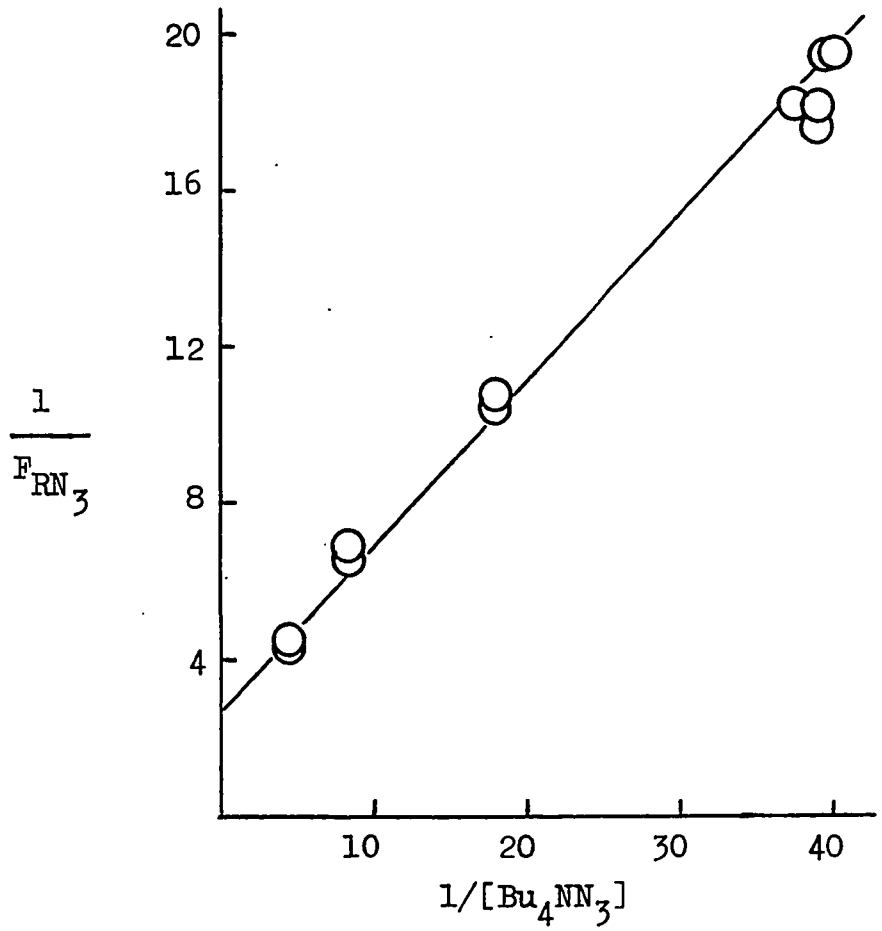


Figure 14. Relationship Between $1/F_{RN_3}$ and $1/[Bu_4NN_3]$, an Intercept Plot for 2-Phenyl-2-propyl Chloride with Lithium Ethoxide.

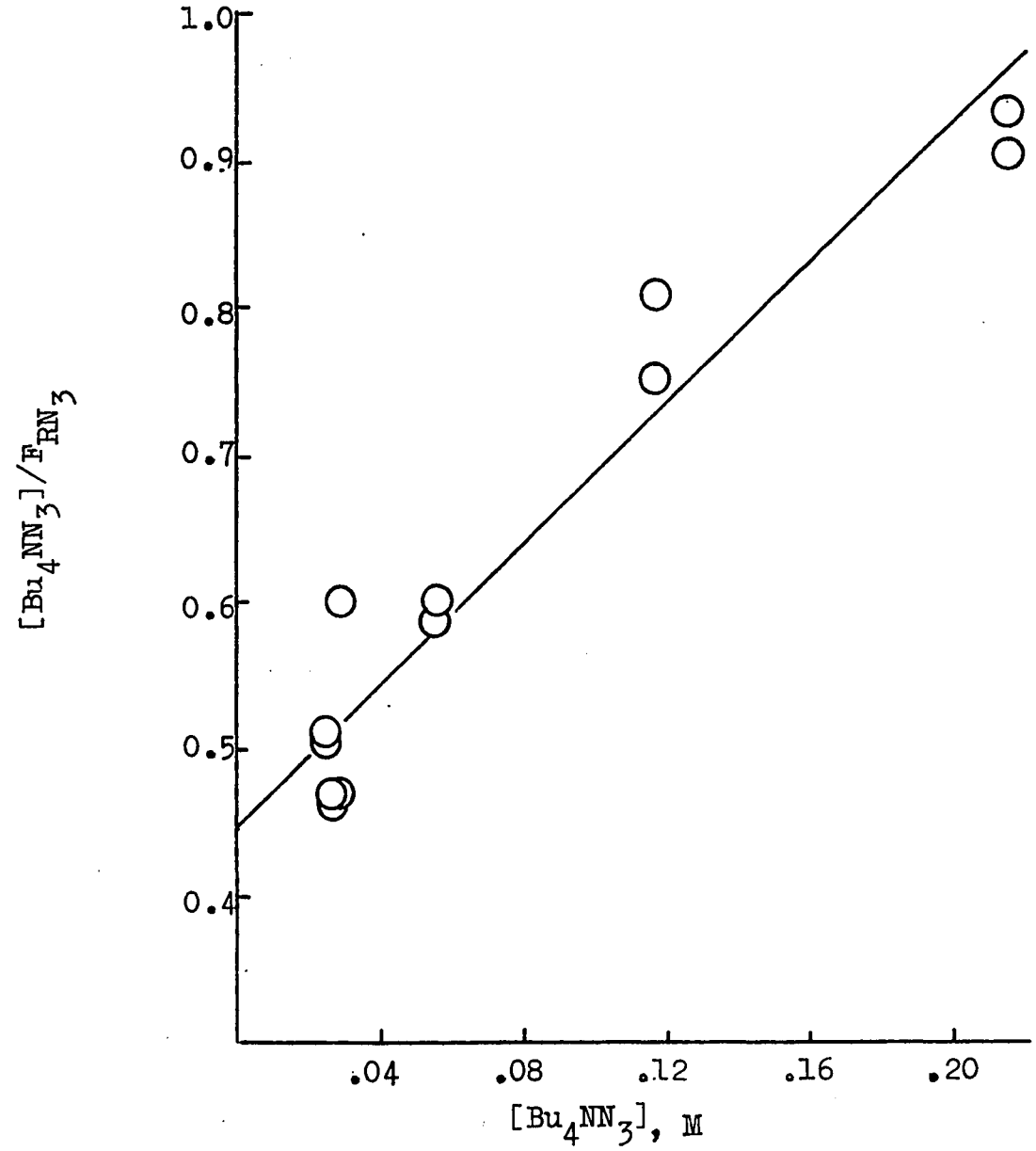


Figure 15. Relationship Between $[Bu_4NN_3]/F_{RN_3}$ and $[Bu_4NN_3]$, a Slope Plot for 2-Phenyl-2-propyl Chloride with Lithium Ethoxide

TABLE XXII

THE RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 14 (INTERCEPT PLOT) AND 15 (SLOPE PLOT), BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
14	0.402	0.012	--	3.01	0.34	--
15	2.38	0.18	--	0.44	0.02	--
b) Weighted Results						
14	0.42	0.01	0.04	2.70	0.18	0.54
15	2.29	0.18	0.33	0.45	0.03	0.04

The second assumption made was that the concentration of tetrabutylammonium azide is a measure of the concentration of the trapping species, represented as $[N_3^-]$. This might not be valid under the experimental conditions employed. The tetrabutylammonium halides have been shown to exist largely in the form of ion pair species in anhydrous ethanol(31). No data are available for tetrabutylammonium azide in this solvent, however, it is reasonable to assume that tetrabutylammonium azide will also be largely associated in ethanol.

If azide ion is the species responsible for trapping, then the concentration of tetrabutylammonium azide added to the solution is not a real measure of the species, because the amount of N_3^- in the solution will be governed by the equilibrium

$$Bu_4N^+N_3^- \rightleftharpoons Bu_4N^+ + N_3^-$$

the concentration being given by the Mass Law equation

$$K_a = \frac{[Bu_4N^+N_3^-]}{[Bu_4N^+][N_3^-]}$$

We have assumed that K_a is reasonably large, i.e. that most of the tetrabutylammonium azide is present in the form of ion pairs; then the concentration of these ion pairs ($[Bu_4N^+N_3^-]$) is approximately equal to the

concentration of salt, Bu_4NN_3, added to the reaction mixture. The concentration of the trapping species ($[N_3^-]$) thus will be proportional to the square root of the salt concentration.

$$[Bu_4N^+][N_3^-] = [N_3^-]^2 = K_a[Bu_4N^+N_3^-] \cong K_a[Bu_4NN_3]$$

If, on the other hand, the ion pair is the trapping species, then the concentration of the species will be directly proportional to the concentration of added salt.

If both the azide ion and the ion pair function as trapping agents, then the relationship between $[Bu_4NN_3]$ and concentration of the species will be more complicated.

The problem can be circumvented. If the concentration of the tetrabutylammonium cation were constant, then the Mass Law equation would become

$$K_a[Bu_4N^+] = K' = \frac{[Bu_4N^+N_3^-]}{[N_3^-]}$$

and $[N_3^-] = K'[Bu_4N^+N_3^-] \cong K'[Bu_4NN_3]$. The concentration of added salt should in this case be a measure of the concentration of trapping agent. If an inert salt of common cation were added to the reaction mixture so that the total concentration of salt were kept constant, then, provided that the K_a values of the two salts were not

too dissimilar, the concentration of tetrabutylammonium cation should remain approximately constant and the concentration of added tetrabutylammonium azide will be directly related to the concentration of the trapping agent. Tetrabutylammonium perchlorate is an obvious choice for the inert salt.

Another assumption made, after having derived equation [II] is that the relationship between $1/F_{RN_3}$ and $1/[N_3^-]$ should be linear. Such a relationship will hold only if the rate constants k_3, k_4, k_5, k_6 and k_7 are truly constants.

When salts are added to a reaction mixture, the ionizing power of the solvent changes; with every change in solvent there is an effect on the rate constant. This effect could be minimized by carrying out all the reactions at the same ionic strength. Again, tetrabutylammonium perchlorate should be a good choice for the inert salt. The effect on the overall rate constant as measured by the "b" value is very similar for tetrabutylammonium perchlorate and tetrabutylammonium azide; it is reasonable to assume that the effect of these salts on the individual rate constants k_3 through k_7 will also be similar.

Studying the formation of alkyl azide while tetrabutylammonium perchlorate is used to adjust the reaction

mixture to constant ionic strength, then, will have a twofold advantage: the concentration of tetrabutylammonium azide will be directly proportional to the concentration of the trapping species; the individual rate constants will not be affected when the concentration of azide salt is changed.

Such a study has been carried out and the results presented in Table VIII. A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$, an intercept plot, is shown in Figure 16. A plot of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$, a slope plot, is shown in Figure 17. The calculated least mean squares fit for each plot is shown in Table XXIII.

The weighted results were calculated assuming that the error in each value is $\pm 1\%$ absolute, in the same manner as was done for other plots of this type.

The results of this experiment are significantly different from those obtained where tetrabutylammonium perchlorate was not present (Tables XXI and XXII). The pertinent values from Table XXIII give a maximum value for k_6/k_3 of 0.13; the standard error is such that this value is well within experimental error of a value of zero. One cannot confidently distinguish between schemes [3] or [4] and [5] on the basis of these results.

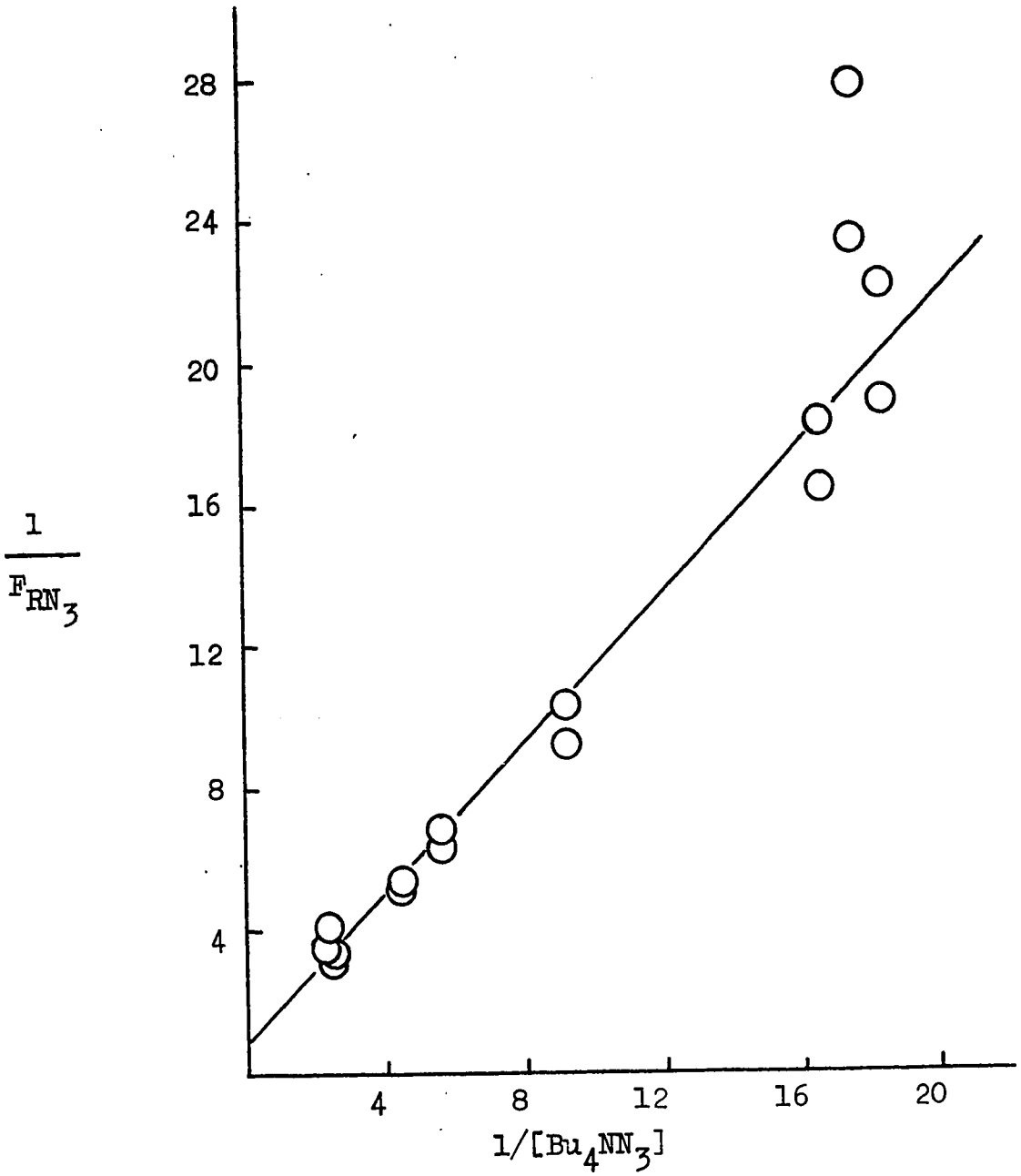


Figure 16. Intercept Plot for 2-Phenyl-2-propyl Chloride at Constant Ionic Strength

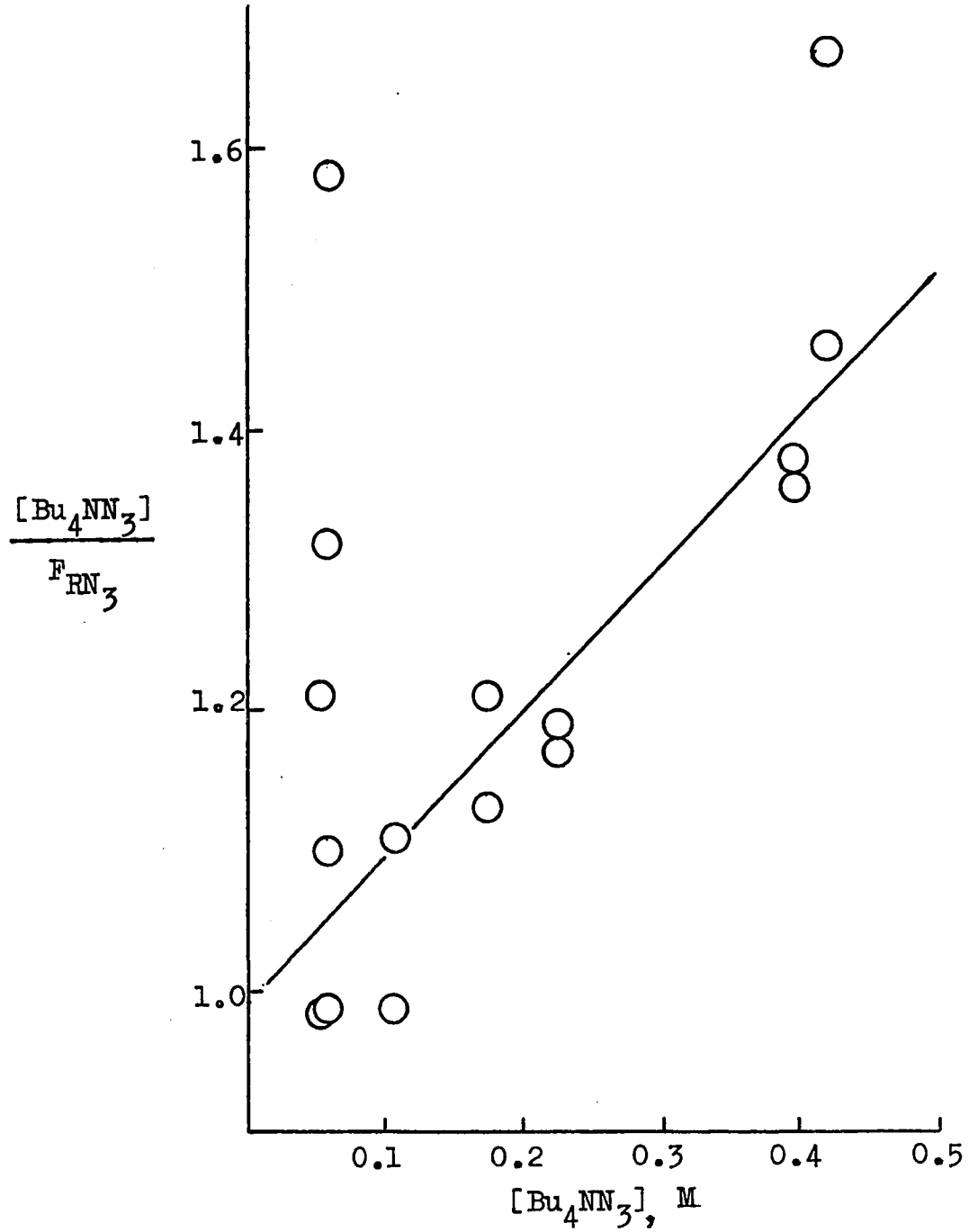


Figure 17. Slope Plot for 2-Phenyl-2-propyl Chloride at Constant Ionic Strength

TABLE XXIII

RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 16 INTERCEPT PLOT) AND 17 (SLOPE PLOT), BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
16	1.18	0.09	--	1.09	0.17	--
17	0.85	0.31	--	1.08	0.07	--
b) Weighted Results						
16	1.04	0.06	0.10	0.92	0.29	0.46
17	1.13	0.21	0.31	0.98	0.06	0.09

No base was present in these runs to neutralize the HCl formed; hence, as discussed earlier, the derived k_6/k_3 ratio is expected to be lower than the real value. Consequently, the experiment was repeated in the presence of lithium ethoxide. The results are recorded in Table X. A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$, an intercept plot, of the new values is shown in Figure 18. A plot of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$, a slope plot, is shown in Figure 19. The best least mean squares fits of the data are recorded in Table XXIV.

The error values calculated for these results appear to be very large. This is not surprising, since the relative error assumed for half of the experimental values, Runs II-81, II-85, and II-88, is almost 20%.

The conditions of this experiment were so designed, that the results should best differentiate among the reaction pathways under consideration; hence, if possible, it would be very desirable to improve the precision of these results. The simplest manner of doing so would be to include more data points in the analysis. Two sets of results that may easily be included are Runs I-295 and II-223 (Table VII). The concentration of tetrabutylammonium azide for these runs is such that they are of the same ionic strength as those in Table X. There is no base present in either of the runs, but this should

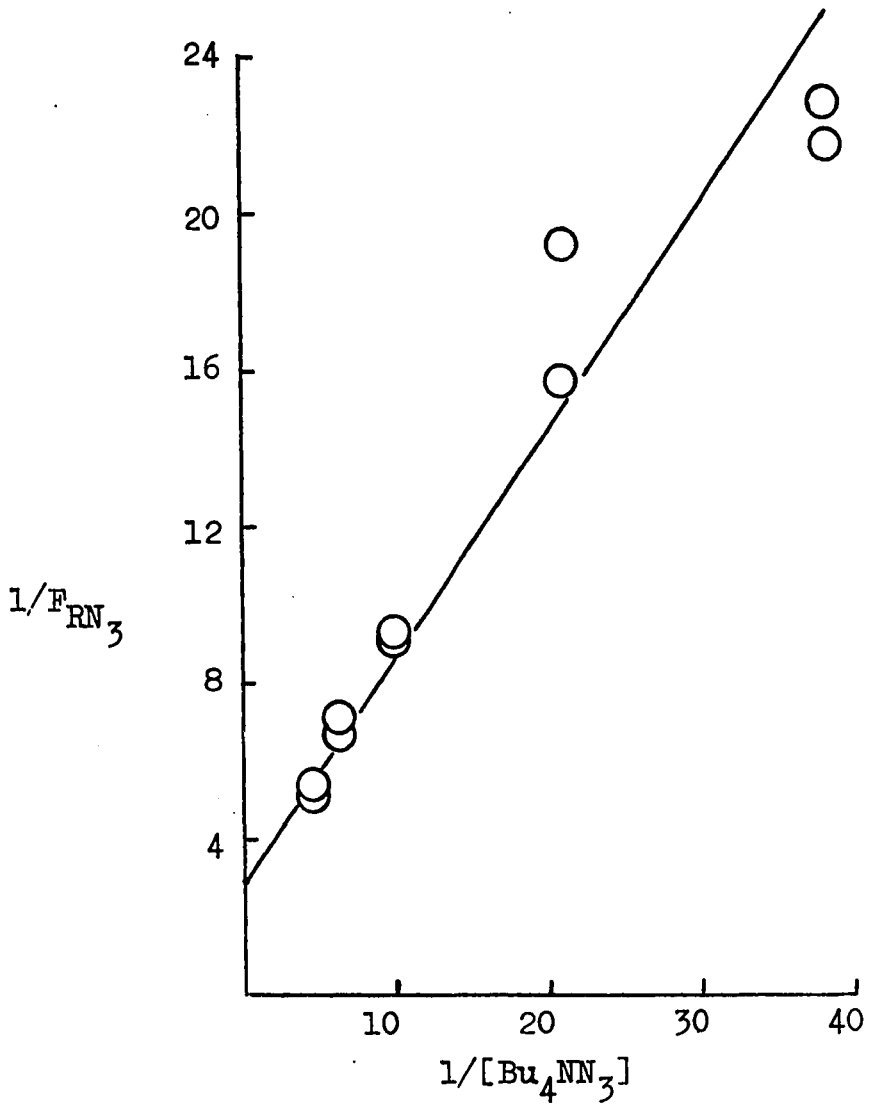


Figure 18. Intercept Plot for 2-Phenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength

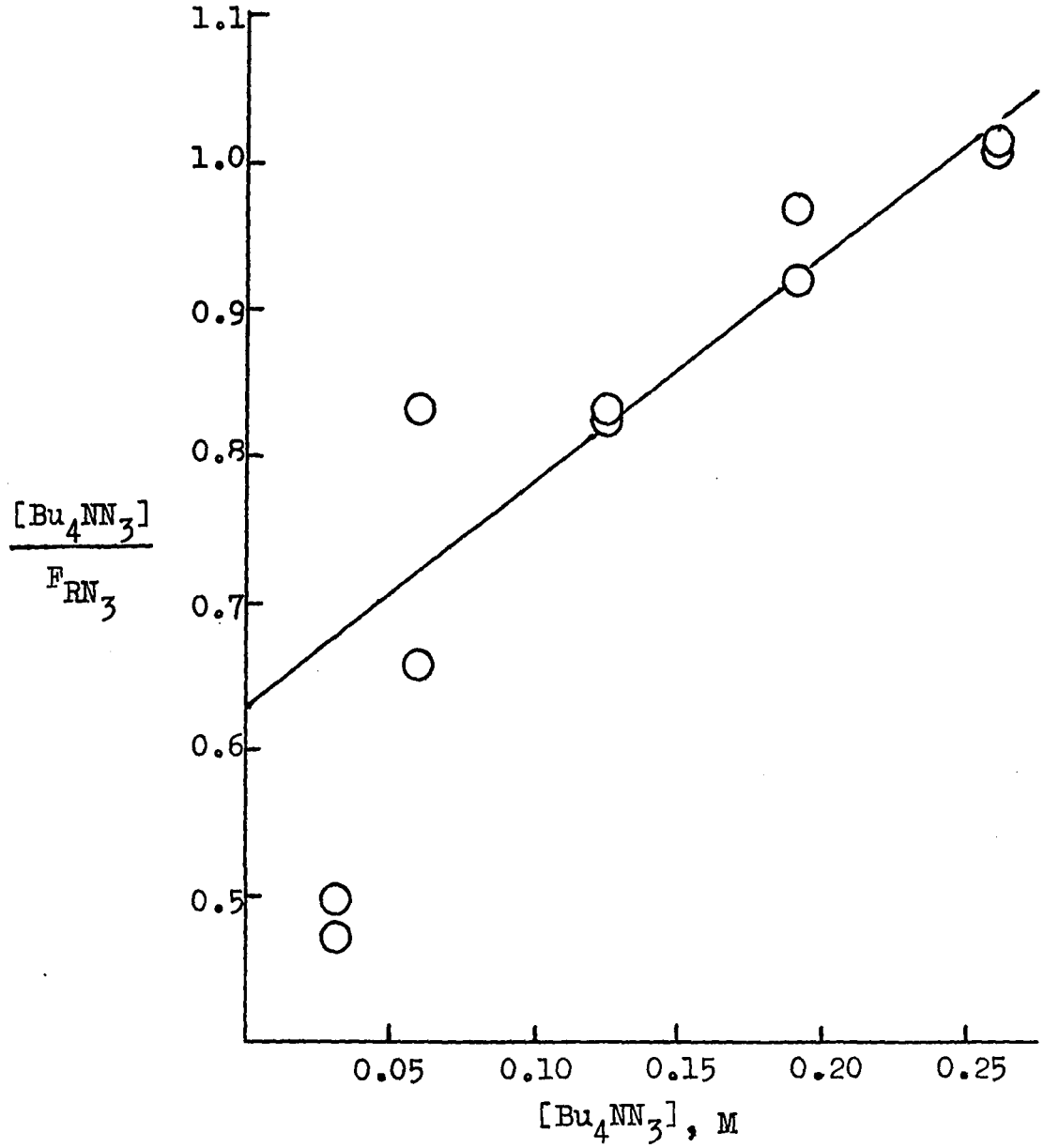


Figure 19. Slope Plot for 2-Phenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength

TABLE XXIV

RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 18 (INTERCEPT PLOT) AND 19 (SLOPE PLOT), BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
18	0.52	0.05	--	3.95	0.99	--
19	2.49	0.42	--	0.63	0.05	--
b) Weighted Results						
18	0.59	0.06	0.09	2.92	0.90	1.49
19	2.42	0.35	0.62	0.63	0.05	0.09

not introduce a serious error, since the maximum amount of acid produced, and therefore the amount of salt removed from the solution as HN_3, is only 0.02 M, 5%. When these two runs are included and a least mean squares analysis of the data obtained, the results are those shown in Table XXV.

These results are within experimental error of those obtained in Table XXIV, but the precision has been very much improved. The calculated values clearly show the advantage of plotting the data in the form of Equation IV, the slope plot, instead of using the format of the intercept plot, Equation III. The advantage of weighting the data according to its relative error is also evident. In each case, the precision of the results is considerably improved.

The results of these experiments rule out the two reaction pathways represented by reaction schemes [3] and [4]. They are consistent with a pathway such as scheme [5], in which there are at least two intermediates capable of reacting with solvent to form products, one of which is not captured by azide ion. The partitioning of the first intermediate between products and a subsequent intermediate, as measured by the value of k_6/k_3, can be assigned a value of 0.9 with an uncertainty, as

TABLE XXV

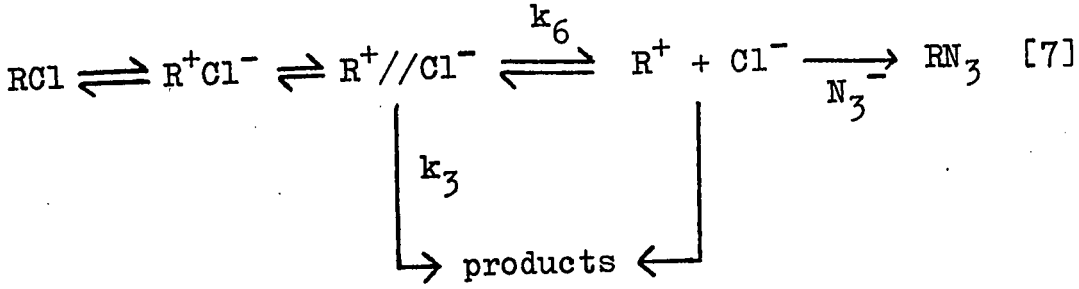
RESULTS OF A LEAST MEAN SQUARES ANALYSIS OF THE DATA FROM TABLE X, TOGETHER WITH RUNS I-295 AND II-223, BY LSEFIT

Type of fit*	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
inter.	0.55	0.04	--	3.12	0.65	--
slope	2.00	0.19	--	0.68	0.05	--
b) Weighted Results						
inter.	0.59	0.06	0.09	2.23	0.23	0.35
slope	1.91	0.17	0.19	0.63	0.04	0.07

* the figures are not shown; inter. refers to the data plotted as an intercept plot, slope refers to the da ta plotted as a slope plot.

measured by the standard error, E, of 0.2.

The evidence presented has given no information about the identity of the two intermediates. One possible reaction pathway might be scheme [7]



[7]

In this scheme, the intimate ion pair (R^+Cl^-) does not give solvolysis products directly.

The only products formed from the solvent separated ion pair ($R^+//Cl^-$) are those of ethanolysis, while the free ions ($R^+ + Cl^-$) can give either alkyl azide (RN_3) or ethanolysis products. The ratio of k_6/k_3 is a measure of the partitioning of $R^+//Cl^-$.

The ability to form free ions, as R^+ and Cl^-, in any system, will depend upon the stability of the ions formed, and upon the ability of the solvent to support the ions formed. The ionizing power of the solvent should be some measure of its ability to support ions.

Summer and Carey(32) have studied the solvolysis of optically active 2-phenyl-2-butyl chloride in 75% aqueous dioxane in the presence of azide ion. The

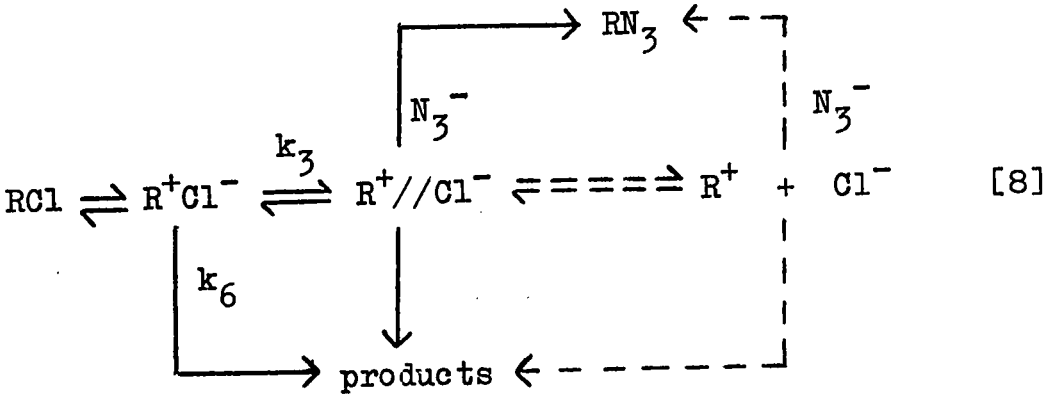
products of the reaction were the 2-phenylbutenes and 2-phenyl-2-butyl azide. 2-Phenyl-2-butyl azide was formed with 17% net inversion of configuration. Thus, in this reaction, the azide cannot be formed solely from free ions.

The stability of the free ions of 2-phenyl-2-butyl chloride should be very similar to those of 2-phenyl-2-propyl chloride, the system under consideration in this study. The ionizing power of anhydrous ethanol, as measured by its Y value is -2.303 (28). Although there is no Y value available for 75% dioxane, it may be estimated to be about -0.40, since Y for 80% aqueous dioxane is -0.83 (33), and Y for 70% dioxane is +0.13 (33); i.e. 75% dioxane is a very much better ionizing solvent than is anhydrous ethanol. Since this is the case, and since the formation of 2-phenyl-2-butyl azide cannot arise solely from free ions in this solvent, then it would be unreasonable to assume that the formation of 2-phenyl-2-propyl azide would arise exclusively from free ions in the much less powerfully ionizing solvent anhydrous ethanol. Hence scheme [7] may be ruled out as the reaction pathway.

These considerations do not rule out, however, the existence of free ions. Rather, they require that there be two intermediates prior to free ions, both capable of

forming solvolysis products and only one of which can be trapped by azide salt.

From the evidence presented, scheme [8] is the best representation of the reaction pathway that can be made.



[8]

Whether the reactions represented by the open arrows (---→) occur is still open to question.

The results obtained for 2-phenyl-2-propyl chloride are similar to those obtained by Mermelstein for 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol. He found $k_6/k_3 = 1.4$. As his value was obtained from data where the ionic strength of the solution was not constant, his results should be accepted only conditionally. The results of Table XX give a value of k_6/k_3 of 1.2 for 2-phenyl-2-propyl chloride under similar conditions. Since the two results are very similar, it may be concluded that the two reactions are proceeding in a similar manner.

ETHANOLYSIS OF SELECTED BENZYL CHLORIDES IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE

CHAPTER 2

INTRODUCTION

In Chapter 1, three reaction mechanisms were considered for the ethanolysis of 2-phenyl-2-propyl chloride. In each scheme, allowance was made for the

diversion of ethanolysis products to 2-phenyl-2-propyl azide observed when the nucleophile tetrabutylammonium azide was added to the reaction mixture. The mathematical relationship between $1/F_{RN_3}$ and $1/[N_3^-]$ was derived for each scheme. For a reaction pathway in which alkyl azide is formed by a nucleophilic displacement on the starting material (scheme [3]), the derived relationship predicts that a plot of $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ should have an intercept of one. For a mechanism wherein the products of solvolysis and the alkyl azide are formed from the same intermediate(s) (scheme [4]), such a plot should also have an intercept of one. If, however, the reaction proceeds through two or more intermediates, one of which is not capable of capture by azide salt (scheme [5]), then the intercept of the plot should be greater than one; the difference between the observed value and unity is a measure of the partitioning of the intermediate not capable of capture by salt (Int. A) between products and a subsequent intermediate (Int. B).

The value of the intercept for 2-phenyl-2-propyl chloride is 1.91. It is concluded from this result that scheme [5] best represents the reaction pathway and that the relative partitioning of Int. A between products and

Int. B is 0.91. An immediate question arises. Is the value of 0.91 a measure of the partitioning of Int. A or is it merely an artifact of the scheme? Have the reaction conditions chosen really been such that the errors due to the assumptions in deriving the $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ relationship have been minimized?

Some insight into the problem might be gained by examining a system for which the value of the intercept can be predicted. If we consider a system where organic azide is formed by nucleophilic displacement, the mechanism of the reaction would be represented by scheme [3]. The predicted intercept value then will be one. If the measured value for such a system is unity, the results found for 2-phenyl-2-propyl chloride could be accepted with confidence because the assumptions in the derivation of the $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ relationship are the same for both schemes [3] and [5]. Any deviation from the value of one would be some indication of the uncertainty of the 2-phenyl-2-propyl chloride results.

The choice of substrate for such an experiment is critical. The chosen compound must be such that direct displacement by tetrabutylammonium azide is competitive with solvolysis. If the substitution reaction is very much faster than solvolysis, the only reaction product

formed would be organic azide; the experiment would be an unsatisfactory test since a plot of $1/F_{RN_3}$ *vs.* $1/[N_3^-]$ would necessarily have an intercept of one because $1/F_{RN_3} = 1/1 = 1$ for any salt concentration. If the solvolysis reaction is very much faster than substitution, the concentration of azide salt required to form organic azide would be so large that the experiment would be impractical.

The systems chosen for study were benzyl chloride and p-methoxybenzyl chloride.

RESULTS

Preparation of Starting Materials and Products

The starting materials used were benzyl chloride and p-methoxybenzyl chloride. The former material was available commercially. The latter was prepared by the reaction of hydrogen chloride with anisyl alcohol.

The corresponding organic azides were required for rate and product studies. Benzyl azide was prepared by the method of Curtius and Erhart(34). p-Methoxybenzyl azide was prepared by the reaction of p-methoxybenzyl chloride with tetrabutylammonium azide in refluxing actone.

Calibration Curves for Azide Analysis

Calibration curves of absorbance at 4.76 μm vs. concentration were made for benzyl azide and p-methoxybenzyl azide. The results are shown in Table XXVI and Figure 20 for benzyl azide, and in Table XXVII and Figure 21 for p-methoxybenzyl azide. The plot for benzyl azide is linear. The plot for p-methoxybenzyl azide shows curvature at high concentrations.

Kinetic Study of the Reaction of Tetrabutylammonium Azide with Benzyl Chloride

A preliminary rate analysis was carried out for benzyl chloride in the presence of 0.016 M tetrabutylammonium azide in anhydrous ethanol at 50°. The study showed that this substrate would not be satisfactory for the experiment we wished to carry out, since even at such a low salt concentration the only reaction observed is that of displacement, the only product found being benzyl azide.

The results of the study are shown in Table XXVIII. The rate was studied by following the appearance of the infrared band due to azide at 4.76 μm. The second-order rate constant was calculated from the expression:

TABLE XXVI

RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION FOR BENZYL AZIDE AT 4.76 μm

4.907 ml aliquot residue dissolved in 2.056 ml of CCl_4

Run No.	10^3 [RN_3] M	log I_o/I
II-234-1	11.11	0.406
		0.391
-4	7.98	0.234
		0.226
-2	4.36	0.129
		0.125
-5	3.13	0.0700
		0.0730
-3	2.18	0.0626
		0.0560
-6	1.57	0.0398
		0.0325

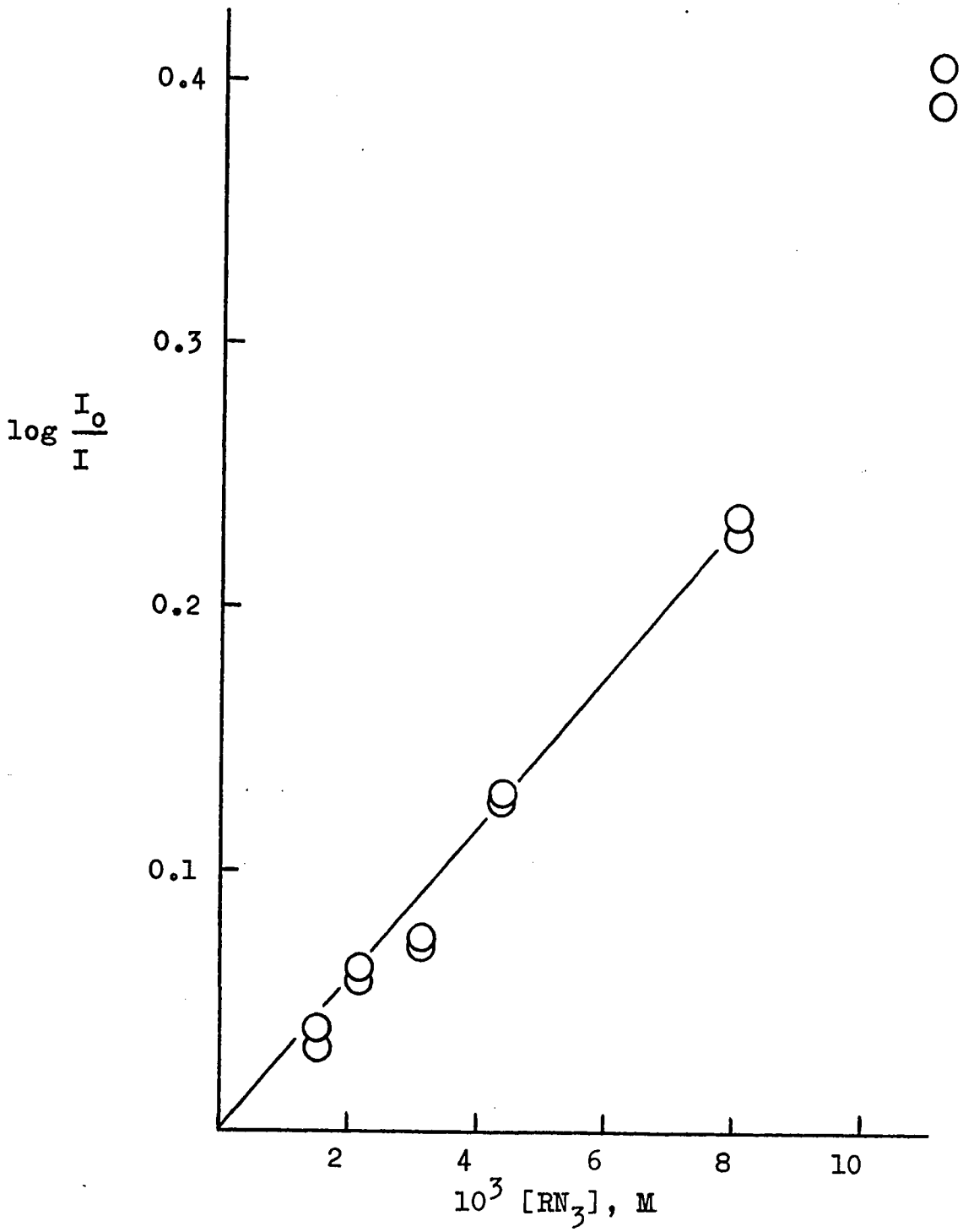


Figure 20. Calibration Curve at 4.76 μm for Benzyl Azide

TABLE XXVII

RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION FOR p-METHOXYBENZYL AZIDE AT 4.76 μm

4.928 ml aliquot residue dissolved in 2.056 ml CCl_4

Run No.	10^3 [RN_3] M	log I_o/I
III-218-1	20.85	1.024
		0.995
-2	14.12	0.854
		0.869
-3	10.43	0.628
		0.646
-4	5.215	0.356
		0.358
-5	4.705	0.318
		0.336
-6	2.171	0.153
		0.150

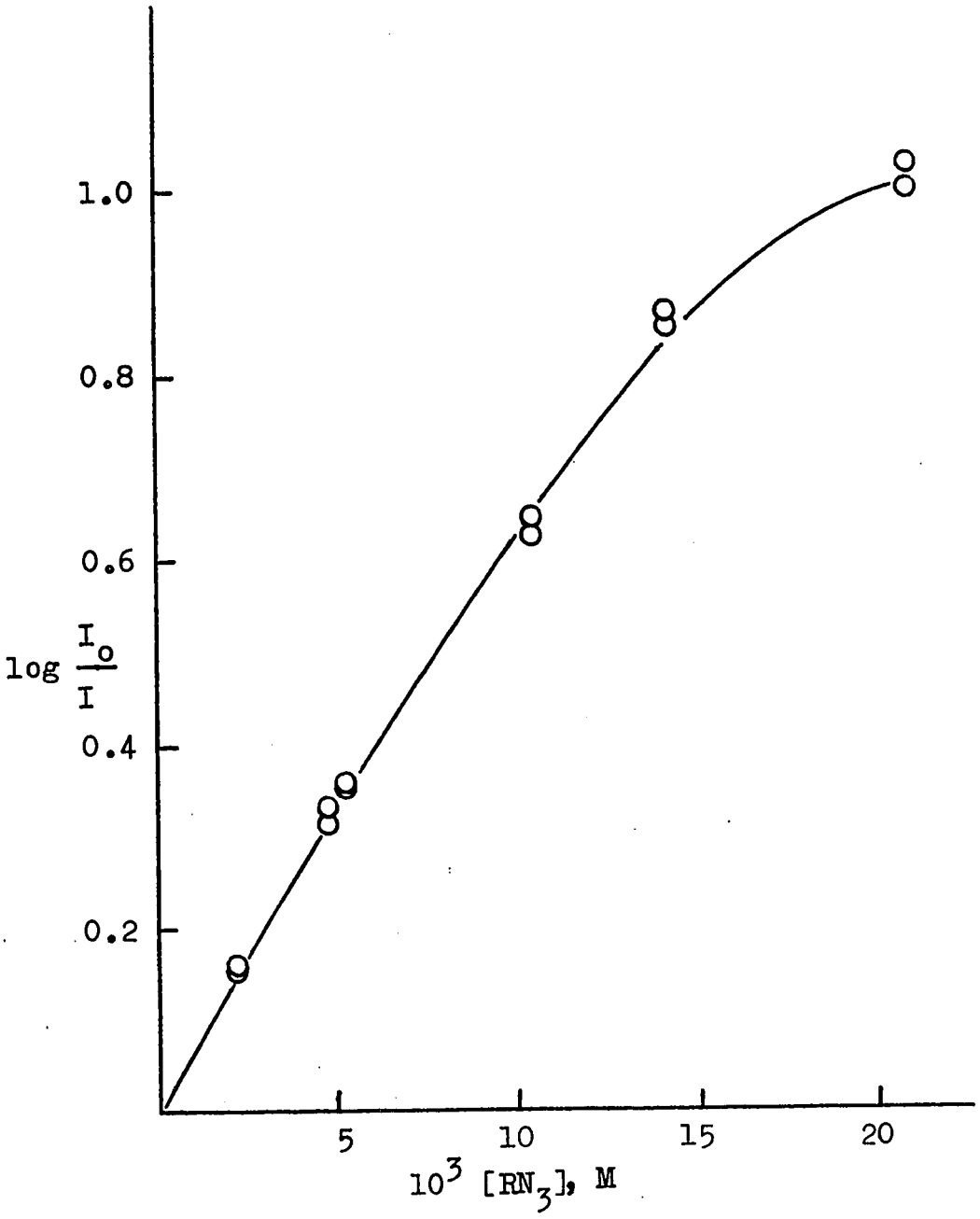


Figure 21. Calibration Curve at 4.76 μm for p-Methoxybenzyl Azide

TABLE XXVIII

REACTION RATE OF BENZYL CHLORIDE IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE IN ANHYDROUS ETHANOL AT 50° BY INFRARED SPECTROSCOPY

$[Bu_4NN_3]$ = 0.0157 M [RCl] = 0.00820 M

Time, sec.	log I_o/I	$[RN_3]$ M	$10^4 k_2$, M^{-1} sec^{-1}
0	---	0	-
3780	0.004	5×10^{-4}	9.7
16440	0.018	9.5×10^{-4}	5.0
258000	0.242	8.2×10^{-3}	-

$$k_2 t = \frac{1}{[Bu_4NN_3]_o - [RCl]_o} \times 2.303 \log \frac{[RCl]_o}{[Bu_4NN_3]_o} \times \frac{[Bu_4NN_3]_t}{[RCl]_t}$$

where subscripts o and t refer to concentrations at zero time and time t respectively.

The discrepancy between the two calculated rate constants is not surprising since both were obtained in the first 10% of the reaction.

Kinetic and Product Studies of the Reaction of Tetrabutylammonium Azide with p-Methoxybenzyl Chloride in Anhydrous Ethanol at 50°

The pseudo-first-order rate constants for the solvolysis of p-methoxybenzyl chloride in 100% ethanol at 50° in the presence and absence of tetrabutylammonium salt were determined using Titrimetric Procedure D (page 249). The results are shown in Table XXIX. Two of the reactions were studied concurrently by infrared spectroscopy and are also included in Table XXIX. These rate constants have very large attendant errors, but the numbers obtained are within experimental error of the titrimetric rate constants.

TABLE XXIX

EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE RATE OF SOLVOLYSIS OF p-METHOXYBENZYL CHLORIDE IN ANHYDROUS ETHANOL AT 50° AS MEASURED BY TITRIMETRY AND INFRARED SPECTROSCOPY

Run No.	[RCl] M	[Bu_4NN_3] M	10^4 k_1, sec^{-1} Titr.	Infrared
II-256	0.02062	0	3.21 ±0.07	
II-261	0.02440	0	3.24 ±0.10	
II-275	0.00637	0.0411	7.6 ±1.2	9.4 ± 1.4
II-293	0.02945	0.04216	5.6 ±0.3	
II-291	0.02677	0.04344	5.7 ±0.3	
II-287	0.01338	0.09127	11.6 ±1.1	15.9 ± 2
II-295	0.02366	0.1001	13.2 ±1.1	

The large increase in rate of reaction of p-methoxybenzyl chloride when tetrabutylammonium azide is added to the reaction mixture is quite different from the behaviour found for the 2-phenyl-2-propyl chloride reaction (Table VI) where the small increase in rate was explained by a normal salt effect. The large increase for the present system may be explained by assuming that azide is carrying out a displacement reaction on p-methoxybenzyl chloride. The observed rate constant, k_{obs}, will be the sum of all the rate constants:

$$k_{obs} = k_1 + k_2[N_3^-]$$

where k_1 is the rate of solvolysis, and k_2 is the rate of displacement by azide ion.

The pseudo-first-order rate constant, k_{obs}, should be constant as long as the azide concentration remains reasonably constant throughout the reaction, or should drift downwards if azide ion is used up during the reaction. The rates being studied were fast, and there was an attendant large error in the observed rate constants, partly due to the speed of the reaction, and partly because of difficulties in the work-up procedure. A sample run, II-275, is shown in Table XXX. In this run the concentration of substrate is small (0.0063 M),

TABLE XXX

RATE OF REACTION OF p-METHOXYBENZYL CHLORIDE (6.372×10^{-3} M) IN ANHYDROUS ETHANOL AT 50.0° IN THE PRESENCE OF TETRA-BUTYLAMMONIUM AZIDE BY TITRIMETRY AND BY INFRARED.

RATE RUN NUMBER II-275

Aliquot size: 4.907 ml $[Bu_4NN_3]$ = 0.0411 M

Calculated infinity: 0.774 ml Indicator: phenolphthalein

Time (sec)	Titre (ml)	log I_o/I	$10^4 k_t$ sec^{-1}	$10^4 k_{ir}$ sec^{-1}
0	0.110	0.042		
120	0.140	0.049	8.7	10.4
180	0.150	0.052	9.5	8.0
240	0.160	0.052	9.9	5.3
360	0.165	0.072	7.2	11.5
480	0.172	0.077	5.5	8.7
600	0.180	0.082	6.0	9.3
720	0.190	0.088	6.2	9.2
900	0.220	0.105	8.4	11.7
1140	0.224	0.106	7.0	9.4
1380	0.250	0.106	8.4	7.6

TABLE XXX (Continued)

Time (sec)	Titre (ml)	$\log \frac{I_o}{I}$	$10^4 k_t$ sec^{-1}	$10^4 k_{ir}$ sec^{-1}
1860	0.266	0.132	7.8	12.7
2280	0.269	0.130	6.9	9.5
$10t_{\frac{1}{2}}$	0.295	0.142		
$30t_{\frac{1}{2}}$	0.308			
		Average	7.6 ± 1.2	9.4 ± 1.4

Average F_{RN_3} calculated from infinity titre: 0.588

F_{RN_3} calculated from infrared results: 0.590

the resulting titre small, and consequently the rate constant is subject to very large errors. Here, 41% of the theoretical amount of HCl was formed, so 59% of the reaction products may be assumed to be p-methoxybenzyl azide; therefore, 10% (0.004 M) of the salt will have been consumed. Any downward drift in rate constant that the loss of this amount of salt might cause would be masked in the large uncertainties in the calculated values.

For rate II-291 (Table XXXI), the initial concentration of tetrabutylammonium azide is the same as that of run II-275. The concentration of starting material for II-291 is 0.0268 M, much larger than that of run II-275; the resulting titres are larger, so that the errors in the calculated rate constants are much smaller.
In run II-291, 47% of the theoretical amount of HCl has been formed, so 53% of the products are p-methoxybenzyl azide; 33% (0.014 M) of the salt will have been consumed. In addition, since no base was added in these runs to neutralize the acid, another 0.013 M of salt will have been removed from the reaction as hydrazoic acid; a total of 66% of the starting azide salt, then, will have been consumed. At first it may seem surprising that there is no observed drift in the rate; however, the

TABLE XXXI

RATE OF ETHANOLYSIS OF p-METHOXYBENZYL CHLORIDE AT 50° IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE BY TITRIMETRY

RUN NUMBER II-291

Aliquot size: 4.974 ml $[Bu_4NN_3]$ = 0.04344 M

Calc. infinity: 3.145 ml Indicator: phenolphthalein

Time (sec)	Titre (ml)	$10^4 k_1$ (sec^{-1})
0	0.600	--
60	0.630	5.91
120	0.648	4.76
180	0.690	6.40
300	0.753	6.50
420	0.772	5.29
600	0.850	5.70
780	0.905	5.60
960	0.950	5.42
1200	1.056	6.26
1500	1.105	5.87
1800	1.151	5.65
2100	1.190	5.48
2460	1.234	5.40
$10t_{\frac{1}{2}}$	1.462	Average: 5.77 $\pm$0.30
$40t_{\frac{1}{2}}$	1.464	

reaction, being rapid, has already reached 30% completion before the first point can be taken. Any rate drift could have already occurred before the rate pattern can be established.

The total amount of p-methoxybenzyl azide formed in run II-291 is less than that found in II-275, as expected, since the overall concentration of salt will be smaller for run II-291 than for II-275; the observed rate constant for run II-291 is the smaller, as would be predicted since the value of $k_2[N_3^-]$ will be smaller.

The fraction of p-methoxybenzyl azide formed when p-methoxybenzyl chloride was allowed to solvolyze in anhydrous ethanol at 50° for 10 half-lives in the presence of tetrabutylammonium azide was studied. These reactions were studied in the presence of lithium ethoxide using tetrabutylammonium perchlorate to adjust the ionic strength to a constant level. The results were obtained by infrared techniques (page 251), and are tabulated in Table XXXII. A plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ is shown in Figure 22. A plot of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$ is shown in Figure 23. The results of the least mean squares fit for the data are shown in Table XXXIII. Again, the standard errors are calculated assuming an absolute error of $\pm 1\%$ in the fraction of RN_3 formed for each run.

TABLE XXXII

EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE PRODUCT DISTRIBUTION FOR THE SOLVOLYSIS OF p-METHOXYBENZYL CHLORIDE IN ANHYDROUS ETHANOL AT 50° IN THE PRESENCE OF LITHIUM ETHOXIDE (0.0285 M) AT CONSTANT IONIC STRENGTH (μ = 0.1) AS MEASURED BY INFRARED SPECTROSCOPY

Run No.	10^3[RCl] M	[Bu_4NN_3] M	[Bu_4ClO_4] M	F_{RN_3}	$\frac{1}{[Bu_4NN_3]}$	$\frac{1}{F_{RN_3}}$	$\frac{[Bu_4NN_3]}{F_{RN_3}}$
III-269-1	8.8851	0.1037	0	0.742	9.65	1.35	0.140
III-269-2	9.207	0.1044	0	0.746	9.60	1.34	0.140
				0.733		1.36	0.142
III-270-1	8.8851	0.08083	0.0256	0.687	12.4	1.46	0.118
				0.717		1.39	0.113
III-270-2	9.207	0.05700	0.0339	0.624	17.5	1.60	0.0914
				0.635		1.57	0.0898
III-271-1	8.8851	0.03854	0.0651	0.508	26.0	1.97	0.0758
				0.515		1.94	0.0747
III-271-2	9.207	0.02334	0.0819	0.376	42.9	2.66	0.0620
				0.373		2.68	0.0625

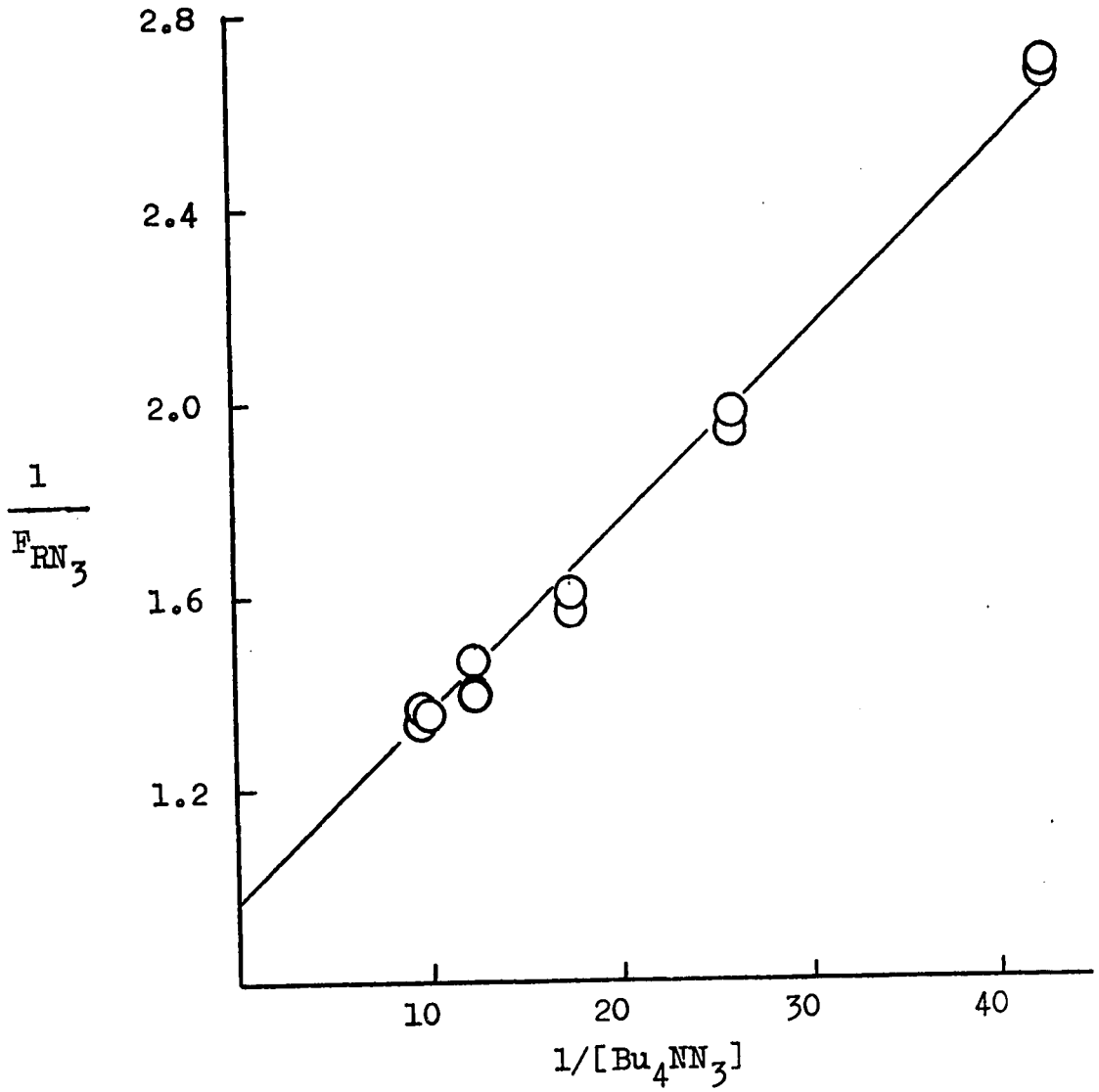


Figure 22. Intercept Plot for p-Methoxybenzyl Azide with Lithium Ethoxide at Constant Ionic Strength

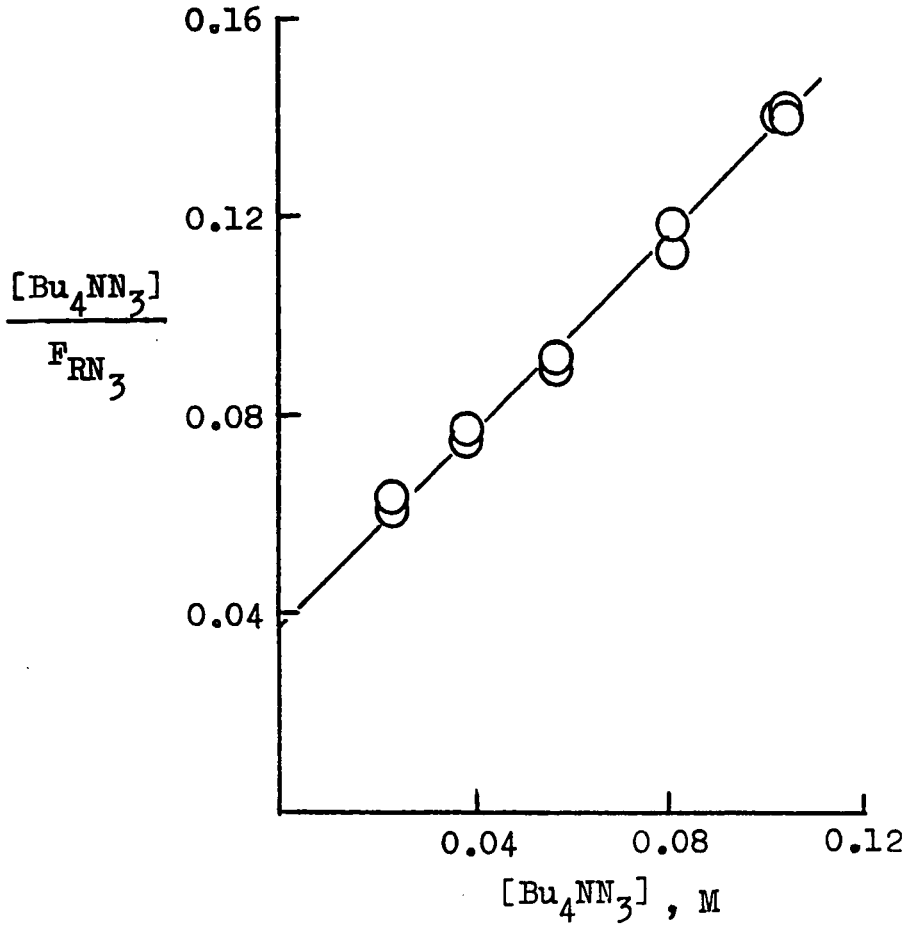


Figure 23. Slope Plot for p-Methoxybenzyl Azide with Lithium Ethoxide at Constant Ionic Strength

TABLE XXXIII

RESULTS OF THE ANALYSIS OF FIGURES 22 (INTERCEPT PLOT) AND 23 (SLOPE PLOT), BY LSEFIT

Figure No.	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
22	0.040	0.001	--	0.932	0.022	--
23	0.977	0.023	--	0.038	0.0015	--
b) Weighted Results						
22	0.039	0.0011	0.0015	0.944	0.023	0.029
23	0.968	0.021	0.027	0.038	0.0013	0.0017

DISCUSSION

It was pointed out in the introduction to this chapter that a study of the direct displacement of tetrabutylammonium azide on a substrate should give some measure of the confidence that can be placed in the results obtained for 2-phenyl-2-propyl chloride. The compound required for study must be such that nucleophilic displacement would be competitive with ethanolysis. It was thought that benzyl chloride might be a suitable substrate.

A preliminary rate study showed that this compound would not be suitable. At 0.016 M salt, the only reaction product formed was benzyl azide. The second-order rate constant, k_2, in ethanol at 50° was found to be 6×10^{-4} M^{-1} sec^{-1}; the pseudo-first-order rate constant for nucleophilic displacement ($k_p = k_2[N_3^-]$), then, is 1×10^{-5} sec^{-1}. The first-order ethanolysis rate constant, k_1, can be estimated as 10^{-8} sec^{-1} at 50°, using Winstein's mY correlation(9) (Y for ethanol = -2.3, Y for 60% aqueous dioxane = 0(33); k_1 in aqueous dioxane at 50° = 1.3×10^{-6} sec^{-1}(35)). Displacement by 0.015 M azide salt should be a thousand-fold faster than ethanolysis of the compound. It was

obvious, then, that a system considerably more reactive towards solvolysis than benzyl chloride would be necessary for the desired study.

p-Methoxybenzyl chloride proved to be a good choice. Simultaneous concerted reaction with the azide salt and ethanolysis were observed; the overall rate constant, k_{obs}, is necessarily the sum of the rate constants for the two reactions; therefore,

$$k_{obs} = k_1 + k_2[Bu_4NN_3]$$

where k_1 is the ethanolysis rate constant and k_2 is the rate constant for nucleophilic attack on the substrate. A plot of k_{obs} *vs.* $[Bu_4NN_3]$ should give an intercept of k_1 and a slope of k_2. Such a plot is shown in Figure 24. From the graph, $k_2 = 1 \times 10^{-2}$ M^{-1} sec^{-1}, and $k_1 = 3.4 \times 10^{-4}$ sec^{-1}; the agreement with the measured value of k_1, 3.2×10^{-4} sec^{-1}, is good. It should be noted that the value of k_2 has not been obtained at constant ionic strength. Consequently, k_2 could be smaller than this value which may include some salt enhancement.

Another estimate of k_2 may be obtained from the results of the product analyses. Equation [I] (Appendix A) predicts for this type of system that a plot of

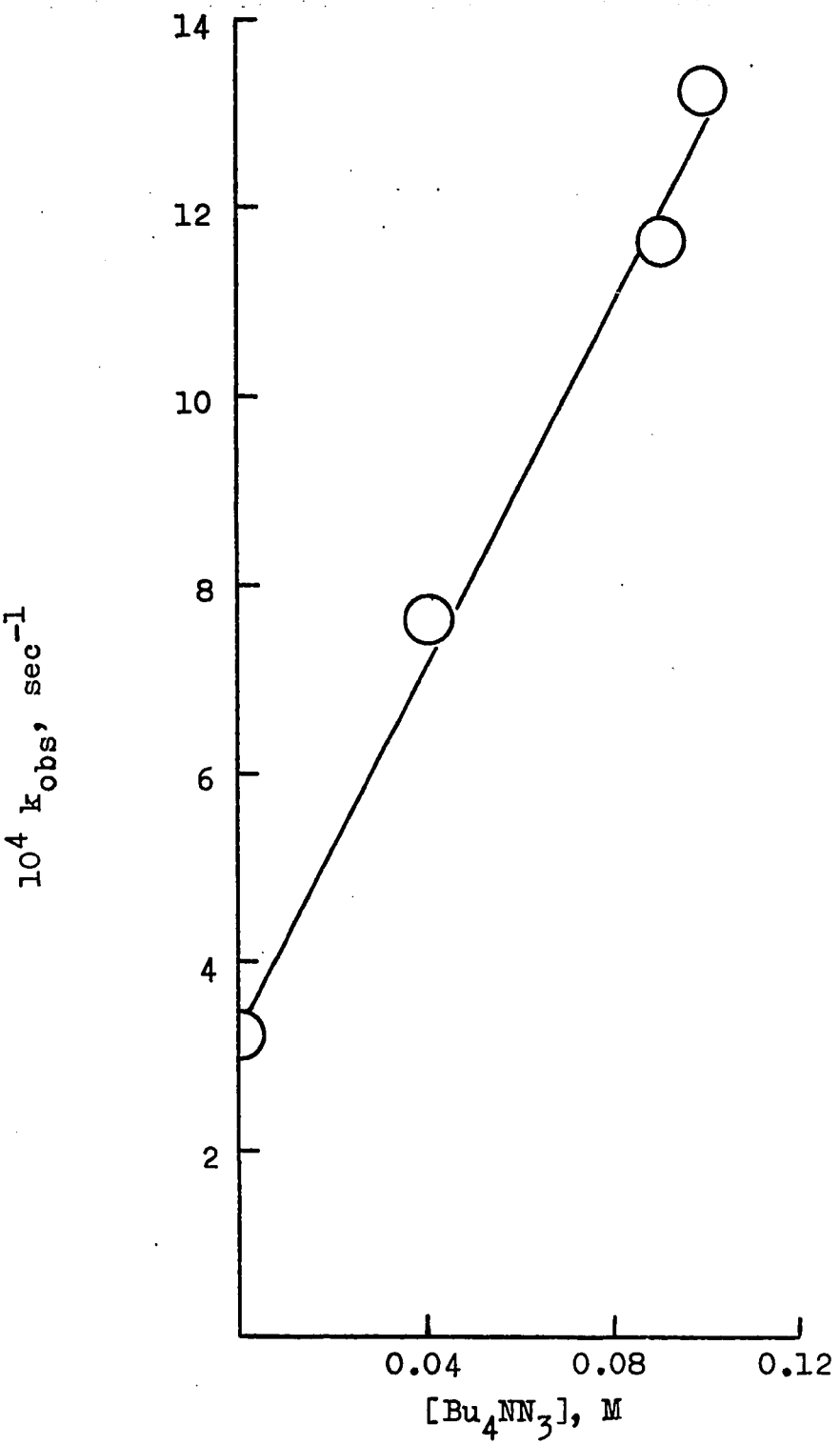


Figure 24. Effect of Tetrabutylammonium Azide on the Reaction Rate of p-Methoxybenzyl Chloride.

$1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ will have a slope of k_1/k_2. The slope of such a plot (Figure 22) has a value of 4×10^{-2}. The measured value of k_1 is 3.2×10^{-4} sec^{-1}; therefore, $k_2 = 0.8 \times 10^{-2}$ M^{-1} sec^{-1}. This value of k_2 is in excellent agreement with that obtained from the kinetic results. Since the product analyses were carried out at constant ionic strength, this value of k_2 will not be enhanced by a salt effect. Both values of k_2 are similar; it may be inferred that there is little rate acceleration due to salt.

The predicted value for the intercept of a plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ is one; as Table XXXIII shows, the results obtained are indeed within experimental error of unity. The excellent agreement between the predicted and measured value found for p-methoxybenzyl chloride certainly lends credence to the conclusions drawn concerning the reaction pathway followed for 2-phenyl-2-propyl chloride. The partitioning of the intermediate, Int. A, as measured by k_6/k_3 can be confidently described as 0.9.

A STUDY OF THE ETHANOLYSIS OF SOME SUBSTITUTED 2-ARYL-2-PROPYL CHLORIDES

CHAPTER 3

INTRODUCTION

In Chapters 1 and 2, mathematical derivations of the relationship between $1/F_{RN_3}$ and $1/[N_3^-]$ were derived for three reaction mechanisms, the assumptions made in the

derivations were justified, and details of the mechanism of reaction of 2-phenyl-2-propyl chloride were elucidated.

In this chapter, a study of the effect of tetrabutylammonium azide on the ethanolysis of some substituted 2-aryl-2-propyl chlorides is examined. The compounds chosen for study were 2-p-tolyl-2-propyl chloride, 2-p-methoxyphenyl-2-propyl chloride, 2-p-nitrophenyl-2-propyl chloride, and 2-p-acetylphenyl-2-propyl chloride. The methods of synthesis of the starting materials and expected products are presented and the results are discussed within the context of the mathematical relationships derived in Chapter 1.

RESULTS

Synthesis of the Starting Materials

2-p-Tolyl-2-propyl Chloride This compound was synthesized by the reaction of dry HCl gas with 2-p-tolyl-2-propanol in the cold, using the procedure developed by Brown and Okamoto(24). The material so prepared had high-field nmr peaks indicative of polymeric material. Only 91% of the theoretical acid was released on solvolysis of the material. This compound resisted

all attempts at purification. In an attempt at distillation, the material decomposed to the olefin, which polymerized. On chromatography over alumina, whether acid, basic, or neutral, only polymeric material was recovered. Attempted preparation by another method, reaction of thionyl chloride with the alcohol, gave material with an nmr spectrum showing about 20% olefin and high-field peaks indicative of polymeric material. The material was finally used without purification. Since 91% of theoretical acid was released, the material was considered to be 91% pure. The nmr showed no indication of olefin, so the impurity was considered to be polymer only. This is in contrast to the results of synthesis of 2-phenyl-2-propyl chloride where the impurity was mainly olefin. Since this material was to be used in product studies, it was important to determine whether only the chloride solvolyzed, or if the impurity would also solvolyze. The most convenient method to find out would be to study the rate of reaction. The chloride and the impurity would not be expected to solvolyze at the same rate, so if both were reacting, a drift in rate as the reaction proceeded should be evident. The solvolysis of 2-p-tolyl-2-propyl chloride was too fast to study in anhydrous ethanol. Instead, it was studied in two other solvent systems.

In 75% acetone-25% ethanol at 25.00°, k_1 = (5.37 ±0.12) x 10^{-4} sec^{-1}; the rate was studied by following the formation of acid by titration with standard base, using phenolphthalein indicator. The rate is shown in Table XXXIV. In 75% dioxane-25% ethanol, k_1 = (1.07 ±.04) x 10^{-4} sec^{-1}; this rate was followed by ultraviolet spectroscopy. Duplicate runs were made. A sample rate is shown in Table XXXV. In both solvent systems, the rate was followed to 95% reaction. There was no observable drift of the rate constant in either solvent system. From these studies, it was concluded that only the desired material, 2-p-tolyl-2-propyl chloride, was undergoing solvolysis.

2-p-Methoxyphenyl-2-propyl Chloride This material could not be obtained satisfactorily from the synthesis developed by Brown and Okamoto. Every attempt, even at very low temperatures and very short reaction times, resulted in material that contained very large amounts of polymeric material, 50% or more as estimated by nmr and by the amount of acid released on solvolysis. Instead, the compound was synthesized by the reaction of thionyl chloride with the alcohol in the presence of 2,6-lutidine. Even this method of synthesis was not very satisfactory and it was necessary to control the

TABLE XXXIV

RATE OF REACTION OF 2-p-TOLYL-2-PROPYL CHLORIDE (0.03868 M) IN 75% ACETONE-25% ETHANOL AT 25.0° BY TITRIMETRY.

Rate Run No. III-90 Indicator: phenolphthalein

Aliquot: 4.928 ml Calculated Infinity: 4.527 ml

Time, sec	Titre, ml	$10^4 k_t$, sec^{-1}	Time, sec	Titre, ml	$10^4 k_t$ sec^{-1}
0	0.67		2160	2.67	5.31
180	0.90	(4.61)	2580	2.92	5.66
360	1.18	5.31	3060	3.05	5.47
600	1.45	5.18	3840	3.24	5.45
750	1.63	5.22	4860	3.41	5.61
960	1.84	5.32	$11t_{\frac{1}{2}}$	3.59	
1230	2.08	5.34	$32t_{\frac{1}{2}}$	3.61	
1530	2.29	5.37	**	4.21	
1800	2.45	5.20		Average:	5.37 ± .12

% of calculated infinity found 92.5

** titre on titrating directly in water solution, without work-up, assumed to be all of acid formed.

TABLE XXXV

RATE OF REACTION OF 2-p-TOLYL-2-PROPYL CHLORIDE IN 75% DIOXANE-25% ETHANOL AT 25.1° BY ULTRAVIOLET SPECTROSCOPY. RATE RUN NO. III-96. [RCl] = 2.004×10^{-4}

Time (sec)	Absorbance	$10^4 k_1$ (sec^{-1})	Time (sec)	Absorbance	$10^4 k_1$ (sec^{-1})
0	0.419		7200	0.739	1.11
60	0.423	1.00	7260	0.742	1.06
180	0.431	1.02	8160	0.783	1.05
480	0.448	1.08	9060	0.796	1.05
540	0.452	1.06	10200	0.821	1.06
840	0.472	1.11	11400	0.846	1.05
1200	0.492	1.10	12540	0.877	1.11
1800	0.530	1.08	13680	0.891	1.08
2400	0.561	1.11	15000	0.916	1.12
3000	0.578	1.07	17340	0.922	1.00
3600	0.620	1.05	19860	0.955	1.06
4380	0.648	1.11	23880	0.977	1.02
5100	0.672	1.03	$10t_{\frac{1}{2}}$	1.030	
6340	0.722	1.03	$22t_{\frac{1}{2}}$	1.032	
			Average: 1.07 ± 0.02		

reaction conditions rigorously. This material was used immediately without attempting to purify it. On solvolysis, 81% of theoretical acid was released, so the compound was considered to be 81% pure. There were several peaks at high field in the nmr, indicative of polymer. The nmr gave no indication of olefin impurity. By analogy to 2-p-tolyl-2-propyl chloride, it was assumed that only the desired material was undergoing solvolysis.

2-p-Nitrophenyl-2-propyl Chloride There was no evidence for reaction on the addition of HCl gas to 2-p-nitrophenyl-2-propanol. On addition of a small amount of sublimed ferric chloride, the reaction proceeded smoothly. The infinity titre of the compound was not determined. No estimate of its purity has been made.

2-p-Acetylphenyl-2-propyl Chloride This compound was synthesized by the reaction of anhydrous HCl with the ethylene ketal of 2-p-acetylphenyl-2-propanol. Both cleavage of the ketal and reaction with the hydroxyl function to yield the chloride were effected. On solvolysis, 96% of the theoretical acid was released. The nmr gave no indication of olefin.

The olefinic products required were 2-p-tolylpropene,

2-p-methoxyphenylpropene, and 2-p-acetylphenylpropene. The 2-p-tolylpropene was obtained by redistillation and chromatography of an alcohol-olefin mixture made by a Grignard reaction. 2-p-Methoxyphenylpropene was available as a by-product from the synthesis of the corresponding azide. 2-p-Acetylphenylpropene was obtained by the reaction of phosphoric acid with the ethylene ketal of 2-p-acetylphenyl-2-propanol.

The ethers required were prepared as follows: 2-p-tolyl-2-propyl ethyl ether was obtained as a by-product of the synthesis of the corresponding azide; 2-p-methoxyphenyl-2-propyl ethyl ether and 2-p-acetylphenyl-2-propyl ethyl ether were synthesized by the method of Bowman and Wallis(26). The azides, 2-p-tolyl-2-propyl azide, 2-p-methoxyphenyl-2-propyl azide, and 2-p-acetylphenyl-2-propyl azide, were synthesized by the reaction of azide salts with the corresponding chlorides.

Calibration Curves for Azide Determination

A calibration curve of absorbance at 4.76 μm *vs.* concentration was constructed for 2-p-methoxyphenyl-2-propyl azide, 2-p-tolyl-2-propyl azide, and 2-p-acetylphenyl-2-propyl azide. The general procedure used was the same in each case. The details are outlined on page 263.

For 2-p-tolyl-2-propyl azide, the results are shown in Table XXXVI and Figure 25. The correlation appears to be linear.

The results of the study for 2-p-methoxyphenyl-2-propyl azide are shown in Table XXXVII and Figure 26. A linear correlation is observed to 0.015 M.

The results for 2-p-acetylphenyl-2-propyl azide are in Table XXXVIII and Figure 27. The relationship observed is not a linear one.

Product and Kinetic Studies

The products of reaction for 2-p-tolyl-2-propyl chloride and 2-p-acetylphenyl-2-propyl chloride were studied using g.c. techniques. For 2-p-nitrophenyl-2-propyl chloride and 2-p-methoxyphenyl-2-propyl chloride, the reaction products were studied by nmr spectroscopy. In addition, the amount of organic azide formed for each of the compounds except 2-p-nitrophenyl-2-propyl chloride was determined by infrared spectroscopy. The concentration of azide was found by comparing the absorbance at 4.76 μm for the sample with the appropriate standard calibration curve. The general procedure used was the same in each case (page 253). The results of each study are discussed below.

TABLE XXXVI

THE RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION AT 4.76 μm FOR 2-p-TOLYL-2-PROPYL AZIDE

4.928 ml aliquot residue dissolved in 2.506 ml CCl_4

Sample No.	$10^3[RN_3]$ M	log I_o/I
III-70-2	11.86	0.658
		0.624
-3	10.48	0.550
		0.542
-4	7.18	0.383
		0.404
-5	6.34	0.346
		0.348
-7	2.97	0.162
		0.152
-6	2.67	0.127
		0.136
-8	2.48	0.114
		0.112
-9	2.18	0.106

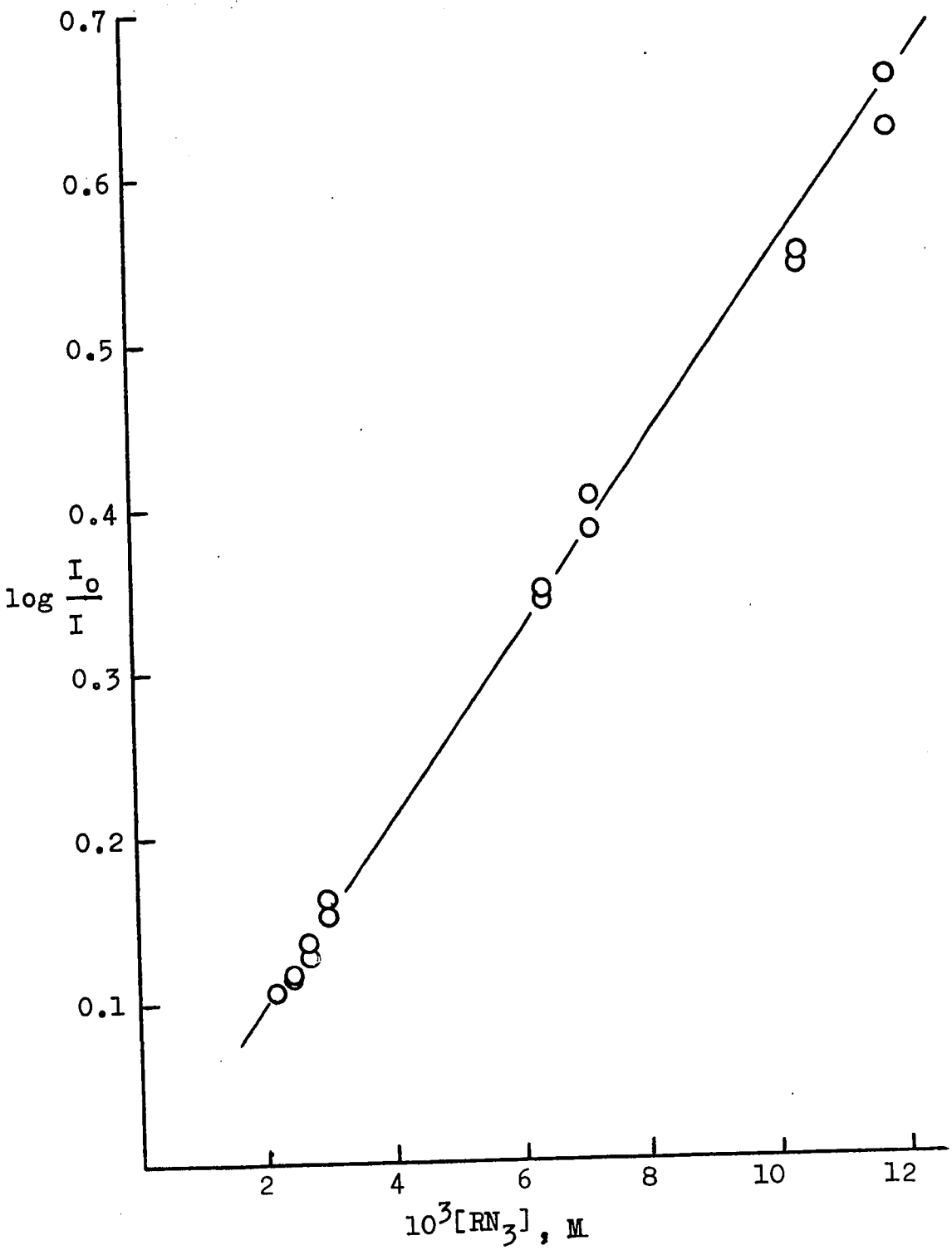


Figure 25. Calibration Curve for 2-p-Tolyl-2-propyl Azide, Measured at 4.76 μm

TABLE XXXVII

THE RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION AT 4.76 μm FOR 2-p-METHOXYPHENYL-2-PROPYL AZIDE

4.928 ml aliquot residue dissolved in 2.056 ml CCl_4

Run No.	$10^3[RN_3]$ M	log I_o/I
III-218-1	20.85	0.9954
		1.024
-2	14.12	0.854
		0.869
-3	10.43	0.628
		0.646
-4	5.215	0.356
		0.358
-5	4.71	0.318
		0.336
-6	2.17	0.153
		0.150

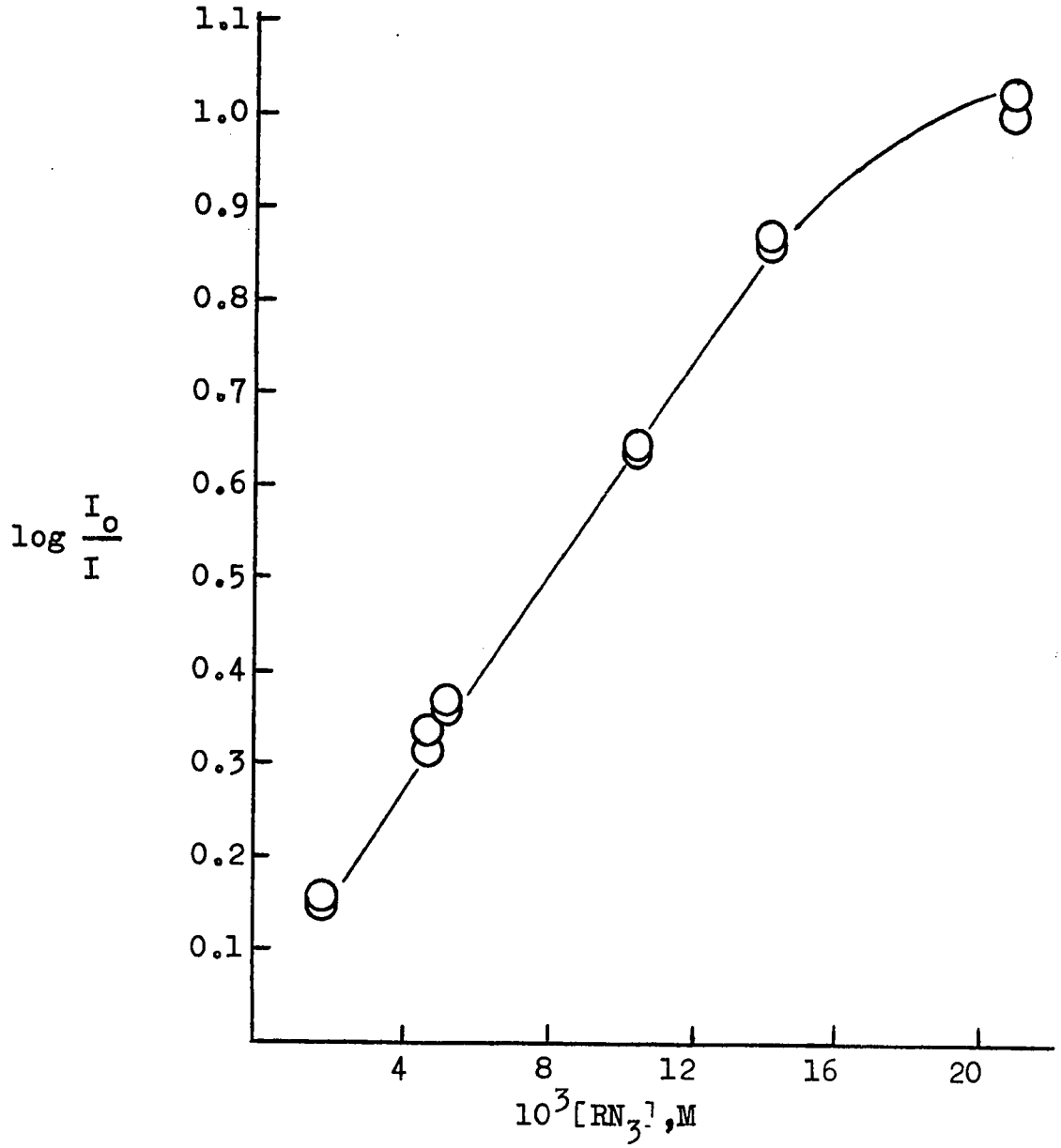


Figure 26. Calibration Curve for 2-p-Methoxyphenyl-2-propyl Azide, Measured at 4.76 μm

TABLE XXXVIII

THE RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION AT 4.76 μm FOR 2-p-ACETYLPHENYL-2-PROPYL AZIDE

4.928 ml sample residue dissolved in 2.056 ml CCl_4

Run No.	$10^3[RN_3]$ M	log I_o/I
III-250-1	13.73	0.758
		0.758
-2	10.11	0.598
		0.605
-3	5.979	0.382
		0.370
III-244	5.30	0.350
III-250-4	2.865	0.204
		0.197
-5	1.247	0.086
		0.086

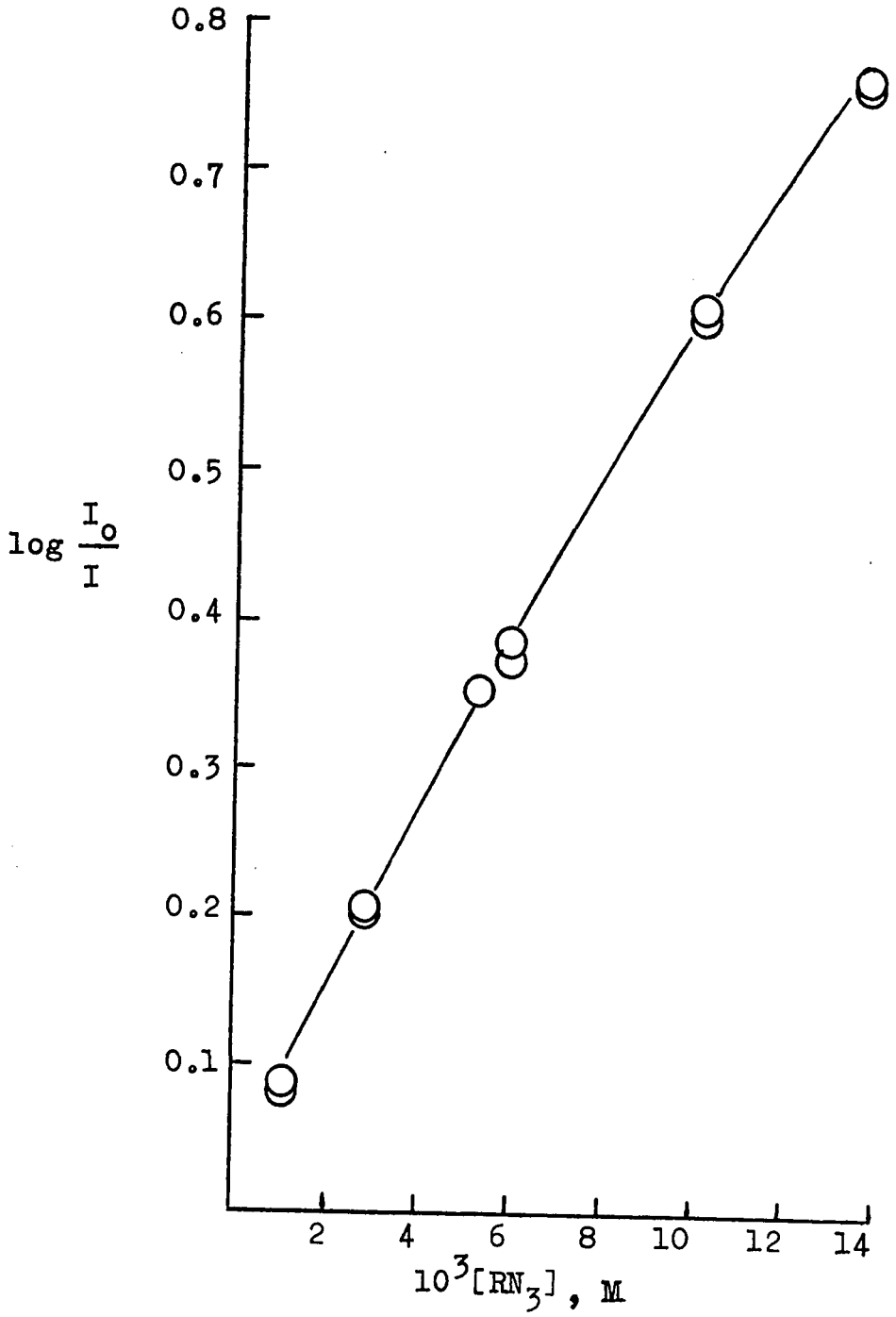


Figure 27. Calibration Curve for 2-p-Acetylphenyl-2-propyl Azide, Measured at 4.76 μm

a) 2-p-Tolyl-2-propyl Chloride

STANDARDS: Synthetic mixtures of the expected products for g.c.: 2-p-tolylpropene, 2-p-tolyl-2-propyl ethyl ether, and 2-p-tolyl-2-propyl azide, were treated in a standard manner and analyzed by g.c., as described on page 257. Plots of RA' *vs.* concentration were constructed for each of the expected products. RA' is defined as the ratio of the area of the g.c. peak of a particular compound to that of the g.c. peak of the internal standard, all multiplied by

the concentration of the particular compound in a 4.928 ml aliquot of the synthetic mixture.

In each case, the relationship was found to be linear. The best straight line for each plot was computed by LSEFIT. The results for 2-p-tolyl-2-propyl ethyl ether are shown in Table XXXIX and Figure 28. The results for 2-p-tolylpropene are shown in Table XL and Figure 29. For 2-p-tolyl-2-propyl azide, the results appear in Table XLI and Figure 30. The least-mean-squares fits for the figures are presented in Table XLII.

PRODUCT STUDIES: The solvolysis of 2-p-tolyl-2-propyl chloride was carried out for one half hour in anhydrous ethanol at 25° in the presence of tetrabutylammonium

TABLE XXXIX

THE RELATIONSHIP BETWEEN [ROEt] AND RA' FOR 2-p-TOLYL-2-PROPYL ETHYL ETHER

4.928 ml sample

Run No.	10^3 [ROEt] M	10^3 RA'
III-67	4.49	7.25 ± 0.26
III-64	6.61	11.25 ± 0.43
III-62	9.29	15.54 ± 0.47
III-63	12.30	20.42 ± 0.64
III-65	16.33	28.50 ± 0.87
III-68	18.07	28.43 ± 0.64
III-66	22.18	38.5 ± 2.1
III-69	24.60	42.47 ± 0.48

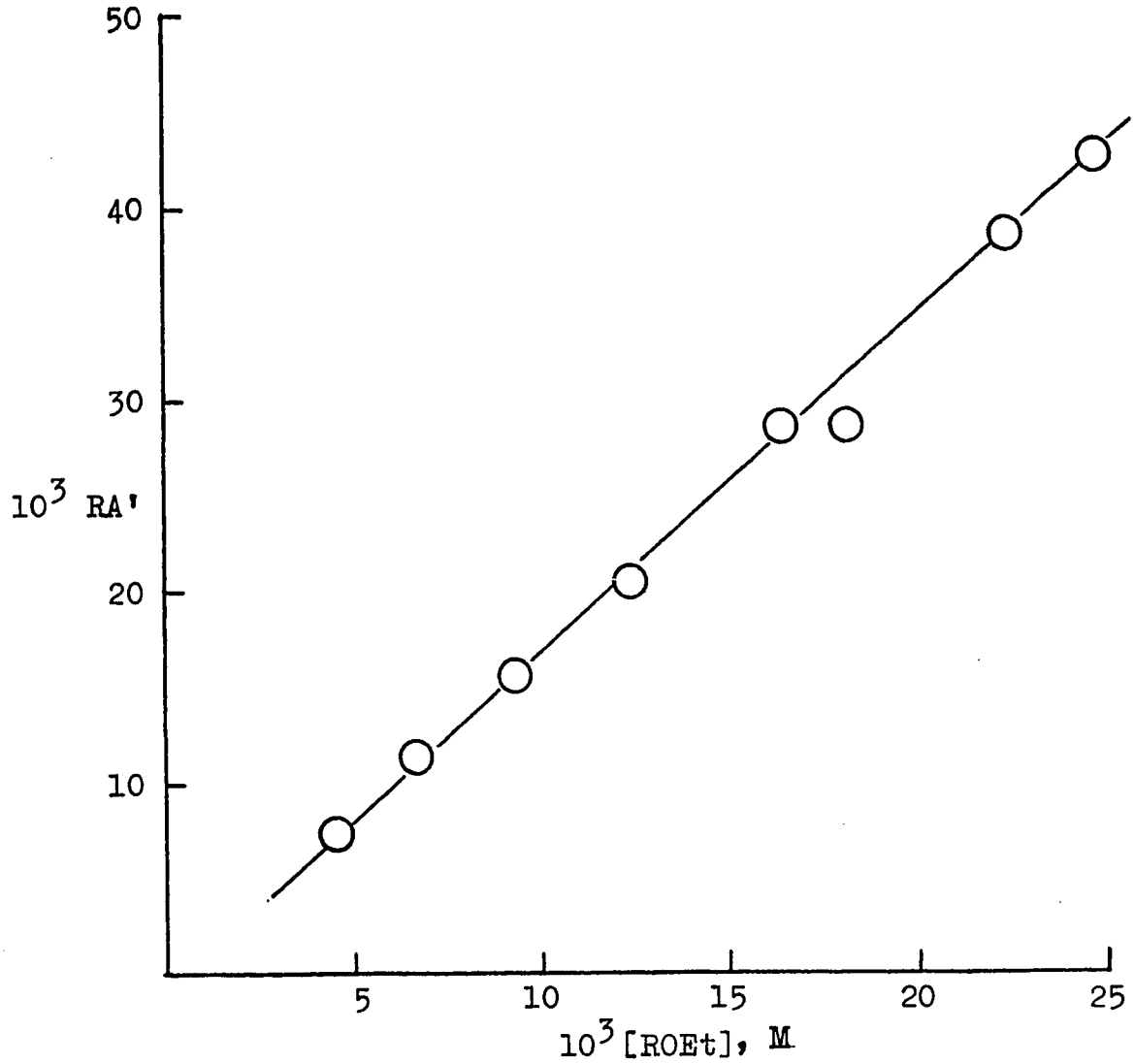


Figure 28. Relationship Between[ROEt] and RA' for 2-p-Tolyl-2-propyl Ethyl Ether.
4.928 ml aliquot.

TABLE XL

THE RELATIONSHIP BETWEEN [OLEFIN] AND RA' FOR 2-p-TOLYLPROPENE

4.928 ml sample

Run No.	10^3[olefin] M	10^3 RA'
III-111	1.24	1.76 ± 0.12
III-110	2.40	3.30 ± 0.28
III- 69	4.71	6.83 ± 0.21
III- 63	4.71	6.79 ± 0.37
III- 68	4.92	7.14
III- 62	6.99	9.70 ± 0.15
III-109	7.20	9.75 ± 0.25
III- 66	7.32	10.62 ± 0.23
III- 65	7.73	11.02 ± 0.30
III- 67	9.14	12.63 ± 0.23
III- 64	9.17	12.36 ± 0.38

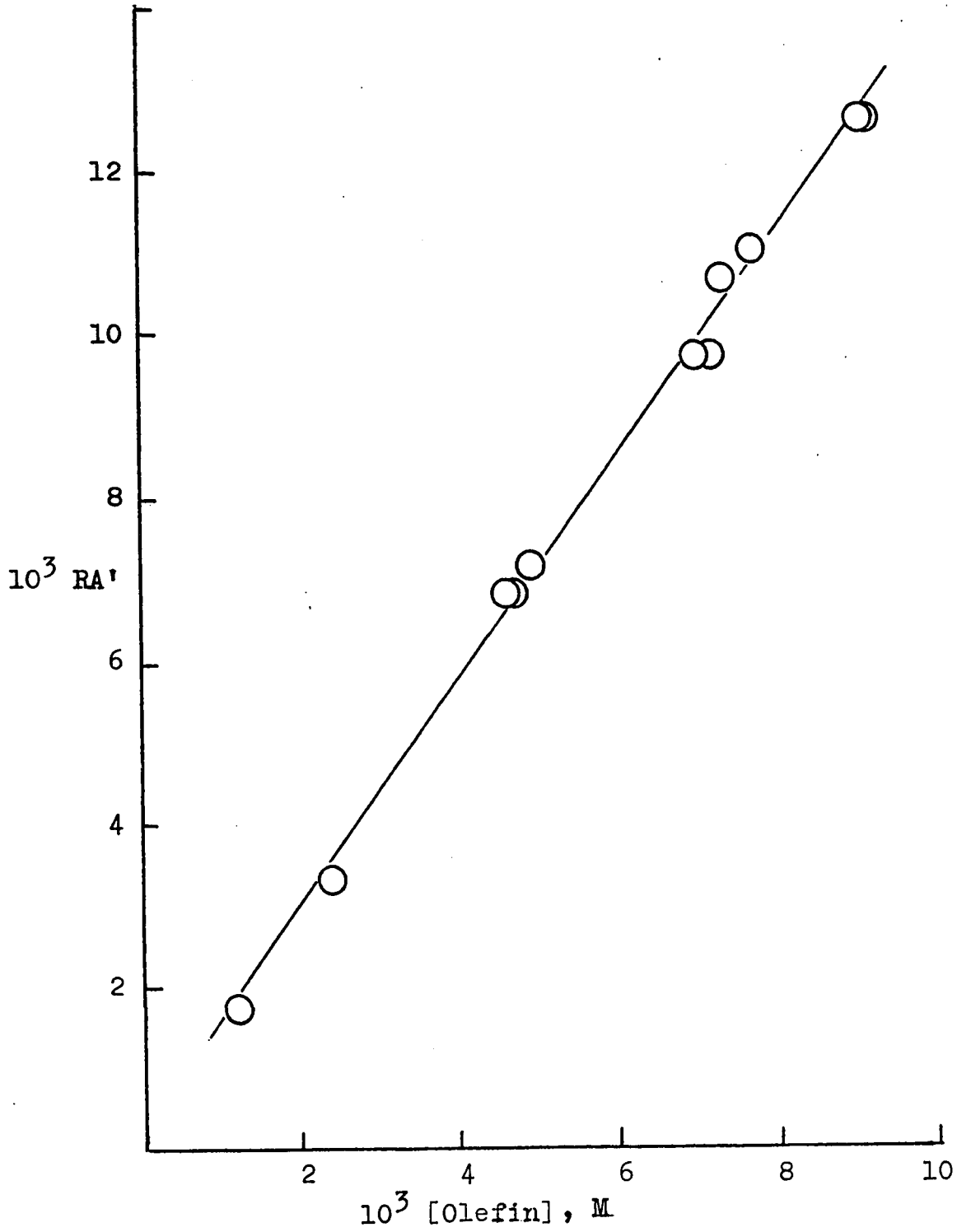


Figure 29. The Relationship Between [olefin] and RA' for 2-p-Tolylpropene. 4.928 ml aliquot.

TABLE XLI

THE RELATIONSHIP BETWEEN $[RN_3]$ AND RA' FOR 2-p-TOLYL-2-PROPYL AZIDE.

Run No.	10^3 $[RN_3]$ M	10^3 RA'
III-68	2.28	3.25 ± 0.11
III-69	2.48	3.54 ± 0.25
III-66	2.87	4.21 ± 0.34
III-67	4.83	6.13 ± 0.28
III-65	6.33	8.85 ± 0.47
III-64	6.38	9.07 ± 0.27
III-63	10.48	14.74 ± 0.36
III-62	11.88	16.96 ± 0.42

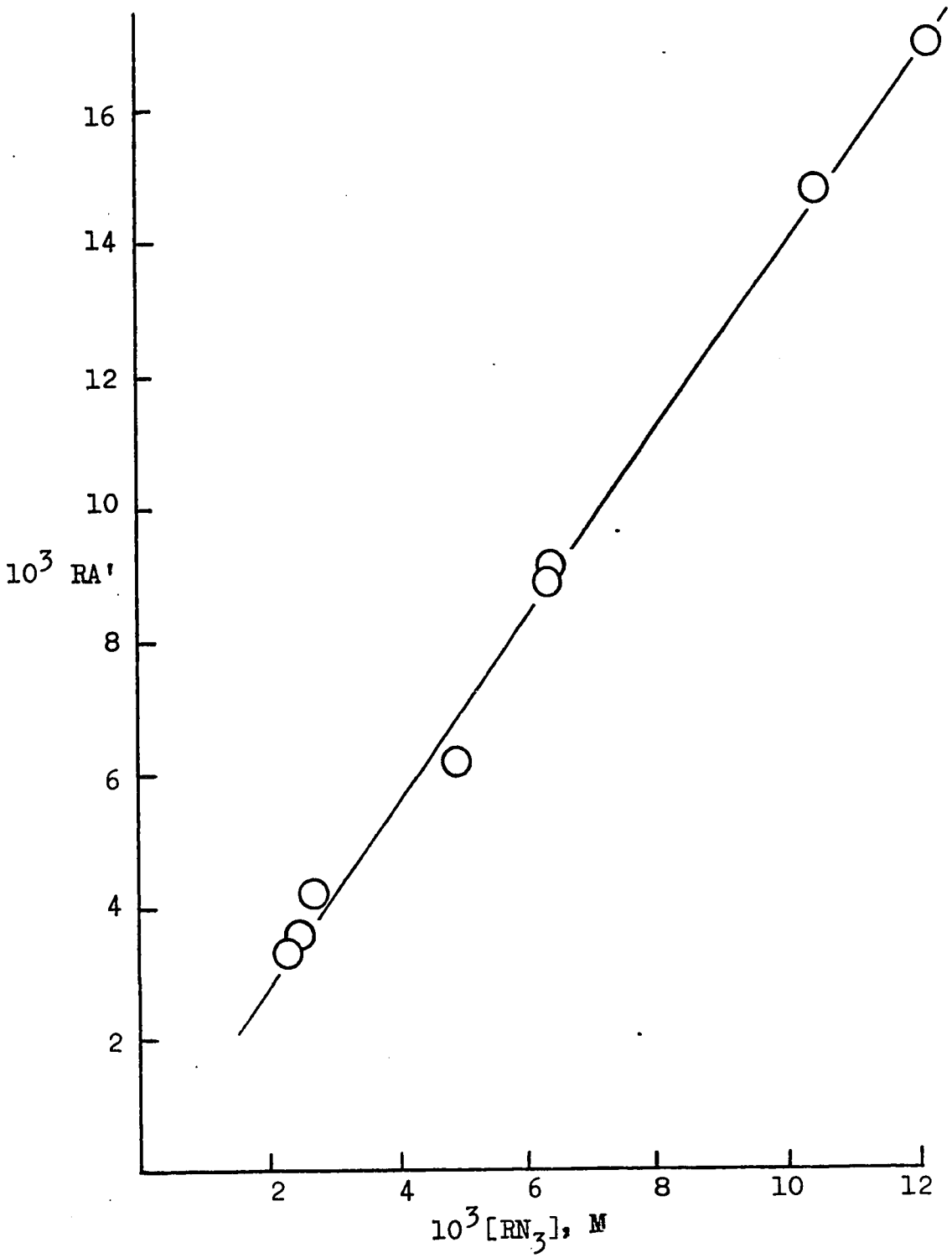


Figure 30. Relationship Between $[RN_3]$ and RA' for 2-p-Tolyl-2-propyl Azide. 4.928 ml aliquot

TABLE XLII

RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 28, 29, AND 30, BY LSEFIT

Figure Number	Slope	σ	E	Intercept	σ	E
28	1.69	0.031	0.039	-0.13	0.033	0.044
29	1.39	0.020	0.030	-0.05	0.11	0.17
30	1.42	0.01	0.03	-0.19	0.03	0.14

azide with added lithium ethoxide. Tetrabutylammonium perchlorate was used to adjust the ionic strength to a constant level. (For this reaction, one half hour should correspond to about 25 half-lives of reaction. This estimate is obtained from the relationship $\log k/k_o = \rho^+\sigma^+$ (24); ρ^+ for 2-aryl-2-propyl chlorides in ethanol at 25° is -4.62 (36); $\sigma^+(p\text{-}CH_3) = -0.311$ (36). For 2-phenyl-2-propyl chloride in ethanol at 25°, $k_o = 3.8 \times 10^{-4}$ (Table II). Therefore, $k = 1 \times 10^{-2}$ sec^{-1}, and $\tau = \ln 2/k = 70$ sec.)

The products of solvolysis were then determined. The procedure used for the g.c. studies is outlined in the Experimental section (page 258); the procedure used for the infrared analysis is described on page 264. Both analyses were carried out in duplicate for every reaction mixture. The results obtained are shown in Table XLIII (infrared) and Table XLIV (g.c.). Two runs were carried out without added tetrabutylammonium azide. The results of these runs are also shown in Table XLIV.

The error estimates in Table XLIV were calculated making the same assumptions as for the 2-phenyl-2-propyl system (Chapter 1, page 63), i.e. the total relative error is the sum of the relative standard deviation of the slope of the standard product curve and the relative

TABLE XLIII

EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE DISTRIBUTION OF PRODUCTS FOR THE ETHANOLYSIS OF 2-p-TOLYL-2-PROPYL CHLORIDE AT 25° IN THE PRESENCE OF LITHIUM ETHOXIDE AT CONSTANT IONIC STRENGTH AS MEASURED BY INFRARED SPECTROSCOPY AT 4.76 μm

Run No.	$[RCl]^a$ M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	μ	[EtOLi] M	F_{RN_3}	$\frac{1}{[Bu_4NN_3]}$	$\frac{1}{F_{RN_3}}$	$\frac{[Bu_4NN_3]}{F_{RN_3}}$
III-116	0.02403	0.03363	0.311	0.345	0.0985	0.042	29.8	24.8	0.80
III-113	0.02408	0.04397	0.300	0.344	0.0985	0.053	22.8	18.9	0.83
III-100	0.02921	0.06431	0.339	0.393	0.0857	0.060	15.6	16.7	0.91
III-101	0.02938	0.1123	0.284	0.396	0.0857	0.104	8.81	9.62	1.08
III-103	0.02342	0.1621	0.239	0.401	0.0857	0.150	6.16	6.66	1.08
III-102	0.02790	0.1646	0.165	0.398	0.0857	0.156	6.08	6.41	1.04
III-117	0.02529	0.1774	0.195	0.395	0.0985	0.162	5.64	6.18	1.10
III-104	0.02513	0.2464	0.149	0.395	0.0857	0.204	4.06	4.91	1.20
III-112	0.02408	0.3967	0	0.397	0.0958	0.283	2.52	3.53	1.39
III-105	0.02594	0.3942	0	0.394	0.0857	0.300	2.54	3.33	1.35

a) [RCl] has been corrected assuming the starting material is 91% pure.

TABLE XLIV

SUMMARY OF PRODUCT ANALYSIS RUNS FOR 2-p-TOLYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE WITH LITHIUM ETHOXIDE (0.09 M) AT CONSTANT IONIC STRENGTH USING TETRABUTYLAMMONIUM PERCHLORATE (μ = 0.4) g.c. analysis

Run No.	[RCl]^a M	[Bu_4NN_3] M	% olefin	% ether	% azide	% products	%' azide^b
III- 98	0.02774	0	6.4 ±0.6	78.1 ±2.5	0	84.5	0
III- 99	0.02494	0	6.5 ±0.5	76.7 ±4.9	0	83.2	0
III-116	0.02641	0.03363	5.7 ±0.3	64.6 ±2.1	2.1 ±0.2	72.4	2.9
III-113	0.02758	0.04397	5.2 ±0.7	72.7 ±1.8	3.0 ±0.4	80.9	3.8
III-100	0.03210	0.06431	6.0 ±0.4	67.5 ±3.0	3.1 ±0.4	76.6	4.1
III-101	0.03229	0.1123	5.7 ±0.3	63.8 ±3.3	6.2 ±0.4	75.7	8.2
III-103	0.02573	0.1621	6.1 ±0.3	65.0 ±3.4	10.9 ±0.3	82.0	13.3
III-102	0.03066	0.1646	6.1 ±0.4	65.0 ±3.1	10.2 ±0.5	81.3	12.6

TABLE XLIV (Continued)

Run No.	[RCl][a] M	[Bu_4NN_3] M	% olefin	% ether	% azide	% products	%' azide[b]
III-117	0.02779	0.1774	5.7 ±0.3	60.9 ±2.7	12.2 ±0.9	78.8	15.5
III-104	0.02762	0.2464	6.0 ±0.5	59.5 ±3.3	14.7 ±1.2	80.2	18.3
III-105	0.02850	0.3942	5.9 ±0.3	57.6 ±2.5	23.1 ±1.7	86.6	26.7

a) [RCl] is computed from the weighed amount of material in the sample; no correction for purity has been made

b) %' azide is the percentage of azide assuming that the percentage of products (% products) represents all of the material solvolyzing

average deviation found in the duplicate runs. The error in the intercept of the standard curve has been ignored, so again the values are conservative estimates.

In addition to the expected products, an extra peak, amounting to about 1% of the starting material, was found in the gas chromatogram. The material was shown to be present in the starting chloride and in the precursor alcohol. The retention time of the material was smaller than that of the olefin and very similar to p-cymene. The material was not identified, but is thought to be a non-polar substance arising as a by-product of the Grignard reaction of methyl magnesium iodide and p-methylacetophenone. Besides this material, a very small peak, amounting to less that 0.5% of the starting material, was found in very concentrated samples. It was identified by its retention time as p-methylacetophenone.

The expected products account for about 80% of the starting material. The purity of the starting material is thought to be 91%, the impurity being polymer. Polymeric material would be deposited on the g.c. inlet and not analyzed, so about 90% of the starting material should have been accounted for in the analysis. The total errors in the analysis are about 6%, making the maximum fraction of materials accounted for 0.86, which is still low.

The fraction of 2-p-tolyl-2-propyl azide found by infrared techniques appears to be greater than that found by g.c.; however, the numbers cannot be compared directly. In calculating the infrared results, the purity of the starting material was assumed to be 91%; the fraction of azide formed was corrected for this. No such correction was applied for the g.c. results. If the assumption is made that the fraction of products found in Table XLIV accounts for all of the starting material undergoing solvolysis, and the percentage of azide is normalized accordingly (to give %' azide), then % azide in Table XLIII and %' azide in Table XLIV should be the same. In fact, even with this correction, the fraction of azide found by g.c. appears to be about 2% lower than the results of the infrared analysis. This is the same type of result as found for 2-phenyl-2-propyl chloride.

The azide fractions, as determined from the infrared data, were used to make plots of $1/F_{RN_3}$ vs. $1/[Bu_4NN_3]$, Figure 31 (intercept plot), and of $[Bu_4NN_3]/F_{RN_3}$ vs. $[Bu_4NN_3]$ (slope plot), Figure 32. Least mean squares fits of both sets of data were made using the LSEFIT programme, and the results are shown in Table XLV.

b) 2-p-Methoxyphenyl-2-propyl Chloride

STANDARDS FOR nmr: The products of ethanolysis of

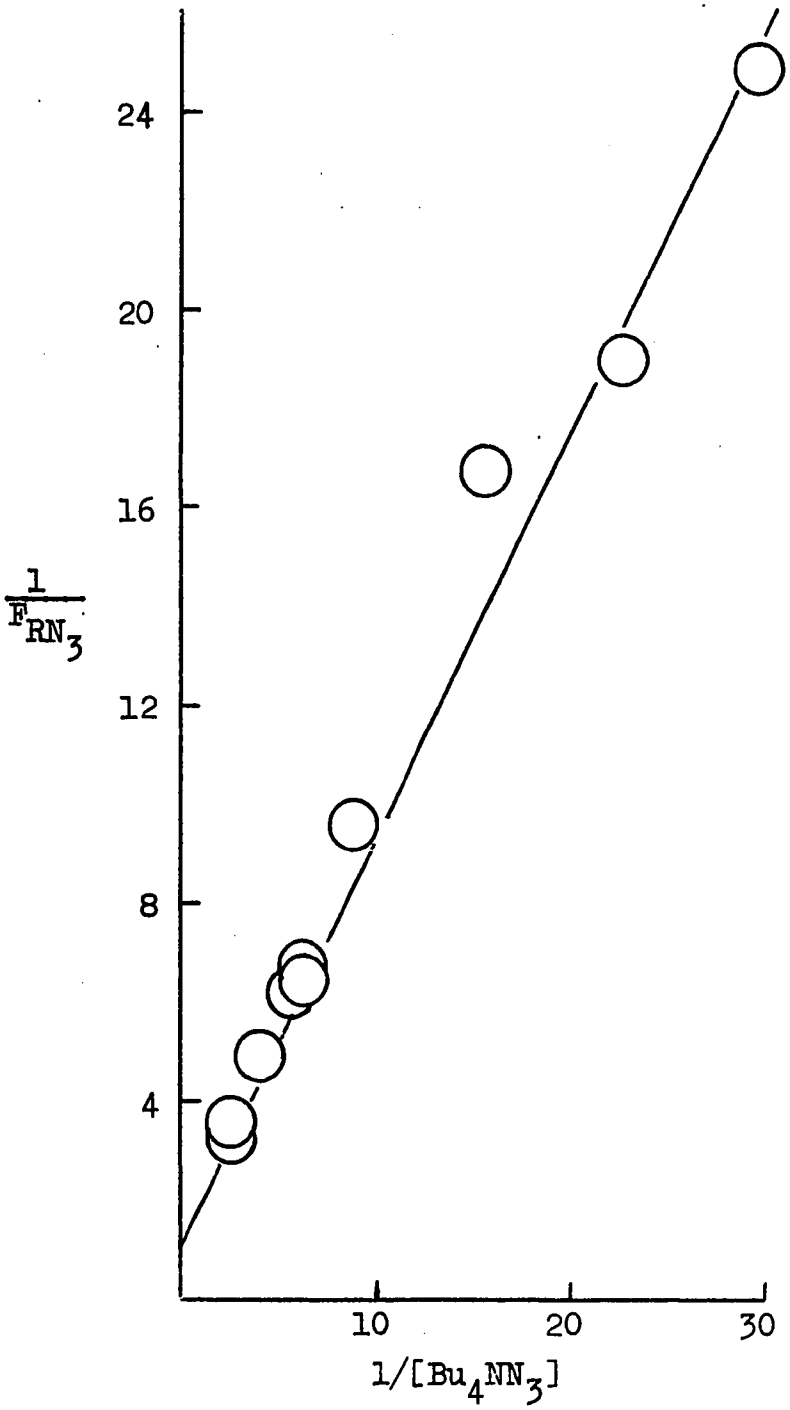


Figure 31. Intercept Plot for 2-p-Tolyl-2-propyl Chloride with Lithium Ethoxide, at Constant Ionic Strength

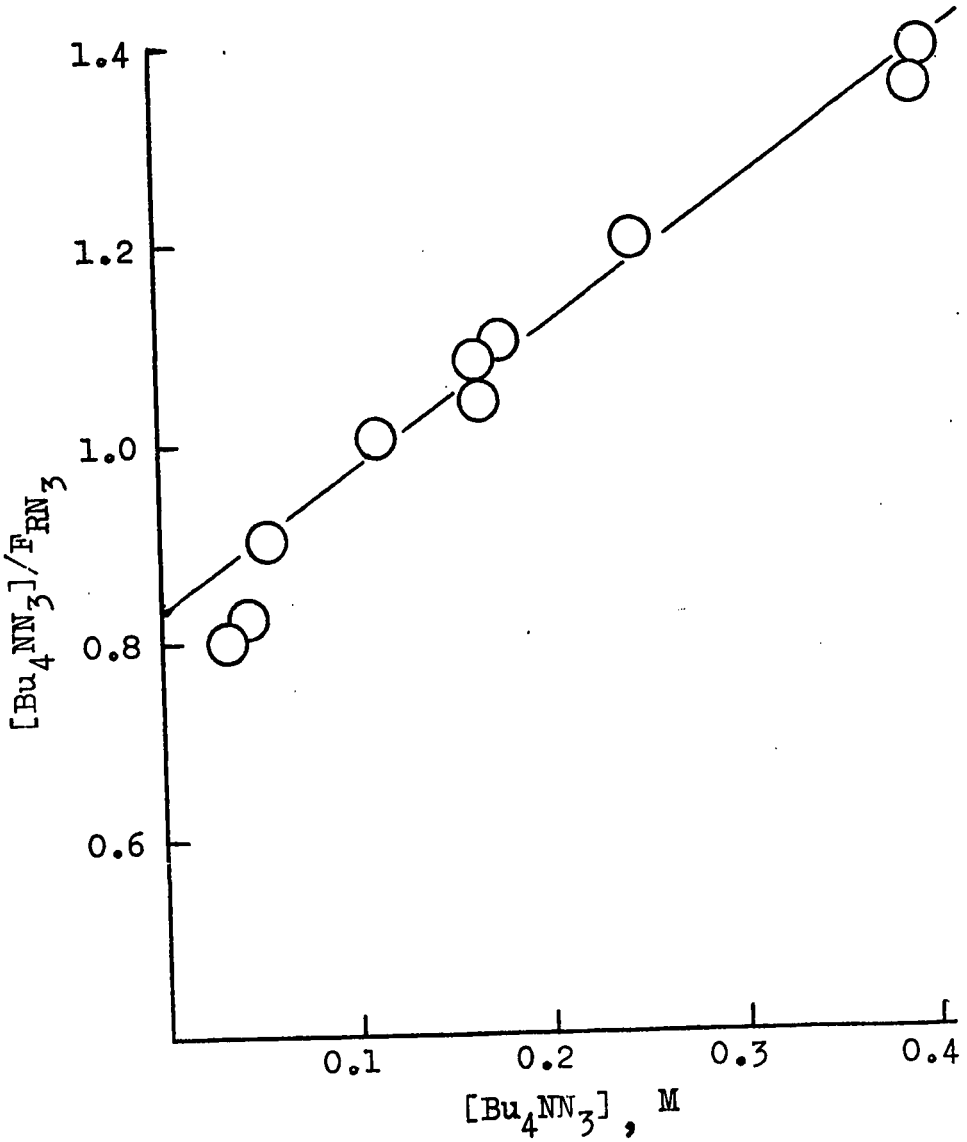


Figure 32. Slope Plot for 2-p-Tolyl-2-propyl Chloride with Lithium Ethoxide, at Constant Ionic Strength

TABLE XLV

RESULTS OF LEAST MEAN SQUARES ANALYSIS OF FIGURES 31 AND 32 (INTERCEPT AND SLOPE PLOTS) FOR 2-p-TOLYL-2-PROPYL CHLORIDE, BY LSEFIT

Figure Number	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
31	0.787	0.037	--	1.91	0.51	--
32	1.47	0.14	--	0.814	0.029	--
b) Weighted Results						
31	0.843	0.038	0.084	1.37	0.21	0.45
32	1.37	0.11	0.26	0.838	0.028	0.070

2-p-methoxyphenyl-2-propyl chloride were found to be too unstable to be analyzed by g.c. Even under the mildest conditions, some decomposition occurred. Instead, the product analysis was carried out by nmr.

Synthetic mixtures of the expected products were made up and carried through a work-up procedure, then analyzed by nmr. Two separate work-up procedures were used. The reason for this, as well as the details, is outlined in the Experimental section (page 261). For 2-p-methoxyphenyl-2-propyl ethyl ether the relationship between nRA and moles (nRA is defined in the same manner as is RA (page 52) except that instead of the g.c. peaks, the nmr peaks are used) was determined directly. The results are shown in Table XLVI and Figure 33. For 2-p-methoxyphenylpropene and 2-p-methoxyphenyl-2-propyl azide, the calculated mole ratio of olefin (azide) to ether was compared with the known mole ratio contained in that sample. The known value for the mole ratio was then converted to number of moles by comparison with the standard plot for the ether. The results for 2-p-methoxyphenyl-2-propyl azide are shown in Table XLVII and Figure 34. The results for 2-p-methoxyphenylpropene are shown in Table XLVIII and Figure 35.

The error values shown in Tables XLVI to XLVIII are the average deviations observed in the measurements.

TABLE XLVI

THE RELATIONSHIP BETWEEN moles AND nRA FOR 2-p-METHOXYPHENYL-2-PROPYL ETHYL ETHER

Run No.	10^4 moles	10^4 nRA
III-220	1.902	1.65 ± 0.09
III-221	1.559	1.33 ± 0.04
III-222	1.018	0.87 ± 0.02

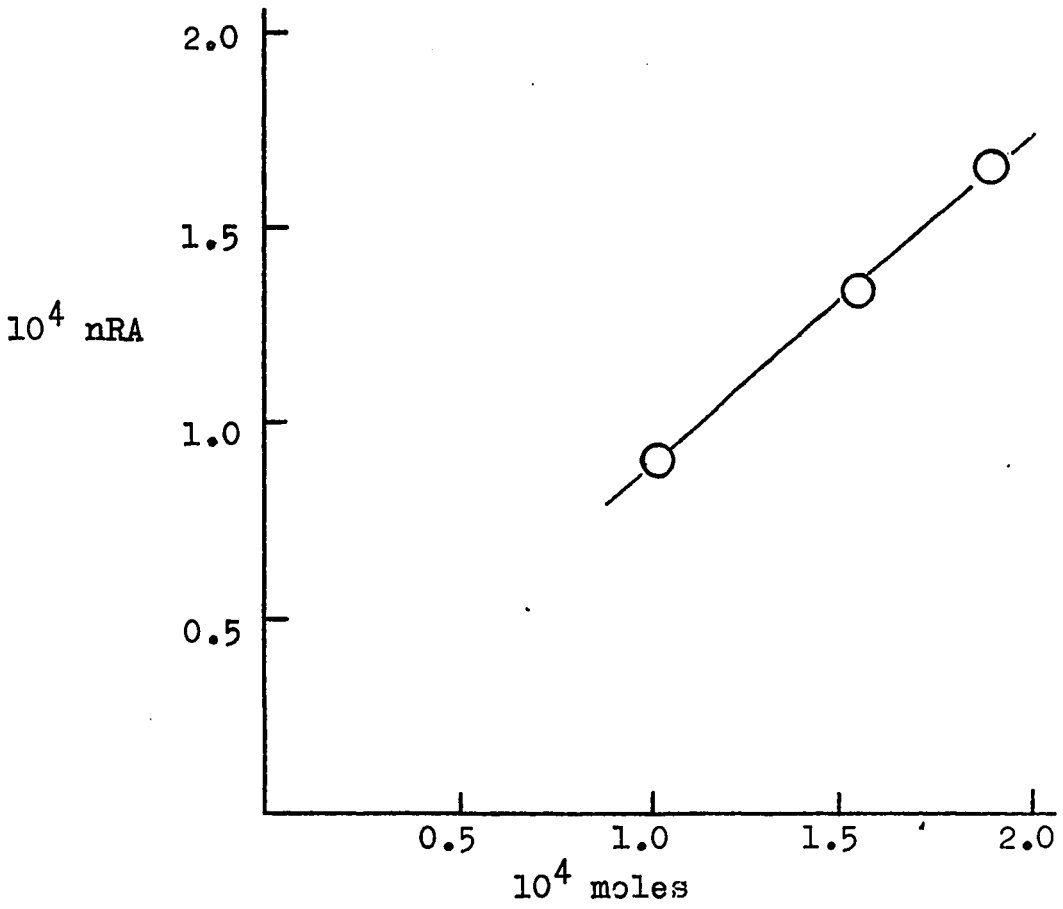


Figure 33. Relationship Between moles and nRA for 2-p-Methoxyphenyl-2-propyl Ethyl Ether

TABLE XLVII

THE RELATIONSHIP BETWEEN KNOWN AND CALCULATED MOLE RATIO OF 2-p-METHOXYPHENYL-2-PROPYL AZIDE RELATIVE TO 2-p-METHOXYPHENYL-2-PROPYL ETHYL ETHER

Run No.	Known mole ratio	Calculated mole ratio
III-212	0.483	0.468 ± 0
III-213	0.377	0.368 ± 0.011
III-214	0.280	0.276 ± 0.006
III-215	0.148	0.140 ± 0.006
III-216	0.120	0.112 ± 0.003
III-217	0.0527	0.0546 ± 0.006

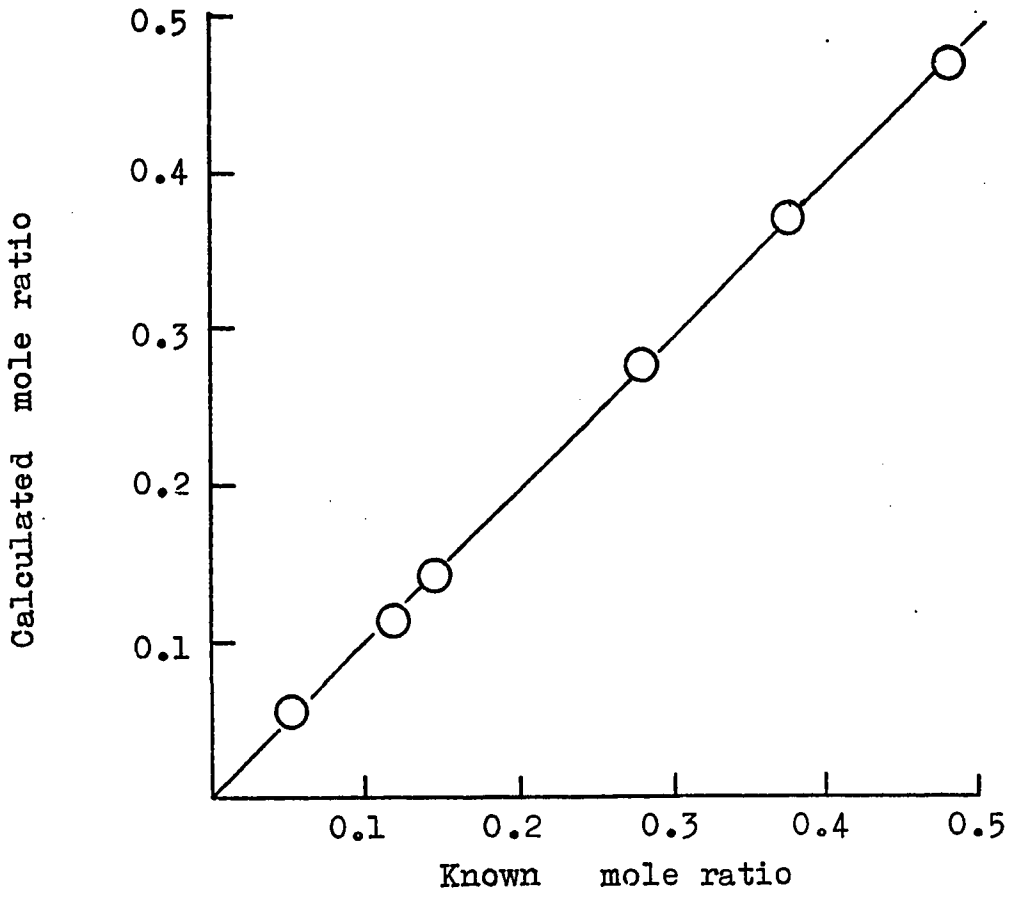


Figure 34. Relationship Between Known and Calculated Mole Ratio; 2-p-methoxyphenyl-2-propyl azide to 2-p-methoxyphenyl-2-propyl ethyl ether

TABLE XLVIII

THE RELATIONSHIP BETWEEN KNOWN AND CALCULATED MOLE RATIO OF 2-p-METHOXYPHENYLPROPENE RELATIVE TO 2-p-METHOXYPHENYL-2-PROPYL ETHYL ETHER

Run No.	Known mole ratio	Calculated mole ratio
III-213	0.287	0.271 ± 0.022
III-217	0.158	0.165 ± 0.008
III-212	0.141	0.148 ± 0.010
III-215	0.135	0.137 ± 0.011
III-214	0.068	0.068 ± 0.007
III-217	0.062	0.068 ± 0.009

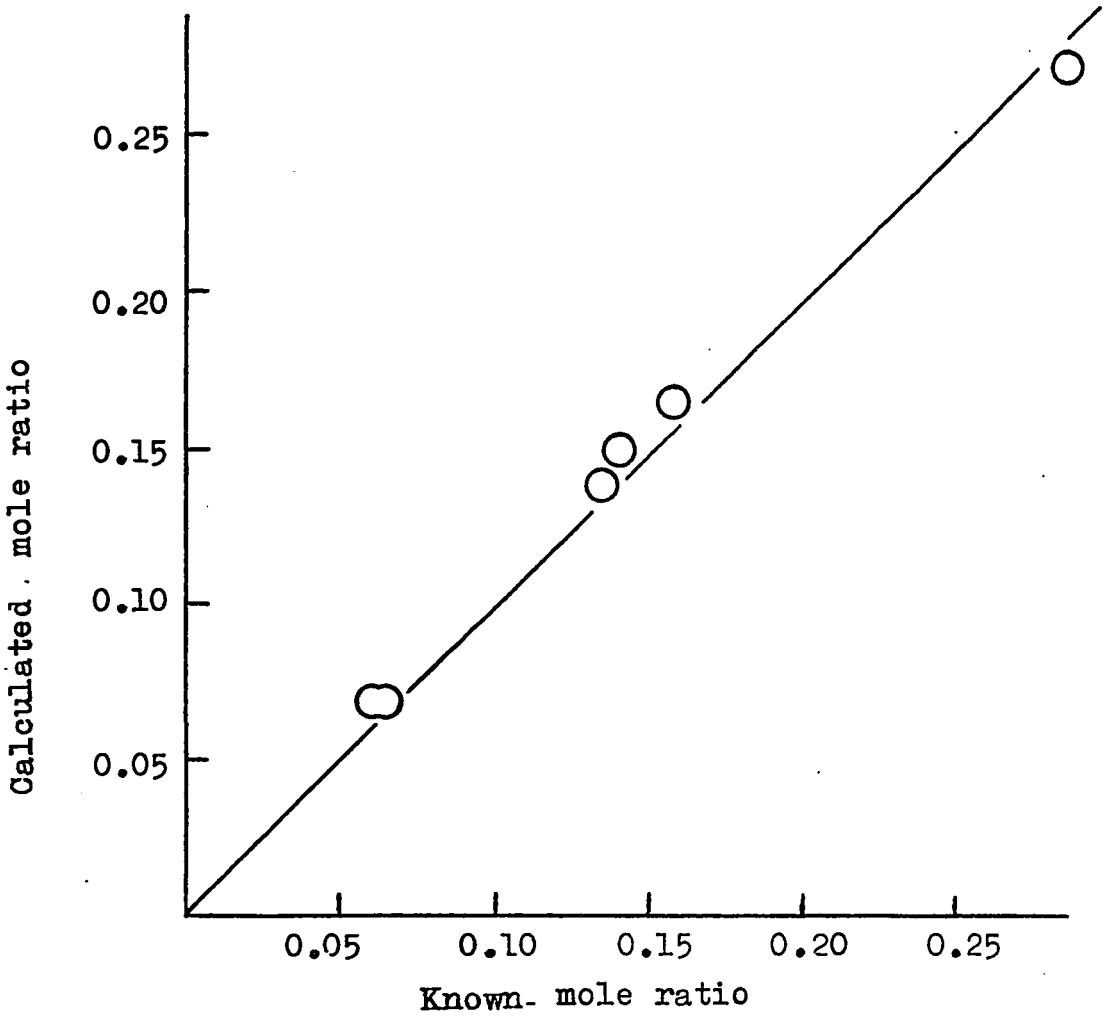


Figure 35. Relationship Between Known and Calculated Mole Ratio; 2-p-Methoxyphenylpropene to 2-p-Methoxyphenyl-2-propyl Ethyl Ether

The rate constant for the ethanolysis at 25° of 2-p-methoxyphenyl-2-propyl chloride can be estimated in the same manner as for 2-p-tolyl-2-propyl chloride, from the $\rho^{+}\sigma^{+}$ relationship (σ^{+}(p-MeO) = -0.778). The value calculated for the rate constant is 1.7 sec^{-1}. Thus, 10 half-lives corresponds to 4 seconds; solvolysis will be essentially instantaneous, limited by the dissolution of the substrate in the solvent. The study of the products formed in the presence of tetrabutylammonium azide becomes a problem in this system, since the reaction could well be over before complete mixing is effected, causing local concentration gradients in the reaction mixture. In order to minimize this problem, the starting material was forcefully injected into a rapidly stirred solution of solvent and salt. The reaction mixtures were analysed by g.c. and by infrared techniques. The procedures are outlined in the Experimental section. Duplicate analyses by both methods were carried out on each reaction mixture. The results are presented in Tables XLIX and L. All of the runs were carried out in the presence of lithium ethoxide. The runs were carried out at constant ionic strength using tetrabutylammonium perchlorate to adjust the mixture to the desired level.

A control was carried out in order to determine whether the method used for mixing in the study of these reactions was

TABLE XLIX

SUMMARY OF PRODUCT ANALYSIS RUNS FOR 2-p-METHOXYPHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25° IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE WITH LITHIUM ETHOXIDE (0.0365 M) AT CONSTANT IONIC STRENGTH USING TETRABUTYLAMMONIUM PERCHLORATE.

μ = 0.40

						nmr analyses			
Run No.	$[RCl]^a$ M	$[Bu_4NN_3]$ M	% ether	% azide	% products	% azide[b]	$\frac{1}{[N_3^-]}$	$\frac{1}{F_{RN_3}}$	$\frac{[N_3^-]}{F_{RN_3}}$
III-286[c]	0.04217	0	76.5 ±3.4	0	76.5				
III-287[c]	0.04387	0	77.9 ±2.7	0	77.9				
III-285	0.03913	0	82.0 ±3.0	0	82.0				
III-284	0.04002	0.04912	67.9 ±1.8	5.5 ±0.5	73.4	7.5	20.4	13.3	0.655
III-283	0.04021	0.0998	63.6 ±4.1	13.5 ±0.3	77.1	17.5	10.0	7.72	0.570
III-281	0.03671	0.1408	62.4 ±1.3	16.5 ±0.1	78.9	21.0	7.10	4.77	0.670

TABLE XLIX (Continued)

Run No.	[RCl]^{a} M	[Bu_4NN_3] M	% ether	% azide	% products	%' azide^{b}	$\frac{1}{[N_3^-]}$	$\frac{1}{F_{RN_3}}$	$\frac{[N_3^-]}{F_{RN_3}}$
III-282	0.03942	0.1455	60.2 ±2.4	17.5 ±0.7	77.7	22.6	6.88	4.43	0.644
III-280	0.04072	0.2291	58.9 ±7.1	24.6 ±0.7	83.5	29.5	4.52	3.40	0.775
III-279	0.03594	0.3816	42.0 ±1.7	32.6 ±0.8	74.6	43.7	2.62	2.29	0.875
III-278	0.03729	0.4034	54.0 ±7.8	33.6 ±3.6	87.4	38.5	2.48	2.60	1.07

a) [RCl] is not corrected for the impurities in the starting material

b) %' azide is the % of azide assuming that % products represents all of the starting material which solvolyzes

c) No added tetrabutylammonium perchlorate

TABLE L

THE EFFECT OF TETRABUTYLAMMONIUM AZIDE ON THE DISTRIBUTION OF PRODUCTS FOR THE SOLVOLYSIS OF 2-p-METHOXYPHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25° IN THE PRESENCE OF LITHIUM ETHOXIDE (0.0365 M) AT CONSTANT IONIC STRENGTH USING TETRABUTYLAMMONIUM PERCHLORATE (μ = 0.40)

				infrared analysis				
Run No.	$[RCl]^a$ M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	F_{RN_3}	$1/[Bu_4NN_3]$	$1/F_{RN_3}$	$[Bu_4NN_3]/F_{RN_3}$	
III-284	0.03020	0.04912	0.355	0.077, 0.071	20.4	13.0, 14.1	0.63, 0.69	
III-283	0.03257	0.0998	0.303	0.168, 0.156	10.0	5.9, 6.3	0.60, 0.64	
III-281	0.02974	0.1408	0.267	0.188, 0.185	7.10	5.32, 5.40	0.74, 0.75	
III-282	0.03191	0.1455	0.264	0.216, 0.205	6.88	4.65, 4.88	0.68, 0.71	
III-280	0.03299	0.2291	0.179	0.300, 0.297	4.52	3.33, 3.46	0.77, 0.77	
III-279	0.02911	0.3816	0.021	0.372, 0.355	2.62	2.69, 2.82	1.03, 1.07	
III-278	0.03020	0.4034	0	0.365, 0.368	2.48	2.75, 2.73	1.14, 1.13	

a) [RCl] has been normalized, assuming the starting material to be 81% pure

satisfactory. A 25 ml quantity of ethanol, which contained 0.4 M tetrabutylammonium azide was cooled to -25°, and 0.15 gm of 2-p-methoxyphenyl-2-propyl chloride added, while the mixture was stirred vigorously. The solution was allowed to warm slowly to -5°, then brought to room temperature. The nmr spectrum of the products formed showed the relative intensity of ether (s, τ8.47) to azide (s, τ 8.40) to be 62:38; therefore, in this run about 38% azide was formed. This value is very similar to that found for runs at 25° that contained 0.4 M salt (43.7%, 38.5%, see Table XLIX). Assuming that the fraction of azide formed at low temperatures would be the same as at 25°, the experiment shows the method of mixing to be satisfactory.

The error estimates shown in Table XLIX are the average deviations for duplicates of the runs. They do not include any error from the standard curve. The actual errors, then, are probably about twice those shown.

Olefin could be detected by the nmr analysis but the quantity of it was so small that an accurate integration could not be made for this reaction product. The product standards show that as little as 0.002 M (Runs III-214, III-216) of 2-p-methoxypropene could be analyzed with some accuracy. Most of the runs contained about 0.04 M starting material, so this amounts to 5% of the

products. There is, then, less than 5% olefin in the products. A check of the starting chloride showed it to contain a small amount of olefin. The peak appears to be similar in size to the peak found in the product runs. Thus we may conclude that little or no olefin is formed on the ethanolysis of 2-p-methoxyphenyl-2-propyl chloride.

The purity of the starting chloride as determined from the infinity acid titre is 81%, with the impurity being mainly polymer, and a small amount of olefin. The nmr peaks of the polymer appear at very high field (τ 9.5-9.9) and do not interfere with the analysis. The total products found would be expected to be 81%. The average of the results, 80 $\pm$7%, for the runs is in agreement with the expected value; however, the errors are large.

The fraction of azide determined by infrared spectroscopy, Table L, was calculated assuming the purity of the starting material to be 81%. The results agree well with %' azide, Table XLIX, which was calculated assuming that products found by g.c. account for all of the starting material which solvolyzed. The agreement at high salt concentrations is not as good as at lower concentrations. But the infrared absorbance for these runs is very high, around 0.75, where the errors in

measurement are largest.

Plots of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ and of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$ were made for both the nmr and infrared results. The plots are shown in Figures 36, 37, 38, and 39. The results of least mean squares fits for these Figures are presented in Table LI.

c) 2-p-Nitrophenyl-2-propyl Chloride

A study of the rate of solvolysis of 2-p-nitrophenyl-2-propyl chloride in anhydrous ethanol at 90° was carried out. In the absence of added base, the acid titre after 10 half-lives was only 50% of the theoretical value. By 20 half-lives, it had dropped to 10%, indicating that the HCl released was being consumed in a subsequent reaction. When 2,6-lutidine was added, the reaction proceeded smoothly, 96% of the theoretical acid was found after 10 half-lives, and the titre remained constant to 20 half-lives. The titrimetrically determined rate constant was $k_1 = (1.44 \pm 0.05) \times 10^{-4}$ sec^{-1}.

One product run was carried out; a mixture of 0.03 M 2-p-nitrophenyl-2-propyl chloride, 0.396 M tetrabutylammonium azide, and 0.04 M 2,6-lutidine was allowed to solvolyze for 10 half-lives at 90°. The resulting mixture was subjected to a standard work-up procedure and analyzed. An intense infrared band at 2090 cm^{-1}

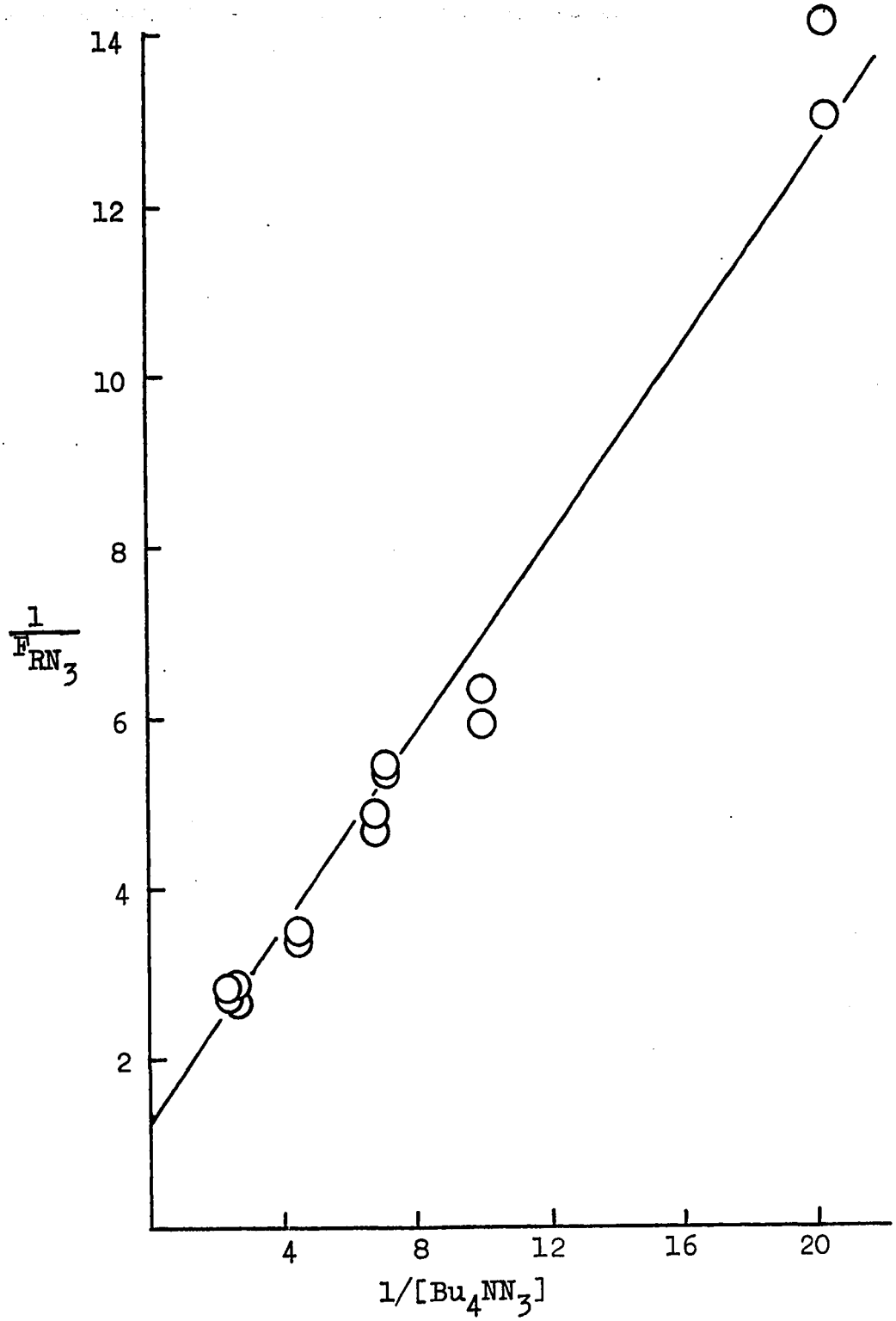


Figure 36. Intercept Plot for 2-p-Methoxyphenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength. Infrared Results

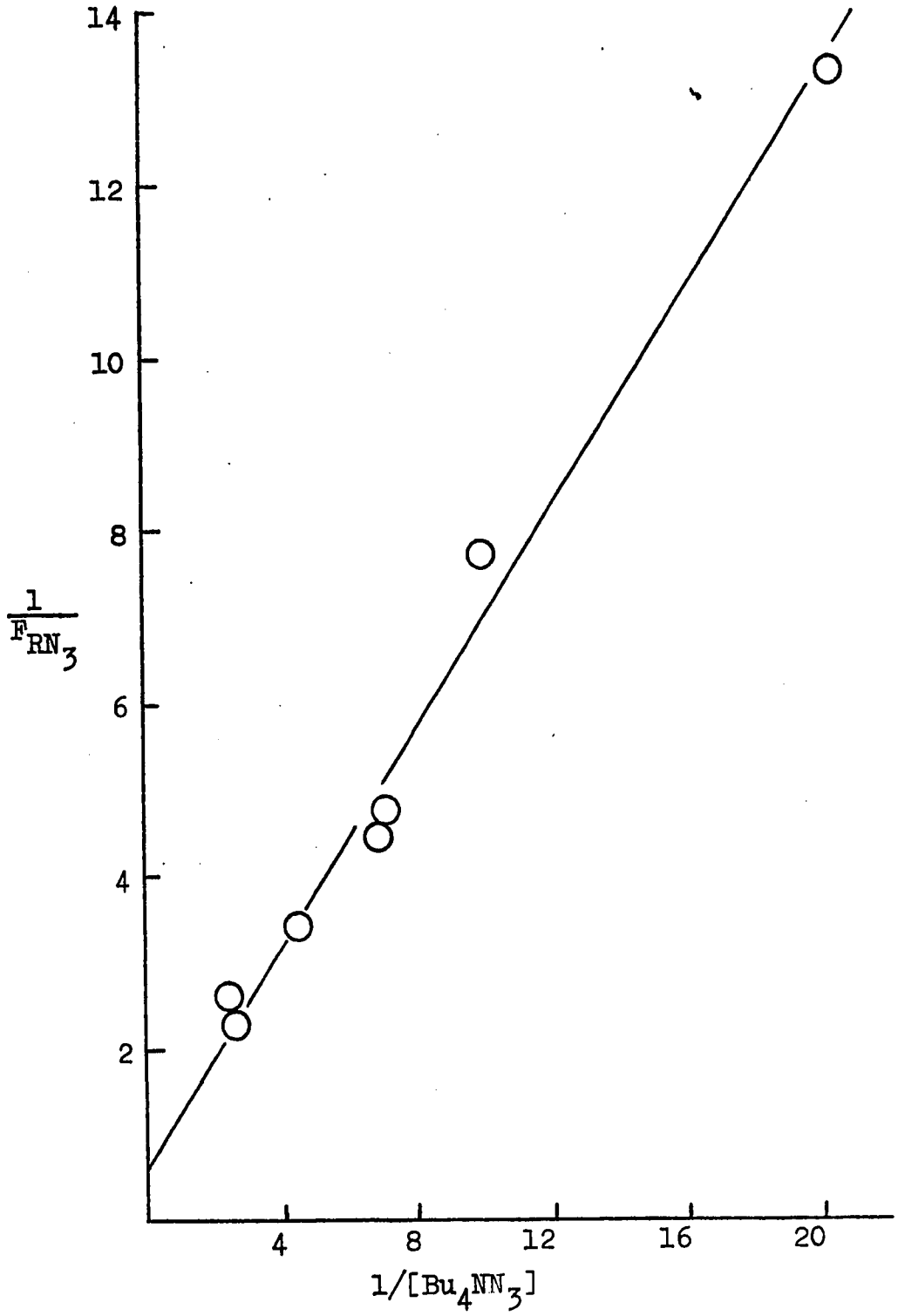


Figure 37. Intercept Plot for 2-p-Methoxyphenyl-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength. Nmr Results

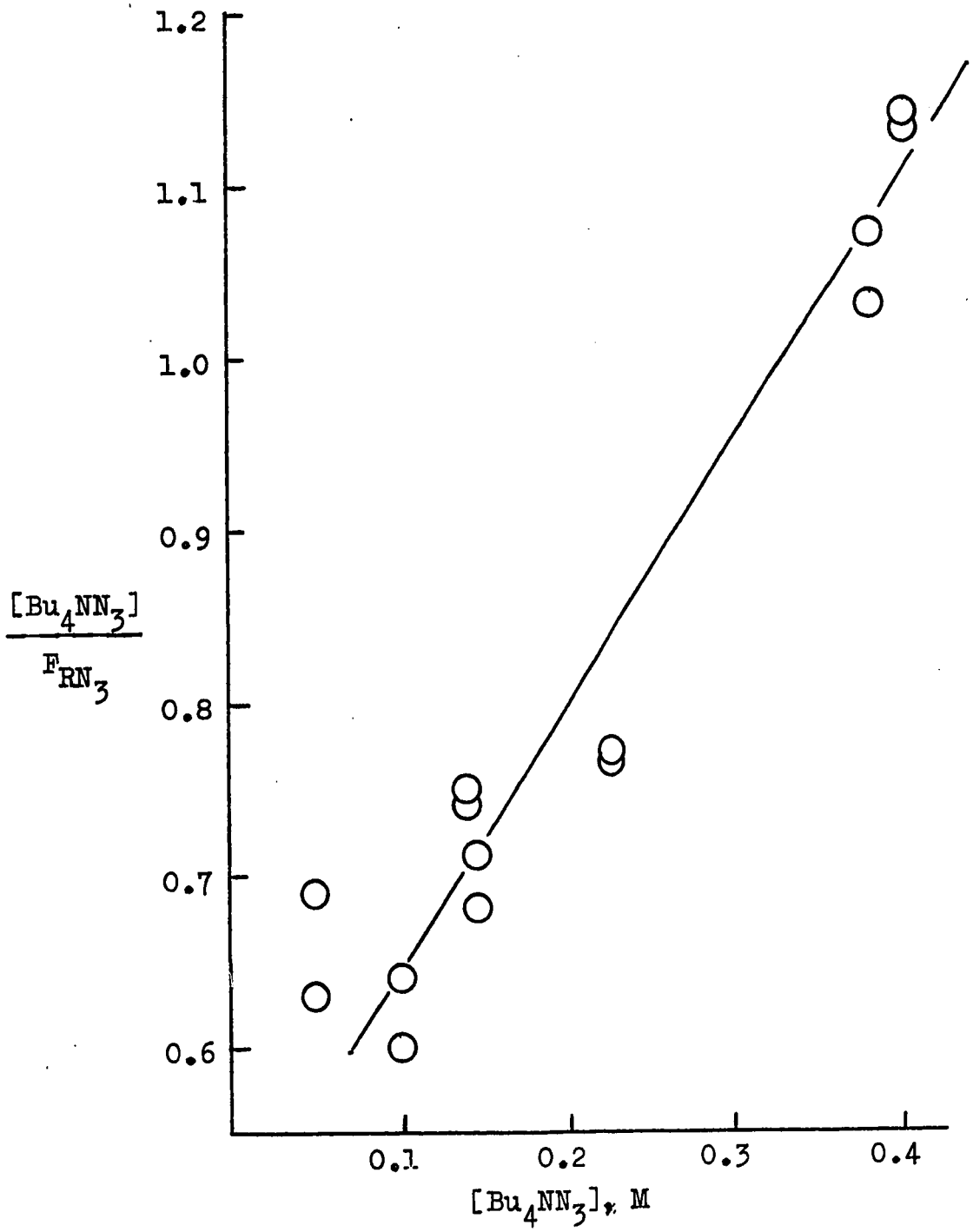


Figure 38. Slope Plot for 2-p-Methoxyphenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength. Infrared Results

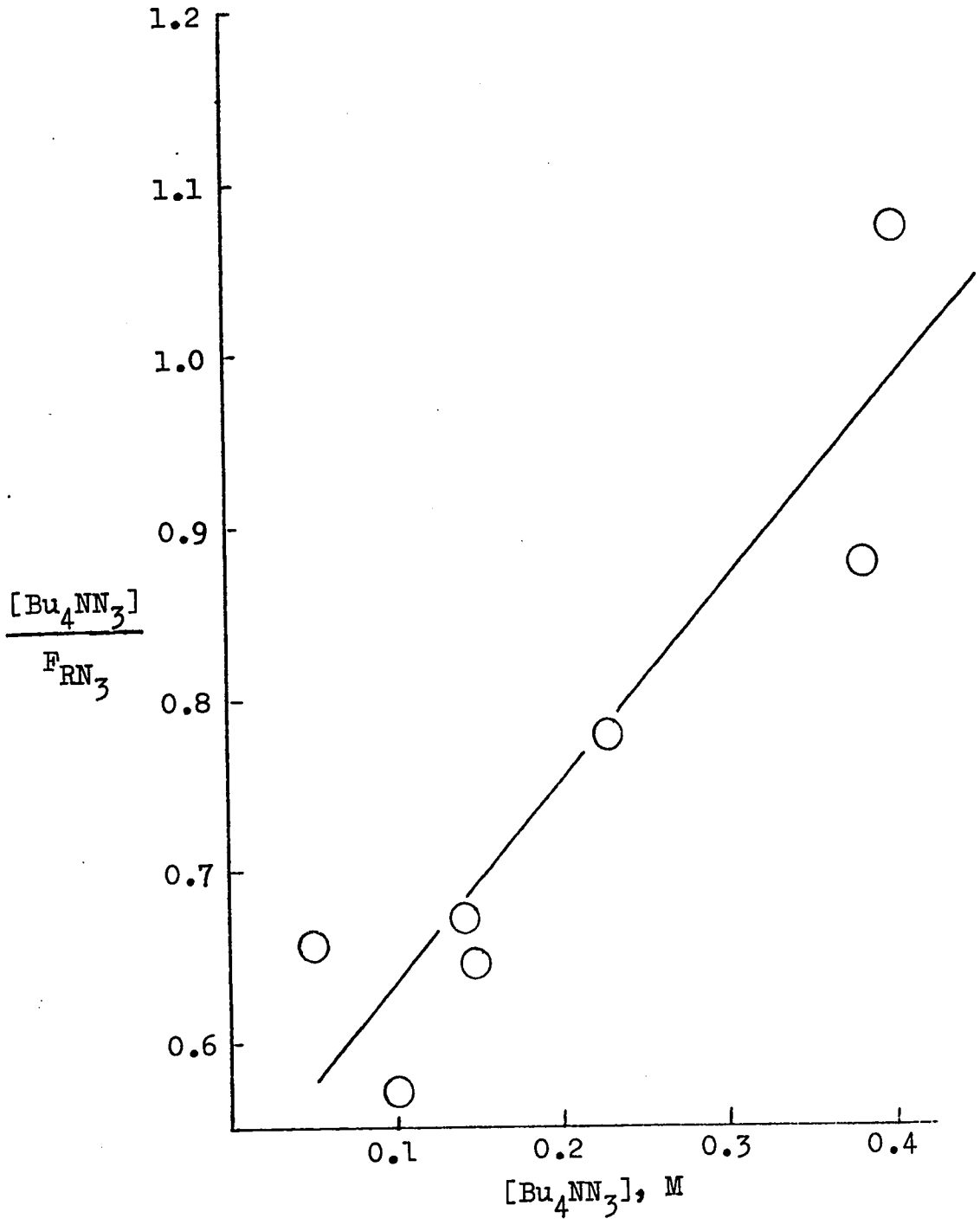


Figure 39. Slope Plot for 2-p-Methoxyphenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength. Nmr Results

TABLE LI

RESULTS OF THE LEAST MEAN SQUARES ANALYSIS OF FIGURES 36 (INTERCEPT PLOT, INFRARED RESULTS), 37 (INTERCEPT PLOT, nmr RESULTS), 38 (SLOPE PLOT, INFRARED RESULTS), AND 39 (SLOPE PLOT, nmr RESULTS), BY LSEFIT

Figure Number	Slope	σ	E	Intercept	σ	E
a) Unweighted Results						
36	0.604	0.023	—	0.865	0.23	—
37	0.622	0.032	—	0.701	0.31	—
38	1.40	0.11	—	0.52	0.028	—
39	1.15	0.21	—	0.513	0.052	—
b) Weighted Results						
36	0.531	0.029	0.039	1.28	0.15	0.21
37	0.683	0.042	0.052	0.603	0.22	0.30
38	1.49	0.11	0.18	0.490	0.028	0.037
39	1.03	0.18	0.25	0.517	0.044	0.060

was indicative of 2-p-nitrophenyl-2-propyl azide. The nmr spectrum of the product mixture showed a broad singlet at τ 7.85, a singlet at τ 8.35, another singlet at τ 8.50, and a series of small peaks from τ 8.6-9.2, which were assigned to the olefinic CH_3, the azide CH_3's, the ether CH_3's, and polymeric material, respectively. The relative intensities of the peaks were 15:61:16:36. Disregarding the polymeric material, the ratio of olefin:ether: azide is 30:16:61, which amounts to approximately 28% olefin, 15% ether, and 57% azide. It is important to note that there was no polymeric material in the substrate, 2-p-nitrophenyl-2-propyl chloride.

The nmr peaks assigned to the polymer are at high field and, even though the exact structure of the polymer is not known, they can reasonably be assigned to methyl and methylene groups. Assuming that only olefin, ether, azide, and polymer are formed, an estimate of the fraction of polymer can be made. If it is assumed that all of the peaks assigned to the polymeric material are due to methyl groups, then the ratio of polymer to other products is 36:106, or 25% of the products are polymeric. If it is assumed that all of the peaks are due to methylene groups, the ratio is 54:106, or 33% of the products are

polymeric. Although this estimate is necessarily rough, it would seem safe to say that a minimum of 25% of the reaction products of this system is polymeric in nature.

These results are dramatically different from the results of the other systems studied. The actual amount of organic azide formed at 0.4 M salt concentration is almost twice as great as was found even for the very reactive 2-p-methoxyphenyl-2-propyl system. Furthermore, the large amount of polymeric material formed is in contrast to that found in the other systems.

d) 2-p-Acetylphenyl-2-propyl Chloride

STANDARDS FOR g.c.: Synthetic mixtures of the expected products were subjected to a standard work-up procedure (page 259). Plots of RA vs. moles (see page 52 for definition of RA) were constructed for each of the expected products of solvolysis. The plots appeared to be linear and were fitted to the best-fit straight line using LSEFIT. The results for 2-p-acetylphenyl-2-propyl ethyl ether are shown in Table LII and Figure 40. The results for 2-p-acetylphenylpropene are shown in Table LIII and Figure 41. The results for 2-p-acetylphenyl-2-propyl azide are shown in Table LIV and Figure 42. In each case, the relationship observed was a linear one. The best fit line for each Figure was obtained by

TABLE LII

THE RELATIONSHIP BETWEEN moles AND RA FOR 2-p-ACETYLPHENYL-2-PROPYL ETHYL ETHER

Run No.	10^5 moles ether	10^5 RA
III-243	10.02	13.07 ± 0.21
III-246	6.99	8.94 ± 0.06
III-249	6.67	8.73 ± 0.05
III-247	5.34	6.81 ± 0.12
III-245	4.68	6.19 ± 0.10
III-244	3.76	5.17 ± 0.06

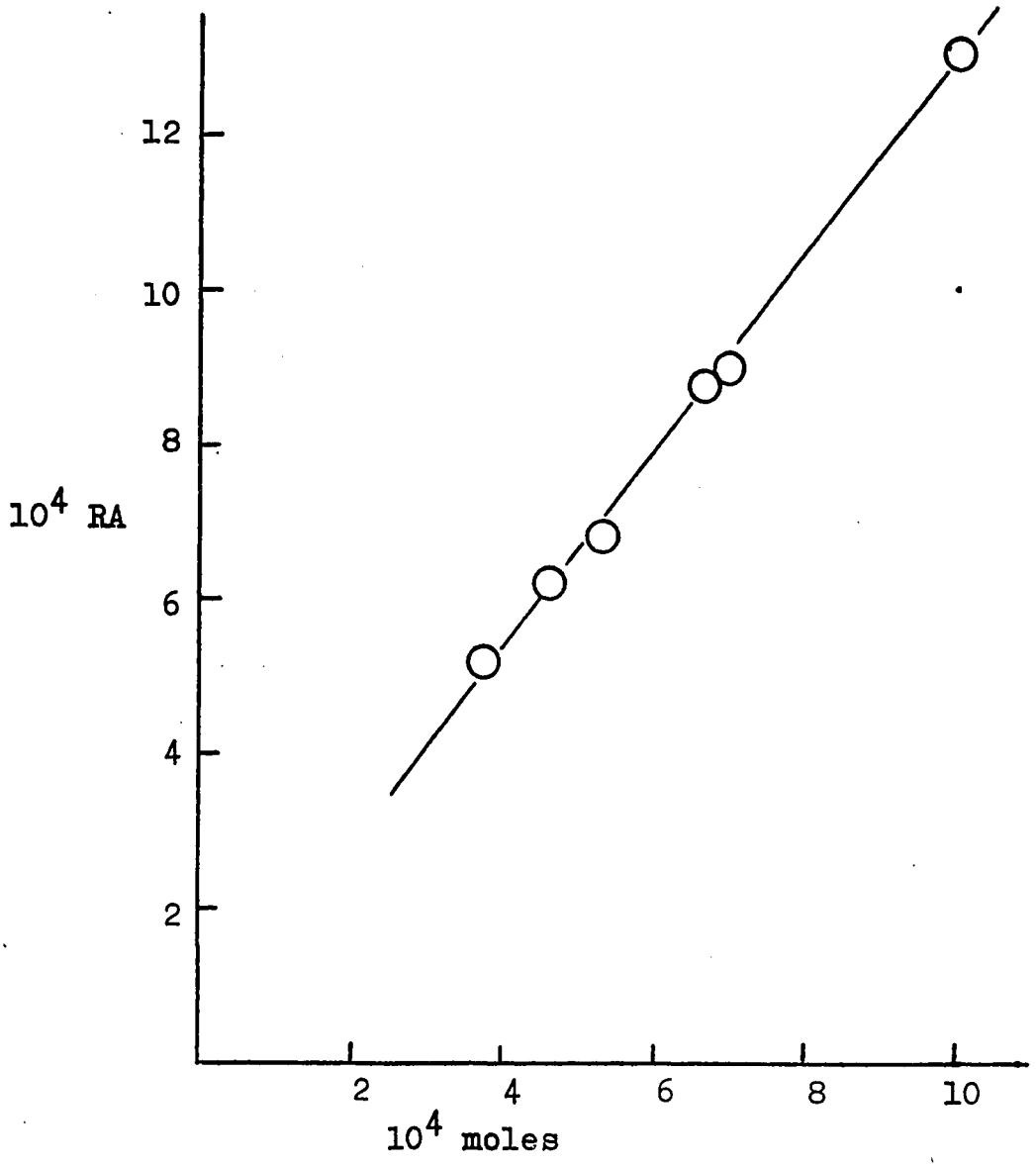


Figure 40. Relationship Between RA and moles for 2-p-Acetylphenyl-2-propyl Ethyl Ether

TABLE LIII

THE RELATIONSHIP BETWEEN moles AND RA FOR 2-p-ACETYL-PHENYLPROPENE

Run No.	10^5 moles olefin	10^5 RA
III-244	6.16	6.81 ± 0.11
III-248	5.01	5.47 ± 0.04
III-249	3.94	4.03 ± 0.06
III-247	2.93	3.12 ± 0.03
III-245	1.30	1.46 ± 0.04
III-246	0.80	0.82 ± 0.04

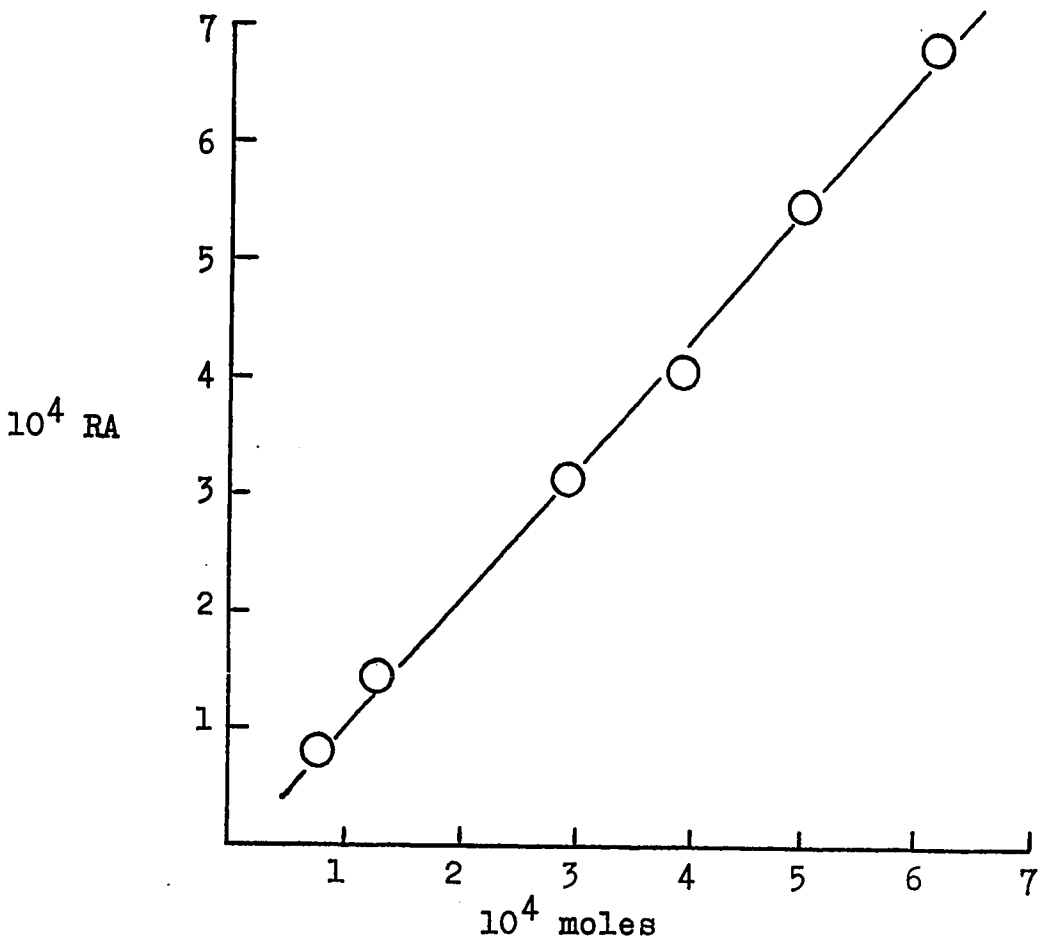


Figure 41. The Relationship Between RA and moles for 2-p-Acetylphenylpropene

TABLE LIV

THE RELATIONSHIP BETWEEN moles AND RA FOR 2-p-ACETYL-PHENYL-2-PROPYL AZIDE

Run No.	10^5 moles azide	10^5 RA
III-245	6.51	7.38 ± 0.17
III-246	4.66	4.97 ± 0.06
III-243	3.48	3.85 ± 0.13
III-244	2.61	3.05 ± 0.13
III-248	1.27	1.24 ± 0.04
III-247	0.52	0.45 ± 0.03

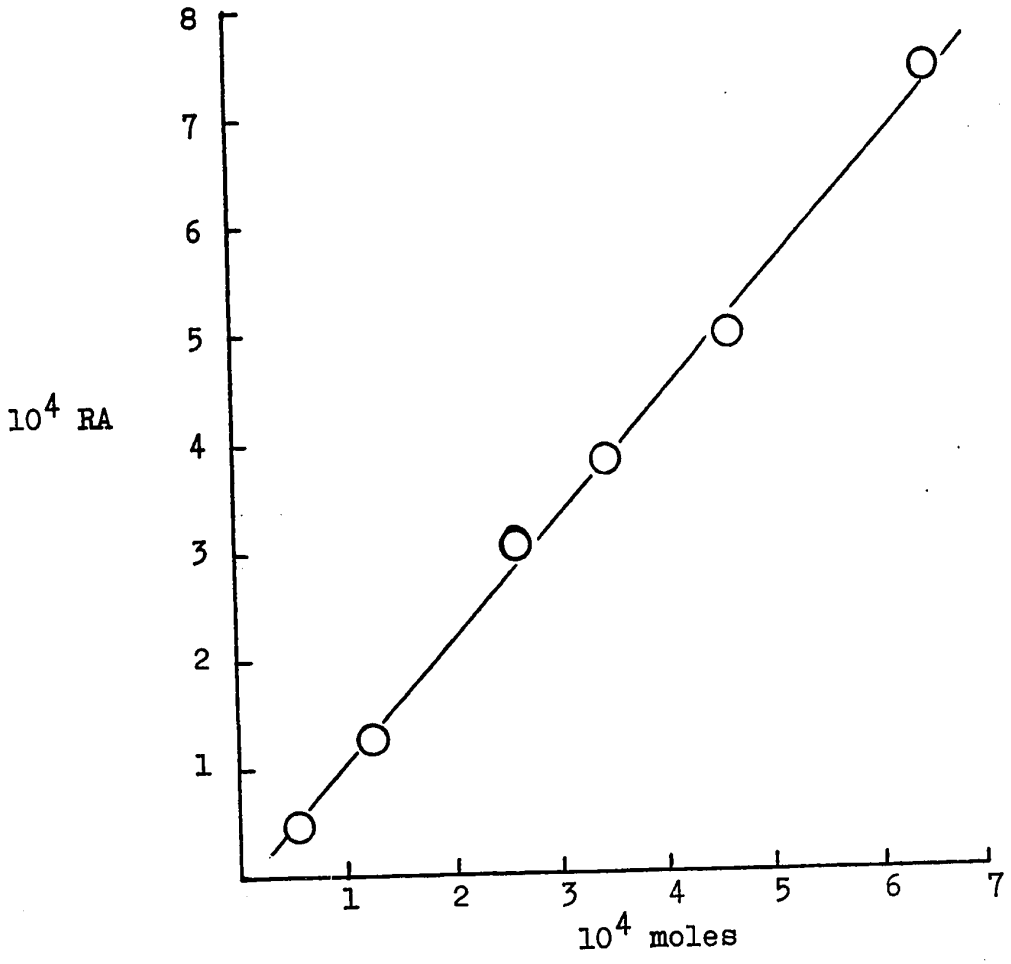


Figure 42. The Relationship Between RA and moles for 2-p-Acetylphenyl-2-propyl Azide

LSEFIT computer analysis and tabulated in Table LV.

PRODUCT STUDIES: 2-p-Acetylphenyl-2-propyl chloride was allowed to react for 21 days (10 half-lives) at 25° in anhydrous ethanol in the presence of tetrabutylammonium azide. 2,6-Lutidine was added to the solution in order to neutralize the acid formed. Tetrabutylammonium perchlorate was added, as necessary, to adjust the ionic strength of the mixture to a constant level. The products were analyzed in the same manner as the standards. The results are shown in Tables LVI (infrared) and LVII (g.c.). Duplicate analyses by both methods were carried out on the same reaction mixture. For purposes of comparison, one run was carried out without added tetrabutylammonium azide, and two others without any added salts. The results of these runs are also presented in Table LVII.

The error estimates in the Tables were calculated in the same manner as for the 2-phenyl-2-propyl system (page 63), and again are conservative estimates.

The fraction of azide found by infrared has been normalized, assuming that 96% (the acid infinity titre) of the starting material should be accounted for in the product analysis. It is also expected that 96% of the starting material should be accounted for in the g.c.

TABLE LV

THE RESULTS OF THE LEAST MEAN SQUARES ANALYSIS OF FIGURES 40, 41, AND 42, BY LSEFIT

Figure Number	Slope	σ	E	Intercept	σ	E
40	1.285	0.023	0.029	0.011	0.013	0.015
41	1.09	0.023	0.026	-0.033	0.015	0.085
42	1.13	0.026	0.031	-0.088	0.091	0.11

TABLE LVI

EFFECT OF TETRABUTYLAMMONIUM AZIDE ON DISTRIBUTION OF PRODUCTS FOR THE ETHANOLYSIS OF 2-p-ACETYLPHENYL-2-PROPYL CHLORIDE AT 25° IN THE PRESENCE OF 2,6-LUTIDINE (0.0323 M) AT CONSTANT IONIC STRENGTH (μ = 0.42) BY INFRARED SPECTROSCOPY

Run No.	[RCl][a] M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	F_{RN_3}	$1/[Bu_4NN_3]$	$1/F_{RN_3}$	$[Bu_4NN_3]/F_{RN_3}$
III-259	0.02037	0.05517	0.366	0.067, 0.066	18.11	14.9, 15.2	0.82, 0.84
III-260	0.02115	0.09767	0.329	0.108, 0.116	10.25	9.25, 8.62	0.90, 0.85
III-258	0.02236	0.1542	0.280	0.171, 0.181	6.46	5.86, 5.33	0.90, 0.85
III-257	0.02079	0.2032	0.218	0.248, 0.243	4.93	4.03, 4.11	0.83, 0.83
III-256	0.02079	0.2073	0.219	0.250, 0.249	4.82	4.00, 4.02	0.83, 0.82
III-255	0.02008	0.4092	0.0188	0.415, 0.414	2.46	2.41, 2.42	0.99, 0.99
III-254	0.02302	0.4242	0	0.420, 0.428	2.36	2.38, 2.34	1.01, 0.99

a) [RCl] corrected assuming the purity of the starting material to be 96%

TABLE LVII

SUMMARY OF PRODUCT ANALYSIS RUNS FOR 2-p-ACETYLPHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25° IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE WITH 2,6-LUTIDINE AT CONSTANT IONIC STRENGTH, BY g.c.

Run No.	$[RCl]^a$ M	$[Bu_4NN_3]$ M	$[Bu_4NClO_4]$ M	μ	% olefin	% ether	% azide	% products
III-263	0.01922	0	0	0	15.7 ±1.1	68.5 ±3.2	0	84.2
III-264	0.02274	0	0	0	15.5 ±1.3	66.5 ±4.0	0	82.0
III-261	0.02170	0	0.428	0.428	20.2 ±1.6	61.0 ±5.4	0	81.0
III-259	0.02139	0.05517	0.366	0.418	18.0 ±1.1	53.8 ±3.7	3.0 ±0.4	76.4
III-260	0.0222	0.09767	0.329	0.426	19.3 ±0.8	55.4 ±2.4	10.0 ±1.5	84.7
III-258	0.02349	0.1542	0.280	0.435	16.5 ±1.0	51.6 ±2.3	14.9 ±1.1	82.0
III-257	0.02184	0.2032	0.218	0.422	17.7 ±1.1	51.7 ±1.5	22.1 ±1.5	91.0
III-256	0.02184	0.2073	0.219	0.426	18.4 ±1.0	51.4 ±2.2	22.5 ±2.3	92.2
III-255	0.02109	0.4092	0.019	0.420	13.5 ±0.8	42.2 ±1.4	39.7 ±1.1	95.4
III-254	0.02418	0.4242	0	0.424	13.0 ±0.9	40.7 ±1.3	40.5 ±2.0	94.2

a) [RCl] not corrected for impurity in the starting material

analysis. In the first four runs analyzed, III-254 through -257, the fraction of products formed is in agreement with this figure. Only 84% is found, however, in the remaining runs. The fraction of azide formed in these runs appears to be quite different from those of the results found by infrared techniques, while the g.c. and infrared results for the first four runs appear to be quite similar. The reason for this discrepancy is not known. If it is assumed that the fraction of all products formed in any run accounts for all of the starting material which has undergone solvolysis and the results normalized accordingly, the values obtained are those presented in Table LVIII. All of the corrected azide values are in agreement with the values in Table LVII. Thus there may be an inadvertent constant error.

Plots of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$, and $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$ have been constructed using the obtained results. They are shown in Figures 43 (intercept plot) and 44 (slope plot). The plots are obviously not linear and they have not been fitted to a least mean squares line. The reason for this lack of linearity will be dealt with in the discussion.

KINETIC STUDIES: The rate of solvolysis of 2-p-acetyl-phenyl-2-propyl chloride in anhydrous ethanol in the

TABLE LVIII

CORRECTED VALUES FOR THE PRODUCT RUNS OF THE SOLVOLYSIS OF 2-p-ACETYLPHENYL-2-PROPYL CHLORIDE IN ANHYDROUS ETHANOL AT 25° WITH 2,6-LUTIDINE

Run No.	$[Bu_4NN_3]$ M	% olefin corrected	% ether corrected	% azide corrected	$1/F_{RN_3}$ corrected
III-263	0	18.7	81.3	0	0
III-264	0	18.9	81.8	0	0
III-261	0	25.0	75.0	0	0
III-259	0.05517	23.6	72.5	3.9	25.6
III-260	0.09767	22.8	65.4	11.8	8.48
III-258	0.1542	20.1	61.5	18.4	5.44
III-257	0.2032	19.5	57.2	23.3	4.29
III-256	0.2072	20.0	56.6	23.4	4.28
III-255	0.4092	14.2	44.2	41.6	2.40
III-254	0.4242	13.8	43.2	43.0	2.32

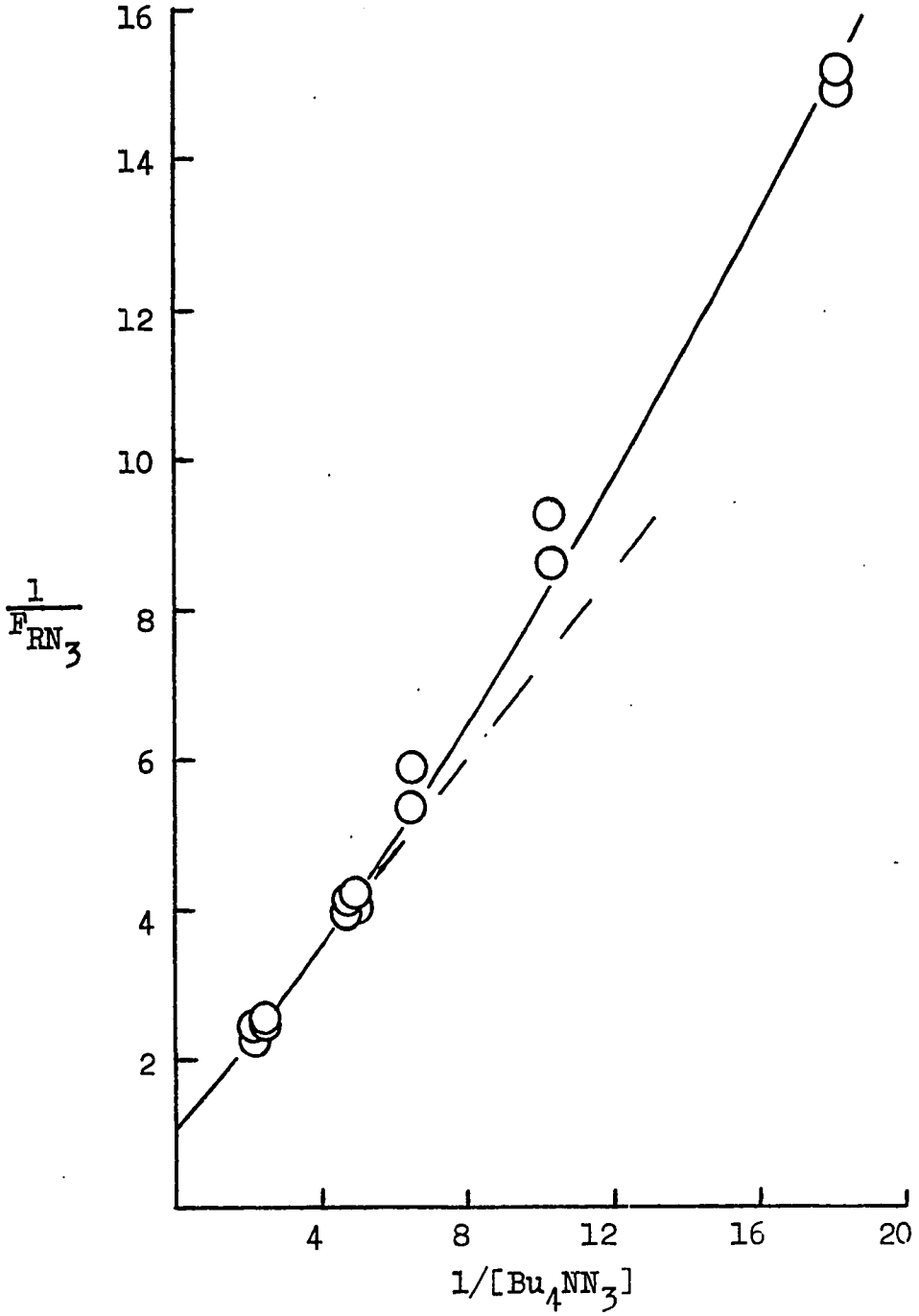


Figure 43. Intercept Plot for 2-p-Acetylphenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength

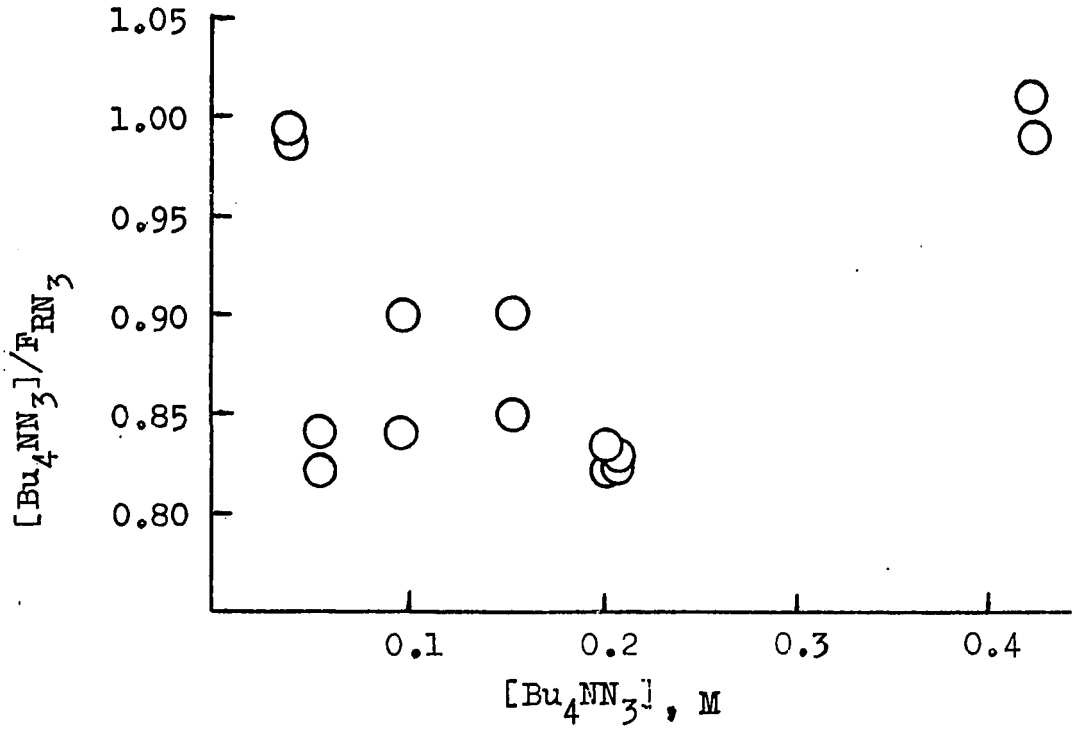


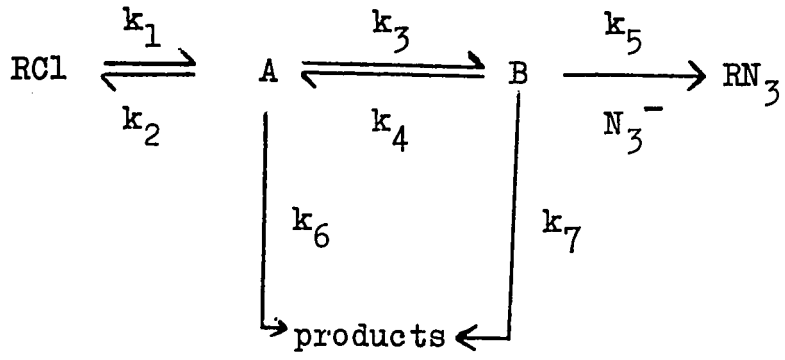
Figure 44. Slope Plot for 2-p-Acetylphenyl-2-propyl Chloride with Lithium Ethoxide at Constant Ionic Strength

presence of 2,6-lutidine was studied at several temperatures. The results are shown in Table LIX. The rate constants were determined titrimetrically.

From the graph of log k *vs.* 1/T (Figure 45), the energy of activation, E_a, is calculated to be 32.1 kcal mole^{-1} for the reaction. Therefore, $\Delta H^{\ddagger} = 31.5$ kcal mole^{-1}, and $\Delta S^{\ddagger} = 18.4$ e.u. at 25°C.

DISCUSSION

In Chapters 1 and 2 the results of the solvolysis of 2-phenyl-2-propyl chloride were shown to be consistent with the reaction scheme



[5]

and a method of evaluating the ratio of k_6/k_3 was

TABLE LIX

THE EFFECT OF TEMPERATURE ON THE RATE OF ETHANOLYSIS OF 2-p-ACETYLPHENYL-2-PROPYL CHLORIDE (RCl) IN THE PRESENCE OF 2,6-LUTIDINE

Run No.	[RCl] M	[2,6-lutidine] M	Temp. °C	k_1, sec^{-1}	$10^3/T$	log k
III-197	0.02839	0.04842	90	$(2.3 \pm .4) \times 10^{-3}$	2.76	-2.63
III-201	0.01343	0.05312	50	$(7.3 \pm .4) \times 10^{-5}$	3.10	-4.13
III-207	0.03070	0.04928	25	$(4.0 \pm .07) \times 10^{-6}$	3.36	-5.40

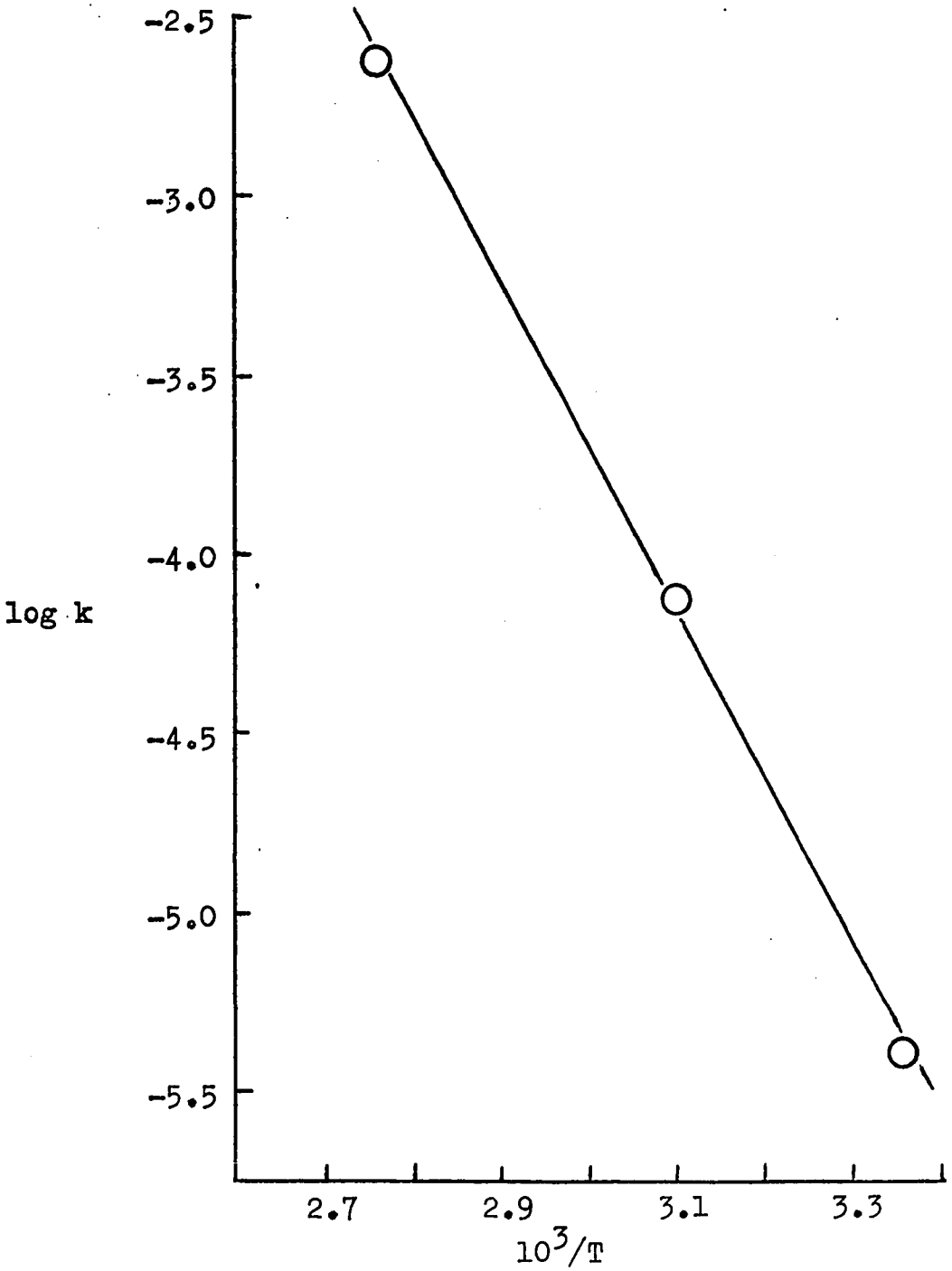


Figure 45. Determination of E_a for 2-p-Acetylphenyl-2-propyl Chloride Solvolysis

presented. In this scheme, the first intermediate, Int. A, an intimate ion pair, has three options available: it may return to starting material, undergo further dissociation, or react with the solvent to form products.

The extent of dissociation of an ionic species depends upon its stability. Compounds such as the trityl arenesulfinates are known to dissociate to free ions while less stable systems dissociate to a lesser extent. In the 2-aryl-2-propyl chloride under study here, the stability of the intermediate may be altered by adding substituents to the benzene ring. Electron-donating substituents would be expected to render the ion more stable and the intimate ion pair should be more likely to undergo further separation rather than react to give products or return to the starting material. The ratio k_6/k_3 is a measure of partitioning of Int. A between products and the second intermediate, so the more stable Int. A is, the smaller k_6/k_3 should be.

For the compounds studied, the electron-donating ability varies as p-OCH_3 > p-CH_3 > H. It would be expected that k_6/k_3 should decrease in the order 2-phenyl-2-propyl chloride > 2-p-tolyl-2-propyl chloride > 2-p-methoxyphenyl-2-propyl chloride.

As was discussed in Chapter 1, the ratio of k_6/k_3 is

best obtained from a plot of $[Bu_4NN_3]/F_{RN_3}$ *vs.* $[Bu_4NN_3]$ when the quantity F_{RN_3} has been determined under basic conditions and at constant ionic strength. The uncertainties in the results can be minimized by assigning weights to the values of F_{RN_3}, then obtaining the best fit line using the LSEFIT computer programme.

The value of k_6/k_3 obtained in this manner for 2-phenyl-2-propyl chloride is 0.91 (Table XXV). For 2-p-tolyl-2-propyl chloride, the calculated value for k_6/k_3 is 0.47 (Table XLV); as predicted, the value is smaller than that obtained for the unsubstituted compound. For both systems, the results are obtained using data obtained by infrared spectroscopy. The values obtained using weighted results are within experimental error of those found in the unweighted cases.

For 2-p-methoxyphenyl-2-propyl chloride, the value of k_6/k_3 found is 0.49 from the infrared data, and 0.03 if the nmr data are used. The two values are slightly outside of experimental error of each other, but they must necessarily represent the same quantity. The errors in this case are sufficiently large that a definitive value of the ratio of k_6/k_3 cannot be assigned. It can only be said that the result obtained is not inconsistent with that predicted.

It is of interest to compare the fraction of olefin formed on solvolysis of each of these three systems. Approximately 7% of olefin is formed in the solvolysis of 2-phenyl-2-propyl chloride, 5% for 2-p-tolyl-2-propyl chloride, and little or no olefin when 2-p-methoxyphenyl-2-propyl chloride is allowed to solvolyze. The uncertainty in each of these numbers is large and it is possible that the differences between them are not significant, but this is considered to be unlikely, since the olefin values for each system are reproducible over a large number of samples, and since there appears to be a regular progression in these values. If the differences are real, this may mean that the olefin is being formed only from the first intermediate; then, as the stability of the system increases and less product formation arises from the intimate ion pair, there is less olefin formed.

It would be of interest to study the effect of electron-withdrawing substituents on the partitioning of the intimate ion pair. Within the framework of scheme [5], it would be expected that the substituent should retard the formation of the second intermediate relative to products, the converse of the behaviour found when electron-donating substituents are added to

the ring. It would be predicted that the ratio of k_6/k_3 for a compound having such a substituent should be greater than 0.91.

Studies were made of two systems containing electron-withdrawing substituents, 2-p-nitrophenyl-2-propyl chloride and 2-p-acetylphenyl-2-propyl chloride.

The result found for the solvolysis of 2-p-nitrophenyl-2-propyl chloride was not that expected. Only one run was carried out in the presence of tetrabutylammonium azide, but the fraction of azide formed in this run was much higher than the amount found for the unsubstituted system. Also, some of the products of the reaction were found to be polymeric in nature. Neither of these results can be explained by a reaction scheme of type [5]. The reaction must proceed by some other pathway, at least in the presence of tetrabutylammonium azide.

Kornblum and coworkers have recently found that 2-p-nitrophenyl-2-propyl chloride(37) and 2-p-nitrophenyl-2-nitropropane(38) react with the base sodium thiophenoxide in dimethylsulphoxide at temperatures around 0° to yield 2-p-nitrophenyl-2-propyl thiophenoxide, as well as polymeric products. The addition of methanol had no effect on the products of the reaction.

It was found that 2-phenyl-2-propyl chloride did not undergo a similar reaction. Kornblum suggested that the reaction may proceed by a radical-anion intermediate.

Regardless of the actual mechanism, it would appear that azide ion is acting as a base to carry out a reaction similar to that observed by Kornblum, and that this is the reason for the unusual product distribution and the appearance of polymeric materials.

The reaction of 2-p-acetyl-2-propyl chloride was slow at 25°. It was decided not to use lithium ethoxide to neutralize the acid formed in the reaction, as it was feared that over a long period of time this base might catalyze undesired side reactions. Instead, 2,6-lutidine was used. The results obtained indicate that this was a poor choice.

The plot of $1/F_{RN_3}$ *vs.* $1/[Bu_4NN_3]$ (Figure 43) made for the 2-p-acetylphenyl-2-propyl azide formed in the solvolysis of the parent chloride in the presence of tetrabutylammonium azide is curved rather than linear. This is the only case of the five systems studied in which this type of behaviour is found. The most reasonable explanation is that the acid formed is removing some of the azide salt from the solution as

hydrazoic acid. As a base, the added 2,6-lutidine is not appreciably stronger than azide ion so cannot prevent formation of hydrazoic acid. This would result in a decrease of available azide ion as the reaction proceeds.

In spite of this problem, some conclusions can still be drawn from the results. By the time the concentration of tetrabutylammonium azide has reached 0.2 M, the amount of HCl released will be small relative to the concentration of salt, so that only a small percentage of it will be removed by the formation of hydrazoic acid, and the approximation that $[Bu_4NN_3]$ is constant throughout the reaction will not be seriously in error. So a straight line correlation may be assumed to hold for Figure 43 at concentrations of salt equal to or greater than 0.2 M. The line so drawn gives an intercept of 1.0. If scheme [5] is an accurate interpretation of the reaction that is occurring, then the ratio of k_6/k_3 is zero. But we have already concluded that k_6/k_3 must be greater than 0.91 if scheme [5] is correct. Therefore, some other mechanism must be in operation for the reaction of 2-p-acetylphenyl-2-propyl chloride with azide ion.

One possibility is that azide ion is carrying out a

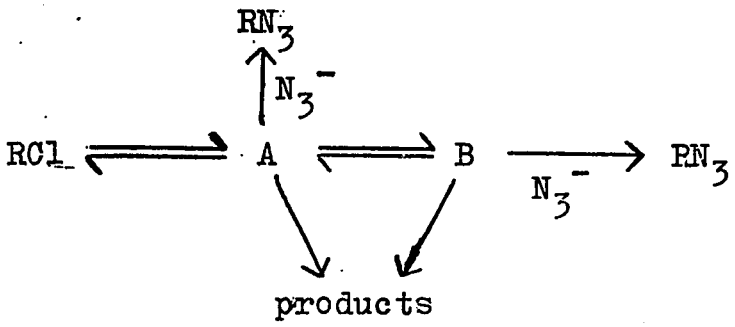
nucleophilic displacement on the starting material. The reaction scheme would then be represented by scheme [3]:

$$RN_3 \xleftarrow[N_3^-]{} RCl \xrightarrow[HOS]{} ROS + HCl \qquad [3]$$

The kinetic expression for this scheme is derived in Appendix B. The equation predicts an intercept of 1.0 for a plot of $1/F_{RN_3}$ vs. $1/[Bu_4NN_3]$. The results are consistent with this reaction pathway.

The results are also consistent with several alternative reaction schemes. A reaction of the type proposed by Kornblum for 2-p-nitrophenyl-2-propyl chloride, where the reaction to form the azide is proceeding through an intermediate formed by basic catalysis, is another possibility. In this case, the base catalyzing the reaction would also be the nucleophile, namely azide ion. It is felt, however, that a reaction scheme of this type is not likely. If it were operating, some of the products would have been expected to be polymeric, and there is no evidence for polymer formation.

The results could also be explained by an expanded form of scheme [5] in which azide ion can compete for the first intermediate, shown here as scheme [6]:



[6]

It is also possible that a combination of the above reaction mechanisms is occurring; for example, both schemes [3] and [6]; the azide ion would then be acting as a trapping agent for an ionic intermediate, and simultaneously competing for the starting material.

The results of this study tentatively rule out the "Kornblum" reaction, but do not allow of distinction among the other possibilities.

The ethanolysis of 2-p-acetylphenyl-2-propyl chloride is almost certainly proceeding through one or more ionic intermediates. The measured values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are consistent with an ionization process. The large percentage of olefin found in the products suggests that much of the solvolysis reaction proceeds through an intimate ion pair.

EXPERIMENTAL

Physical Measurements

Melting points were measured using a Hershberg melting-point apparatus with Anschutz thermometers. The melting points recorded are uncorrected values.

Refractive indices were taken using a Bausch & Lomb Abbe-3L refractometer, thermostated to the temperature stated by means of a Colora water bath assembly.

Infrared spectra were recorded on Perkin Elmer Recording Infrared Spectrophotometers, Models 337, 21, and 421. The Model 21 was used for all analytical work.

Nuclear magnetic resonance spectra were recorded on Varian Spectrometers, Models A-60, A-56/60 A, HA-60 I, and HA-100. The model HA-100 was used for analytical work.

Gas chromatography work was carried out using a Varian Aerograph Model A-90-P3, equipped with a linear temperature programmer, and a Honeywell pen recorder, Model 15, with a disc chart integrator, Model 201-B.

Ultraviolet measurements were made using a Beckman DU Spectrophotometer having a thermostated cell compartment in conjunction with a Colora water bath assembly.

SOLVENTS

Anhydrous Ethanol

Anhydrous ethanol was the solvent used for almost all of the kinetic and product studies in this work. The solvent was prepared from "98%" ethanol. It was

distilled through a glass helices column and the centre cut collected and dried with magnesium metal turnings using the method of Lund and Bjerrum(25) as described by Fieser(39). The ethanol so prepared was found to contain less than 0.01 volume percent. water, as determined by a Karl Fischer titration. Ethanol prepared in this manner had little absorbance in the 210-280 nm range and was a suitable solvent for ultraviolet spectroscopic studies.

Dioxane

Dioxane that had been previously purified by the method of Brown et al.(40) was refluxed with freshly-cut sodium until the metal was shiny, then distilled, the first and last 20% being discarded. The colourless liquid was collected: b.p. 98-98.5° (710 mm).

Pentane

12 litres of Phillips commercial grade pentane were shaken with nine pounds of concentrated sulphuric acid for one-half hour. The acid was removed and the pentane treated an additional half-hour with nine pounds more of acid. The pentane layer was then washed three times with water, heated at reflux for two hours with one pound of phosphorus pentoxide, and distilled, collecting

the centre cut.

Acetone

Acetone for rate studies was prepared by drying over, and distilling from, molecular sieves. The freshly prepared solvent was used immediately: b.p. 53-54° (702 mm).

Ethyl Acetate

Five pounds of ethyl acetate (Analar A.R.) was heated at reflux temperature with one pound of anhydrous potassium carbonate. The ethyl acetate was distilled, and stored in a dark bottle: b.p. 74-75° (705 mm).

Diethyl Ether

Mallinckrodt AR anhydrous ether was used without further purification.

Mixed Solvent

The mixed solvents used were prepared by mixing appropriate volumes of purified solvents. The composition of the mixtures recorded is volume percent; e.g. 75%acetone-25% ethanol was prepared by mixing three volumes of acetone and one volume of ethanol.

Standardized Sodium Methoxide

A solution of sodium methoxide was prepared by adding an appropriate amount of freshly cleaned sodium to five pounds of reagent methanol (Shawinigan). The solution was standardized against potassium hydrogen phthalate (B.D.H. primary standard) using 10 drops of phenolphthalein indicator. Sodium methoxide so prepared was stored in a dark, tightly-stoppered bottle. It showed no change in titre over long periods of time.

Standardized Lithium Ethoxide

Freshly cut lithium was added to anhydrous ethanol. The solution of lithium ethoxide was standardized against standard HCl, using 10 drops of phenolphthalein indicator. Lithium ethoxide so prepared was used within 24 hours of preparation.

2,6-Lutidine

Purified 2,6-lutidine was kindly donated by Mr R. L. Tomilson.

2-Phenyl-2-propanol

A 34.0 gm (1.41 mole) quantity of magnesium metal turnings (Fisher) was placed in a 2-litre, 3-necked

flask equipped with Hershberg stirrer, water condenser, and dropping funnel. A mixture of 200 gm (1.42 moles) of methyl iodide in 400 ml of anhydrous ether was added at a rate sufficient to maintain the reaction at reflux temperature. The dark-coloured Grignard solution was cooled to $0^{o}C$, and a 120 gm (1.0 mole) quantity of acetophenone dissolved in 300 ml of ether was added dropwise. After completion of the reaction, 100 ml of saturated ammonium chloride solution were added to the grey reaction mixture. The ether solution was decanted, and the residual white solid washed three times with ether. The ether layer and washings were combined and washed once with 10% sodium carbonate solution, and eight times with water.

The ethereal solution was dried over anhydrous K_2CO_3. The ether was removed at the rotary evaporator and the residue distilled to give 85.8 gm (63%) of the colourless liquid: b.p. 74-75° (42 mm) (reported(41) b.p. 94° (13 mm)); n_D^{25} = 1.5188 (reported (18) n_D^{25} = 1.5188); ir (CS_2) 3580, 1600, 1030 cm^{-1}; nmr (CCl_4) τ3.0 (m, 5H), τ 6.7 (s, 1H), τ8.12 (s, 6H).

2-p-Tolyl-2-propanol

Reaction of 130 gm (0.97 mole) of p-methylaceto-phenone with 1.41 moles of methylmagnesium iodide at

0° gave the alcohol contaminated with about 20% olefin. Redistillation under vacuum afforded 56.5 gm (39%) of the desired 2-p-tolyl-2-propanol: b.p. 88.0-88.5° (4.8 mm) (reported(24) b.p. 101° (10 mm)); n_D^{25} = 1.5168 (reported(24) n_D^{20} = 1.5180); ir (neat) 3400, 1015 cm^{-1}; nmr (CCl_4) τ2.3 (m, 4.3H), τ 7.38 (s,1.1H), τ 7.76 (s, 3H), τ 8.58 (s, 6H).

2-p-Methoxyphenyl-2-propanol

The Grignard reagent was prepared from 100 gm (0.70 mole) of iodomethane and 17 gm (0.70 mole) of magnesium. p-Methoxyacetophenone (60 gm (0.40 mole)), dissolved in 200 ml of ether, was added while keeping the temperature of the reaction below -10°. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours, then cooled to 0° and hydrolyzed with saturated ammonium chloride solution. The work-up procedure was the same as that used for 2-phenyl-2-propanol. Redistillation under vacuum gave 20 gm (30%) of 2-p-methoxyphenyl-2-propanol: b.p. 117-120° (6 mm), n_D^{25} = 1.5267 (reported(18) b.p. 110-112° (4.3 mm), n_D^{25} = 1.5270); ir (CCl_4) 3580, 3400, 3020, 2810, 1500 cm^{-1}; nmr (CCl_4) τ3.0 (m, 3.9H), τ6.41 (s, 3H), τ 7.35 (s, 1H), τ8.55 (s, 6H).

2-p-Nitrophenyl-2-propanol

This compound was donated by D. Darwish. The ir and nmr spectra of the material were superimposible with the spectra of authentic material. It was used without purification.

2-Methyl-2-p-bromophenyl-1,3-dioxolane

A 60 gm quantity of p-bromoacetophenone, Eastman white label, was dissolved in 1000 ml of benzene, and 0.5 gm of p-toluenesulfonic acid monohydrate, together with 260 ml of ethylene glycol, added. The mixture was distilled at the rate of one drop per second for 26 hours, while benzene was added through a dropping funnel to maintain a constant volume. The distilling flask was immersed in an oil bath which was maintained at 85°. The mixture was cooled to room temperature. Excess powdered sodium acetate was added. The mixture was stirred vigorously for one hour, poured into a separatory funnel, washed once with 5% sodium carbonate solution, 5 times with distilled water, and dried over anhydrous potassium carbonate. The solvent was removed using a rotary evaporator. The light yellow residual liquid was distilled under vacuum and the centre cut collected to yield 62 gm (86%) of colourless liquid: b.p. 125-126°

(4 mm) (reported(42) 175-180° (20-30 mm)); ir (CCl_4) 2980, 2880, 1590, 1380, 1300, 1200, 1090, 950 cm^{-1}; nmr (CCl_4) τ 2.6 (m, 1H), τ 6.2 (m, 4H), τ 8.5 (s, 3H).

A peak in the nmr at τ 7.5 indicated about 5% impurity of p-bromoacetophenone. The material was used immediately without further purification.

2-Methyl-2-p-(α-hydroxyisopropyl)-1,3-dioxolane

In a 3-necked flask, fitted with dropping funnel, stirrer, and reflux condenser, were placed 14 gm (0.57 mole) of magnesium metal turnings and 70 ml of sodium-dried tetrahydrofuran. A mixture of 4 gm of iodomethane in 30 ml of tetrahydrofuran was added. The resulting mixture was heated at reflux temperature overnight and maintained at this temperature while 109 gm (0.45 mole) of 2-methyl-2-p-bromophenyl-1,3-dioxolane, dissolved in 150 ml of tetrahydrofuran, was added. The mixture was allowed to continue boiling at reflux temperature for one hour, then cooled to 50°, and 120 ml (2.0 mole) of freshly-prepared acetone added. The resultant solution was stirred for one hour, and hydrolyzed with 225 ml of saturated ammonium chloride solution. The organic layer was decanted, poured into 1000 ml of ether, washed five times with water, and dried over anhydrous potassium carbonate. The solvent was removed at the rotary

evaporator. The residual yellow oil was extracted with 100-ml portions of pentane until no more of the material dissolved (about 20 treatments with the solvent). The yellow crystals obtained when the solvent was removed from the resultant pentane solution were recrystallized three times from 35% ether-65% pentane to yield 19.5 gm (21%) of white flakes: m.p. 80.4-81.0°; ir (CCl_4) 3580, 2960, 2870 cm^{-1}; nmr (CCl_4) τ 2.68 (s, 4H), τ 6.20 (m, 4H), τ 7.8 (s, 1H), τ 8.50 (s, 8.8H).

Analysis: Calculated for $C_{12}H_{18}O_3$: C, 70.24; H, 8.15

Found: C, 69.92, 70.35; H, 8.16, 7.89.

2-Phenyl-2-propyl Chloride

A 13.6 gm (0.1 mole) quantity of 2-phenyl-2-propanol was dissolved in 40 ml of CH_2Cl_2 and cooled to -10° in a methanol-ice bath. Anhydrous HCl was bubbled through the mixture for one hour. The reaction mixture was allowed to warm to room temperature, poured into a separatory funnel, and the water layer removed. The organic layer was dried over anhydrous potassium carbonate, and filtered. The bulk of the methylene chloride was removed at the water aspirator; that remaining was removed at the vacuum pump.

The residual light yellow liquid was distilled under

nitrogen to give 10.2 gm (89.5%) of colourless liquid: b.p. 77-78° (10.5 mm), n_D^{25} = 1.5228 (reported(24) b.p. 56-58° (1.5 mm), n_D^{20} = 1.5210); ir (CCl_4) 3040, 2980, 1490, 1440, 1260, 1120, 1090 cm^{-1}; nmr (CCl_4) τ 2.7 (m, 5H), τ 8.05 (s, 5.8H).

The purity of the sample was checked by carrying out a solvolysis reaction in 50% acetone, and titrating the acid formed; % purity as obtained by titre was 96 ±1%.

2-p-Tolyl-2-propyl Chloride

In a typical preparation, 3.0 gm (0.02 mole) of 2-p-tolyl-2-propanol were dissolved in 75 ml of purified pentane. The solution was cooled to -80° in a dry ice-acetone bath and dry HCl bubbled through the mixture for 30 seconds. The water formed was removed by drying the mixture over anhydrous potassium carbonate and filtering. The solvent was removed at the rotary evaporator. The 2-p-tolyl-2-propyl chloride (3.0 gm, 88%) so prepared contained about 10% polymeric material: ir (CCl_4) 2970, 2900, 1510, 1260, 1085 cm^{-1}; nmr (CCl_4) τ 2.8 (m, 4H), τ 7.62 (s, 3H), τ 8.08 (s, 5H), and small peaks at τ 8.5, 8.9 and 9.22, totalling about 10% of the integration.

Attempts to purify the compound by vacuum distil-

lation caused the material to decompose to olefin, which polymerized. The material also decomposed on chromatography over basic, neutral or acidic alumina, or on g.c. It was used without further purification. Solvolysis of the compound in 50% aqueous acetone released 91% of the theoretical HCl; hence, the 2-p-tolyl-2-propyl chloride used in the study was assumed to be 91% pure.

2-p-Methoxyphenyl-2-propyl Chloride

Attempts to synthesize this material utilizing the reaction of HCl with the alcohol in the cold gave material containing 50-60% polymeric material, as estimated from the nmr.

The compound was synthesized from 2-p-methoxyphenyl-2-propanol by the following procedure: 2.1 gm (0.0125 mole) of 2-p-methoxyphenyl-2-propanol and 1.38 gm (0.0125 mole) of 2,6-lutidine were dissolved in 170 ml of methylene chloride. Thionyl chloride (0.94 ml, 1.55 gm, 0.0125 mole), in 70 ml of pentane, was added while keeping the temperature of the reaction mixture below -18°. The supernatant liquid was decanted and the 2,6-lutidinium chloride which remained was washed twice with 5-ml portions of pentane. The decantate and washes were combined and the solvent

removed at the rotary evaporator to yield 1.5 gm (65%) of yellow liquid: ir (CCl_4) 1500, 1390, 1045 cm^{-1}; nmr (CCl_4) τ3.0 (m, 4.1H), τ6.35 (s, 3H), τ8.08 (s, 5.1H), and a series of small peaks at τ8.5-9.6.

Solvolysis of a sample of material in 95% ethanol for ½ hour yielded 81% of the theoretical amount of HCl; hence, the material was considered to be 81% pure. The nmr spectrum indicated that the remainder of the material was polymeric in nature. On standing in the freezer for a few days, 2-p-methoxyphenyl-2-propyl chloride turned black. When needed for product studies, it was always prepared and used immediately.

2-p-Nitrophenyl-2-propyl Chloride

2-p-Nitrophenyl-2-propanol (0.5 gm) was dissolved in 40 ml of benzene, 20 mg of sublimed ferric chloride was added, and HCl gas was bubbled through the mixture for 15 minutes. Anhydrous potassium carbonate was added to remove the water formed, then the mixture was filtered and the solvent removed at the rotary evaporator to yield 0.4 gm (73%) of bright yellow liquid: ir (CCl_4) 2980, 1525, 1350, 960 cm^{-1}; nmr (CCl_4) τ2.1 (m, 4H), τ8.0 (s, 6H).

2-p-Acetylphenyl-2-propyl Chloride

A 2.6 gm quantity of 2-methyl-2-p-(α-hydroxyisopropyl)-phenyl-1,3-dioxolane was dissolved in 50 ml of methylene chloride and HCl gas bubbled through the reaction mixture for 10 minutes. The solution turned a dark red colour. The solution was treated with anhydrous potassium carbonate, filtered, and the solvent removed. The residual yellow oil was recrystallized twice from pentane in a dry-ice-acetone bath to yield 1.0 gm (42%) of yellow solid: m.p. 25°; ir (CCl_4) 2980, 1680, 1600, 1350, 950 cm^{-1}; nmr (CCl_4) τ 2.35 (m, 4.1H), τ 7.50 (s, 3H), τ 8.05 (s, 6H).

Benzyl Chloride

Benzyl chloride, Fisher reagent, was distilled under vacuum and the centre cut collected: b.p. 62-62.5° (10 mm).

p-Methoxybenzyl Chloride

p-Methoxybenzyl alcohol (30 gm, 0.22 mole) was dissolved in 400 ml of benzene and cooled to -10°. Dry HCl was bubbled through the mixture for 2 hours. The reaction mixture was washed 5 times with water, dried over anhydrous calcium chloride, and filtered.

Following removal of the solvent, the residual yellow liquid was distilled to yield 31.1 gm (91%) of clear liquid: b.p. 105-106° (8 mm), n_D^{25} = 1.5474 (reported(43) b.p. 101-102° (7 mm)); ir (CCl_4) 2980, 1509, 1240, 1030, 1005 cm^{-1}; nmr (CCl_4) τ2.7-3.5 (m, 3.7H), τ5.60 (s, 2H), τ6.34 (s, 3H).

2-Phenylpropene

Eastman white label 2-phenylpropene was distilled and the centre cut collected: b.p. 48.5-49° (9.3 mm); n_D^{25} = 1.5361 (reported(44) b.p. 54-55° (14 mm), n_D^{18} = 1.5384).

2-p-Tolylpropene

Treatment of methyl magnesium iodide with p-tolyl methyl ketone gave an alcohol-olefin mixture. Fractional distillation under vacuum gave two fractions, one mostly alcohol with some olefin: b.p. 92-94° (4 mm), and the other mostly olefin with some alcohol, b.p. 42-45° (4 mm). The latter fraction was chromatographed over alumina Activity II. The olefin was eluted with pentane: n_D^{25} = 1.5334 (reported(18) n_D^{25} = 1.5331); ir (CCl_4) 1625, 1510, 1370, 890 cm^{-1}; nmr (CCl_4) τ2.6-3.1 (m, 4.1H), τ4.76 (m, 1H), τ5.05 (m, 3H), τ7.70 (s, 3H), τ7.81 (m, 3H).

2-p-Methoxyphenylpropene

This compound was obtained as a by-product of the synthesis of 2-p-methoxyphenyl-2-propyl azide. It was purified by distillation under vacuum: b.p. 72-74° (2 mm); m.p. 31.8-32.4° (reported(45) b.p. 63.0-63.5° (0.5 mm); m.p. 34°); ir (CCl_4) 3080, 2840, 1600, 1280, 1240, 1030, 890 cm^{-1}; nmr (CCl_4) τ2.9 (m, 4H), τ4.78 (s, 1H), τ5.05 (s, 1H), τ6.25 (s, 2.9H), τ7.90 (s, 3H).

2-p-Acetylphenylpropene

2-Methyl-2-p-(α-hydroxyisopropyl)-phenyl-1,3-dioxolane (2.0 gm) was heated on the steam bath for 3 hours with 0.5 gm of phosphoric acid. The reaction mixture was poured onto an ice-ether mixture. The ether layer was separated and washed successively 3 times with water, twice with 5% sodium carbonate solution and 3 times with water. The ether layer was dried over potassium carbonate, filtered, and the solvent removed at the rotary evaporator. The residual light yellow solid was further purified by chromatography over Woelm alumina Activity IV using 5% ether-95% pentane eluant. A 0.76 gm quantity (59%) of white crystals was obtained: m.p. 48.2-49.4°; ir (CCl_4) 1680, 1600, 1450, 1350, 900 cm^{-1}; nmr (CCl_4) τ 2.4 (m, 3.9H), τ4.62 (s, 1H), τ4.95 (m, 1H), τ7.54 (s, 3H), τ7.91 (m, 3H).

Analysis: Calculated for $C_{11}H_{12}O$: C, 82.46; H, 7.55.
Found: C, 82.34, 82.71; H, 7.24, 7.49.

2-Phenyl-2-propyl Ethyl Ether

A mixture of 2.0 ml of conc. H_2SO_4 and 100 ml of anhydrous ethanol were placed in a 500 ml Erlenmeyer flask, and equilibrated to 25°. 2-Phenyl-2-propanol (10.0 gm, 0.073 mole) was added and the mixture stirred for 24 hours. The solution was poured onto an ice-ether mixture. The water layer was separated and washed three times with 15-ml portions of ether. The ethereal solution and the extracts were combined and washed successively, twice with water, once with 10% sodium carbonate solution, and three times with water. The solvent was then removed at the water aspirator. The residual oil was chromatographed over alumina Activity IV, using pentane as eluant. The light yellow liquid obtained from chromatography was distilled under vacuum, taking the centre cut, to yield 6.2 gm (51%) of colourless 2-phenyl-2-propyl ethyl ether: b.p. 75-7° (9.5 mm); n_D^{25} = 1.4875 (reported( ) b.p. 48-9° (2.5 mm); n_D^{22} = 1.491); ir (CCl_4) 1600, 1492, 1385, 1375, 1305, 1160, 1060 cm^{-1}; nmr (CCl_4) τ 2.7 (m, 5H), τ6.85 (q, 2H J = 7 Hz), τ8.55 (s, 6H), τ8.92 (t, 3H J = 7 Hz).

2-p-Tolyl-2-propyl Ethyl Ether

This material was obtained as a by-product of the synthesis of 2-p-tolyl-2-propyl azide. The 2-p-tolyl-2-propyl ethyl ether from the preparative g.c. was further purified by distillation: b.p. 58-59° (3 mm); n_D^{25} = 1.4876; ir (CCl_4) 2908, 1510, 1350, 1250, 1090 cm^{-1}; nmr (CCl_4) τ 2.95 (m, 4H), τ 6.88 (q, 2.1H, J = 14 Hz), τ 7.70 (s, 3H), τ 8.55 (s, 6H), τ 8.90 (t, 3H, J = 14 Hz). Analysis: Calculated for $C_{12}H_{18}O$: C, 80.85; H, 10.18

Found: C, 81.02, 81.23; H, 10.09, 10.07.

2-p-Methoxyphenyl-2-propyl Ethyl Ether

Conc. sulfuric acid (0.5 ml) was dissolved in 50 ml of anhydrous ethanol and allowed to equilibrate to room temperature in a water bath. 2-p-Methoxyphenyl-2-propanol (4.0 gm, 0.02 mole) was added and the mixture stirred for 35 minutes. The same work-up procedure was used as for 2-phenyl-2-propyl ethyl ether. The crude ether, containing 10% olefin, was chromatographed over Harshaw alumina. The olefin was eluted with pentane. The 2-p-methoxyphenyl-2-propyl ethyl ether was eluted with 50% ether-pentane. 2.0 gm (45%) of colourless liquid was obtained: n_D^{25} = 1.5003; ir (CCl_4) 1500, 1430, 1390, 1045 cm^{-1}; nmr (CCl_4) τ 2.95 (m, 4H),

τ6.25 (s, 3H), τ6.78 (q, 2H, J = 7 Hz), τ8.47 (s, 6H), τ8.95 (t, 3H, J = 7 Hz).

Analysis: Calculated for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.12, 74.50; H, 9.19, 8.82.

2-p-Acetylphenyl-2-propyl Ethyl Ether

A mixture of 1.5 gm of 2-methyl-2-p-(α-hydroxy-isopropyl)-phenyl-1,3-dioxolane, 1.0 ml of conc. sulfuric acid, and 25 ml of anhydrous ethanol were stirred together for 4 days at room temperature. After work-up, using the same procedure as for 2-phenyl-2-propyl ethyl ether, the recovered crude material was shown by nmr to be a mixture of about 8% olefin, 5% alcohol, and 87% of the desired ether. Chromatography of the red oil over Woelm alumina Activity IV using 5% ether-95% pentane eluant gave 0.6 gm (40%) of the desired material, a light yellow liquid: n_D^{25} = 1.5125; ir (CCl_4) 2980, 1680, 1360, 1290, 1170, 1070, 950 cm^{-1}; nmr (CCl_4) τ2.30 (m, 4H), τ6.82 (q, 2H, J = 13 Hz), τ7.49 (s, 3H), τ8.51 (s, 6H), τ8.86 (t, 3H, J = 13 Hz).

Analysis: Calculated for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79

Found: C, 75.75, 75.97; H, 8.46, 8.60.

2-Phenyl-2-propyl Azide

A 10.0 g. quantity (0.154 mole) of sodium azide was

dissolved in 40 ml of water, then 110 ml of reagent acetone added, followed by 13.5 gm (0.082 mole) of 2-phenyl-2-propyl chloride. The reaction mixture was stirred for two hours at room temperature, poured into water, and extracted three times with ethyl ether. The combined ether extracts were washed successively, twice with water, once with 10% sodium carbonate solution and four times with water, and dried over anhydrous potassium carbonate. The potassium carbonate was filtered off and the ether removed at the aspirator to give a pale yellow oil which had absorption in the infrared at 3580 cm^{-1}, indicative of some alcohol. The alcohol was removed by chromatography on alumina, Activity II. The material obtained from the chromatography was distilled to give 4.2 gm (30%) of colourless liquid: b.p. 87-88° (9.5 mm), n_D^{25} = 1.5197 (reported(18) b.p. 84-85° (8 mm), n_D^{25} = 1.5195); ir (CCl_4) 2100, 1490, 1385, 1364, 1250, 1142, 1023, 690 cm^{-1}; nmr (CCl_4) τ 2.75 (m, 5H), τ 8.45 (s, 6H).

Analysis: Calculated for $C_9H_{11}N_3$: C, 67.06; H, 6.88; N, 26.06

Found: C, 66.94, 66.93; H, 6.73, 6.53; N, 26.01, 26.31.

2-p-Tolyl-2-propyl Azide

2-p-Tolyl-2-propyl chloride (10.1 gm, 0.05 mole) was dissolved in a mixture of 25 gm (0.5 mole) of lithium azide and 500 ml of anhydrous ethanol and allowed to stand overnight, then most of the ethanol was removed at the rotary evaporator. The mixture was poured into 1000 ml of pentane, washed 5 times with water, and dried over anhydrous potassium carbonate. The solvent was removed at the rotary evaporator. The residual oil was a mixture of the composition 5% olefin, 45% azide, 50% ether, as estimated from the nmr. Preparative g.c. on a 3 m x 3/8 in. Carbowax 1500 column maintained at 157°, using a helium gas flow of 300 ml/min., of 3.0 gm of the crude material yielded 0.5 gm of a colourless liquid which was very light-sensitive. The 2-p-tolyl-2-propyl azide so obtained was purified by molecular distillation immediately before using: $n_D^{25} = 1.5184$; ir (CCl_4) 2980, 2105, 1510, 1350, 1290, 1090 cm^{-1}; nmr (CCl_4) τ2.95 (m, 4H), τ 7.65 (s, 3H), τ8.48 (s, 5.9H).

A satisfactory analysis could not be obtained for this compound.

2-p-Methoxyphenyl-2-propyl Azide

A 3.5 gm quantity (0.016 mole) of 2-p-methoxyphenyl-2-propyl chloride was dissolved in a mixture of 9.4 gm (0.033 mole) of tetrabutylammonium azide and 25 ml of acetone. The reaction mixture was stirred at room temperature for 2 hours, the solvent was removed at the rotary evaporator. The residue was taken up in 500 ml of ether, washed 8 times with water, and dried over anhydrous potassium carbonate. The solvent was removed at the rotary evaporator. The crude oil remaining contained about 50% olefin. On chromatography over Woelm alumina Activity III, the olefin was eluted with pentane, after which 0.55 gm (15%) of the desired compound was eluted using 10% ether-pentane: $n_D^{25} = 1.5270$; ir (CCl_4) 2950, 2815, 2090, 1230, 1040 cm^{-1}; nmr (CCl_4) τ 3.0 (m, 4H), τ 6.28 (s, 3H), τ 8.40 (s, 3H). Analysis: Calculated for $C_{10}H_{13}N_3O$: C, 62.81; H, 6.85; N, 21.97.

Found: C, 62.13, 62.80; H, 6.91, 6.58; N, 21.91, 22.16.

2-p-Acetylphenyl-2-propyl Azide

A mixture of 2.5 gm of 2-p-acetylphenyl-2-propyl chloride and 9.5 gm (0.034 mole) of tetrabutylammonium azide dissolved in 50 ml of acetone was heated overnight.

The solution was worked up using the same procedure as for 2-p-methoxyphenyl-2-propyl azide. The crude material was chromatographed over Woelm alumina Activity IV with 5% ether-95% pentane eluant to give 0.95 gm (38%) of a light yellow liquid: n_D^{25} = 1.5429; ir (CCl_4) 2980, 2100, 1680, 1350, 1250, 1000 cm^{-1}; nmr (CCl_4) τ 2.30 (m, 4H), τ 7.52 (s, 3H), τ 8.40 (s, 6H).

Analysis: Calculated for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.44; N, 20.68.

Found: C, 65.37, 65.51; H, 6.36, 6.30; N, 20.33, 20.57.

Benzyl Azide

This compound was prepared according to the method of Curtius and Ehrhart(34) in 71.5% yield: b.p. 77-78° (11 mm); n_D^{25} = 1.5342 (reported(34) b.p. 108° (23 mm); n_D^{25} = 1.5341).

p-Methoxybenzyl Azide

p-Anisyl chloride (8.0 gm, 0.06 mole) was dissolved in a mixture of 15 gm (0.05 mole) of tetrabutylammonium azide and 100 ml of acetone. After the mixture was allowed to boil at reflux for 6 hours, it was poured into 500 ml of ether, washed 5 times with water, and dried over anhydrous calcium chloride. The solvent was

removed and the residual oil distilled to yield 3.5 gm (36%) of colourless liquid: b.p. 82-83° (3.5 mm), n_D^{25} = 1.5417; ir (CCl_4) 2940, 2100, 1510, 1250, 1035 cm^{-1}; nmr (CCl_4) τ2.8-3.4 (m, 4H), τ5.90 (s, 2H) τ6.35 (s, 3H).

Analysis: Calculated for $C_8H_9N_3O$: C, 58.88; H, 5.56; N, 25.76.

Found: C, 58.79, 58.96; H, 5.60, 5.50; N, 25.74, 25.43.

Tetrabutylammonium Bromide

1-Bromobutane (BDH reagent) and tri-n-butyl amine (Eastman practical) were purified by distillation.

A mixture of 1.6 moles of 1-bromobutane (218 gm) and 1.6 moles of tri-n-butyl amine (296 gm) was heated on the steam bath for ten days. The dark red oil obtained was washed with ether until crystallization occurred. The crude material was recrystallized three times from purified ethyl acetate to give 180 gm (35%) of white crystals; m.p. 117.8-118.3° (reported(47) 118°).

A Volhard titration showed 98.4% of theoretical bromide.

Later, commercial tetrabutylammonium bromide, Eastman Kodak, was recrystallized once from ethyl acetate and used.

Tetrabutylammonium Azide

Tetrabutylammonium bromide (80.5 gm, 0.25 mole) was dissolved in 225 ml of water and stirred with excess silver oxide until the supernatant liquid gave a negative test for bromide. The silver halide-oxide mixture was filtered off, and the filtrate treated with excess hydrazoic acid until acidic to litmus; then the water was removed at the rotary evaporator. The solid material remaining was dissolved in chloroform, allowed to digest for ten minutes over potassium carbonate, and filtered. The chloroform was removed at the aspirator leaving a crystalline solid which was recrystallized twice from purified ethyl acetate to give 42.7 gm (62%) of white, hygroscopic crystals: m.p. 80-82°. The salt was stored under vacuum with phosphorus pentoxide desiccant.

ANALYSIS: Various methods of analysis of this salt proved less than successful. On attempted analysis of the material for the azide ion, using the method of van de Meulen(27), a method shown to be satisfactory for both lithium azide and for sodium azide, the tetrabutylammonium cation decomposed and interfered with the determination. Attempted analysis by comparison of the infrared spectrum of a model compound such a lithium

azide was not possible because of the solvent limitations of cells used for infrared work.

The azide ion has a moderate intensity absorption band at 230 μm (ϵ = 400 mole^{-1}) which has been assigned to $^1\Sigma_g \Rightarrow {}^1\Delta_u$ transition(48). It was hoped that comparison of the absorption of tetrabutylammonium azide at 230 μm to a calibration curve of absorbance vs. concentration at the same wavelength of a model compound might be a suitable method of determining the purity of the salt. When this was attempted, however, 130% of the theoretical amount of tetrabutylammonium azide was found. It was assumed that a small amount of impurity having an intense absorption band in this region was interfering with the analysis.

Direct carbon and hydrogen analysis of the material was impossible, since the salt was too hygroscopic to be weighed on the microanalytical balance. Carbon, hydrogen and nitrogen analysis could be carried out indirectly, however. The salt was dried, accurately weighed and then dissolved in a known weight of water; the resulting syrup was not appreciably hygroscopic. The salt lowered the vapour pressure of the water to such an extent that loss of water by evaporation was not a problem. The result of such an analysis for a

sample of 3.5887 gm of tetrabutylammonium azide dissolved in 0.9411 gm of water were:

Calculated: C, 53.51; H, 12.43; N, 15.60

Found: C, 53.28, 53.73; H, 12.38, 12.32; N, 15.33.

Tetrabutylammonium Perchlorate

Tetrabutylammonium hydroxide prepared by the treatment of 40 gm of tetrabutylammonium bromide with silver oxide was neutralized with 70% perchloric acid. The white crystals formed were recrystallized twice from ethyl acetate to yield 35.0 gm (82%) of the desired salt: m.p. 212-213° (reported(49) m.p. 212-212.5°).

Lithium Perchlorate

Lithium perchlorate trihydrate was quantitatively dehydrated over phosphorus pentoxide in an Aberhalden drying apparatus.

Lithium Chloride

Reagent grade lithium chloride was dried to constant weight over phosphorus pentoxide in an Aberhalden drying apparatus.

Acetophenone

Reagent grade acetophenone was distilled and the

centre cut collected: b.p. 197-198° (702 mm).

Naphthalene

Eastman white label naphthalene, recrystallized from alcohol, was used: m.p. 80.0-80.5°.

Standard Acid

0.03 N HCl was prepared from boiled distilled water and reagent grade hydrochloric acid. It was standardized against sodium methoxide standard base.

STANDARD EXTRACTION PROCEDURES

Three different extraction procedures were used throughout kinetic measurement and product analysis work. They are listed below.

Extraction Procedure I

A 5-ml aliquot of solution was withdrawn using a calibrated automatic pipette and delivered into a 60 ml separatory funnel containing 40 ml of pentane and 10 ml of boiled distilled water. The mixture was shaken vigorously 50 times. The aqueous layer was withdrawn and the pentane mixture was washed successively with two 10-ml portions of water. The organic layer was decanted

into an Erlenmeyer flask. The separatory funnel was rinsed twice with 5-ml portions of pentane. The organic layer and rinses were combined and dried over anhydrous potassium carbonate, then filtered through glass wool. The flask and glass wool were rinsed twice with 5-ml portions of pentane.

Extraction Procedure II

Whenever tetrabutylammonium perchlorate was present in the reaction mixture, it precipitated out when the reaction mixture was added to the pentane. Since the salt was also insoluble in water, it interfered with washing. In cases where this salt was present, the aliquot of solution was delivered into an Erlenmeyer flask containing 35 ml of pentane, then filtered into a 60 ml separatory funnel through a glass wool plug. The insoluble salt and plug were rinsed twice with 5 ml of pentane. The mixture and washes were combined and treated as described in Extraction Procedure I.

Extraction Procedure III

This procedure was used for all extractions where 2,6-lutidine was present in the reaction mixture.

A 5-ml aliquot of the solution was withdrawn using

a calibrated automatic pipette. When the reaction mixture contained tetrabutylammonium perchlorate, it was delivered into 35 ml of pentane and filtered, in the manner described in Procedure II. Otherwise, it was delivered directly into a 60 ml separatory funnel containing 40 ml of pentane. The pentane solution was washed successively with two 10-ml portions of 0.1 N HCl, 10 ml of 5% sodium carbonate solution and two 10-ml portions of water. Each wash was shaken 50 times. The organic layer was withdrawn and the funnel washed twice with 5-ml portions of pentane. The combined solution and washes were dried over anhydrous potassium carbonate, then filtered through glass wool; the wool was rinsed twice with 5-ml portions of pentane.

KINETIC MEASUREMENTS

Kinetic measurements were carried out by titrimetry, infrared spectroscopy, and ultraviolet spectroscopy. Each method is described in detail below.

a) Titrimetry

Several different procedures were used in the titrimetric runs. In each case, the first-order rate constants were calculated using the expression:

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V}$$, where V = volume of titre at time t

i) Titrimetric Procedure A

Procedure A was used for rate studies on 2-phenyl-2-propyl chloride in 100% ethanol at 25.00°.

The starting material was weighed accurately in a 100 ml volumetric flask, filled to the mark with ethanol previously equilibrated to 25°, and shaken. The volumetric flask containing the mixture was then placed in a water bath thermostated at 25.00° and allowed to equilibrate. After two minutes, a 5-ml aliquot was withdrawn for a "zero" point, using an automatic pipette. Further aliquots were withdrawn at appropriate intervals and quenched in a mixture of cold (-10°) reagent acetone and 10 drops of 0.1% phenolphthalein indicator solution. The acetone-indicator mixture had been previously titrated to the pink end-point. The mixture was titrated to a pink end-point again, using standard base.

ii) Titrimetric Procedure B

This procedure was used for most titrimetric rate studies on 2-phenyl-2-propyl chloride in ethanol at

25.00° to which salts were added.

The salt used was previously dried, if necessary, then accurately weighed in a volumetric flask and completely dissolved in ethanol previously equilibrated to 25°. The starting material was accurately weighed in a weighing boat and quantitatively transferred into the flask. Solvent was added to the mark, the solution shaken, and allowed to equilibrate for two minutes in a water bath thermostated at 25.00° before a 5-ml aliquot was withdrawn for a "zero" point. Other aliquots were withdrawn at appropriate time intervals. The aliquots were delivered into pentane and washed in the manner described in Extraction Procedure I or II, depending upon which was appropriate. The pentane layer was discarded or saved for infrared measurements and the separatory funnel rinsed once with 5 ml of water. The water washings and rinse were combined, and 10 drops of 0.1% phenolphthalein indicator solution added. The resulting solution was titrated to the pink end-point with standard base.

iii) Titrimetric Procedure C

Procedure C differs from Procedure B in that the reaction mixtures contained lithium ethoxide. The

solutions were prepared in the same manner as for Procedure B, using a solution of standard lithium ethoxide as solvent rather than ethanol. The reaction mixtures were treated exactly as in Procedure B except that the combined water washings and rinse were titrated to the colourless end-point of the indicator with standard HCl.

iv) Titrimetric Procedure D

Procedure D was used for titrimetric rate studies on benzyl chloride and p-methoxybenzyl chloride at 50.00° in 100% ethanol.

The reaction mixtures were prepared in the same manner as for Procedure B. Aliquots (6 ml) were transferred into ampoules, sealed, and equilibrated in an oil bath thermostated at 50.00°. After 4 minutes, a "zero" point" was withdrawn. Further ampoules were withdrawn at appropriate time intervals. Each ampoule was plunged into an ice-water bath and left for at least two minutes, then equilibrated in a water bath at 25° for 5 minutes. The ampoule was opened and a 5-ml aliquot, withdrawn using an automatic pipette, was delivered into pentane and washed in the manner described in Extraction Procedure I or II. The pentane layer was

reserved for infrared measurements or discarded. The water washings were combined and titrated to the pink end-point of phenolphthalein using standard base.

v) Titrimetric Procedure E

Procedure E was used for the titrimetric rate study of 2-p-nitrophenyl-2-propyl chloride at 90.00° in ethanol with added 2,6-lutidine, and for titrimetric rate studies of 2-p-acetylphenyl-2-propyl chloride in ethanol at several temperatures.

An appropriate amount of 2,6-lutidine was placed in a volumetric flask, weighed, and dissolved in ethanol. The starting material was weighed accurately in a weighing boat and transferred quantitatively into the flask. The mixture was made up to the mark with solvent, shaken, and transferred into ampoules which were thereupon sealed. The ampoules were placed in the appropriate thermostated bath. After 4 minutes, one ampoule was withdrawn for a "zero" point. Other ampoules were withdrawn at suitable intervals. The ampoules were plunged into an ice-water bath, then equilibrated for 5 minutes at 25°. A 5-ml aliquot was withdrawn from each, transferred into a mixture of 15 ml of reagent methanol and 0.2 ml of 0.1% p-naphthylbenzein indicator

which had been previously titrated to the green end-point. The mixture was again titrated to the green end-point of the indicator using standard base.

When the reaction temperature was 25.00°, the ampoules were not plunged into ice-water. They were withdrawn, opened, and titrated. The time recorded was that at the beginning of the titration in this case.

b) Infrared Spectroscopy

Several rates were studied simultaneously by infrared spectroscopy and titrimetry. In these cases, the reaction mixtures were made up and treated in the manner outlined in Titrimetric Procedure B or D, depending on which was appropriate. The water washings were reserved for the titrimetric measurements. The pentane layer was decanted and the separatory funnel rinsed twice with 5-ml portions of pentane. The pentane layer and washes were combined and placed in a pear-shaped flask. The pentane was removed and the residue treated in the same manner as used in constructing the appropriate calibration curve (page 253). The concentration of organic azide in the sample ($[RN_3]$) was obtained by comparison with the calibration curve. The concentration was used to calculate the first-order rate constant from the expression:

$$k = \frac{2.303}{t} \log \frac{[RN_3]_\infty - [RN_3]_o}{[RN_3]_\infty - [RN_3]}$$

where $[RN_3]_\infty$ and $[RN_3]_o$ are the concentrations of organic azide at complete reaction and "zero" time, respectively.

c) Ultraviolet Spectroscopy

The rate of reaction of 2-phenyl-2-propyl chloride in ethanol at 25° was often studied by monitoring the increase in intensity of a band due to 2-phenylpropene (λ_{max}= 242 nm; ϵ = 1.09 x 10^4). This method was particularly useful for reactions studied in the presence of added salts, where the precision of titrimetric studies was very low.

The salt, if used, was weighed out into a volumetric flask and dissolved in the appropriate solvent, which had been previously equilibrated to 25°. An aliquot of solution containing an accurately determined amount of starting material sufficient to give an absorbance of about 1 at complete reaction was then added and the mixture made up to the mark. The solution was shaken vigorously and an aliquot of the mixture transferred to one of a pair of dry, matched cells. The other cell was filled with the solvent and used as a blank. Both cells

were placed in the thermostated cell compartment of a Beckman Model DU instrument. The absorbance of the reaction mixture was measured at 242 nm at appropriate time intervals. The instrument null needle was balanced against the blank immediately before each reading was taken.

The first-order rate constant was calculated from the expression:

$$k = \frac{2.303}{t} \log \frac{A_\infty - A_o}{A_\infty - A}$$

where A is the absorbance at time t.

Calibration Curves of Absorbance vs. Concentration

The infrared spectra of organic azides exhibit a very strong absorption band at or near 4.76 μm, assigned to the N=N stretching frequency. Calibration curves of absorbance at 4.76 μm vs. concentration were made for 2-phenyl-2-propyl azide, 2-p-tolyl-2-propyl azide, 2-p-methoxyphenyl-2-propyl azide, 2-p-acetylphenyl-2-propyl azide, benzyl azide, and p-methoxybenzyl azide. The general procedure used in each case was identical except as noted.

In each case, two stock solutions of the organic

azide were made up by weighing an appropriate amount of the material in a volumetric flask, dissolving, and making up to the mark with anhydrous ethanol. Other solutions of the material were then prepared by dilution of the stock solutions. For each solution, a 5-ml sample was withdrawn by automatic pipette and treated as in Extraction Procedure II. The pentane solution and washings were placed in a pear-shaped flask and carborundum chips added. For 2-phenyl-2-propyl azide, the pentane was removed at the aspirator while keeping the flask in a cold water bath. For all the other systems, the pentane was removed by slow distillation through a Vigreux column. The small amount of solvent remaining was removed by drawing a gentle stream of air over the residue. The residue was dissolved in 2.056 ml of carbon tetrachloride. The optical density, I, of the resulting solution was measured between 4.4 and 5.1 μm on a Perkin Elmer Model 21 infrared recording spectrophotometer. A variable spacer cell of the same thickness containing only carbon tetrachloride was used as a blank to compensate for any absorbance due to the solvent; I_o and I were measured and a plot of log I_o/I vs. concentration was made; see Figures 2, 20, 21, 25, 26, 27.

PRODUCT ANALYSES

The products of solvolysis of the systems studied were determined by g.c., nmr, or infrared spectroscopic measurements.

a) g.c.

Product analyses of several systems were carried out by g.c. using a Varian Aerograph A-90-P3. In each case, controls were carried out on a series of solutions containing various amounts of the expected products. An aliquot of each solution was carried through a standard work-up procedure, internal standard added, and the mixture analyzed by g.c.

The details for each system are given below.

i) 2-Phenyl-2-propyl System

Standard plot: A series of synthetic mixtures of 2-phenylpropene, 2-phenyl-2-propyl ethyl ether, and 2-phenyl-2-propyl azide in ethanol was prepared. Each mixture was allowed to stand for 5 hours at 25°, 10 half-lives of reaction of the starting material. A 5-ml aliquot of the solution of the starting material was withdrawn using an automatic pipette, and delivered into pentane. A 1-ml solution of an internal standard was added and the resulting mixture was treated in the manner

described in Extraction Procedure I. The internal standard was prepared by weighing an appropriate amount of naphthalene in a 25-ml volumetric flask, dissolving the material and making the solution up to the mark with ethanol. The pentane and washings from the extraction were combined and placed in a 100 ml round-bottomed flask, and the solvent removed by slow distillation through a Vigreux column. A 1-ml portion of ether was added to the residue to ensure complete solubility of the standard. Aliquots (25 μl) of the solution were analyzed in triplicate on g.c. column K (20% Carbowax on Chromosorb W), 3 m x $\frac{1}{4}$ in. using the conditions:

inlet temperature:	196°
column temperature:	150°
detector temperature:	183°
filament current:	150 ma.
helium gas flow:	63 ml $min.^{-1}$, 62 p.s.i.

The retention time of each material under these conditions was:

2-phenylpropene	110 sec.
2-phenyl-2-propyl ethyl ether:	170 sec.
2-phenyl-2-propyl azide:	340 sec.
naphthalene:	545 sec.

The area of each peak was determined using a disc chart

integrator. Duplicate determinations were made for each standard solution. A plot of RA (see page 52 for definition) vs. moles was made for each of the expected products. They are shown in Figures 7, 8, and 9.

Product Runs: Salt (or 2,6-lutidine), if used, was dried as necessary, weighed in a volumetric flask, and dissolved in the appropriate solvent. A known amount of 2-phenyl-2-propyl chloride was added, the flask made up to the mark with solvent, mixed, and allowed to solvolyze for 5 hours, 10 half-lives of reaction, at 25.00°. A 5-ml aliquot of the solution was withdrawn, treated, and analyzed in the same manner as were the standards. Comparison of RA for each product with that of the appropriate standard gave the number of moles of each material in the reaction mixture.

ii) 2-p-Tolyl-2-propyl System

Standard Plots: A series of synthetic mixtures of 2-p-tolylpropene, 2-p-tolyl-2-propyl ethyl ether, and 2-p-tolyl-2-propyl azide was made up in ethanol and each mixture allowed to stand for one-half hour at 25.00°. A 5-ml aliquot of solution was withdrawn and run into pentane and a 1-ml aliquot of an ethanol solution containing a known amount of acetophenone, internal standard added. The solution was treated in

the same manner as the standards of the 2-phenyl-2-propyl system. After most of the pentane was removed, 25-μl aliquots of the residual solutions were analyzed in triplicate using a 2 m x 3/8 in. column (20% Carbowax 1500 on Chromosorb W). The conditions used were:

inlet temperature:	222°
column temperature:	154°
detector temperature:	228°
filament current:	175 ma.
helium gas flow:	150 ml $min.^{-1}$; 60 p.s.i.

The retention time for each of the expected products under the conditions used was:

2-p-tolylpropene:	225 sec.
2-p-tolyl-2-propyl ethyl ether:	312 sec.
acetophenone:	512 sec.
2-p-tolyl-2-propyl azide:	640 sec.

The area of each peak was recorded using a disc chart integrator. Plots of the average value of RA' (see page 154 for definition) vs. the concentration of the material in a 4.918 ml aliquot of the standard solution was made for each of the expected products; see Figures 28, 29, and 30.

Product Runs: Salts, if used, were dried as necessary, weighed in a volumetric flask, dissolved in

the appropriate solvent, and made up to within ¼ ml of the mark. A sample of 2-p-tolyl-2-propyl chloride was accurately weighed in a weighing boat, then quickly added to the mixture which was immediately shaken vigorously. The weighing boat was then reweighed and the amount of starting material obtained by difference. A few drops of solvent sufficed to bring the volume of solution up to the mark. The reaction mixture was allowed to stand for 3 hours at 25.00°, then a 5-ml aliquot withdrawn and treated in the same manner as were the standards. In cases where tetrabutylammonium perchlorate was present in the solution, Standard Extraction Procedure II was substituted for I. Comparison of the average value for each of the products to that of the appropriate standard gave the concentration of each material in the reaction mixture.

iii) 2-p-Acetylphenyl-2-propyl System

Standard Plots: A series of synthetic mixtures of 2-p-acetylphenylpropene, 2-p-acetylphenyl-2-propyl ethyl ether, and 2-p-acetylphenyl-2-propyl azide was prepared. The solvent used in the mixtures was a solution of anhydrous ethanol, 0.02 M in 2,6-lutidine. A 5-ml aliquot of each solution was withdrawn using an automatic pipette and treated in the manner outlined in Standard

Extraction Procedure III. The pentane solution and washings were combined and placed in a 100 ml round-bottom flask and the solvent removed by slow distillation through a Vigreux column. A 1-ml aliquot of an ethanol solution containing a known amount of naphthalene was then added and 25-μl aliquots of the mixture analyzed in triplicate on a silicone oil, SE-30 (20% on Chromosorb W) column, 2 m x ¼ in. The conditions were:

inlet temperature: 202°

column temperature: 159°

detector temperature: 198°

filament current: 150 ma.

helium gas flow: 93 ml $min.^{-1}$; 60 p.s.i.

The retention time of each of the expected products was:

naphthalene (internal standard): 220 sec.

2-p-acetylphenylpropene: 450 sec.

2-p-acetylphenyl-2-propyl ethyl ether: 860 sec.

2-p-acetylphenyl-2-propyl azide: 1080 sec.

The area of each peak was determined using a disc chart integrator. Plots of the average value of RA (see page 52 for definition) vs. moles was made for each of the expected products; see Figures 40, 41, and 42.

Product Runs: Salts, if used, were dried as necessary, weighed in a volumetric flask and dissolved

in a solution of ethanol, 0.03 M in 2,6-lutidine. A known weight of 2-p-acetylphenyl-2-propyl chloride was added, and the mixture made up to the mark and shaken. Aliquots of the solution were sealed in ampoules and allowed to react at 25.00° for 21 days, corresponding to 10 half-lives of reaction. The ampoules were then opened and 5-ml aliquots of solution withdrawn, treated, and analyzed in the same manner as were the standards. Comparison of the average RA found for each product to that of the standards gave the number of moles of each material in the reaction mixture.

b) Nmr

The products of solvolysis of 2-p-methoxyphenyl-2-propyl chloride decomposed on attempting analysis by g.c. techniques. Therefore, the product analysis of this system was carried out by nmr.

Standard Plots: A series of synthetic mixtures containing 2-p-methoxyphenylpropene, 2-p-methoxyphenyl-2-propyl ethyl ether, and 2-p-methoxyphenyl-2-propyl azide were prepared in ethanol. After mixing, a 5-ml aliquot of each solution was withdrawn and run into pentane. A 1-ml aliquot of an ethanolic solution containing an appropriate amount of acetophenone as internal standard was added and the mixture carried

through Standard Extraction Procedure I. The combined pentane solution and washings were placed in a 100 ml round bottom flask and the solvent removed at the rotary evaporator. The residue was then pumped for an hour to remove the last traces of solvent. A 0.519-ml aliquot of carbon tetrachloride was added, the flask shaken and the mixture filtered through a cotton wool plug into clean nmr medium wall tubes. TMS was added to the sample in order to provide a signal for the internal lock. The spectrum of the sample was scanned on a Varian Model HA-100 spectrometer between τ6.5 and 9.3. Duplicate integrations of each sample were taken. Duplicates of each standard solution were analyzed.

After these runs had been completed, it was found that part of the acetophenone added as standard had been lost during the work-up procedure. A new set of standards containing only 2-p-methoxyphenyl-2-propyl ethyl ether was prepared, mixed, and carried through the same procedure, except that the solution containing the internal standard (acetophenone) was not added. The residue was taken up in 0.519 ml of carbon tetrachloride containing a known amount of acetophenone, with TMS added, and the spectrum run as before. The average area ratio for the quartet, singlet and triplet signals of

the ether (τ 6.78, q, 2H, J = 7 Hz; τ 8.47, s, 6H; τ 8.95, t, 3H, J = 7 Hz) was found to be within experimental error of that expected, for every sample. A plot of nRA (see page 171 for definition) vs. the number of moles of ether in the sample was made; see Figure 33. Duplicate runs were made for each standard solution.

The area ratios of the methyl signals of 2-p-methoxyphenylpropene (τ 7.90, s, 3H) and 2-p-methoxyphenyl-2-propyl azide (τ 8.40, s, 6H) was not determined directly. Instead, the relative mole ratio of olefin or azide to ether was compared to the actual mole ratio contained in the standard: see Figures 34 and 35.

Product Runs: Any salts used were dried as necessary, weighed in a volumetric flask, and made up to the mark using as solvent an ethanol solution, 0.04 M in lithium ethoxide. The salt-solvent mixture was equilibrated for 10 minutes in the 25.00° bath, then a 23.22-ml aliquot was withdrawn using an automatic pipette, and transferred to a 200 ml round bottom flask equipped with a Hershberg stirrer. A 0.15-gm sample of 2-p-methoxyphenyl-2-propyl chloride was drawn into a 1 ml syringe, accurately weighed, and forcefully injected into the rapidly stirred solution. The syringe was reweighed and the difference taken to be the weight

of starting material in the mixture. The reaction mixture was stirred for 5 minutes, then allowed to stand for an additional 25 minutes. A 5-ml aliquot of solution was withdrawn, treated and analyzed in the same manner as was done for the standards containing only 2-p-methoxyphenyl-2-propyl ethyl ether. Comparison of the results for each product to the appropriate standard curve gave the number of moles of ether and of azide in the reaction mixture. The amount of olefin in the mixture was so small that the noise level of the instrument precluded accurate integration of the signal. Therefore, no accurate measure of the amount of olefin formed in the solvolysis of 2-p-methoxyphenyl-2-propyl chloride is available.

c) Infrared Spectroscopy

Whenever one of the products of a solvolysis reaction was an organic azide, an independent check on the amount of azide formed was possible by infrared spectroscopic techniques.

Product Runs: A 5-ml aliquot of the solution to be analyzed was carried through the same work-up and analysis procedure as was used in constructing the calibration plot of the appropriate azide. Comparison of the absorbance at 4.76 μm of the sample to that of the standard gave the concentration of azide in the reaction mixture.

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APPENDIX A

For a reaction scheme [3]

$$RN_3 \xleftarrow[N_3^-]{k_2} RX \xrightarrow[HOS]{k_1} ROS + HX$$

the relationship between $1/[N_3^-]$ and $1/F_{RN_3}$ may be

derived as follows:

$$-\frac{d}{dt}[RX] = k_1[RX] + k_2[RX][N_3^-]$$

and $$\frac{d}{dt}[RN_3] = k_2[RX][N_3^-]$$

Therefore,

$$-\frac{d[RX]}{d[RN_3]} = \frac{k_1 + k_2[N_3^-]}{k_2[N_3^-]}$$

$$-\int_{[RX]_o}^{[RX]_t} d[RX] = \frac{k_1 + k_2[N_3^-]}{k_2[N_3^-]} \int_{[RN_3]=0}^{[RN_3]_t} d[RN_3]$$

$$[RX]_o - [RX]_t = \left(\frac{k_1}{k_2[N_3^-]} + 1\right)[RN_3]_t$$

Define: $[RX]_o - [RX]_t = [RN_3]_t + [ROS]_t$;

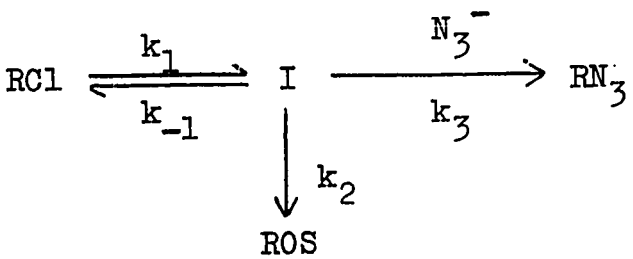
$$F_{RN_3} = \frac{[RN_3]}{[RN_3] + [ROS]}$$

Then, $$\frac{[RN_3]_t + [ROS]_t}{[RN_3]_t} = \frac{k_1}{k_2[N_3^-]} + 1$$

and $$1/F_{RN_3} = 1 + k_1/k_2\,(1/[N_3^-]).$$

APPENDIX B

For the reaction scheme



the relationship between $1/F_{RN_3}$ and $1/[N_3^-]$ may be derived as follows:

$$\frac{d}{dt}[ROS] = k_2[I] \; ; \qquad \frac{d}{dt}[RN_3] = k_3[N_3^-][I]$$

Applying the steady state approximation:

$$\frac{d}{dt}[I] = 0 = k_1[RCl] - k_{-1}[I] - k_3[N_3^-][I]k_2[I]$$

$$[I] = \frac{k_1[RCl]}{k_1 + k_2 + k_3[N_3^-]}$$

$$\frac{d}{dt}[RN_3] = \frac{k_1k_3[N_3^-][RCl]}{k_1 + k_2 + k_3[N_3^-]} \qquad (1)$$

$$\frac{d}{dt}[ROS] = \frac{k_2k_1[RCl]}{k_1 + k_2 + k_3[N_3^-]} \qquad (2)$$

Dividing (1) by (2) and simplifying:

$$\frac{d[ROS]}{d[RN_3]} = \frac{k_2}{k_3[N_3^-]}$$

So, $$\int_{[ROS]=0}^{[ROS]_t} d[ROS] = \frac{k_2}{k_3[N_3^-]} \int_{[RN_3]=0}^{[RN_3]_t} d[RN_3]$$

Then,

$$[ROS]_t = \frac{k_2}{k_3[N_3^-]} [RN_3]_t$$

Define:

$$F_{RN_3} = \frac{[RN_3]}{[ROS] + [RN_3]}$$

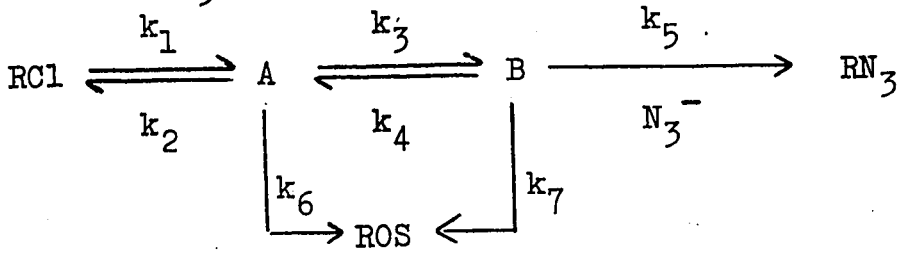
Then,

$$\frac{1}{F_{RN_3}} = 1 + \frac{[ROS]}{[RN_3]}$$

$$\frac{1}{F_{RN_3}} = 1 + \frac{k_2}{k_3} \frac{1}{[N_3^-]}$$

APPENDIX C

For the reaction scheme shown, the relationship between $1/F_{RN_3}$ and $1/[N_3^-]$ may be derived.



$$\frac{d[ROS]}{dt} = k_6[A] + k_7[B] \qquad \frac{d[RN_3]}{dt} = k_5[N_3^-][B]$$

Applying the steady state approximation, then:

$$\frac{d[A]}{dt} = 0 = k_1[RCl] + k_4[B] - k_2[A] - k_3[A] - k_6[A]$$

$$[A](k_2 + k_3 + k_6) = k_1[RCl] + k_4[B]$$

$$[A] = \frac{k_1[RCl] + k_4[B]}{k_2 + k_3 + k_6}$$

$$\frac{d[B]}{dt} = 0 = k_3[A] - k_4[B] - k_5[B][N_3^-] - k_7[B]$$

Substitute for [A] and rearrange:

$$\frac{k_3k_1[RCl]}{k_2 + k_3 + k_6} = [B]\left(k_4 + k_5[N_3^-] + k_7 - \frac{k_3k_4}{k_2 + k_3 + k_6}\right)$$

Rearranging and cancelling terms:

$$k_3k_1[RCl] = [B]\ (k_4 + k_5[N_3^-] + k_7)(k_3 + k_2 + k_6) - k_3k_4$$

$$[B] = \frac{k_1k_3}{(k_4 + k_5[N_3^-] + k_7)(k_2 + k_3 + k_6) - k_3k_4}[RCl] = Z[RCl]$$

$$[A] = \frac{k_1[RCl] + k_4Z[RCl]}{k_2 + k_3 + k_6} = Y[RCl]$$

$$Y = \frac{k_1 + k_4Z}{k_2 + k_3 + k_6}$$

Then solving in the rate expressions:

$$\frac{d[ROS]}{dt} = k_6Y[RCl] + k_7Z[RCl] \qquad (1)$$

$$\frac{d[RN_3]}{dt} = k_5Z[N_3^-][RCl] \qquad (2)$$

Dividing (1) by (2) and simplifying:

$$\frac{d[ROS]}{d[RN_3]} = \frac{k_6Y + k_7Z}{k_5[N_3^-]\ Z}$$

So,

$$\int_0^{[ROS]_t} d[ROS] = \frac{k_6Y + k_7Z}{k_5[N_3^-]\ Z} \int_0^{[RN_3]_t} d[RN_3]$$

Then,

$$\frac{[ROS]_t}{[RN_3]_t} = \frac{k_6Y + k_7Z}{k_5[N_3^-]\ Z}$$

Define: $$F_{RN_3} = \frac{[RN_3]}{[ROS] + [RN_3]}$$, and $$\frac{1}{F_{RN_3}} = 1 + \frac{[ROS]}{[RN_3]}$$

Then:

$$\frac{1}{F_{RN_3}} = 1 + \frac{k_6 Y + k_7 Z}{k_5[N_3^-]\ Z} \quad ;$$

or

$$\frac{1}{F_{RN_3}} = 1 + \frac{k_6(k_1 + k_4 Z)}{k_5[N_3^-](k_2 + k_3 + k_6)Z} + \frac{k_7}{k_5[N_3^-]}$$

$$\frac{1}{F_{RN_3}} = 1 + \frac{k_7}{k_5[N_3^-]} + \frac{k_1 k_6}{k_5[N_3^-](k_2+k_3+k_6)Z} +$$

$$\frac{k_4 k_6}{k_2+k_3+k_6}\ \frac{1}{k_5[N_3^-]}$$

Substituting for Z:

$$\frac{k_1 k_6}{k_5[N_3^-](k_2+k_3+k_6)Z} = \frac{k_1 k_6\{(k_4+k_5[N_3^-]+k_7)(k_2+k_3+k_6) - k_3 k_4\}}{k_5[N_3^-](k_2 + k_3 + k_6)k_1 k_3}$$

$$= \frac{k_6(k_4+k_7+k_5[N_3^-])}{k_3 k_5[N_3^-]} - \frac{k_4 k_6}{k_5(k_2+k_3+k_6)}\ \frac{1}{[N_3^-]}$$

$$= \frac{k_6(k_4+k_7)}{k_3 k_5[N_3^-]} + \frac{k_6}{k_3} - \frac{k_4 k_6}{k_5(k_2+k_3+k_6)}\ \frac{1}{[N_3^-]}$$

Then:

$$\frac{1}{F_{RN_3}} = \frac{k_6}{k_3} + 1 + \left\{\frac{k_6(k_4+k_7)}{k_3 k_5} + \frac{k_4 k_6}{k_5(k_2+k_3+k_6)}\right.$$

$$\left. + \frac{k_7}{k_5} - \frac{k_4 k_6}{k_5(k_2+k_3+k_6)}\right\}\frac{1}{[N_3^-]}$$

$$\frac{1}{F_{RN_3}} = \frac{k_6}{k_3} + 1 + \frac{k_7k_3 + k_6k_4 + k_6k_7}{k_3k_5} \frac{1}{[N_3^-]}$$

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