

THE EFFECT OF HALOGEN ATOMS ON THE S₂ REACTIVITY
N
OF OTHER HALOGEN ATOMS IN THE SAME MOLECULE

A THESIS

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the Faculty of the Graduate Division

by

Walter Howe Brader Jr.

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

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June 1954

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THE EFFECT OF HALOGEN ATOMS ON THE S_N2 REACTIVITY
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Date approved by Chairman June 8, 1954

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SUMMARY

One of the most thoroughly studied reactions in organic chemistry is the nucleophilic displacement reaction on carbon, of the type:



Many investigations have been carried out on the influence of the R group on the reactivity of R-X. For example, it is well known that the substitution of alpha-methyl groups tend to inhibit S_N2 reactivity and to enhance S_N1 reactivity. The substitution of an alpha-halogen has also been found to inhibit S_N2 reactivity; however it was somewhat surprising to find that beta-halogen compounds were reported to accelerate the S_N2 Reactivity. On the other hand, gamma-, delta-, and epsilon-halo compounds were reported to be of about the same reactivity as the unsubstituted compounds. As a result, it was of interest to study quantitatively the influence of beta-, gamma-, delta-, and epsilon-halogens on the S_N2 reactivity of other halogens.

A study of the reactions of the ethylene halides with many of the nucleophilic reagents previously used indicated that elimination reactions were occurring to a large extent. Thus, the conclusions that beta-halogens increased the S_N2 reactivity were found to be based on data for elimination reactions rather than for substitution reactions. In order to obtain accurate data for the influence of halogens on S_N2 reactivity, nucleophilic reagents were sought which would produce

displacements on carbon rather than on hydrogen or halogen. It was found, however, that no substitution reactions could be measured in the ethylene iodide series; the various ethylene halobromides on the other hand, were found to react with sodium thiophenolate in methanol at a convenient rate to form substitution products.

The reaction rates were measured by pipetting measured volumes of solutions of the halogen compounds and sodium thiophenolate together in a reaction flask. At a measured interval of time 2.0 ml. of acetic acid was added, and the unreacted thiophenol analyzed by titration against standard iodine using the iodine color as an end point. Since many of the halogen compounds were light sensitive, the reaction vessels were shielded from the light in order to prevent interference.

The results are tabulated as follows:

Table 1. Alkyl Halide Plus Thiophenolate Ion

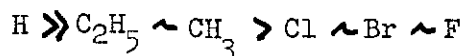
Alkyl	$k \times 10^4$			ΔH_a kcal.	ΔS_a e.u.
	0°C	20°C	34.6°C		
$\text{CH}_3\text{CH}_2\text{Br}$	3.79 ± 0.06	39.1 ± 0.60	182 ± 3	18.1	-10
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	2.56 ± 0.03	25.6 ± 0.30	112 ± 2	17.7	-12.3
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	2.77 ± 0.03	26.9 ± 0.3	121 ± 1	17.7	-12.3
$\text{C}_4\text{H}_9\text{CH}_2\text{CH}_2\text{Br}$	3.14 ± 0.02	77.8 ^b ± 0.4	----	17.1	-13.7
$\text{FCH}_2\text{CH}_2\text{Br}$	0.403 ± 0.006	4.95 ± 0.04	25.5 ± 0.2	19.4	-9.6
$\text{ClCH}_2\text{CH}_2\text{Br}$	0.486 ± 0.006	5.61 ± 0.03	28.5 ± 0.5	19.1	-10.6
$\text{BrCH}_2\text{CH}_2\text{Br}$	0.446 ^a ± 0.01	4.99 ^a ± 0.15	24.3 ^a ± 1	18.7	-12
$\text{FCH}_2\text{CH}_2\text{CH}_2\text{Br}$	1.86 ± 0.02	52.6 ^b ± 0.4	----	17.9	-12
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Br}$	2.54 ± 0.04	70.6 ^b ± 0.40	----	17.8	-11.8
$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{I}$	21.8 ± 0.4	191 ± 4	----	16.7	-11.3
$\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$	20.1 ^a ± 0.3	181 ^a ± 2	----	16.9	-10.7
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{I}$	15.7 ± 0.1	138 ± 1	----	16.8	-11.8

$\text{FCH}_2\text{CH}_2\text{CH}_2\text{I}$	11.2 ± 0.2	104 ± 1	----	17.2 - 11.0
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$	23.8 ± 0.1	204 ± 4	----	17.2 - 11.8
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$	22.9 ± 1.6	195 ± 1	----	16.5 - 12
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	14.7 ± 0.3	128 ± 1	----	16.6 - 12.4

^aThese rate constants contain a statistical factor of one-half

^bThese rate constants were determined at 29.8°C.

From the data tabulated above it can immediately be seen that a halogen in the beta position decreases the reactivity as compared to the reactivity of the ethyl halide. For the beta substituent the rates vary thus:



It is also readily observable that a substituent further removed from the reaction site has little influence on the S_N2 reactivity.

An effort was made to find to what extent the order of reactivities observed earlier by Thomas in the reaction between sodium methoxide and various of the methylene halide compounds was due to steric or electronic effects. Since the previous studies were carried out using ionic nucleophilic reagents, it was thought desirable to study the kinetics of the reactions between the same halogen compounds and a nucleophilic reagent of neutral charge type. The reagent chosen which possessed the desired properties was triethylamine in nitrobenzene.

The reaction kinetics were carried out by pipetting measured volumes of triethylamine and the halogen compound into a conductivity cell, and the cell resistance measured from time to time. Utilizing the resistance of the solution found, the concentration of the products formed can be easily determined by use of a plot correlating resistance of the solution and product concentration.

The results are tabulated as follows:

Table 2. Alkyl Iodide Plus Triethylamine

Alkyl Iodide	$k \times 10^6$	$l. \text{ mole}^{-1} \text{ sec.}^{-1}$
	24.8°C	
CH ₃	34,200	± 600
ClCH ₂	39.3	± 0.5
ICH ₂	6.78	± 0.08

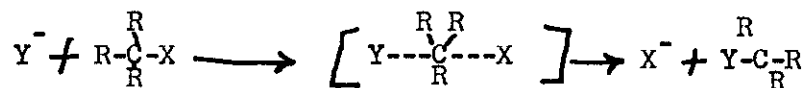
The decrease in S_N2 reactivity caused by the substitution of a halogen for an alpha-hydrogen of an alkyl halide results from the increased difficulty of bond cleavage. Within the group of alpha-halo substituents, however, the variation of reactivity appears to be due largely to the size of the substituent.

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CHAPTER 1

INTRODUCTION

Perhaps one of the most thoroughly studied reactions in organic chemistry is the one-step bimolecular displacement reaction on carbon which is more commonly known as the S_N2 reaction.¹ Many investigations have led chemists to believe that the reaction occurs according to the scheme shown below in which an attack is made by the nucleophilic reagent, Y^- ,



on the carbon atom in a line co-linear with the group being displaced i. e. X. In this discussion it will be assumed that the formation of the transition state, the structure shown in brackets, involves a partial formation of the Y-C bond and simultaneously a partial rupture of the C-X bond, both of which are in a line perpendicular to the plane of the carbon and its substituents. This transition state then gives a product of inverted configuration.

Considerable evidence is available concerning the effect of an alpha-alkyl group relative to alpha hydrogen on the S_N2 reactivity; however the data are insufficient for allowing one to theorize with regard to the influence of substituents on S_N2 reactivity. Since the alkyl groups are electron donors, it was thought necessary to have

¹For a discussion of the S_N2 reaction see C. K. Ingold, Structure and Mechanisms in Organic Chemistry, Cornell University Press, Ithaca, New York, 1953, Chapter VII.

information concerning the influence of electron withdrawing groups before a logical conclusion could be reached. In this laboratory a recent study has been made concerning the influence of substituting a halogen atom for one of the alpha-hydrogen atoms of a methyl halide (1). It was found that the alpha-halogen diminished the reactivity by a large factor.

At this point, it was thought desirable to learn whether a decrease also occurred in cases where a halogen was substituted in the beta, gamma, or delta position for a corresponding hydrogen atom. Surprisingly enough, however, several reports have been made to the effect that such substitutions served to increase the reactivity (2-5). The data, however, from which most of these statements were derived concerned reactions which involved rather strong bases as the nucleophilic reagent. For example, Tronov and Gershevich studied the kinetics of the reaction between various

-
- (1) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.
 - (2) E. R. Alexander, Principles of Ionic Organic Reactions, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 89.
 - (3) M. J. S. Dewar, The Electronic Theory of Organic Chemistry, Oxford University Press, London, 1949, p. 71.
 - (4) A. E. Remick, Electronic Interpretations of Organic Chemistry, 2nd, Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 394.
 - (5) B. V. Tronov and A. I. Gershevich, J. Russ. Phys. Chem. Soc., 59, 727 (1927); C. A., 22, 3389 (1928).

bromine derivatives of propane and sodium methoxide (5). Taylor also found that the reaction rate between ethylene bromide and ethanolic alkali was greater by a factor of two or three than that of ethyl bromide (6). Similar results were observed by other investigators using various 1,2-dihalo compounds and strongly basic nucleophilic reagents (7-9). In the reactions of such polyhalogen compounds with strong bases one might suspect that considerable dehydrohalogenation was occurring. For example, it was found by Lespieau and Bourguel that 1,2,3-tribromopropane gives an 80 per cent yield of 2,3-dibromopropene upon reaction with sodium hydroxide (10).

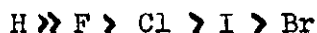
Although sodium thiosulfate is not a strong base, Slator found that ethylene iodide was more reactive by a factor of approximately 20 toward sodium thiosulfate than ethyl iodide (11). Previous theorists, however, have not regarded the fact that Slator also found ethyl bromide to be considerably more reactive toward the same reagent

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- (5) B. V. Tronov and A. I. Gershevich, J. Russ. Phys. Chem. Soc., 59, 727 (1927); C. A., 22, 3389 (1928).
- (6) W. Taylor, J. Chem. Soc., 1514 (1935).
- (7) B. V. Tronov and L. V. Laduigina, J. Russ. Phys. Chem. Soc., 62, 2165 (1930); C. A., 25, 3957 (1931).
- (8) P. Petrenko-Kritchenko and V. Opotsky, Ber., 59II, 2131 (1926).
- (9) A. L. Bernoulli and W. Kampli, Helv. Chem. Acta, 16, 1187 (1933).
- (10) R. Lespieau and M. Bourguel, Organic Synthesis, Collective Volume I 2nd., Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 209.
- (11) A. Slator, J. Chem. Soc., 85, 1286 (1904).

than ethylene bromide. Thus, it is believed that no reliable conclusions can be drawn from the data cited above since one is dubious concerning the extent of occurrence of elimination in these reactions.

It was, thus, decided to measure substitution reactions on some beta-, gamma-, and delta-haloalkyl halides. Specifically it was desired to compare the relative influence of the various substituents on the reactivity of both alkyl iodides and bromides. Thus, the various ethylene, trimethylene, and tetramethylene bromides and iodides were chosen as the compounds to be studied.

The alpha-substituent has been found to increase the S_N2 reactivity in the order (1):



It is, thus, observed that the order is roughly one of decreasing size and increasing electronegativity of the substituents.

In an effort to distinguish between the size and electronegativity factors it was thought desirable to study the reactivity of the methylene halide series toward a nucleophilic reagent of neutral charge type. A reaction previously studied by several

(1) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.

workers using a tertiary amine as the nucleophilic reagent appeared to satisfy the conditions desired (12-15). The reaction is the well known Menshutkin reaction which involves the reaction of a tertiary amine with an alkyl halide to form a quaternary ammonium salt.

-
- (12) H. C. Brown and N. R. Eldred, J. Am. Chem. Soc., 71, 455 (1949).
- (13) H. C. Brown and W. H. Bonner, ibid., 75, 14 (1953).
- (14) C. N. Hinshelwood et al, J. Chem. Soc., 860 (1938).
- (15) W. C. Davies et al, ibid., 412 (1939).

CHAPTER II

PROCEDURE

Experimental

Kinetic Runs on the Reaction of C_6H_5SNa and R-X.--Standard

thiophenolate ion solutions were prepared by weighing thiophenol accurately into a volumetric flask and adding a two per cent excess of standard sodium methoxide. Absolute methanol was then added to dilute the solution to the desired concentration. Solutions of the halogen compounds were prepared in a similar manner by accurately weighing them in a volumetric flask and diluting to volume with absolute methanol.

The reactions studied at temperatures other than $0^{\circ}C$ were carried out in a fashion described in this and the following paragraph. One hundred milliliter volumetric flasks, whose necks and stoppers had been painted black, were used as the reaction vessels. The reactions were carried out in a constant temperature bath to which several bottles of Script black ink had been added. In an effort to prevent light catalysis the painted flasks were immersed with about one-half of the painted necks submerged.

The reactions were started by pipetting measured volumes of the solutions of the halogen compounds and sodium thiophenolate together in a reaction flask. The initial time was observed when the pipet containing the later reactant was one-half delivered; a stopwatch was utilized for observing the time to the nearest one-fourth minute. At a measured interval of time 2.0 ml. of glacial acetic acid

was added to one of the reaction flasks in order to stop the reaction by converting the sodium thiophenolate to unreactive thiophenol. The thiophenol concentration was then determined by titration against standard iodine using a faint iodine color as the end point (16).

The procedure followed for the reactions at 0° C was modified somewhat as a matter of convenience. These reactions were carried out by weighing into 100 ml. volumetric flask containing 50 ml. of methanol the desired amount of halogen compound. The reaction vessels were then placed in a one-gallon Dewar flask containing an ice water slurry and allowed to equilibrate, after which 50 ml. of a sodium thiophenolate solution, prepared as described above, was pipetted into the flask containing the halogen compound, and the solution diluted to volume with cold methanol. The reaction vessels were then shaken and allowed to stand for about 10 minutes in order to equilibrate. Two 10 ml. samples were withdrawn from each vessel and allowed to flow into flasks containing methanol and two ml. of acetic acid. The solution was analyzed for thiophenol by the method described above. Since mercaptans in basic solutions are oxidized easily (17).

(16) P. Klason and T. Carlson, Ber., 39, 738 (1906).

(17) J. Xan et al., J. Am. Chem. Soc., 63, 1139 (1941).

a stream of nitrogen was directed at the top of the reaction flask while samples were being withdrawn in order to maintain an inert atmosphere above the solution. It was also found that best results were obtained by keeping the Dewar flask in a refrigerator when samples were not being withdrawn and by cooling the pipets in a refrigerator before use.

Kinetic Runs on the Reaction of R_3N and R-X.--Standard solutions

of triethylamine were prepared by weighing triethylamine into a volumetric flask and diluting the contents to volume with nitrobenzene. Solutions of known concentration of the halogen compounds were prepared in a similar manner. Flasks containing each reactant were then placed in a constant temperature bath and allowed to equilibrate for at least one hour. Following equilibration, measured volumes of each reactant were pipetted into a conductivity cell, and the cell shaken. The initial time was recorded when the pipet containing the second reactant was one-half delivered. Care was taken at all times to maintain the volume of the reaction mixture at 30 ml. in order to have the solution surface well above the cell electrodes.

At intervals the conductivity cell was placed in the bridge circuit, and the bridge adjusted until a null point was obtained. From the resistance observed the concentration of product formed was found by the use of a curve correlating the concentration of quaternary ammonium salt and corresponding resistances.

Reaction of Ethylene Iodide with Sodium Thiosulfate.--In an effort to analyze the gas evolved during the course of the reaction between

sodium thiosulfate and ethylene iodide in 50 per cent aqueous ethanol, a solution was prepared in a one liter three-neck flask containing 5.2 grams (0.0184 mole) of ethylene iodide and 20 grams (0.08 mole) of sodium thiosulfate in 500 ml. of solvent. The gas evolved was allowed to pass through a condenser with an attached "cold nose", and into a two liter bottle containing water saturated with potassium carbonate. When the reaction was complete, the mixture was refluxed until the dissolved gases ceased to be given off. The mixture was then cooled, and refluxed again in order to correct for the expansion of the solvent and its atmosphere. The gas volume was then measured to be 300 ml. at 738 mm. and 29°C; the volume of gas collected corresponded to a 64 per cent yield.

Using a bromine solution which contained some mercuric ions in an Orsat arrangement, a derivative was made of the gas which was assumed to be unsaturated. After the gas was absorbed, the absorbing solution was treated with an aqueous solution of sodium thiosulfate in order to discharge the bromine, and the resulting solution extracted several times with methylene chloride in order to remove all organic products. Distilling the extracted solution under vacuum to remove the solvent gave a small volume of an organic liquid. A yield of one to two ml. of a liquid boiling over a range of 130-134°C was obtained upon distilling the above liquid.

A derivative was prepared by mixing the distilled product, thought to be ethylene bromide, with sodium thiophenolate in methanol.

The reaction mixture was allowed to react for about two days in a constant temperature bath at 35°C after which the sample was removed and placed in water in order to precipitate the derivative. The white solid was filtered and then recrystallized from ethanol. A melting point of 68-69°C was obtained which corresponded to that of 1,2-bis-(phenylmercapto)-ethane (18). One might then conclude that the liquid obtained was ethylene bromide and the gas evolved ethylene.

Reaction of Ethylene Bromide with Sodium Thiophenolate.--Four hundred ninety milliliters of a solution containing 21.383 grams of ethylene bromide (0.114 mole), 39.354 grams (0.357 mole) of thiophenol, and 100 ml. of 3.64 N (0.364 mole) of sodium methoxide were placed in a constant temperature bath at 35°C. As a precaution against light catalysis the flask which was used as the reaction vessel had previously been painted. After three days the solution was removed from the bath, dilute sodium hydroxide added, and then filtered. While being filtered, the product, part of which had separated during the course of the reaction, was maintained under an atmosphere of nitrogen in order to prevent oxidation of the excess thiophenol (17). The residue was washed several times with dilute sodium hydroxide solution and then with water. After several recrystallizations from ethanol a residue was obtained which melted at 68.5°C; the product expected, 1,2-bis-(phenylmercapto)-ethane, was reported to melt at 69°C (18).

(18) E. V. Bell and G. M. Bennett, J. Chem. Soc., 3189 (1928).

(19) J. Xan et al, J. Am. Chem. Soc., 63, 1139 (1941).

The crystals were placed on a watch glass in a desiccator over calcium chloride and allowed to remain for one week. The dry material was found to weigh 26.9 grams corresponding to a yield of 96 per cent. A derivative was prepared by dissolving some of the above material in glacial acetic acid, adding 30 per cent hydrogen peroxide, and allowing the solution to digest for several hours. The resulting solution was poured into a large volume of water to precipitate the product and then filtered. A residue was obtained which after recrystallization from ethanol gave a melting point of 180-181^o C. This melting point corresponds to that of 1,2-bis-(phenylsulfonyl)-ethane (19), the product expected from a two-step substitution reaction on ethylene bromide.

Reaction of Ethylene Bromide and Sodium Hydroxide.--In an effort to determine the extent of substitution in the reaction between sodium hydroxide and ethylene bromide, 15.00 ml. of 0.0275 M ethylene bromide containing diphenylamine in dioxane were pipetted into 100 ml. volumetric flasks which contained 15.00 ml. of 0.0573 N sodium hydroxide in water. At intervals samples were removed and titrated with standard hydrochloric acid. The results in Table 49 indicate that substitution occurred to an extent of about two per cent.

Reaction of Diiodomethane with Triethylamine.--Ten ml. of diiodomethane (0.125 mole) and 25 ml. of triethylamine (0.25 mole) were each added to two 100 ml. volumetric flasks. To one flask were added 25 ml. of nitrobenzene and to the other 25 ml. of methyl ethyl ketone.

(19) H. Gilman and N. J. Beaber, J. Am. Chem. Soc., 47, 1451 (1925).

The crude product obtained from the nitrobenzene solution weighed 47 grams as opposed to 45.5 grams expected from a reaction between one mole of triethylamine and one mole of diiodomethane. The product was recrystallized several times from a mixture of methanol and ethyl acetate using ether to precipitate and dry the salt; the melting point observed, with decomposition, was 182°C. The product obtained from the methyl ethyl ketone solution was also found to melt, with decomposition, at 182°C after several recrystallizations. Weighed samples of the product were analyzed for ionic iodide by titration against standard silver nitrate using dichlorofluorescein as the indicator in the absence of sunlight. The per cent ionic iodide was found to be 33.6, 34.8, 34.2 and 34.6 as compared to the theoretical value of 34.4 for a one step reaction (a value of 54.0 per cent is calculated for the ionic iodide in a two step reaction). The low value, 33.6, occurred with a sample which required only 1.87 ml. of 0.1034 N silver nitrate.

Investigation of the Reversal of the Menschutkin Reaction.--In order to explain decreases observed in some of the rate data for the formation of quaternary ammonium salts, the reaction between triethylamine and certain halogen compounds were investigated for a possible reversal. Investigations were carried out by dissolving a sample, taken from a reaction mixture which had proceeded until the resistance of the solution no longer changed, in an aqueous acetone solution. Analysis of the triethylamine was then carried out by titration against standard hydrochloric acid using equal volumes of bromcresol green in

acetone and methyl red in water as the indicator. Upon titrating 5.00 ml. samples obtained from the reaction of triethylamine with methyl iodide, 0.437 milliequivalent of triethylamine was found as compared to 0.439 expected if no reversal occurred. A similar analysis on the solution obtained from the reaction of bromodimethane showed 0.0213 milliequivalent of triethylamine present as compared with 0.0216 expected. Further evidence against reversibility was obtained by preparing a solution of triethyliodomethylammonium iodide in nitrobenzene and allowing it to stand for ten days at 60.8°C. Samples were removed and titrated with standard hydrochloric acid; however no base was observed to be present.

Calibration of the Conductivity Cells.--The greatest problem encountered in using a conductometric method was that of determining the relationship between measured resistance and product concentration. The most convenient method consisted of allowing a solution to react until the resistance no longer changed. Measured volumes of solvent were then added to the reaction cell and the corresponding resistances observed. Such a procedure had merits in that the concentration of quaternary ammonium salt was known at the end of the reaction from the quantities of reactants added. The data obtained were then plotted, and the unknown concentrations read directly from the plot.

Since some decomposition of product was observed while awaiting completion of the reaction, a somewhat more laborious but more accurate method was devised. In this case the pure products expected from the reactions were synthesized, and several solutions of known

"salt" concentration prepared. Then the necessary conductivity measurements were made and the previous method continued.

Determination of the pK_a of Thiophenol in Absolute Methanol.--

Using the method of Kolthoff, a spectrophotometric determination of the pK_a of thiophenol in absolute methanol was carried out. The pK_i for bromcresol purple was reported to be 11.3 in methanol by Kolthoff (20). Thus, using equal volumes of 0.0242 N sodium thiophenolate and 0.0151 M thiophenol, a value of 11.2 was obtained for the pK_a of thiophenol. In a similar manner equal volumes of 0.0121 N sodium thiophenolate and 0.0492 M thiophenol gave a value of 11.1.

(20) I. M. Kolthoff and L. S. Guss, J. Am. Chem. Soc., 60, 2516 (1938)

Preparation and Purification of Reagents

Methanol.--To about four liters of commercial methanol in a five liter round-bottom flask was added 10 grams of magnesium metal turnings (21), and the mixture allowed to react, under reflux, until all of the magnesium had disappeared. The dry methanol was then distilled and stored under nitrogen.

Ethylene Chlorobromide.--Ethylene chlorobromide obtained as a sample from Dow Chemical Co. was twice fractionated, and the fraction boiling at 106°C was collected and stored under nitrogen. The refractive index at 20°C was observed to be 1.4899 .¹

Sodium Thiosulfate.--Eimer and Amend C. P. Grade sodium thiosulfate was dissolved in freshly boiled water and diluted to the desired concentration with the boiled water. A fresh solution was prepared for each reaction in order to avoid difficulties due to decomposition of the sodium thiosulfate.

Thiophenol.--Matheson Company thiophenol was used without further purification. However, titration of weighed samples of the thiophenol against standard iodine indicated that the thiophenol was 99.6 per cent pure.

Sodium Methoxide.--Freshly cut sodium was added to a polythene bottle containing methanol in which a stream of nitrogen was played over the surface of the methanol while the reaction was in progress.

(21) L. F. Fieser, Experiments in Organic Chemistry, Part II, 2nd ed., D. C. Heath and Co., New York., N. Y., 1941, p. 359.

¹All of the refractive indices reported herein were measured with an Abbe refractometer (manufactured by the Bausch and Lomb Co.) utilizing the D line of sodium.

Absolute methanol was then added to bring the solution to approximately the desired concentration; the solution was stored in a polythene container under nitrogen.

Trimethylene Chlorobromide.--Dow Chemical Company trimethylene chlorobromide was fractionated through a Todd Column having an inside diameter of 1.2 cm, a length of three feet, and packed with one-eighth inch single turn glass helices. The fractionation was carried out under nitrogen, and the fraction boiling at 144°C (740 mm.) was collected and stored in brown bottles in the refrigerator. The refractive index at 24.5°C was found to be 1.4841, the density at the same temperature was observed to be 1.5599. The molar refraction was then found by experiment to be 28.9 as compared with 28.7 calculated.¹

Trimethylene Bromide.--Eastman Kodak White Label trimethylene bromide was fractionated under nitrogen and the fraction boiling 167-168°C collected. The index of refraction at 25°C was observed to be 1.5209.

Trimethylene Chloriodide.--Trimethylene chloriodide was prepared by refluxing trimethylene chlorobromide and sodium iodide in acetone for about five hours. The sodium bromide which had precipitated was filtered, the acetone distilled, and the organic material remaining washed with aqueous sodium thiosulfate. The material was dried over CaSO₄ and fractionated. The fraction boiling at 71°C (35 mm.) was

¹Molar refractions reported herein were calculated from atomic refractions listed in Handbook of Chemistry, 6th. Ed., Handbook Publishers Inc., Sandusky, Ohio, 1946, p. 1025.

collected and stored in the usual manner. The refractive index was found to be 1.5475 at 20.5°C; the density at the same temperature was 1.9393. The molar refraction observed was 33.5 as compared with the calculated value of 33.7.

Trimethylene Iodide.--Trimethylene iodide was prepared by the method of M. T. Bogert and E. M. Slocum (22). The material was fractionated under vacuum and the material boiling 110°C (19 mm) was collected. The refractive index measured at 25°C was 1.6402; the density at the same temperature was found to be 2.5531. The molar refraction calculated was 41.7 as compared with 41.8 observed.

Trimethylene Bromiodide.--Trimethylene bromiodide was prepared from the reaction of sodium iodide and trimethylene bromide in acetone in the same manner described for the preparation of trimethylene chloriodide. The fraction collected boiled at 88°C (17.5 mm.). The refractive index at 25°C was found to be 1.5810, and the density at the same temperature was 2.2804. The molar refraction was observed to be 36.4 as compared with 36.6 calculated.

Propyl Iodide.--Eastman Kodak White Label propyl iodide was fractionated and the fraction boiling 102°C (740 mm.) collected. The refractive index at 20°C was observed to be 1.5051 as compared with the value 1.5051 reported in the Chemical Rubber Handbook (23).

(22) M. T. Bogert and E. M. Slocum, J. Am. Chem. Soc., 46, 763 (1924).

(23) Handbook of Chemistry and Physics, 32nd. Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p. 1088.

Trimethylene Fluorobromide.--Trimethylene fluorobromide was prepared according to the method of F. W. Hoffmann (24). The material was fractionated, and the material boiling between 101.5° and 102°C , (740 mm.) was collected. The refractive index, 1.4295 at 23°C was found to agree with that reported by Hoffmann.

Trimethylene Fluoriodide.--Trimethylene fluoriodide was prepared by the reaction of sodium iodide and trimethylene fluorobromide in acetone according to the method described for the preparation of trimethylene chloriodide. The material was fractionated and the fraction boiling at 46°C (39 mm.) was collected. The refractive index was observed to be 1.4991 at 20°C , and the density 1.9655 at the same temperature. The molar refraction was observed to be 28.1 as compared with 28.8 calculated.

Tetramethylene Chloriodide.--Tetramethylene chloriodide obtained from Columbia Organic Chemical Company was fractionated under nitrogen, and the material boiling at 91°C (16 mm) was collected. The refractive index at 25.3°C was 1.7850. The molar refraction was found by experiment to be 38.3 as compared with 38.3 calculated.

Hexyl Bromide.--Hexyl bromide obtained from the Eastman Kodak Company was fractionated, and the fraction boiling at 156°C (740 mm.) was collected. The refractive index, 1.4478 at 20°C corresponded to that reported in the Chemical Rubber Handbook (25)

(24) F. W. Hoffmann, J. Org. Chem., 14, 1056 (1940).

(25) Handbook of Chemistry and Physics, 32nd. Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, p. 928.

Pentamethylene Chloriodide.--Pentamethylene chloriodide obtained from the Columbia Organic Chemical Co. was fractionated and the fraction boiling at 85°C (5 mm.) was collected. The refractive index at 20°C was 1.5304.

Ethylene Bromide.--Eastman Kodak White Label ethylene bromide was twice fractionated through a Todd Column; the fraction boiling at 131°C (738 mm.) was collected and stored under nitrogen. The index of refraction at 21.5°C was found to be 1.5379.

Vinyl Bromide.--Approximately 20 grams (0.106 mole) of ethylene bromide was added to a 500 ml round-bottom flask containing four grams of KOH and 29 ml. of ethanol. The solution was refluxed for one hour using an ice water condenser to condense the vapors; the vinyl bromide was then distilled into a receiver which was cooled by an ice-brine solution. The product was then fractionated through a Todd Column, and the fraction boiling at about 6°C collected and a small amount of diphenylamine added to inhibit polymerization.

Ethylene Iodide.--Into a flask containing a slurry of iodine in ethanol was slowly passed ethylene at a rate such that most of the ethylene was absorbed. After the ethylene was no longer absorbed, the contents of the flask was diluted with water, the iodine color discharged with bisulfite, and the white crystals filtered. The product was immediately recrystallized from hot ether since its decomposition was catalyzed by iodine. The ethylene iodide obtained melted at 82°C, and was stored under nitrogen in a brown container.

Ethylene Fluorobromide.--Ethylene fluorobromide was prepared by the method of Hoffmann (24) in which ethylene bromide was reacted with potassium fluoride in ethylene glycol. Since the product formed was the lowest boiling component, it was collected as it was formed. The product obtained was fractionated through the Todd Column, and the Fraction boiling $70.5-71^{\circ}\text{C}$ (738 mm.) was collected and stored under nitrogen. The index of refraction at 25°C was found to be 1.4226.

n-Propyl Bromide.--n-Propyl bromide was prepared according to the procedure in Organic Synthesis (26). Two fractionations gave a product which boiled $70.5-70.9^{\circ}\text{C}$ (738mm.). The index of refraction at 15°C was found to be 1.4370.

Ethanol.--U. S. P. absolute ethanol was used without further treatment.

Ethyl Bromide.--Merck reagent grade ethyl bromide was twice fractionated, and the fraction boiling at 38.4°C was collected and stored under nitrogen. The index of refraction at 20°C was found to be 1.4239.

Nitrobenzene.--Eastman Kodak White Label nitrobenzene was fractionated over phosphorous pentoxide through a Todd Column. The fraction boiling at 89.5°C (12 mm.) was collected. The refractive index at 29.5°C was found to be 1.5478.

Methyl Iodide.--Eastman Kodak White Label methyl iodide was fractionated thorough a Todd Column Column under an atmosphere of nitrogen. The fraction boiling 42.5°C (738 mm.) was collected and stored in a brown bottle. The refractive index at 20°C was observed to be 1.5305.

(24) F. W. Hoffmann, J. Org. Chem., 14, 1056 (1949).

(26) R. F. Goshorn, T. Boyd, and E. F. Degering, Organic Synthesis, Collective Volume I, John Wiley and Sons, Inc., 2nd. Ed., New York, N. Y., 1941, p. 37.

Methylene Chloriodide.--Methylene chloriodide was prepared by the reaction of sodium iodide in acetone with methylene chlorobromide in a manner similar to that described for the preparation of trimethylene chloriodide. Fractionation thorough a Todd Column gave a fraction boiling at 108°C (740 mm.). The material was collected and stored under nitrogen; a refractive index of 1.5828 was observed at 20°C.

Methylene Bromiodide.--Methylene bromiodide was prepared by the action of sodium iodide in acetone on methylene bromide as described for the preparation of trimethylene chloriodide. Fractionation through a Todd Column gave a fraction boiling at 44.5°C (23 mm.). A refraction index of 1.6384 was observed at 20°C.

Triethylamine.--Eastman Kodak White Label triethylamine was fractionated through a Todd Column over sodium. A fraction was obtained which boiled at 89.5°C (739 mm.). The refractive index was observed to be 1.4003 at 20°C.

Apparatus

The instrument arrangement used for the measurement of electrolytic conductivities was a modification of that described in the Leeds and Northrup catalogue EN-95 (42). The principle difference in the instrument arrangement was the use of a cathode-ray oscilloscope as the null point indicator, as described by Jones (43), rather than the usual audio method. A diagram of the modified circuit is shown in Figure 1, which is located in Appendix C.

(42) Apparatus for Electrolytic Conductivity Measurements, Leeds and Northrup Company, Catalogue number EN-95, 1953, p. 16.

(43) G. Jones, K. J. Mysels, and W. Juda, J. Am. Chem. Soc., 62, 2919 (1940).

Experimental determinations of the electrolytic conductivities were carried out by (1) placing the conductivity cell, X, in the bridge circuit, (2) making an approximate setting of the decade resistance box, R, and (3) varying the ratio arms of the slidewire for a null point in the bridge circuit. Measurements were normally carried out with the oscillator adjusted for a frequency of 2200 cycles per second. In general it was found that the conductivity was independent of the frequency; however the current phase in the circuit was found to vary with the frequency. The phasing difficulties were taken care of by means of a condenser in parallel with the decade resistance box. The oscilloscope was arranged and used in the manner described by Jones (43).

Specifications of the apparatus are listed as follows:

Decade resistance box, General Radio Co., Model 1432-L.

Audio frequency Oscillator, Hewlett-Packard, Model 200-CD.

Cathode-Ray Oscillograph, Du Mont Co., Model 304-A.

Variable Capacitor, Leeds and Northrup, Model 1185.

Conductivity Cell, Sargaent Co., No. S-29865.

Isolation Transformers, War Surplus.

Student Potentiometer, Leeds and Northrup, Model 7651.

CHAPTER III

Discussion

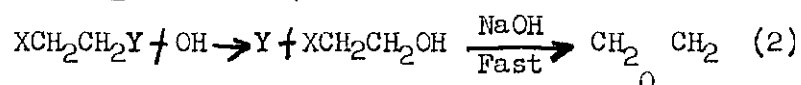
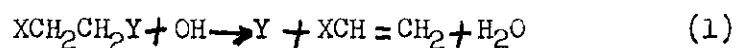
Previous studies have been made in this laboratory on the influence of alpha-halogens upon the S_N2 reactivity of other halogens (1). However, the study of the influence of beta-, gamma-, and delta-halogens on the S_N2 reactivity of other halogens in the same molecule is complicated in one respect in that elimination reactions may occur as well as substitution reactions.¹ The literature indicated that the existing experimental data was inconclusive with regard to the type of reaction occurring (5,6,7,8, and 11).

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- (1) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.

¹For a discussion of the mechanism of substitution reactions see C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

- (11) A. Slator, J. Chem. Soc., 85, 1290 (1904).
- (6) W. Taylor, ibid., 1514 (1935).
- (8) P. Petrenko-Kritchenko and V. Opotsky, Ber., 59 II, 2131 (1926).
- (5) B. V. Tronov and A. I. Gershevich, J. Russ. Phys. Chem. Soc., 59, 727 (1927); C. A., 22, 3389 (1928).
- (7) B. V. Tronov and L. V. Iadugina, ibid., 62, 2165 (1930); C. A., 25, 3957 (1931).

An investigation of the various possible nucleophilic reagents was undertaken in an effort to find one which gave only the desired substitution reactions. Since the ethylene halides were expected to give the greatest difficulty in this respect, they were the first group of compounds to be studied. The first nucleophilic reagent investigated was sodium hydroxide with which a mixture of dioxane and water was used as the solvent in order to dissolve both the organic and the inorganic compounds involved. One may write ionic reactions which may occur in the case of the ethylene halides as follows:



In the examples above X and Y are both halogens and in some cases both are the same halogen.

If the reaction rate of sodium hydroxide with a vinyl halide, the product of an elimination reaction between sodium hydroxide and an ethylene halide, is negligible, only one mole of base will be required per mole of ethylene halide in an elimination reaction (example 1). On the other hand, if the halohydrin produced from the first step of the substitution reaction (example 2) reacts rapidly with sodium hydroxide as compared with the ethylene halide, two moles of base will be required per mole of ethylene halide. Thus, one can experimentally determine the extent of elimination and substitution by measuring the quantity of base required in the reaction between an ethylene halide and sodium hydroxide provided, of course, the limitations cited above are observed.

An investigation of the literature showed that the rate constant for the reaction of 2-bromoethanol with sodium hydroxide in 25.1 per cent dioxane at 0°C was 4.58 l. mole⁻¹min.⁻¹ (27). In this laboratory the rate constant for the reaction of ethylene bromide with sodium hydroxide in 50 per cent dioxane at 36.5°C was found to be 0.0760 l. mole⁻¹min.⁻¹ (Table 47). A comparison of the values shown above indicates that the halohydrin, the product formed in the first step of a substitution reaction, reacts much faster with sodium hydroxide than does ethylene bromide.

Vinyl bromide was prepared and its reaction rate with sodium hydroxide observed. The data, Table 48, indicate that a subsequent reaction of vinyl bromide, if any, is negligible. The solvolysis of ethylene bromide was also shown not to occur. Since the assumptions for distinguishing between substitution and elimination reactions appeared to be valid, experiments were carried out in which it was found that substitution occurs to an extent of about 1.9 per cent (Table 49). It was concluded, therefore, that sodium hydroxide and other strong bases, e. g., sodium alkoxides, were unsuitable for use in measuring substitution reactions.

The search for a nucleophilic reagent which would give predominantly substitution narrowed to two possibilities: sodium thiosulfate and sodium thiophenolate.

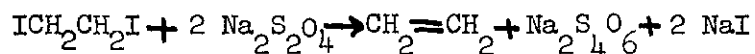
Preliminary experiments using sodium thiophenolate in absolute methanol indicated a convenient reaction rate with ethylene chlorobromide. Ethylene iodide, on the other hand, was completely reacted within one minute at 0°C and very low concentrations.

(27) J. C. Warner and C. L. McCabe, J. Am. Chem., 70, 4031 (1948)

Efforts to slow the rate by the addition of water to the reaction mixture proved to be futile.

Slator had shown in a previous work that the reaction rate of ethylene iodide with sodium thiosulfate was measurable (11). As a result of the convenient reaction rate, it was decided to study more thoroughly the reaction of the ethylene halides with sodium thiosulfate in 50 per cent aqueous ethanol. As reported by Slator, two moles of sodium thiosulfate were to be required per mole of ethylene iodide (11); however a gas was observed to be evolved during the course of the reaction. An investigation showed the gas to be ethylene.

An experiment similar to the one described above using sodium thiosulfate was arranged using instead sodium thiophenolate as the nucleophilic reagent in order to see whether a gas was evolved in its reaction with ethylene iodide. A gas which was assumed to be ethylene was found to be evolved, as in the case of sodium thiosulfate. The reactions appear, therefore to involve an attack by the sulfur anion on iodine rather than on carbon according to the reaction scheme:



At this point it appeared advisable to discontinue efforts to measure a substitution reaction with the ethylene iodides. However, preliminary experiments showed that the ethylene bromohalides did not evolve a gas in their reaction with sodium thiophenolate in methanol. Since these compounds were also found to react at a convenient rate with sodium thiophenolate, the problem was pursued along these lines.

(11) A. Slator, J. Chem. Soc., 85, 1290 (1904).

Sodium thiophenolate was chosen rather than sodium thiosulfate as the nucleophilic reagent because of several advantages of the former reagent. For example, the latter yields Bunte salts which are susceptible to hydrolysis to sulfuric acid and mercaptans which interfere with the analytical method. (28). One may also observe oxygen substituted products (28).

In order to establish that the reaction between the ethylene halobromides and sodium thiophenolate was one involving substitution an experiment was arranged in which the product was isolated and identified. Since ethylene bromide was thought to be the most likely of the series to undergo elimination reactions, it was chosen as the example to be studied. A product separated from the reaction mixture whose physical properties corresponded to 1,2-bis(phenylmercapto)-ethane. This material was oxidized and the product found to be 1,2-bis-(phenylsulfonyl)-ethane. The above compounds were those expected from a two step substitution reaction. Sodium thiophenolate therefore, appeared to yield the desired substitution reactions with the ethylene halobromide series.

A two per cent excess of sodium methoxide was used in the procedure for measuring the kinetics of the reactions involving sodium thiophenolate in order to insure that the thiophenol was completely converted to its anion. In order to find whether the excess of the sodium methoxide was sufficient to interfere in the comparison of S_N2 reactivities an experiment was arranged in which the reactivity of ethylene bromide toward sodium thiophenolate and sodium methoxide was compared. The thiophenolate ion was found to be more reactive by a

(28) P. M. Dunbar and L. P. Hammett, J. Am. Chem. Soc., 72, 109 (1950).

factor of about 25 which indicated that no difficulty should be encountered.

It was also desirable to know whether the two ml. of acetic acid added as a means of converting the thiophenolate ion to unreactive thiophenol was sufficient. A spectrophotometric determination of the pK_a for thiophenol in absolute methanol was carried out using bromcresol purple as the indicator. From the value of 11.1 obtained for the pK_a of thiophenol in absolute methanol one can show that the concentration of thiophenolate ion was reduced to a negligible amount by the addition of two ml. of acetic acid. Kolthoff found the pK_a of acetic acid in methanol to be 9.65 (20).

All of the experimental values for the specific rate constant in the reactions involving sodium thiophenolate were calculated by the unmodified second order rate equation. The maximum average deviation tolerated was two per cent. However, ethylene bromide was the only compound studied which did not conform to such a simple equation since beta-bromoethyl phenyl sulfide appears to react with sodium thiophenolate at a rate comparable to that of ethylene bromide. An effort was made to find whether the kinetics of the reaction conformed to a rate equation modified for a two step reaction which assumed the second step of the reaction to be fast compared to the first. Such an equation, however, did not represent the reaction kinetics. As a consequence, to obtain the initial specific rate constant the quantity shown below versus time was plotted on a large graph paper,

$$\log \frac{b}{a} \cdot \frac{a-x}{b-x}$$

(20) I. M. Kolthoff and L. S. Guss, J. Am. Chem. Soc., 60, 2516 (1938).

the curve extrapolated to the initial time, and the desired specific rate constant calculated from the initial slope of the curve. Since the effect of beta-bromine on the reactivity of alkyl bromides was desired, it seems that the above results should be satisfactory. Since each bromine was equally capable of being displaced, the specific rate constant quoted for ethylene and trimethylene bromide are divided by two in order to give the rate constant per bromine. The specific rate constant for trimethylene iodide was treated similarly.

The heats and entropies of activation listed in the tables were calculated from the absolute rate equation using the method of least squares (29). The average deviation of activation energies from the mean was thought accurate within 0.3 kcal/mole and the corresponding values for the activation entropies were thought accurate within 0.7 e. u./mole.

In a previous study in this laboratory on the influence of a second halogen on the S_N2 reactivity of another halogen attached to the same carbon atom it was found that the alpha-halogen decreased the reactivity (1). In an effort to determine whether the steric influences were responsible for the decrease in reactivity, it was thought desirable to study the reaction using a nucleophilic reagent which was of a neutral charge type. The nucleophilic reagent chosen was triethylamine, and the reaction the well known Mentschutkin reaction. of the type:

(29) S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(1) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.



Similar reaction rates have been studied in the past by measuring the rate of formation of the halide ion (30) i. e., Y^- , or by measuring the rate of decrease of base concentration (14). However, it was decided to measure the kinetics of the reaction by measuring the rate of change of the conductance of the solution. Such a method offered advantages in that only small quantities of reactants were needed, and very fast reactions could be measured conveniently and with accuracy.

In order to achieve the results desired it was decided to study the relative reactivities in nitrobenzenes. Nitrobenzene was chosen as the solvent because of its superior ability to facilitate the rate of formation of the quaternary ammonium salts. Further advantages existed in that there appeared to be less likelihood of subsequent salt hydrolysis, and the relatively high boiling point allowed one to study the reaction at high temperatures without the difficulty of evaporation losses due to handling.

The instrument arrangement was that of a simple conductivity bridge whose circuit diagram is described under the instrument section. However, a Leeds and Northrup student potentiometer was arranged in the circuit as the bridge's ratio arms in such a way that only the slide-wire and end coils were used. This allowed one to make rapid measurements by merely placing the cell in the circuit, making an approximate setting.

(30) G. E. Edwards, Trans. Faraday Soc., 33, 129 (1937).

(14) C. N. Hinshelwood et al, J. Chem. Soc., 360 (1933).

of the resistance box, and adjusting the slidewire until a null point was obtained. The cell resistance was then calculated from the resistance box reading, R, and the slidewire ratio, A, by the equation:

$$R_x = R \cdot \frac{4500 + A}{5500 - A}$$

Utilizing the resistances measured, the concentration of product formed can easily be obtained by use of the plots described in the experimental section.

Some difficulty was encountered in that the phase of the current in each side of the conductivity bridge was not in balance. Since an adjustable air condenser of sufficient size was not available, the problem was overcome by adding an identical cell containing 30 ml. of solvent in parallel with the resistance box.

An increase was encountered in some of the kinetic data; it was thought that a subsequent reaction might explain these data since it had been reported by Davies and his associates that trimethylamine would form a bis compound when reacted with the dihalomethanes (15).

An experiment was arranged in which a two fold excess of triethylamine was reacted with diiodomethane in nitrobenzene. In order to be certain that no unexpected influence of solvent was occurring, a similar experiment was carried out using methyl ethyl ketone as the solvent. Although the crude product from the reaction using nitrobenzene as the solvent weighed 3.3 per cent more than theoretically

(15) W. C. Davies et al, J. Chem. Soc., 412 (1939).

expected from a one step reaction, the analysis for ionic iodide corresponded to that for a product from a one step reaction. Further, the products obtained from reactions using different solvents were identical.

Although Hartman and coworkers had shown that no reversal of the Menschutkin reaction occurred in examples which they investigated (31), a possible reversal of the reactions involving triethylamine were considered in an effort to explain certain decreases in the rate data.¹ Experiments were arranged in which an excess of triethylamine was used and in which the product was dissolved in nitrobenzene; however no reversal could be detected. A more probable explanation of the difficulties in the rate data can be attributed to the procedure used for cell calibration since decomposition of the reaction mixture was observed in many cases while awaiting completion of the reaction. In such cases the final resistance did not correspond to the correct concentration of quaternary ammonium salt, and the entire calibration curve was incorrect by a small factor.

In Chapter I brief mention was made of the mechanism for the S_N2 reaction. It is desired now to consider in greater detail the electronic influences expected from such a mechanism. Two factors appear to determine reactivity by this mechanism, namely the extent of bond making and the extent of bond breaking in the transition state. Thus, the extent of bond making and bond breaking in the transition state will determine the magnitude of the electron density around the alpha-carbon

(31) D. Hartman et al, J. Am. Chem. Soc., 64, 2294 (1942).

atom. Electron supply is expected to aid reactions in which the central carbon is relatively positive, i. e., where bond breaking is favored over bond making, and electron withdrawal to aid in cases in which bond making is favored. However, one should be aware that this simplification is somewhat exaggerated in that those factors which favor bond formation also tend to increase the strength of the bond undergoing cleavage due to contributions from the ionic terms of the bond energy equation (32).

$$E = \frac{1}{2}(A_2 + B_2) + 23.06(X_A^2 + X_B^2) \bar{e}$$

In the above equation the first term represents the average of the bond energies of the diatomic molecules A_2 and B_2 ; the remaining term is a function of the difference in Pauling's electronegativity values between the atoms A and B. Thus, the latter term accounts for the added stabilization of the bond due to its unsymmetrical character. Thus, those factors which favor bond cleavage will also decrease the ease of approach of nucleophilic reagents.

In compounds which possess electron donor groups many examples exist for which bond cleavage has been favored to such an extent that bond formation is not of significance. These are, of course, the well known uni-molecular or S_N1 reactions many of which even show no dependence at all on the concentration or the nature of the nucleophilic reagent. It seems reasonable too that with sufficiently strong withdrawing substituents one might observe examples in which little dependence

(32) L. Pauling, Nature of the Chemical Bond, 2nd. Ed., Cornell University Press, Ithaca, N. Y., 1945, p. 60.

is attached to bond cleavage. A similar idea has recently been introduced by Swain and Langsdorf (37). Intermediate cases are known, thus, in the reaction of various para substituted beta-phenylethyl chlorides with iodide ion in acetone a minimum in the relative reactivities was observed in the series of substituents; p-MeO 1.04, p-H 0.735, p-F 1.53, p-Cl 1.65, p-Br 1.63, p-I 1.40, p-NO₂ 3.76 (33). Other data are available which show a similar minimum (34-36). However, it should be noted that those minima are observed in aromatic series within which steric factors are constant. A rate minimum due to steric rather than electronic effects should also be possible.

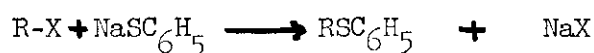
Since the beta-, gamma-, delta-, and epsilon-haloalkyl halides are electron withdrawing groups, one should expect their reactivity relative to an alkyl halide to be determined by competition between bond cleavage and bond formation. Further, with regard to the influence of the specific substituent the energy necessary for cleavage of the old bond should be expected to decrease and the energy for the formation of a new bond to increase in the series of beta substituents:

F, Cl, Br

-
- (33) G. Baddeley and G. M. Bennett, J. Chem. Soc., 1819 (1935).
 (34) S. Sugden and J. B. Willis, ibid., 1360 (1951).
 (35) G. M. Bennett and B. Jones, ibid., 1815 (1935).
 (36) C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N. Y., 1953, p. 327.
 (37) C. G. Swain and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951).

An examination of the data in Table 3 shows that the reactivity of the various ethylene bromides is less than that of ethyl by a factor of about eight. However, the various trimethylene bromides are observed to be of about the same reactivity as propyl. Unfortunately, it was not found possible to measure the S_N2 reactivity of the ethylene iodides; however a consideration of the trimethylene, tetramethylene, and pentamethylene iodides show that the reactivities are only slightly greater than that of propyl iodide. One is led to conclude in the ethylene bromide series that bond cleavage is still the dominating factor while in the higher series the substituents are sufficiently far away that little influence is observed.

Table 3 Summary of Results for the Reaction



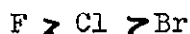
R-X	$k \times 10^4$ l. mole ⁻¹ sec. ⁻¹			ΔH_a	ΔS_a
	0°C	20°C	34.6°C	kcal	e.u.
HCH ₂ CH ₂ Br.	3.79 ± 0.06	39.1 ± 0.6	182 ± 3	18.1	- 10
CH ₃ CH ₂ CH ₂ Br	2.56 ± 0.03	25.6 ± 0.3	112 ± 2	17.7	- 12.3
C ₂ H ₅ CH ₂ CH ₂ Br	2.77 ± 0.03	26.9 ± 0.3	121 ± 1	17.7	- 12.3
C ₄ H ₉ CH ₂ CH ₂ Br	3.14 ± 0.02	77.8 ^b ± 0.4	---	17.1	- 13.7
FCH ₂ CH ₂ Br	0.403 ± 0.006	4.95 ± 0.04	25.5 ± 0.2	19.4	- 9.6
ClCH ₂ CH ₂ Br	0.436 ± 0.006	5.61 ± 0.03	28.5 ± 0.1	19.1	- 10.6
BrCH ₂ CH ₂ Br	0.446 ^a ± 0.01	4.99 ^a ± 0.15	24.3 ^a ± 1	18.7	- 12
FCH ₂ CH ₂ CH ₂ Br	1.86 ± 0.02	52.6 ^b ± 0.4	----	17.9	- 12
ClCH ₂ CH ₂ CH ₂ Br	2.54 ± 0.04	70.6 ^b ± 0.4	----	17.3	- 11.3
BrCH ₂ CH ₂ CH ₂ Br	2.89 ^a ± 0.04	29.8 ^a ± 0.1	----	18.1	- 10.5
BrCH ₂ CH ₂ CH ₂ I	21.8 ± 0.4	191 ± 4	----	16.7	- 11.3
ICH ₂ CH ₂ CH ₂ I	20.1 ± 0.3	181 ^a ± 3	----	16.9	- 10.7
ClCH ₂ CH ₂ CH ₂ I	15.7 ± 0.2	138 ± 1	----	16.3	- 11.3

$\text{FCH}_2\text{CH}_2\text{CH}_2\text{I}$	11.2 ± 0.1	104 ± 1	----	17.2	-10.0
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$	23.8 ± 0.1	204 ± 4	----	17.2	-11.3
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$	22.9 ± 0.2	195 ± 1	----	16.5	-12
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	14.7 ± 0.3	128 ± 1	----	16.6	-12.4

^aThese rate constants contain a statistical factor of one-half.

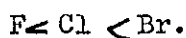
^bThese rate constants were determined at 29.3°C.

Within the ethylene bromide series, somewhat surprising results were found in that the various substituents had about the same influence on reactivity. A closer examination of the reactivity, however, shows the correspondence to be largely fortuitous since the decrease in reactivity caused by a beta-fluorine results from a more unfavorable activation energy while at the other extreme that of beta-bromine results from a more unfavorable activation entropy. Considering only the activation energy, one finds that the beta-halogen increases the activation energy of the alpha-bromine in the order;



This suggests that the overall decrease in activation energy relative to the unsubstituted alkyl halide is due to difficulty in cleavage of the old halogen bond.

Of interest also is the entropy of activation term which is observed to increase in the order:



Assuming the model proposed by Ivanhoff and Magat (38), it is found that the small size of size of beta-fluorine makes its ΔS_a of about the same magnitude as that for a beta-hydrogen. On the other hand, it is less probable that a molecule with a beta-bromine attached would be in the proper configuration for reaction. According to calculations by Mozushima's method (41), the *gauche* form of ethylene bromide in methanol is about

(38) N. Ivanhoff and M. Magat, J. Chim. Phys., 47, 914 (1950).

(41) S. I. Mizushima, Journal of Chemical Physics, 18, 754 (1950).

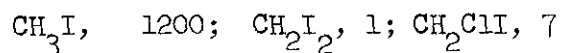
0.7 kcal per mole less stable than the trans form. Thus, an examination of Table 3 shows that the ΔS_a for ethyl bromide to be about equal to that for ethylene fluorobromide and about two entropy units greater than that for ethylene bromide. As might be suspected, the ΔS_a for ethylene chlorobromide is intermediate between that for ethyl bromide and ethylene bromide.

An examination of Table 3 also indicates that the electronic effects are constant when the substitution is more than two carbon atoms removed from the reaction site. Thus, it is observed that the gamma-, delta-, and epsilon-haloalkyl halide are of approximately the same reactivity as the propyl halide.

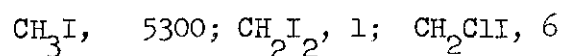
In an earlier portion of this chapter consideration was given to the electronic influences exerted in an S_N2 reaction. The reactions previously considered, however, were those in which the charge types of the reactants were similar to those of the products. The formation of a quaternary ammonium salt from a tertiary amine and an alkyl halide, on the other hand, involves a reaction between neutral molecules to form an ionic product. Since the alpha-carbon atom of the quaternary ammonium salt is more positive in the product than in the initial state, one should expect the alpha-carbon atom to be more positive in its transition state than in the ground state. As a result, bond cleavage should be made more difficult. A rate minimum, if any, should be expected to occur with considerably stronger electron withdrawing groups.

A comparison of the relative reactivities of the methylene halides toward sodium methoxide in methanol indicate a rate minimum

as is seen by the order:



In a consideration of the data in Table 2 a similar minimum in the relative reactivities of the methylene halides toward triethylamine is seen by the order:



Thus, the increased reactivity caused by the substitution of an alpha-chlorine for an alpha-iodine atom is more probably due to steric factors since a rate minimum is not expected to occur with these substituents.

One might tentatively conclude that the order of reactivities observed by Thomas (1) is also due to steric factors. However, the above conclusions should be regarded as tentative until more reliable data on the reactivities of the various methylene halides toward triethylamine and quinuclidine are collected.

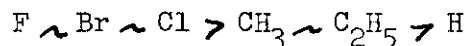
(1) C. H. Thomas, Ph. D. Thesis, Georgia Institute of Technology, 1953.

CHAPTER IV

CONCLUSIONS

In this investigation the substitution of a halogen atom for a beta-hydrogen atom in an ethyl halide was found to decrease the reactivity of that halide toward sodium thiophenolate in absolute methanol. Previous reports that a beta-halogen increased the S_N2 reactivity were shown to be based on kinetic evidence for an E2 reaction.

The order with which the beta-substituent decreases the reactivity of the ethyl halide is:



The order of reactivities were somewhat surprising, however, in that the various beta-halogens had about the same influence on reactivity. An inspection of the heats and entropies of activation show the similarity of reactivities to be fortuitous since the more unfavorable heat of activation for the beta-fluorine is balanced by the less favorable activation entropy for the beta-bromine.

One should also note that the heats of activation increase with increasing electronegativity of the substituent while the activation entropy decreases with increasing size of the substituent.

Electronic influences exerted by substituents situated in the gamma, delta, or epsilon position are observed to be minor as evidenced by similar rates and heats of activation.

Preliminary experiments on the reactivity of triethylamine toward various of the methylene halides suggest that the order of re-

activity observed by Thomas in the reaction of the same compounds with sodium methoxide was due to steric as well as electronic effects.

CHAPTER V

RECOMMENDATIONS

It is felt that further work should be carried out on the relative reactivities of the methylene halides toward triethylamine and toward a less sterically hindered tertiary amine such as quinuclidine or 1-azabicyclo(2,2,1)heptane. Such data would give stronger evidence concerning the importance of steric factors on the course of the reaction.

APPENDIX A
SAMPLE CALCULATIONS

I. Derivation of rate equations.

See any text on kinetics, e. g. Laidler (40).

The equation used for the calculations is:

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (1)$$

II. Calculation of H_a from the absolute rate equation.

$$k = \frac{eKT}{h} e^{-\frac{\Delta H_a}{RT}} e^{\frac{\Delta S_a}{R}} \quad (2)$$

k Boltmann's constant

h Planck's constant

A Derivation of the equation used when two sets of data are available:

$$\ln k_1 = \ln \frac{eKT_1}{h} - \frac{\Delta H_a}{RT_1} + \frac{\Delta S_a}{R} \quad (3)$$

$$\ln k_2 = \ln \frac{eKT_2}{h} - \frac{\Delta H_a}{RT_2} + \frac{\Delta S_a}{R} \quad (4)$$

$$\Delta H_a = \frac{RT_1 T_2}{T_1 - T_2} (\ln k_1 - \ln k_2 + \ln \frac{T_2}{T_1}) \quad (5)$$

B. Derivation of the least squares method used when three sets of data are available.

$$\ln k = \ln \frac{eKT}{h} + \frac{\Delta S_a}{R} - \frac{\Delta H_a}{RT} \quad (6)$$

let $A = \frac{eKT}{h} e^{\frac{\Delta S_a}{R}}$

$$a_1 = \ln A$$

$$a_2 = -\frac{\Delta H_a}{R}$$

V_i = the minimum deviation

Equation 6 then becomes

$$\ln k = a_1 + a_2 \frac{T_i^{-1}}{T_i} \quad (7)$$

$$\ln k - a_1 - \frac{a_2}{T_i} = v_i \quad (8)$$

$$(\ln k - a_1 + a_2)^2 = v_i^2 \quad (9)$$

$$\frac{\delta v_i^2}{\delta a_1} = (\ln k_i - a_1 - \frac{a_2}{T_i}) (-1) = 0 \quad (10)$$

$$\frac{\delta v_i^2}{\delta a_2} = (\ln k_i - a_1 - \frac{a_2}{T_i}) (-\frac{1}{T_i}) \quad (11)$$

$$\sum_{i=1}^3 (a_1 + a_2 \frac{-1}{T_i} - \ln k_i) = 0$$

$$\sum_{i=1}^3 (a_1 T_i^{-1} + a_2 T_i^{-2} - T_i^{-1} \ln k_i) = 0$$

III. Calculation of ΔS_a from the absolute rate equation.

a. Derivation of the equation used when two sets of data are available.

Using equation 3 or 4, the following equation is found:

$$\Delta S_a = R \ln \frac{eKT}{h} - R \ln k - \frac{\Delta H_a}{T}$$

B. Derivation of the least squares equation used when three sets of data are available. Using the value of a_1 from equations 10 or 11 derived in part II. B. of the Sample Calculations, the value of ΔS_a can be readily calculated.

APPENDIX B

TABLES

Table 4

C₅H₅SNa and C₂H₅Br in CH₃OH at 34.6°C.

Thirty ml. of 0.01439 N C₅H₅SNa and 0.01623 M C₂H₅Br were titrated against 0.0245 N I₂.

Time in Min.	Titer in ml.	k ⁻¹ 1. mole ⁻¹ min. ⁻¹
1	17.92	-----
9	15.70	1.060
22	12.37	1.092
29	11.70	1.092
43	9.00	1.091
52	7.09	1.103
63	6.10	1.110
15	14.22	1.110
72	7.40	1.109
154	4.00	1.110

Thirty ml. of 0.02034 N C₅H₅SNa and 0.02044 M C₂H₅Br were titrated against 0.0329 N I₂.

1	18.70	-----
10	15.60	1.037
20.5	13.14	1.072
30	11.53	1.072
60	8.30	1.068
90	6.43	1.075
43	9.92	1.057
150	4.51	1.036
249	3.00	1.103

$K = (1.32 \pm 0.003) \times 10^{-2}$ 1. mole⁻¹ sec.⁻¹

$K = (1.09 \pm 0.016) \times 10^{-1}$ 1. mole⁻¹ min.⁻¹

Table 5

C_6H_5SNa and C_2H_5Br in CH_3OH at $20^\circ C$.

Thirty ml. of $0.03770 \text{ N } C_6H_5SNa$ and $0.04423 \text{ M } C_2H_5Br$
were titrated against $0.0468 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
1	23.94	-----
23	19.41	0.2395
44	16.39	0.2377
83	12.61	0.2349
125	9.93	0.2355
169	8.01	0.2364
211	6.68	0.2370
281	5.16	0.2370
322	4.43	0.2407

Thirty ml. of $0.03622 \text{ N } C_6H_5SNa$ and $0.04303 \text{ M } C_2H_5Br$
were titrated against $0.0468 \text{ N } I_2$.

1	22.97	-----
21	19.11	0.2384
41	16.32	0.2347
63	14.00	0.2323
96	11.42	0.2321
138	9.28	0.2306
175	7.78	0.2300
211	6.70	0.2297
275	5.36	0.2262

$$K = (3.91 \pm 0.06) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$K = (2.35 \pm 0.03) \times 10^{-1} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

Table 6

C_6H_5SNa and C_2H_5Br in CH_3OH at $0^\circ C$.

Fifty ml. of 0.03328 N C_6H_5SNa and 0.7351g. C_2H_5Br
per 100 ml. of solution. Ten ml. samples were titrated against
0.0297 N I_2 .

Time in Min.	Titer in ml.	$k \times 10^2$ l. mole ⁻¹ min. ⁻¹
0	13.03	-----
71	11.76	2.203
209	9.66	2.255
311	8.39	2.301
402	7.47	2.319
1441	2.53	2.32 ³

Fifty ml. of 0.03400 N C_6H_5SNa and 0.7365 g. of C_2H_5Br
per 100 ml. of solution. Ten ml. samples were titrated against
0.0297 N I_2 .

0	13.86	-----
30	12.33	2.266
136	10.69	2.262
327.5	9.01	2.23 ³
453.5	7.86	2.290
1515	2.93	2.292

$$K = (3.79 \pm 0.06) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$K = (2.276 \pm 0.03) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 7

C_6H_5SNa and C_3H_7Br in CH_3OH at $34.6^\circ C$.

Thirty ml. of $0.02563 \underline{N} C_6H_5SNa$ and $0.02853 \underline{M} C_3H_7Br$
were titrated against $0.0297 \underline{N} I_2$.

Time in Min.	Titer in ml.	$k \times 10^1$ l. mole ⁻¹ min. ⁻¹
1	24.81	-----
11	20.80	6.829
20	18.31	6.596
35.5	15.03	6.690
51	12.69	6.638
75	10.23	6.514
100	8.34	6.584
124	7.12	6.524
146	6.26	6.477

Thirty ml. of $0.02320 \underline{N} C_6H_5SNa$ and $0.02827 \underline{M} C_3H_7Br$
were titrated against $0.0297 \underline{N} I_2$.

1	22.36	-----
11	18.76	6.977
24	15.48	6.839
40	12.61	6.817
61	10.02	6.807
91	7.63	6.704
117	6.20	6.748
151	4.89	6.712
181	4.09	6.654

$$k = (1.12 \pm 0.02) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (6.697 \pm 0.112) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 8

C_6H_5SNa and C_3H_7Br in CH_3OH at $20^\circ C$.

Thirty ml. of $0.03816 \text{ N } C_6H_5SNa$ and $0.04354 \text{ M } C_3H_7Br$
were titrated against $0.0466 \text{ N } I_2$.

Time in Min	Titer in ml.	$k \times 10^{-1}$ 1. mole ⁻¹ min. ⁻¹
1	23.84	----
27.5	20.19	1.595
51	17.88	1.530
85	15.24	1.538
182	16.68*	1.507
260.5	13.15*	1.509
492	7.96*	1.460

Thirty ml. of $0.03412 \text{ N } C_6H_5SNa$ and $0.05707 \text{ M } C_3H_7Br$
were titrated against $0.0297 \text{ N } I_2$.

2	32.50	----
23	27.34	1.559
45	23.27	1.548
107	15.54	1.554
188	9.87	1.570
245	7.40	1.580

Thirty ml. of $0.03202 \text{ N } C_6H_5SNa$ and $0.06085 \text{ M } C_3H_7Br$
were titrated against $0.04137 \text{ N } I_2$.

2	21.73	----
20.25	18.49	1.569
43	15.44	1.543
71	12.59	1.532
102	10.20	1.530
168	6.86	1.513
240	4.62	1.510
341	2.75	1.513

$$k = (2.56 \pm 0.03) \times 10^{-3} \text{ 1. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.54 \pm 0.02) \times 10^{-1} \text{ 1. mole}^{-1} \text{ min.}^{-1}$$

* represents ml. of $0.0297 \text{ N } I_2$.

Table 9

C_6H_5SNa and C_3H_7Br in CH_3OH at $0^\circ C$.

Fifty ml. of $0.03350 \text{ N } C_6H_5SNa$ and $0.7247 \text{ g. of } C_3H_7Br$
per 100 ml. of solution. Ten ml. samples were titrated against
 $0.0214 \text{ N } I_2$.

Time in Min.	Titer in ml.	$k \times 10^2$ 1. mole ⁻¹ min. ⁻¹
0	18.35	-----
139	16.40	1.491
299.5	14.46	1.533
372.5	13.77	1.503
1335	7.69	1.540
1674	6.51	1.538

Fifty ml. of $0.08136 \text{ N } C_6H_5SNa$ and $1.1562 \text{ g. of } C_3H_7Br$
per 100 ml. of solution. Ten ml. samples were titrated against
 $0.0214 \text{ N } I_2$.

0	17.40	-----
198	13.38	1.542
305	11.75	1.533
411	10.34	1.542
1387	3.70	1.564
1834	2.49	1.544
2970	0.93	1.538

$$k = (2.56 \pm 0.03) \times 10^{-4} \text{ 1. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.533 \pm 0.01) \times 10^{-2} \text{ 1. mole}^{-1} \text{ min.}^{-1}$$

Table 10

C_6H_5SNa and C_4H_9Br in CH_3OH at $34.6^\circ C$.

Thirty ml. of $0.01704 \text{ N } C_6H_5SNa$ and $0.02683 \text{ M } C_4H_9Br$ were titrated against $0.0297 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
1	16.65	-----
10	14.20	0.7041
25	11.10	0.7225
45	8.36	0.7258
70	6.16	0.7476
110	4.02	0.7231

Thirty ml. of $0.02553 \text{ N } C_6H_5SNa$ and $0.02788 \text{ M } C_4H_9Br$ were titrated against $0.0297 \text{ N } I_2$.

1	25.39	-----
20	18.23	0.7489
28	16.27	0.7390
42	13.72	0.7314
61	11.34	0.7147
87	9.01	0.7049
119	7.03	0.7293
160	5.51	0.7206
230	3.90	0.7141
268	3.36	0.7109

$$k = (1.21 \pm 0.001) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (7.241 \pm 0.111) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 11

C_6H_5SNa and C_4H_9Br in CH_3 at $20^\circ C$.

Thirty ml. of $0.0500 \text{ M } C_4H_9Br$ and $0.03348 \text{ N } C_6H_5SNa$
were titrated against $0.0297 \text{ N } I_2$.

Time in Min	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
1	21.29	----
15	19.05	0.1655
25	17.76	0.1613
47	15.27	0.1620
79	12.49	0.1632
125	9.79	0.1607
173	7.73	0.1617
234	5.92	0.1614
299	4.58	0.1613
345	3.86	0.1612

Thirty ml. of $0.3559 \text{ N } C_6H_5SNa$ and $0.05415 \text{ M } C_4H_9Br$
were titrated against $0.0468 \text{ N } I_2$.

1	22.60	----
13	20.35	0.1675
23.75	18.78	0.1602
43	16.21	0.1636
71	13.52	0.1600
100	11.32	0.1609
161	8.20	0.1595
218	6.23	0.1605
304	4.40	0.1573

$$k = (2.69 \pm 0.03) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.62 \pm 0.016) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 12

C_6H_5SNa and C_4H_9Br in CH_3OH at $0^\circ C$.

Fifty ml. of $0.08043 \underline{N}$ C_6H_5SNa and 0.7766 g. of C_4H_9Br per 100 ml. of solution. Ten ml. samples were titrated against $0.0297 \underline{N}$ I_2 .

Time in min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	13.55	----
100	12.39	0.01659
236	11.11	0.01590
1233	5.53	0.01665
1523	4.83	0.01676
2379	2.65	0.01660
1662	4.54	0.01664

Fifty ml. of $0.08328 \underline{N}$ C_6H_5SNa and 0.9231 g. of C_4H_9Br per 100 ml. of solution. Ten ml. samples were titrated against $0.0297 \underline{N}$ I_2 .

0	13.73	-----
73	12.69	0.01635
319	9.90	0.01680
401	9.19	0.01671
1427	4.31	0.01647
1320	3.29	0.01695
2341	1.87	0.01679
3254	1.54	0.01655

$$k = (2.77 \pm 0.03) \times 10^{-4} \text{ l. mole}^{-1}\text{sec.}^{-1}$$

$$k = (1.66 \pm 0.017) \times 10^{-2} \text{ l. mole}^{-1}\text{min.}^{-1}$$

Table 13

C_6H_5SNa $C_6H_{13}Br$ in CH_3OH at $29.4^\circ C$.

Twenty-five ml. of $0.01391 \text{ N } C_6H_5SNa$ and 0.03450 M

$C_6H_{13}Br$ were titrated against $0.02068 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ sec. ⁻¹
0	16.10	----
25	11.14	0.007740
36	9.52	0.007873
45	8.48	0.007825
68	6.38	0.007795
88	5.05	0.007773
120.5	3.52	0.007757
158	2.34	0.007777

Twenty-five ml. of $0.01391 \text{ N } C_6H_5SNa$ and 0.03955 M

$C_6H_{13}Br$ were titrated against $0.02068 \text{ N } I_2$.

0	16.00	----
9	13.62	0.007876
24	10.63	0.007779
34	9.08	0.007773
45	7.68	0.007779
55	6.66	0.007742
69	5.40	0.007823
85	4.34	0.007799
105	3.34	0.007745
129	2.48	0.007668

$$k = (7.783 \pm 0.037) \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (4.670 \pm 0.022) \times 10 \text{ l. mole}^{-1} \text{ min.}$$

Table 14

C_6H_5SNa $C_6H_{13}Br$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.04712 \text{ N } C_6H_5SNa$ and $1.5678 \text{ g. of } C_6H_{13}Br$ per
100 ml. of solution. Ten ml. of solution were titrated against
 $0.00923 \text{ N } I_2$.

Time in Min.	Titer in ml.	k $l. \text{ mole}^{-1} \text{ sec.}^{-1}$
0	24.59	-----
47.5	22.59	0.0003223
147	19.03	0.0003177
249.25	16.12	0.003143
404	12.63	0.0003127
540	10.23	0.0003133
647	8.78	0.0003106
1520	2.49	0.0003141

Fifty ml. of $0.04712 \text{ N } C_6H_5SNa$ and $1.3871 \text{ g. of } C_6H_{13}Br$ per
ml. of solution. Ten ml. samples were titrated against $0.00923 \text{ N } I_2$.

0	24.63	-----
70.75	22.17	0.0003091
152	19.65	0.0003091
250.75	16.96	0.0003143
404.5	13.65	0.0003146
539	11.41	0.0003133
643.75	9.86	0.0003160
1519	3.32	0.0003153

$$k = (3.141 \pm 0.023) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.354 \pm 0.014) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 15

C_6H_5SNa and $C_2H_4Br_2$ in CH_3OH at $34.6^\circ C$.

Thirty ml. of $0.03407 \text{ N } C_6H_5SNa$ and $0.01679 \text{ M } C_2H_4Br_2$
 were titrated against $0.0535 \text{ N } I_2$.

Time in Min.	Titer in ml.	$k \times 10^{-1}$ l. mole ⁻¹ min. ⁻¹
1	18.97	-----
16	17.42	3.56
31	16.19	3.54
81	12.55	4.04
121	10.45	4.07
174	8.33	4.61
242	6.50	5.06
300	5.31	5.48
362	4.48	5.73

Thirty ml. of $0.01110 \text{ N } C_6H_5SNa$ and $0.18287 \text{ M } C_2H_4Br_2$
 were titrated against $0.0245 \text{ N } I_2$.

1	12.59	-----
5	9.71	3.58
10	7.27	3.39
14	5.60	3.49
18	4.34	3.52
24	2.91	3.60
30	1.89	3.71

$$k = (2.43 \pm 0.10) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (2.92 \pm 0.12) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

This k was obtained by plotting the term shown below

$$\log \frac{b}{a} \cdot \frac{a-x}{b-x}$$

versus time, obtaining the initial slope to the curve, and dividing the initial slope by the difference in initial concentration of the of the reactants.

Table 16

C_6H_5SNa and $C_2H_4Br_2$ in CH_3OH at $20^\circ C$.

Thirty ml. of $0.03770 \text{ N } C_6H_5SNa$ and $0.07947 \text{ M } C_2H_4Br_2$
were titrated against $0.0463 \text{ N } I_2$.

Time in Min.	Titer in ml.	$k \times 10^2$ l. mole ⁻¹ min. ⁻¹
1	23.95	-----
27	21.03	6.40
59	17.92	6.73
101	14.62	6.93
165	10.54	7.49
237	7.22	8.10

Thirty ml. of $0.03595 \text{ N } C_6H_5SNa$ and $0.09340 \text{ M } C_2H_4Br_2$
were titrated against $0.0463 \text{ N } I_2$.

1	22.34	-----
23	20.13	6.379
70	15.19	6.371
100	12.77	7.00
153	9.27	7.407
196	7.12	7.63
236	5.42	8.14

$$* k = (4.99 \pm 0.15) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$* k = (5.00 \pm 0.19) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

* This k was obtained as described at the bottom of Table

* This k contains a statistical factor of one-half.

Table 17

C_6H_5SNa and $C_2H_4Br_2$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.08136 \underline{N} C_6H_5SNa$ and 1.7182 g. of $C_2H_4Br_2$.
per 100 ml. of solution. Ten ml. samples were titrated against
 $0.0214 \underline{N} I_2$.

Time in Min.	Titer in ml.	$k \times 10^{10}$ l. mole ⁻¹ min. ⁻¹
0	18.77	-----
344	15.89	5.51
1359	9.81	5.97
1807	7.98	6.13
2946	4.49	6.83
3223	3.86	7.03
4551	1.79	8.14

Fifty ml. of $0.08136 \underline{N} C_6H_5SNa$ and 1.5029 g. of $C_2H_4Br_2$
per 100 ml. of solution. Ten ml. samples were titrated
against $0.0214 \underline{N} I_2$.

0	18.78	-----
323	16.57	5.028
1344	10.31	5.89
1788	9.02	6.07
2925	5.57	6.75
3201	4.91	6.95
4529	2.59	7.92

$$* k = (0.446 \pm 0.010) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$* k = (5.35 \pm 0.06) \times 10^{-3} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

* This k was obtained as described at the bottom Table 15.

* This k contains a statistical factor of one-half.

Table 18

C_6H_5SNa and C_2H_4ClBr in CH_3OH at $34.6^\circ C$.

Thirty ml. of $0.02682 \text{ N } C_6H_5SNa$ and $0.08129 \text{ M } C_2H_4ClBr$ were titrated against $0.0329 \text{ N } I_2$.

Time in Min.	Titer in ml.	$k \text{ l. mole}^{-1} \text{ min.}^{-1}$
1	24.04	-----
5	22.79	0.1668
8	21.96	0.1621
12	20.65	0.1680
20	18.65	0.1725
35	15.21	0.1782
53	12.81	0.1640
69	10.31	0.1735
90	8.00	0.1764
130	5.36	0.1720

Thirty ml. of $0.02534 \text{ N } C_6H_5SNa$ and $0.6635 \text{ M } C_2H_4ClBr$ were titrated against $0.0329 \text{ N } I_2$.

1	22.82	-----
12	20.20	0.1711
30	16.73	0.1714
60	12.45	0.1721
45	14.35	0.1728
88	9.62	0.1725
113	7.75	0.1722
190	4.03	0.1751

$k = (2.85 \pm 0.05) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$
 $K = (1.71 \pm 0.03) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$

Table 19

C_6H_5SNa and C_2H_4ClBr in CH_3OH at $20^\circ C$.

Thirty ml. of $0.03166 \text{ N } C_6H_5SNa$ and $0.04097 \text{ M } C_2H_4ClBr$
were titrated against $0.04137 \text{ N } I_2$.

Time in Min.	Titer in ml.	k $l. \text{ mole}^{-1} \text{ min.}^{-1}$
2	22.96	-----
100	20.23	0.03346
153	18.96	0.03333
319	15.75	0.03353
450	13.80	0.03358

Thirty ml. of $0.02821 \text{ N } C_6H_5SNa$ and $0.07810 \text{ M } C_2H_4ClBr$
were titrated against $0.04137 \text{ N } I_2$.

2	20.46	-----
34	18.83	0.03355
112	15.53	0.03364
193.5	12.90	0.03316

Thirty ml. of $0.03130 \text{ N } C_6H_5SNa$ and $0.07210 \text{ M } C_2H_4ClBr$
were titrated against $0.04137 \text{ N } I_2$.

2	22.64	-----
20	21.68	0.03363
45	20.45	0.03357
74	19.05	0.03455
130	16.89	0.03378
222	13.97	0.03360
311	11.65	0.03399
465	8.84	0.03355

$$k = (5.61 \pm 0.03) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (3.36 \pm 0.02) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 20

C_6H_5SNa and C_2H_4ClBr in CH_3OH at $0^\circ C$.

Fifty ml. of $0.03126 \underline{N} C_6H_5SNa$ and 1.1554 g. of C_2H_4ClBr per 100 ml. of solution. Ten ml. samples were titrated against $0.0297 \underline{N} I_2$.

Time in Min.	Titer in ml.	$k \times 10^3$ l. mole ⁻¹ min. ⁻¹
0	13.68	-----
1019	10.97	2.839
1488	9.97	2.85
2502	8.14	2.91
3983	6.25	2.91
5477	4.93	2.89

Fifty ml. of $0.08136 \underline{N} C_6H_5SNa$ and 1.3267 g. of C_2H_4ClBr per 100 ml. of solution. Ten ml. samples were titrated against $0.0214 \underline{N} I_2$.

0	18.87	----
303	17.43	2.89
1262	13.59	3.02
2902	9.44	2.96
3179	8.96	2.94
4512	6.90	2.91

$$k = (0.486 \pm 0.006) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (2.92 \pm 0.037) \times 10^{-3} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 21

C_6H_5SNa and C_2H_4FBr in CH_3OH at $34.6^\circ C$.

Thirty ml. of $0.01810 \text{ N } C_6H_5SNa$ and $0.03955 \text{ M } C_2H_4FBr$
were titrated against $0.0245 \text{ N } I_2$.

Time in Min.	Titer in ml.	k $l. \text{ mole}^{-1} \text{ min.}^{-1}$
1	22.05	-----
30	18.51	0.1590
63	15.55	0.1539
91	13.50	0.1532
127	11.40	0.1520
208	7.93	0.1525
260	6.43	0.1518
302	5.49	0.1503

Thirty ml. of $0.08256 \text{ M } C_2H_4FBr$ and $0.03386 \text{ N } C_6H_5SNa$
were titrated against $0.0535 \text{ N } I_2$.

1	18.75	-----
10	16.79	0.1527
20	14.89	0.1548
31	13.16	0.1538
54	10.28	0.1540
64	9.33	0.1531
90	7.27	0.1523
120	5.51	0.1527
170	3.59	0.1525
275	1.60	0.1500

$$k = (2.55 \pm 0.02) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.529 \pm 0.009) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 22

C_6H_5SNa and C_2H_4FBr in CH_3OH at $20^\circ C$.

Thirty ml. of 0.02428 N C_6H_5SNa and 0.04680 M C_2H_4FBr
were titrated against 0.0297 N I_2 .

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
1	24.53	-----
17	23.98	0.03036
50	22.92	0.02943
116	21.05	0.02936
192	19.06	0.03000
263	17.57	0.02960
349	15.93	0.03048
433	14.49	0.02966

Thirty ml. of 0.03741 N C_6H_5SNa and 0.06454 M C_2H_4FBr
were titrated against 0.0518 N I_2 .

1	21.66	-----
40	20.12	0.02978
90	18.41	0.02957
140	16.93	0.02934
186	15.72	0.02941
275	13.66	0.02961
338	12.45	0.02963
942	5.78	0.03000
1300	3.99	0.02982

$$k = (4.95 \pm 0.04) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (2.97 \pm 0.03) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 23

C_6H_5SNa and C_2H_4FBr in CH_3OH at $0^\circ C$.

Fifty ml. of $0.07604 \text{ N } C_6H_5SNa$ and 0.9617 g. of FCH_2CH_2Br per 100 ml. of solution. Ten ml. samples were titrated against $0.0214 \text{ N } I_2$.

Time in Min.	Titer in ml.	$k \times 10^3$ $l. \text{ mole}^{-1} \text{ min.}^{-1}$
0	17.58	-----
1274	14.11	2.417
2306	11.11	2.413
4757	8.57	2.342
5762	7.26	2.472

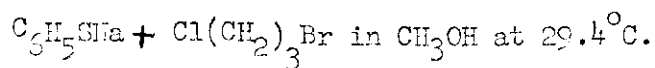
Fifty ml. of $0.07604 \text{ N } C_6H_5SNa$ and 0.9113 g. of FCH_2CH_2Br per 100 ml. of solution. Ten ml. samples were titrated against $0.0214 \text{ N } I_2$.

0	17.62	-----
1257	14.63	2.407
2736	11.91	2.472
4766	9.63	2.359
5741	8.47	2.452
10151	5.50	2.437

$k = (0.403 \pm 0.006) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

$k = (242 \pm 0.023) \times 10^{-3} \text{ l. mole}^{-1} \text{ min.}^{-1}$

Table 24



Twenty-five ml. of 0.02417 N $\text{C}_6\text{H}_5\text{SNa}$ and 0.07093 M $\text{Cl}(\text{CH}_2)_3\text{Br}$ were titrated against 0.02307 N I_2 .

Time in Min.	Titer in ml.	k 1. mole ⁻¹ min. ⁻¹
0	26.19	-----
10.	19.61	0.4264
15.	17.24	0.4180
20.	14.99	0.4276
29.	11.93	0.4255
38.	9.61	0.4273
50.	7.31	0.4249
70.	4.81	0.4173
92.	3.00	0.4199

Twenty-five ml. of 0.02378 N $\text{C}_6\text{H}_5\text{SNa}$ and 0.07101 M $\text{Cl}(\text{CH}_2)_3\text{Br}$ were titrated against 0.02307 N I_2 .

0	25.77	-----
7	20.90	0.4210
15.	16.81	0.4220
23.	13.61	0.4253
31.	11.18	0.4236
43.	8.40	0.4239
55.	6.45	0.4202
70.	4.53	0.4236

$$k = (7.058 \pm 0.040) \times 10^{-3} \text{ 1. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (4.235 \pm 0.024) \times 10^{-1} \text{ 1. mole}^{-1} \text{ min.}^{-1}$$

Table 25

C_6H_5SNa $Cl(CH_2)_3Br$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.01918 N C_6H_5SNa and 0.8356 g. of $Cl(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against 0.007735 N I_2 .

Time in Min.	Titer in ml. of 0.007735 N I_2	l. mole ⁻¹ min. ⁻¹
0	12.34	-----
230.5	10.27	0.01519
258.5	9.26	0.01539
530	8.12	0.01531
1466	4.10	0.01515
1665	3.61	0.01496

Fifty ml. of 0.02025 N C_6H_5SNa and 0.9432 g. of $Cl(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against 0.007735 N I_2 .

0	12.81	-----
112	11.52	0.1597
207	10.64	0.1521
301.5	9.72	0.1566
417.25	8.90	0.1502
1445	3.93	0.1473

$$k = (2.543 \pm 0.042) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.526 \pm 0.026) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 26

$C_6H_5SNa + F(CH_2)_3Br$ in CH_3OH at $29.4^\circ C$.

Twenty-five ml. of $0.01743 \text{ M } C_6H_5SNa$ and $0.05139 \text{ M } F(CH_2)_3Br$ were titrated against $0.02276 \text{ M } I_2$.

Time in Min.	Titer in ml.	k^{-1} l. mole ⁻¹ min. ⁻¹
0	18.54	-----
10.	15.88	0.3118
17.	14.32	0.3111
25.	12.69	0.3165
38.5	10.50	0.3160
51.	8.82	0.3186
65.	7.36	0.3174
120.	3.72	0.3183

Twenty-five ml. of $0.01683 \text{ M } C_6H_5SNa$ and $0.03974 \text{ M } F(CH_2)_3Br$ were titrated against $0.02276 \text{ M } I_2$.

Twenty-five ml. of $0.01683 \text{ M } C_6H_5SNa$ and $0.03974 \text{ M } F(CH_2)_3Br$ were titrated against $0.02276 \text{ M } I_2$.

0	20.00	-----
12.	16.75	0.3106
15.	15.94	0.3210
23.5	14.19	0.3157
30.	12.95	0.3179
38.5	12.04	0.3134
45.	10.66	0.3155
61.	8.71	0.3164
92.	3.04	0.3158
123.	5.06	0.3131

$$k = (5.26 \pm 0.037) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (3.157 \pm 0.022) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 27

$C_6H_5SNa + F(CH_2)_3Br$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.02426 \underline{N} C_6H_5SNa$ and 1.4890 g. of $F(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against $0.00685 \underline{N} I_2$.

Time in Min.	Titer in ml.	k $l. \text{ min.}^{-1} \text{ mole}^{-1}$
0	17.64	-----
93	15.83	0.01110
261	13.06	0.01111
409.25	11.10	0.01099
522.25	9.75	0.01107
734	7.28	0.01190
1495	3.50	0.01091
1917	2.21	0.01102

Fifty ml. of $0.01970 \underline{N} C_6H_5SNa$ and 1.6723 g. of $F(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against $0.00685 \underline{N} I_2$.

0	14.28	-----
122	12.19	0.01103
255	10.25	0.01110
379	8.72	0.01117
563	6.95	0.01106
758	5.37	0.01122
1474	2.30	0.01094

$$k = (1.855 \pm 0.023) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.113 \pm 0.014) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 28

C_6H_5SNa $Br(CH_2)_3Br$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.009858 \text{ N } C_6H_5SNa$ and $0.114357 \text{ M } Br(CH_2)_3Br$ were titrated against $0.00923 \text{ N } C_6H_5SNa$ and $0.114357 \text{ M } Br(CH_2)_3Br$

Time in Min.	Titer in ml.	k $l. \text{ mole}^{-1} \text{ min.}^{-1}$
0	24.44	-----
5	19.98	0.3579
7	18.40	0.3610
10	16.37	0.3580
13	14.53	0.3587
17	12.46	0.3569
25	9.03	0.3615
37	5.70	0.3603
43	4.52	0.3607
55	2.85	0.3613

Twenty-five ml. of $0.008569 \text{ N } C_6H_5SNa$ and $0.11085 \text{ M } Br(CH_2)_3Br$ were titrated against $0.00923 \text{ N } I_2$.

0	22.20	-----
4	18.98	0.3561
8	16.31	0.3528
10	15.01	0.3591
15	12.41	0.3376
20	10.29	0.3561
26	8.15	0.3588
33.5	6.13	0.3596
40.25	4.82	0.3578
50	3.37	0.3561

$$* K = (2.987 \pm 0.014) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$* K = (1.792 \pm 0.009) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

* This k contains a statistical factor of one-half

Table 29

C_6H_5SNa $Br(CH_2)_3Br$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.02025 N C_6H_5SNa and 1.5778 g. of $Br(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against 0.00735 N I_2 .

Time in Min.	Titer in ml.	k $l. mole^{-1} min.^{-1}$
0	12.71	-----
32.	11.65	0.03439
64.5	10.68	0.03505
111.5	9.42	0.03514
165.5	8.26	0.03409
241.5	6.81	0.03433
303.	5.81	0.03453
364.	3.96	0.03450

Fifty ml. of 0.01921 N C_6H_5SNa and 1.2306 g. of $Br(CH_2)_3Br$ per 100 ml. of solution. Ten ml. samples were titrated against 0.007735 N I_2 .

0	12.42	-----
103.	9.93	0.03454
176.	8.61	0.03505
232.5	7.64	0.03545
320.	6.59	0.03390
493.5	4.60	0.03508
1425.	0.89	0.03396

$$k = (2.898 \pm 0.037) \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$(1.737 \pm 0.022) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

This k contains a statistical factor of one-half.

Table 30

$C_6H_5SNa + C_3H_7I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.008569 \text{ N } C_6H_5SNa$ and 0.03984 M

C_3H_7I were titrated against $0.00923 \text{ N } I_2$.

Time in Min.	Titer in ml.	k_{-1} l. mole ⁻¹ min. ⁻¹
0	22.71	-----
5.	19.52	0.7743
8.	17.83	0.7712
14.	15.09	0.7652
25.	11.05	0.7743
38.5	7.34	0.7595
50.	5.76	0.7675
60.	4.56	0.7569
90.	2.22	0.7509

Twenty-five ml. of $0.01811 \text{ N } C_6H_5SNa$ and 0.02862 M

C_3H_7I were titrated against $0.02276 \text{ N } I_2$.

0	19.40	-----
9.	16.12	0.7745
17.	13.96	0.7596
25.	12.00	0.7594
38.	9.91	0.7653
46.	8.87	0.7592
60.	7.23	0.7731
90.	4.99	0.7735
124.	3.43	0.7633

$$K = (1.276 \pm 0.010) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$K = (7.655 \pm 0.062) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 31

$C_5H_5SNa + C_3H_7I$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.04712 N C_5H_5SNa and 1.6959 g. of C_3H_7I per 100 ml. of solution. Ten ml. samples were titrated against 0.00922 N I_2 .

Time in Min.	Titer in ml.	k l. mole ⁻¹ sec. ⁻¹
0	23.91	----
23.	19.70	0.001461
36.25	17.53	0.001502
52.	15.51	0.001474
81.75	12.15	0.001497
108.75	9.87	0.001496
173.25	6.00	0.001513
225.5	4.10	0.001510
290.75	2.61	0.001498

Fifty ml. of 0.06214 N C_5H_5SNa and 1.1927 g. of C_3H_7I per 100 ml. of solution. Ten ml. samples were titrated against 0.02276 N I_2 .

0	13.00	-----
13.25	12.03	0.001449
39.25	10.47	0.001437
67.75	8.90	0.001465
100.5	7.20	0.001601
135.	6.38	0.001466
189.25	5.00	0.001459
244.75	3.95	0.001454
397.75	2.15	0.001450

$$k = (1.473 \pm 0.028) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (3.838 \pm 0.168) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 32

$C_6H_5SNa + I(CH_2)_3I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.008140 \text{ N } C_6H_5SNa$ and $0.04071 \text{ M } I(CH_2)_3I$ were titrated against $0.01375 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	13.56	-----
3	10.62	2.078
5	8.89	2.136
7	7.60	2.165
9	6.50	2.161
14	4.33	2.207
14.3	4.19	2.2266
18	3.21	2.197
21.5	2.42	2.2224

Twenty-five ml. of $0.007181 \text{ N } C_6H_5SNa$ and $0.03910 \text{ M } I(CH_2)_3I$ were titrated against $0.00923 \text{ N } I_2$.

0	17.92	-----
3	13.98	2.193
5	12.03	2.135
8	9.54	2.143
11	7.68	2.120
14	6.05	2.161
20	3.88	2.172
25	2.71	2.171
29	1.93	2.229

$$k = (1.811 \pm 0.026) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.087 \pm 0.016) \text{ l. mole}^{-1} \text{ min.}^{-1}$$

This k contains a statistical factor of one-half

Table 33

$C_6H_5SNa + I(CH_2)_3I$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.02026 N C_6H_5SNa and 2.4935 g. of $I(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.007735 N I_2 .

Time in Min.	Titer in ml.	k_{-1} l. mole ⁻¹ min. ⁻¹
0.	10.96	-----
14.75	8.31	0.230
19.50	7.41	0.247
26.25	6.53	0.244
35.5	5.50	0.242
43.5	4.27	0.243
59.75	3.47	0.243
83.1	2.00	0.241

Fifty ml. of 0.01918 N C_6H_5SNa and 1.2343 g. of $I(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.007735 N I_2 .

0.	11.26	-----
14.75	8.98	0.241
24.5	7.79	0.238
35.5	6.53	0.246
52.5	4.53	0.237
91.5	2.94	0.242
156.25	1.16	0.246

$$k = 0.242 \pm 0.003 \text{ l. mole}^{-1}$$

$$(2.014 \pm 0.037) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

This k contains a statistical factor of one-half.

Table 34

$C_6H_5SNa + Br(CH_2)_3I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.01193 \text{ M } C_6H_5SNa$ and $0.04828 \text{ M } Br(CH_2)_3I$ were titrated against $0.02950 \text{ M } I_2$.

Time in Min.	Titer in ml.	k , $l.$ mole ⁻¹ min. ⁻¹
0	13.60	-----
5.	10.36	1.179
6.	9.00	1.133
14.	6.61	1.163
23.	4.33	1.150
25.	3.98	1.151
30.	3.09	1.174
35.5	2.40	1.177
44.25	1.62	1.178

Twenty-five ml. of $0.01207 \text{ M } C_6H_5SNa$ and $0.04332 \text{ M } Br(CH_2)_3I$ were titrated against $0.01375 \text{ M } I_2$.

0	20.60	-----
5.	16.57	1.099
6.	14.51	1.103
12.	12.14	1.120
15.	10.67	1.126
20.	8.65	1.130
25.	6.99	1.147
30.	5.66	1.159
40.	3.90	1.163

$$k = (1.913 \pm 0.037) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.148 \pm 0.022) \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 35

$C_6H_5SNa + Br(CH_2)_3I$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.01970 \text{ N } C_6H_5SNa$ and 1.9590 g. of $Br(CH_2)_3I$
per 100 ml. of solution. Ten ml. samples were titrated against $0.00685 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	13.44	----
15.5	11.72	0.1229
30.25	10.13	0.1313
53.5	8.11	0.1342
78	6.57	0.1317
110.5	4.92	0.1320
146.5	3.54	0.1335
215	1.93	0.1346

Fifty ml. of $0.02754 \text{ N } C_6H_5SNa$ and 1.8903 g. of $Br(CH_2)_3I$ per 100
ml. of solution. Ten ml. samples were titrated against $0.00685 \text{ N } I_2$.

	Titer in ml.	
0	16.87	----
12.5	16.79	0.1283
27	14.61	0.1331
47	12.43	0.1278
70	10.31	0.1275
100.25	7.97	0.1312
138.25	5.95	0.1317
197.25	3.88	0.1316
283	2.06	0.1343

$$k = (2.183 \pm 0.040) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.310 \pm 0.024) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 36

$C_6H_5SNa + Cl(CH_2)_3I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.01751 \text{ M } C_6H_5SNa$ and $0.03311 \text{ M } Cl(CH_2)_3I$ were titrated against $0.02276 \text{ N } I_2$.

Time in Min.	Titer in ml.	k_{-1} l. mole ⁻¹ min. ⁻¹
0	17.37	-----
5.	15.33	0.8595
18.	10.79	0.8433
28.	8.54	0.9255
40.	6.43	0.8304
48.	5.53	0.8180
58.	4.40	0.8340
83.	2.71	0.8295

Twenty-five ml. of $0.01865 \text{ N } C_6H_5SNa$ and $0.03393 \text{ M } Cl(CH_2)_3I$ were titrated against $0.02276 \text{ N } I_2$.

0	19.12	-----
10.	14.29	0.8242
14.5	12.68	0.8207
23.	10.21	0.8248
31.	8.36	0.8371
41.	6.79	0.8202
58.	4.72	0.8255
92.	2.45	0.8253

$$k = (1.382 \pm 0.012) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec}^{-1}$$

$$k = (8.294 \pm 0.073) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 37

$C_6H_5SNa + Cl(CH_2)_3I$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.02622 N C_6H_5SNa and 1.8282 g. of $Cl(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.00685 N I_2 .

Time in Min	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	17.47	----
15.25	15.38	0.09497
34.5	13.07	0.09670
55.75	11.06	0.09528
81	9.12	0.09422
111.5	7.20	0.09444
170.5	4.64	0.09376
321.5	1.57	0.09265

Fifty ml. of 0.01223 N C_6H_5SNa and 1.8959 g. of $Cl(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.00685 N I_2 .

0	16.37	-----
16	14.33	0.09164
32	12.42	0.09578
52.75	10.51	0.09373
85.75	8.08	0.09309
119.5	5.98	0.09639
180	3.78	0.09430

$$k = (1.573 \pm 0.019) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (9.438 \pm 0.112) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 38

C_6H_5SNa $F(CH_2)_3I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.008272 \text{ N } C_6H_5SNa$ and $0.01938 \text{ M } F(CH_2)_3I$ were titrated against $0.02068 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	14.13	-----
14	12.08	0.6146
28	10.40	0.6274
42	9.11	0.6221
60.2	7.71	0.6272
80.5	6.54	0.6225
113	5.11	0.6195
160	3.75	0.6144
242	2.22	0.6267

Twenty-five ml. of $0.02341 \text{ N } C_6H_5SNa$ and $0.03834 \text{ M } F(CH_2)_3I$ were titrated against $0.02276 \text{ N } I_2$.

0	24.54	-----
7.25	20.79	0.6415
10	19.66	0.6344
17	17.22	0.6191
25	14.77	0.6306
38	12.00	0.6168
45	10.91	0.6042
60	8.62	0.6180
79	6.70	0.6155
100	5.09	0.06224

$$k = (1.037 \pm 0.010) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (6.222 \pm 0.062) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 39

$C_6H_5SNa + F(CH_2)_3I$ in CH_3OH at $0^\circ C$.

Fifty ml. of 0.08030 N C_6H_5SNa and 1.1766 g. of $F(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.02276 N I_2 .

Time in Min.	Titer in ml.	k_{-1} 1. mole ⁻¹ sec. ⁻¹
0	16.73	-----
26.25	15.11	0.001105
70.5	12.82	0.001128
109.	11.33	0.001109
172.	9.34	0.001111
248.5	7.50	0.001123
341.25	5.91	0.001127
474.75	4.37	0.001120

Fifty ml. of 0.05508 N C_6H_5SNa and 2.0928 g. of $F(CH_2)_3I$ per 100 ml. of solution. Ten ml. samples were titrated against 0.01375 N I_2 .

Time in Min.	Titer in ml.	k_{-1}
0	13.95	-----
13.75	17.13	0.001123
34.25	14.82	0.001113
54.25	12.90	0.001121
79.25	10.92	0.001117
119.	8.38	0.001126
163.75	6.11	0.001127
233.	4.01	0.001124
283.25	3.07	0.001122

$$k = (1.120 \pm 0.005) \times 10^{-3} \text{ 1.mole}^{-1} \text{ sec.}^{-1}$$

$$k = (6.720 \pm 0.030) \times 10^{-2} \text{ 1.mole}^{-1} \text{ min.}^{-1}$$

Table 40

$C_6H_5SNa + Cl(CH_2)_4I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of 0.009800 N C_6H_5SNa and 0.03695 M $Cl(CH_2)_4I$ were titrated against 0.00923 N I_2 .

Time in Min.	Titer in ml.	k l. mole ⁻¹ min. ⁻¹
0	24.10	-----
3.	21.16	1.221
5.	19.41	1.232
11.	15.17	1.229
16.	12.48	1.224
20.	10.77	1.213
29.	7.63	1.227
40.	5.08	1.235
61.5	2.42	1.226

Twenty-five ml. of 0.01391 N C_6H_5SNa and 0.03714 M $Cl(CH_2)_4I$ were titrated against 0.02068 N I_2 .

0.	15.40	-----
5.	12.12	1.386
8.5	10.94	1.194
13.	9.11	1.220
16.	8.19	1.210
24.	6.19	1.209
20.	7.10	1.209
29.	5.22	1.209
45.	3.20	1.137
60.25	2.00	1.193

$$k = (2.041 \pm 0.037) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.224 \pm 0.022) \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 41

C_6H_5SNa $Cl(CH_2)_4I$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.06237 N C_6H_5SNa$ and 1.4242 g. of $Cl(CH_2)_4I$ per 100 ml. of solution. Ten ml. samples were titrated against $0.02068 N I_2$.

Time in Min.	Titer in ml.	k 1. mole ⁻¹ sec. ⁻¹
0	13.91	-----
17	12.00	0.002379
30.5	10.71	0.002409
57	8.71	0.002406
81.75	7.30	0.002390
112.75	5.90	0.002393
145.5	4.76	0.002401
197.75	3.51	0.002371

Fifty ml. of $0.04015 N C_6H_5SNa$ and 1.7958 g. of $Cl(CH_2)_4I$ per 100 ml. of solution. Ten ml. samples were titrated against $0.02276 N I_2$.

	Titer in ml.	
0	16.07	-----
14.75	13.74	0.002332
30	11.73	0.002385
51	9.66	0.002360
73.5	7.79	0.002427
92.25	6.76	0.002371
121.75	5.30	0.002393
157.25	4.10	0.002369
237.5	2.32	0.002384

$$k = (2.385 \pm 0.13) \text{ 1. mole}^{-1}\text{sec.}^{-1}$$

$$k = (1.431 \pm 0.010) \text{ 1. mole}^{-1}\text{min.}^{-1}$$

Table 42

$C_6H_5SNa + Cl(CH_2)_5I$ in CH_3OH at $19.95^\circ C$.

Twenty-five ml. of $0.01973 \text{ N } C_6H_5SNa$ and 0.04116 N

$Cl(CH_2)_5I$ were titrated against $0.02068 \text{ N } I_2$.

Time in Min.	Titer in ml.	k_1 l. mole ⁻¹	-1 sec.
0	22.65	-----	
4.5	19.50	0.01967	
7.	16.62	0.01972	
10.	14.79	0.01943	
15.	12.21	0.01947	
20.	10.25	0.01940	
30.	7.32	0.01947	
45.	4.66	0.01935	
60.	3.01	0.01945	

Twenty-five ml. of $0.01856 \text{ N } C_6H_5SNa$ and 0.03523 N

$Cl(CH_2)_5I$ were titrated against $0.02068 \text{ N } I_2$.

0	21.50	-----	
4.	18.40	0.01955	
7.	16.45	0.01978	
10.5	14.66	0.01938	
20.	10.81	0.01952	
29.	8.39	0.01941	
40.	6.21	0.01960	
50.	4.89	0.01942	
73.5	2.81	0.01956	

$$k_1 = (0.01951 \pm 0.00010) \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k_2 = (1.171 \pm 0.006) \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 43

C_6H_5SNa $I(CH_2)_5Cl$ in CH_3OH at $0^\circ C$.

Fifty ml. of $0.05692 \text{ N } C_6H_5SNa$ and 2.3226 g. of $I(CH_2)_5Cl$ per 100 ml. of solution. Ten ml. samples were titrated against $0.02068 \text{ N } I_2$.

Time in Min.	Titer in ml.	k l. mole ⁻¹ sec. ⁻¹
0	12.23	----
18	9.68	0.002305
30.5	8.36	0.002249
49	6.63	0.002308
68	5.32	0.002308
84.5	4.49	0.002268
103.75	3.60	0.002293

Fifty ml. of $0.06232 \text{ N } C_6H_5SNa$ and 1.4319 g. of $I(CH_2)_5Cl$ per 100 ml. of solution. Ten ml. samples were titrated against $0.02068 \text{ N } I_2$.

0	14.02	-----
14.75	12.43	0.002356
35.75	10.67	0.002285
60	8.99	0.002299
95.75	7.10	0.002315
122.75	6.09	0.002280
155.75	5.02	0.002290
212	3.78	0.002250
291	2.50	0.002282

$$k = (2.292 \pm 0.020) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k = (1.375 \pm 0.012) \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 44

$(C_2H_5)_3N$ and CH_3I in $C_6H_5NO_2$ at $24.8^\circ C$

Thirty ml. of $0.02552 \text{ M } (C_2H_5)_3N$ and $0.02530 \text{ M } CH_3I$

Time in Min.	Resistance in Ohms	Moles Per Liter Salt Formed	k l. Mole ⁻¹ sec. ⁻¹
5.5	1924	0.00584	0.03511
7.25	1622	0.00728	0.03590
9	1431	0.00850	0.03638
10	1353	0.00911	0.03634
11.5	1153	0.00992	0.03609
16.25	1069	0.01200	0.03602
19	1006	0.01290	0.03542
23	935	0.01415	0.03557
37	810	0.01692	0.03504

Thirty ml. of $0.02939 \text{ M } (C_2H_5)_3N$ and $0.01671 \text{ M } CH_3I$

7.5	2017	0.00551	0.03374
9	1847	0.00614	0.03267
10.75	1654	0.00810	0.03385
13.25	1456	0.00832	0.03535
17	1289	0.00956	0.03593
19.5	1221	0.01031	0.03557
24.25	1122	0.01131	0.03490
46.25	933	0.01420	0.03517
31.5	1027	0.01260	0.03513

$k = (3.52 \pm 0.064) \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 45

$(C_2H_5)_3N$ and ICH_2I in $C_6H_5NO_2$ at 24.8°

Thirty ml. of $0.09338 \text{ M } (C_2H_5)_3N$ and $0.04412 \text{ ICH}_2\text{I}$

Time in Min.	Resistance in Ohms	Moles Per Liter Salt Formed	$k_{-1} \times 10^6$ l. mole ⁻¹ sec.
2734	5177	0.00444	6.98
3864	3953	0.00592	6.39
4150	3767	0.00628	6.85
4335	3650	0.00656	6.88

Thirty ml. of $0.11547 \text{ M } (C_2H_5)_3N$ and $0.06421 \text{ M } ICH_2I$

1502	5284	0.00432	6.84
2152	3982	0.00588	6.63
2450	3596	0.00669	6.70
3838	2563	0.01027	6.89
5032	2102	0.01299	6.83
5602	1974	0.01403	6.80

$$k = (6.80 \pm 0.03) \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

Table 46

$(C_2H_5)_3N$ and $ClCH_2I$ in $C_6H_5NO_2$ at $24.8^\circ C$.

Thirty ml. of $0.11547 \text{ M } (C_2H_5)_3N$ and $0.04207 \text{ M } ClCH_2I$

Time in Min.	Resistance in Ohms	moles Per Liter Salt Formed	$k \times 10^5$ l. mole ⁻¹ sec. ⁻¹
271	4252	0.00300	3.99
304	3881	0.00331	3.94
352	3467	0.00377	3.91
440	2897	0.00473	3.99
530	2509	0.00548	3.89

$$k = (3.93 \pm 0.05) \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

Table 47

NaOH and $C_2H_4Br_2$ in 50 Per Cent Aqueous

Dioxane at $36.5^\circ C$.

Thirty ml. of 0.02365 N NaOH and 0.02305 M $C_2H_4Br_2$
were titrated against 0.0307 N HCl.

Time in Min.	Titer in ml.	$k \times 10^2$ l. mole ⁻¹ min. ⁻¹
0	28.33	-----
40	26.26	7.53
65	25.19	7.81
130	23.05	7.48
200	21.14	7.45
280	19.24	7.57
359	17.87	7.64
1443	9.69	7.73

$$k = (7.60 \pm 0.15) \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Table 48 NaOH and $CH_2=CHBr$ in 50 Per Cent Aqueous-

Dioxane at $36.5^\circ C$.

Thirty ml. of 0.0289 N NaOH and 0.0274 M
vinyl bromide were titrated against 0.1071 N NaOH.

Time in Min.	Titer in ml.	$k \times 10^{-4}$ l. mole ⁻¹ min. ⁻¹
0	3.26	-----
1200	7.97	5.1
4095	7.35	7.0
6870	7.65	2.34
8310	5.59	10.4
10320	7.58	8.9

Table 1

Extent of substitution in the Reaction

Between NaOH and $C_2H_4Br_2$ in 50 Per Cent Dioxane at $36.5^\circ C$.Thirty ml. of 0.02865 N NaOH and 0.01373 M $C_2H_4Br_2$

H Cl.

Time in Hrs.	Titer in ml.	NaOH used moles/l.	NaOH used if no substitution occurs.	Fraction of Substitution
45	14.74	0.01365	0.01336	0.0217
69	14.57	0.01363	0.01366	0.0161

APPENDIX C
GRAPHS

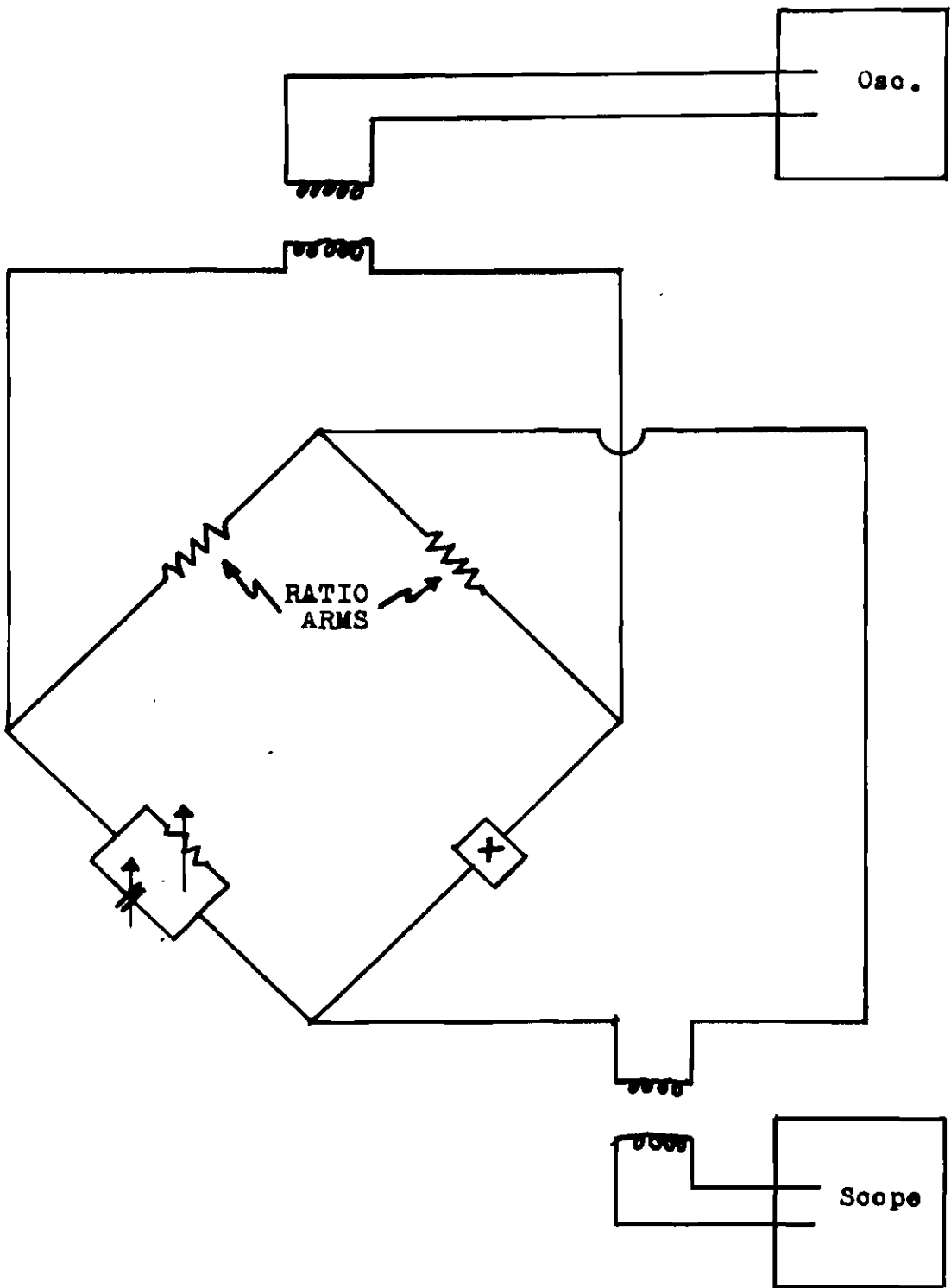


Figure 1.--Circuit Diagram of Conductivity Bridge.

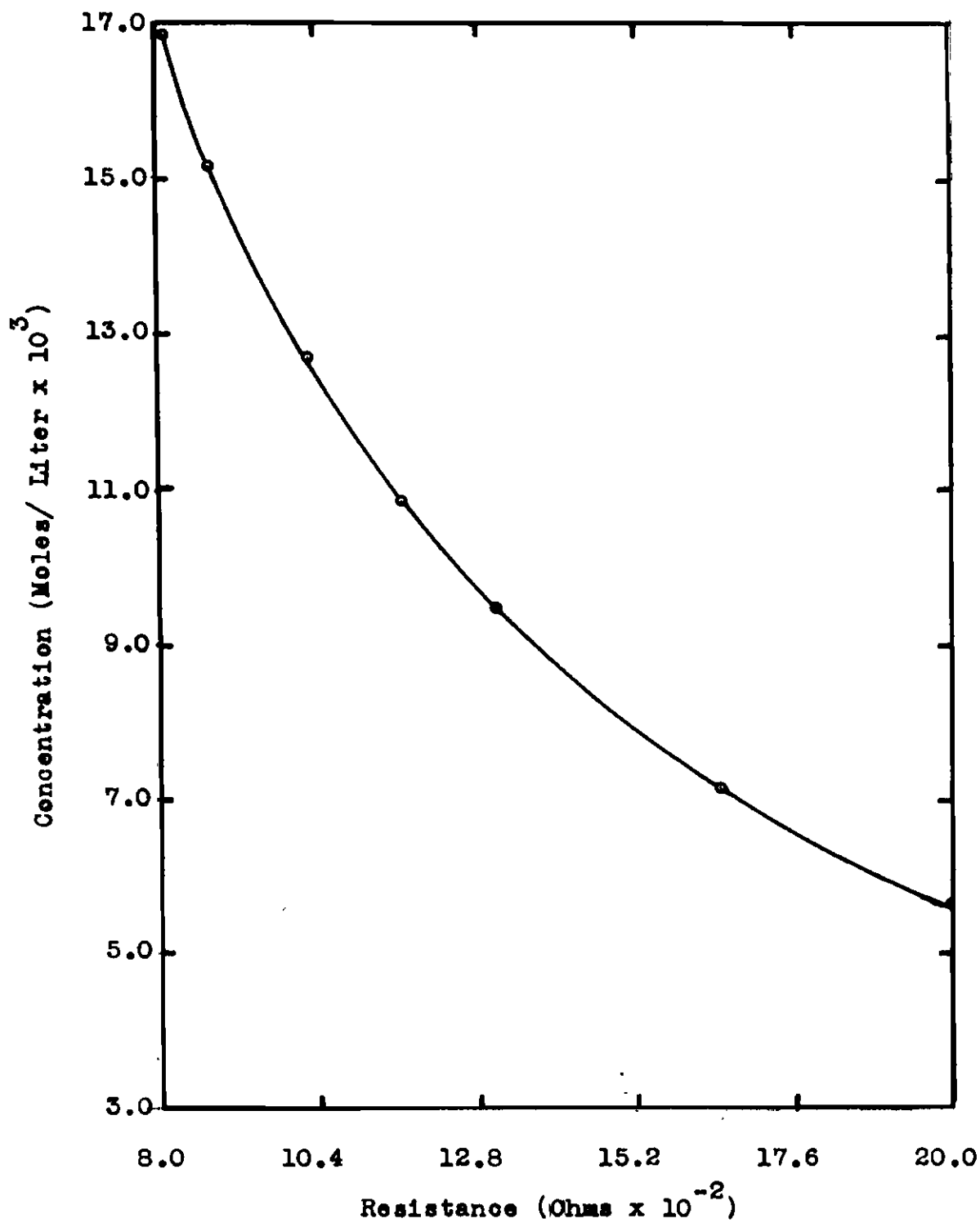


Figure 2.--Concentration Versus Resistance of $\text{CH}_3\text{N}(\text{C}_2\text{H}_5)_3\text{I}$ Solutions in Nitrobenzene at 24.8°C .

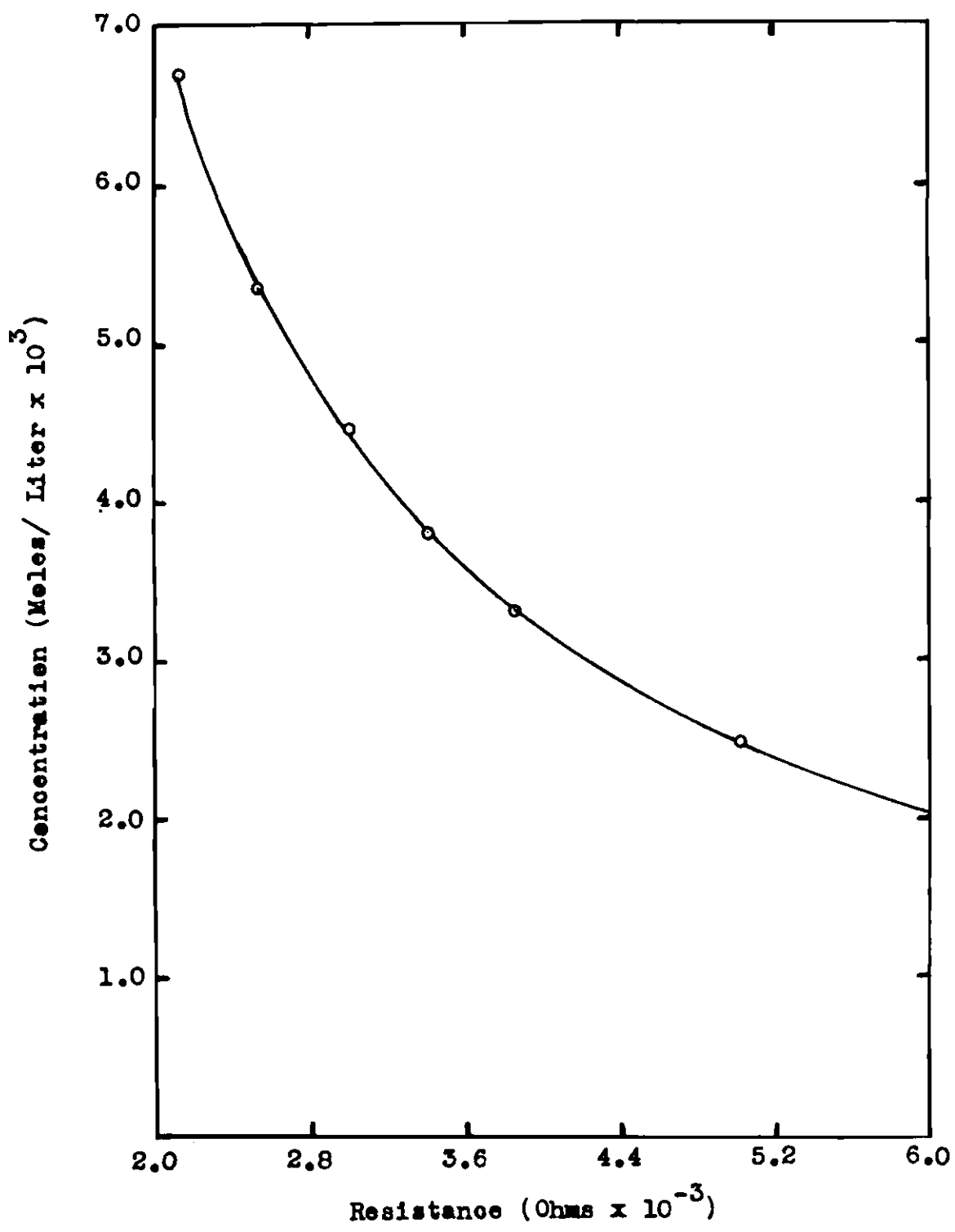


Figure 3.--Concentration Versus Resistance of $\text{ClCH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{I}$ Solutions in Nitrobenzene at 24.8°C .

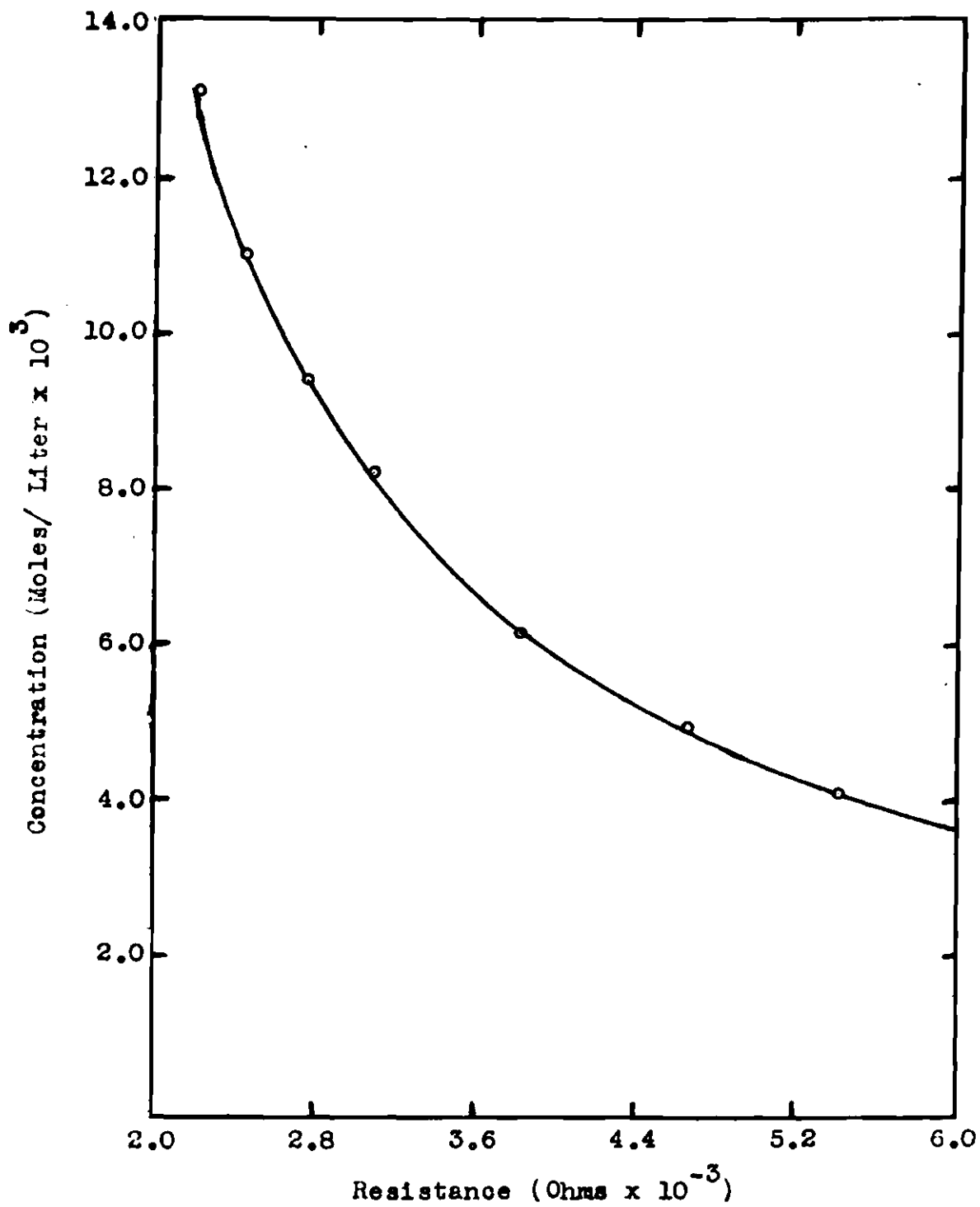


Figure 4.--Concentration Versus Resistance of $\text{ICH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{I}$ Solutions in Nitrobenzene at 24.8°C .

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VITA

Walter Howe Brader Jr. was born October 30, 1927 in Beaumont, Texas. His elementary and high school education were received at the South Park Schools in Beaumont, Texas; graduation from high school occurred May 22, 1944. While working at night in the Sun Oil Company garage in Beaumont, Texas, further education was pursued at Lamar Junior College from February, 1945 until graduation in June of 1946 with an A. A. degree. Studies were begun at the Rice Institute in September of 1947, and a B. A. degree in Chemistry completed in June of 1950. After receiving the B. A. degree a position was taken with the Sun Oil Company at their Delhi, Louisiana gasoline plant; however that position was resigned January, 1951 in order to accept a graduate assistantship at Georgia Tech. While at Georgia Tech research grants from the Research Corporation of New York and the National Science Foundation were held.