

RELATIVE NUCLEOPHILICITIES OF ANIONS IN ACETONITRILE WHOSE
COUNTERION, POTASSIUM, IS COMPLEXED BY 18-CROWN-6

A THESIS

Presented to

The Faculty of the Division of Graduate Studies

By

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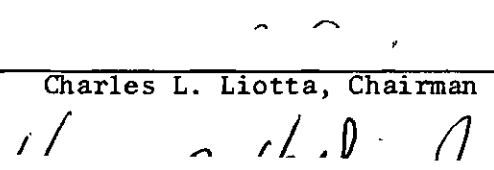
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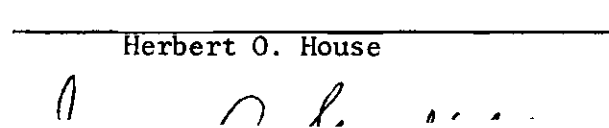
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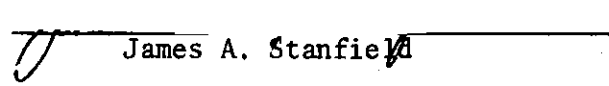
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SUMMARY

An order of nucleophilicities of bromide, chloride, iodide, fluoride, acetate, azide, cyanide, and thiocyanide ions, plus thiourea, were determined by reacting the potassium salt ($4-8 \times 10^{-4} \text{M}$) of each with the substrate, benzyl tosylate (0.01M), in an acetonitrile solution containing 0.10M 18-crown-6. The reactions were followed by conductance techniques. Pseudo first order and second order rate constants were calculated by standard methods and provide the basis for the relative order of nucleophilicities. This order is $\text{N}_3^- \geq \text{OAc}^- > \text{CN}^- > \text{F}^- > \text{Cl}^-, \text{Br}^- > \text{I}^- > \text{SCN}^- \gg \text{thiourea}$. The magnitude of the relative nucleophilicities varies by a factor of 50 if thiourea is neglected.

CHAPTER I

HISTORICAL INTRODUCTION

It has only been in the last few decades that relative nucleophilicities of anions toward organic and inorganic substrates have been the subject of extensive research. Probably the most intensified area of this research involved the bimolecular substitution reaction (S_N-2) which was proposed by Hughes, Ingold, and coworkers in 1935 [1] to explain the observations of second order kinetics in many reactions.

The first attempt to correlate a large number of nucleophilic reactivities (i.e., water, halides, hydroxide ion, etc.) for the bimolecular substitution reaction was made by Swain and Scott in 1953 [2]. A two parameter equation was used with methyl bromide being designated the standard substrate with a value of 1.00 and water the standard nucleophile with a nucleophilicity of 0.00. This equation is,

$$\text{Log } \frac{k}{k_o} = SN$$

where S = constant characteristic of the substrate
 N = nucleophilicity of the nucleophile
 k_o = rate constant for water as the nucleophile
 k = rate constant for any other nucleophile.

A second attempt at correlating nucleophilic order was made by Edwards [3] in 1954. He proposed a four parameter equation relating

basicity and polarizability to nucleophilicity. This equation is,

$$\text{Log } \frac{k}{k_0} = AP + BH$$

where P is a measure of the nucleophile's polarizability,
H is a measure of the nucleophile's basicity, and
A and B are constants characteristic of the substrate.

The order of reactivities found by both Edwards and Swain and Scott are in good agreement although there are differences in the magnitude of reactivity for some nucleophiles. Exceptions to these nucleophilic orders have also been found [4]. Iodide ion, for example, is about ten times as reactive as hydroxide ion towards 2,3-epoxypropanol in aqueous solution, but is about 12 times less reactive toward the ethylene- β -chloroethylsulfonium ion. Similarly, pyridine is about six times as reactive as triethylamine towards isopropyl iodide, whereas triethylamine is about 26 times as reactive as pyridine towards methyl iodide.

These anomalies have been discussed by several authors with numerous factors being recognized as important in determining nucleophilicities. Bunnett [5] has listed 17 factors which he feels influence nucleophilic reactivity. The Alpha effect (i.e., the enhancement of nucleophilicity caused by an atom adjacent to the attacking atom of the nucleophile having one or more pairs of unshared electrons), polarizability, basicity, and more recently ion pairing, solvation, and sybotic effects have all been used to explain deviations from the nucleophilic order found by Edwards, and Swain and Scott.

Winstein and coworkers [6] observed that the nucleophilic order of halide ions in acetone is the reverse of that observed in water by Edwards, and Swain and Scott in the second order reaction of tetra(n-butyl)ammonium halides with n-butyl brosylate at 25°C and iso-butyl tosylate at 50°C. The nucleophilic order for both substrates was $\text{Cl}^- > \text{Br}^- > \text{I}^-$ with the relative reactivities of both series being similar in magnitude. Lithium halides were also investigated in acetone and were observed to have the same nucleophilic order ($\text{I}^- > \text{Br}^- > \text{Cl}^-$) as found in water. This result also agrees with work done by Ingold and coworkers [7a,b,c] who observed the order to be $\text{I}^- > \text{Br}^- > \text{Cl}^-$ for the reaction between various alkyl bromide substrates and lithium salts in acetone at 25°C. Winstein and coworkers suggested the difference in nucleophilic order of the halide ions in acetone is due to ion-association (ion pairing). They found that if the apparent second order rate constant (k') found for each salt was divided by the degree of dissociation (α) of the salt at the concentration employed in the kinetic experiment, the resulting second order rate constants (k) were almost identical (Table 1) for the lithium and ammonium salts. Furthermore, the relative order of reactivity of the halide ions was $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in both systems.

The observation that the same order of nucleophilicity and similar reactivity for halide ions can be obtained in acetone with different salts by correcting for ion association led Winstein and coworkers to suggest that ion pairing can control the apparent nucleophilicity of ions and that the dissociated ion is much more reactive than the ion pair.

Table 1. Summary of Rate Constants for the Reaction of n-Butyl Brosylate with 0.04M Salts in Acetone at 25°C

Salt	$10^3 k'$ (l/m-sec)	$10^3 k$ (l/m-sec)
(<u>n</u> -Bu) ₄ NCI	33.5	58
LiCl	0.493	51
(<u>n</u> -Bu) ₄ NBr	9.09	13
LiBr	2.81	12
(<u>n</u> -Bu) ₄ NI	1.68	2.0
LiI	2.97	3.6

The apparent reversal of the nucleophilic order for the halide series from that found in water was confirmed by Weaver and Hutchison [8] who observed the second order rate constants for the reactions between methyl tosylate and lithium halides in dimethylformamide at 0°C are in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. The relative rates were found to be $\text{Cl}^- (7.8) : \text{Br}^- (3.3) : \text{I}^- (1.0)$. When corrections were made for ion pairing the order remained the same, but an increase in relative rates $\text{Cl}^- (9.1) : \text{Br}^- (3.4) : \text{I}^- (1.0)$ was observed.

Weaver and Hutchison believed the difference in nucleophilic order and relative rates obtained in DMF from that in water was caused by preferential solvation of anions with high charge density (e.g., Cl^-) in protic solvents. This was demonstrated by reacting methyl tosylate with lithium halides in 9% water-DMF solution and obtaining a 24-fold reduction in the observed rate of displacement for the chloride ion but only a two-fold retardation for iodide.

These results substantiate the hypothesis by Acree [9] who earlier (1912) stated the decrease in second order rate constants with an increase in salt concentration was due to incomplete salt dissociation, and that ion pairs were much less reactive than the dissociated ion. It is also apparent that the extent of ion pairing in aprotic solvents decreases with increasing ionic size and is relatively unimportant for large cations such as tetra(n-butyl)ammonium.

The reversal in reactivity observed for the halide series when going from water to acetone or DMF indicates solvation of the anion plays an important role in determining nucleophilic order. This was further elucidated by studies of Parker and coworkers who observed that going from protic (e.g., methanol, 10% dioxane-formamide) to dipolar aprotic (e.g., CH_3CN , acetone, DMSO, DMF) solvents, large increases in rates of reactions occurred. Thus, aromatic nucleophilic substitution ($\text{S}_{\text{N}}\text{Ar}$) [10] reactions have been observed to have a rate enhancement of as much as 10^5 when going from protic to dipolar aprotic solvents, whereas a 10^7 increase has been observed for aliphatic nucleophilic substitution [11]. Parker [11] also observed that the nucleophilic order ($\text{CN}^- > \text{F}^-, \text{Cl}^-, \text{N}_3^-, \text{Br}^- > \text{SCN}^- > \text{picrate}$) obtained from the reaction of methyl iodide with various potassium, sodium, and lithium salts in dimethylformamide was the reverse of that found in water.

Parker [12] has described these results in terms of the varying abilities of the anion to hydrogen bond to the solvent molecules. The greater reactivity of the large, highly polarizable nucleophiles such as iodide and thiocyanide ions in protic solvents is thought to be due to the lack of strong hydrogen bonding of these anions to the solvent.

The large nucleophiles should exhibit a smaller increase in reactivity as compared to the smaller, more strongly hydrogen bonded nucleophiles such as fluoride and chloride ions when the solvent is changed from protic to dipolar aprotic. An order of susceptibility of the anion to hydrogen bond to the solvent is suggested to be $F^- > Cl^-, CN^- > Br^-, N_3^- > I^- > SCN^-$. Fuchs and coworkers [13] have challenged the order of solvation of anions in dipolar aprotic solvent proposed by Parker and coworkers and claim to "find no compelling evidence that large anions are, in fact, more strongly solvated than small anions in dipolar aprotic solvents." Instead, they observed the solvation order for the halide series to be the same as in water, $Cl^- > Br^- > I^-$. This conclusion arrived at from an analysis of the measured enthalpies of solution for LiCl, LiBr, LiI, KBr, and KI in DMSO by calorimetric methods. The enthalpy change accompanying the transfer of the salt from the gas phase to solution, ΔH_{solv} , was calculated using the relationship $\Delta H_{solv} = \Delta H_{soln} - \text{crystal lattice energy}$. These values for DMSO are tabulated in Table 2 and compared to the values for water.

Table 2. Enthalpies of Solvation and Solution of Some Alkali Halides in DMSO and Water at 25°C

Salt	ΔH_{soln} (DMSO)	ΔH_{soln} (H ₂ O)	Lattice Energy	ΔH_{solv} (DMSO)	ΔH_{solv} (H ₂ O)
LiCl	-10.9	-8.85	203.4	-214.3	-212.2
LiBr	-12.1	-11.62	191.4	-208.4	-203.0
LiI	-24.2	-15.13	177.0	-201.2	-192.1
KBr	-2.7	-4.75	162.1	-164.8	-157.4
KI	-6.5	-4.86	151.1	-157.6	-146.2

Recently the study of bimolecular substitution reactions and the association of acetonitrile with halide ions in the gas phase has produced some interesting results. Yamdagni and Kebarle [14] have observed that as the size of the halide ion increased, association by acetonitrile becomes more favorable in the order $I^- > Br^- > Cl^- > F^-$ relative to water.

Young, Lee-Ruff, and Bohme [15] have shown for the bimolecular substitution reaction of H^- , NH_2^- , OH^- , and F^- with methyl chloride in the gas phase at $300^\circ K$, $X^- + CH_3Cl \rightarrow CH_3X + Cl^-$, that the nucleophilic reactivities (Table 3) are the same within experimental error ($\pm 30\%$) and do not follow the gas phase basicity order ($NH_2^- > H^- > OH^- > F^-$). This suggests that solvation of the anions is responsible for the observed differences found for the reactivities of the anions in solution.

Table 3. Rate Constants for the Nucleophilic Substitution with CH_3Cl in the Gas Phase at $300^\circ K$

Nucleophile	Rate Constants, $k \times 10^9$ ($cm^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)
H^-	2.5
F^-	1.8
OH^-	1.9
NH_2^-	2.1

However, Brauman and coworkers [16] have observed for the gas phase reactions of the nucleophiles F^- , Cl^- , and SCH_3^- with the substrates CH_3Cl and CH_3Br a nucleophilic order of $F^- > SCH_3^- > Cl^-$. The

relative nucleophilicity is 10:1:0.1 towards methyl chloride and 8:2:1 towards methyl bromide. The order of reactivity of the halide ions, fluoride, and chloride is similar to that found in acetone as mentioned earlier.

The number of reversals in the nucleophilic order relative to water has generally been limited to the halide series and to dipolar aprotic solvents. Recently, however, several reversals over a wide range of nucleophiles have been reported.

The reaction of tetraphenylarsonium salts with methyl iodide [17] in acetonitrile at 25°C and also with methyl tosylate [18] under the same conditions was observed to follow a significantly different nucleophilic order when compared to the water results, as can be seen in Table 4.

Table 4. Rate Constants for Various Nucleophiles Reacting with Methyl Iodide and Methyl Tosylate in Acetonitrile at 25°C and at Concentrations less than $10^{-2}M$

Nucleophiles	k_{MeI} (l/m-sec)	k_{OTs} (l/m-sec)
CN^-	26.5	---
OAc^-	4.8×10^{-1}	2.6×10^{-1}
N_3^-	2.4×10^{-1}	2.5×10^{-2}
Cl^-	7.0×10^{-2}	2.3×10^{-2}
Br^-	---	5.0×10^{-3}
NCS^-	2.1×10^{-2}	2.3×10^{-4}

Interestingly, the reactivity of the cyanide ion was found to be greater than that of the other nucleophiles when the substrate was methyl iodide. This is just the opposite to the results of Bohme and coworkers [19] who found CN^- to be much slower relative to other anions in the gas phase.

It is interesting to note that the nucleophilic order corresponding to both of the substrates, methyl iodide and methyl tosylate, are the same but the magnitude of the nucleophilic orders differs by a factor of 50 if the cyanide ion is neglected.

Fuchs and coworkers [20] have obtained similar results in DMSO at temperatures adjusted to 25°C. Reacting tetra(n-butyl)ammonium salts with n-propyl tosylate, they obtained a larger spread in the rate constants (Table 5) than Engemyr and Songstad. This should be expected since DMSO is a much stronger dipolar aprotic solvent and according to Parker, solvation although weak, does play an important role in nucleophilic reactivity.

Pedersen [21a,b,c] discovered that macrocyclic polyethers (crown ethers) possess the ability to form crystalline complexes with a variety of inorganic salts and, furthermore, increased the solubility of many salts in aprotic organic solvents. This has led to investigations by several workers on the effects of crown ether on bimolecular nucleophilic substitution reactions.

It has been observed that potassium salts (F^- , Cl^- , Br^- , I^- , CN^- , N_3^- , and OAc^-) dissolved in acetonitrile containing 0.10M 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) are much more soluble than in identical solutions without 18-crown-6 [22]. Several workers [23,24,25] have

Table 5. Rate of Tosylate Displacement in DMSO Adjusted to 25°C

Nucleophile	k (l/m-sec)
$S_2O_3^{-2}$	9.4×10^{-1}
F^{-*}	2.0×10^{-1}
N_3^{-}	2.7×10^{-3}
Cl^{-}	9.5×10^{-4}
Br^{-}	4.1×10^{-4}
I^{-}	1.2×10^{-4}
SCN^{-}	3.4×10^{-5}

*Hexyl tosylate was used as the substrate

also observed that many potassium salts are more highly dissociated in aprotic solvents containing 18-crown-6. Liotta has termed these free anions "naked anions."

Studies by Liotta and coworkers on the bimolecular nucleophilic substitution reactions of the nucleophiles F^{-} [26], CN^{-} [27], OAc^{-} [28] in acetonitrile containing 18-crown-6 with a large number of substrates have shown them to be extremely reactive. Fluoride and acetate ions, which are usually thought of as poor nucleophiles, are now shown to be two of the best.

The research described herein was conducted to develop an order of nucleophilicities in the hope that it will be similar to the inherent scale of nucleophilicities both in order and magnitude for a large number of nucleophiles. To date, most studies reported on relative nucleophilicities have been performed in solvents of high dielectric

constant and solvating power (water, DMF, $\text{CH}_3\text{CH}_2\text{OH}$ -water, etc.), thus increasing the probability that major external factors such as solvation and ion pairing may markedly influence the nucleophilicities of the anion. The recently reported success of Liotta and coworkers to solubilize successfully potassium salts in acetonitrile containing 18-crown-6 resulting in increased reactivity even for such nucleophiles as fluoride and acetate ions which are usually considered weak nucleophiles, has led to the proposal that the anions are relatively "free" in acetonitrile containing 18-crown-6. Conductance studies [23] on these solutions have supported this idea. Consequently, the development of a scale of relative nucleophilicities in acetonitrile containing 18-crown-6 should be similar to the inherent scale.

CHAPTER II

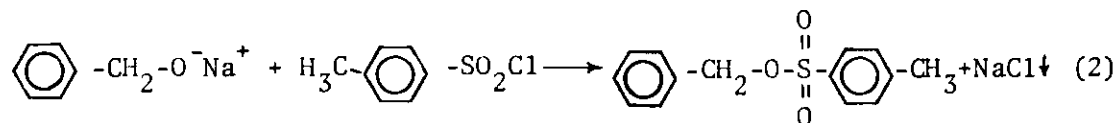
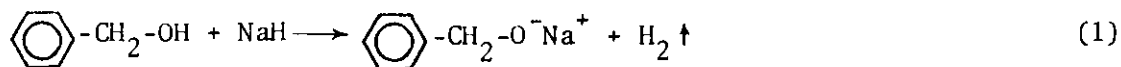
EXPERIMENTAL

Reagents

Acetonitrile. A.C.S. certified acetonitrile was obtained from Fisher Scientific Company, Atlanta, Georgia. It was dried by refluxing a minimum of four hours over CaH_2 , then distilling into another vessel containing CaH_2 and refluxed again for a minimum of four hours. The acetonitrile was distilled from the second vessel just prior to use.

Potassium Salts. Each of the potassium salts used in this study were Fisher Certified A.C.S. Reagent grade, except for potassium azide which was obtained from Ventron, Beverly, Massachusetts and was of Highest Purity. All salts were vacuum (0.3mm Hg) dried for a minimum of 24 hours.

Thiourea. Baker Analyzed Reagent thiourea was sublimed, then dried under vacuum (0.3mm Hg) for a minimum of 24 hours. M.P. 181°C (Lit. 182°C) [41].

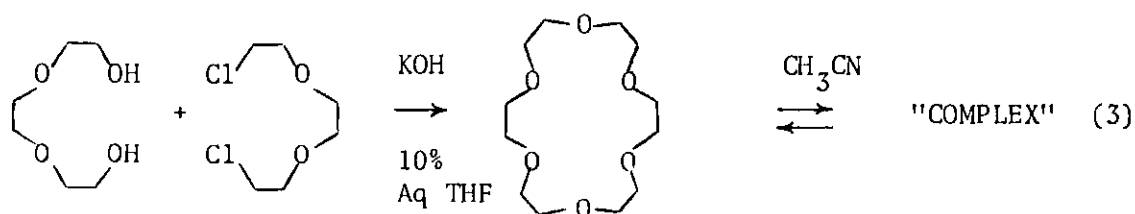
Preparation of Benzyl Tosylate [29].

Benzyl tosylate was prepared by the method of Kochi and Hammond [29]. A 500 ml three-necked round-bottomed flask equipped with a reflux condenser, water-cooled bearing, Drierite drying tube, mechanical

stirrer, and a gas outlet tube was charged with 10 ml (0.097 mol) benzyl alcohol (Fisher) and 100 ml anhydrous ether. After stirring for a few minutes, 2.4 g. (0.10 mol) NaH (Ventron) was added; the solution was then stirred and refluxed for 12 hours under nitrogen. The resulting sodium alkoxide was then cooled to about -20°C with a dry ice bath and a mixture of 19.5 g. (0.10 mol) p-toluenesulfonyl chloride (Eastman) and 100 ml anhydrous ether added dropwise to the suspension over a period of about 30 minutes. The reaction was then stirred for two hours at -10°C and one hour at room temperature. To avoid exposure to moist air, a filter stick (Figure 1) was used to filter the mixture. The mixture was filtered several times under reduced pressure, until a clear solution was obtained and then the filtrate cooled in a dry ice-acetone bath until a copious white precipitate formed. The precipitate was quickly filtered and recrystallized several times with petroleum ether. Yield 3.0 g.; 12%; M.P. $57-57.5^{\circ}\text{C}$ (Lit. $58-58.4^{\circ}\text{C}$).

Preparation of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

[31].



18-Crown-6 was prepared and purified by the method of Gokel, Cram, Liotta, Harris, and Cook [31]. The preparation was accomplished by adding 60% KOH (218 g. of 85% KOH in 140 ml water) to 225 g. (0.75 mol) triethylene glycol (Matheson, Coleman, and Bell) and 1000 ml

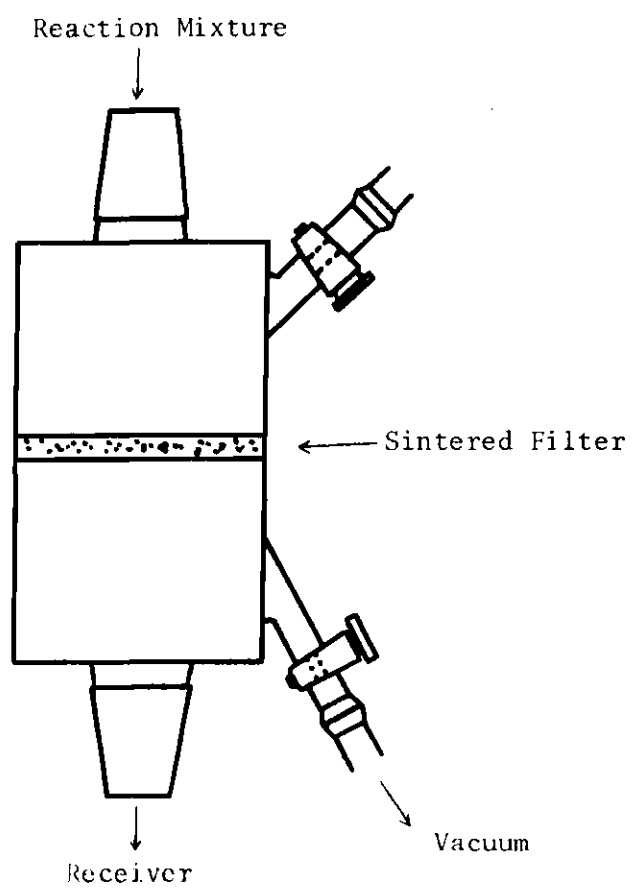


Figure 1. Filterstick [30]

THF (Fisher) in a 3000 ml three-necked round-bottomed flask equipped with a reflux condenser, 500 ml dropping funnel, and a mechanical stirrer with a water-cooled bearing. After the mixture was stirred for about one hour, a solution 3,6 dioxo-1,8 dichlorooctane (Eastman, 380 g. 0.75 mol) in 200 ml THF was added in a thin stream. The reaction mixture was stirred vigorously and heated at reflux for 18 hours after which it was allowed to cool and the major portion of the THF removed under reduced pressure. The resulting slurry was diluted with 1000 ml dichloromethane (Fisher) and filtered. The filtrate was dried over MgSO_4 . Dichloromethane was removed under reduced pressure and the remaining liquid distilled under vacuum (0.3-0.4mm Hg). The 18-crown-6 was collected between 100-160°C. To purify the crude crown ether a 250 ml Erlenmeyer flask was charged with 137 ml acetonitrile (Fisher) and the crown ether, and then gently heated, with stirring, until the slurry dissolved. The top of the flask was then equipped with a Drierite drying tube and the solution allowed to cool to ambient temperature. The flask was then cooled with stirring in an ice-acetone bath and the precipitate quickly filtered under reduced pressure. After transferring the crystals to a 250 ml round bottomed flask, the excess acetonitrile was removed under high vacuum (0.2-0.3mm Hg) with gentle heating (ca. 40°C) over 2-3 hours. M.P. 36-37.5°C (Lit. 39-40°C) [32].

Instrumentation

Nuclear Magnetic Resonance Spectrometer. All N.M.R.'s were obtained using a Varian T-60 spectrometer.

Conductivity Bridge. All conductance data were obtained using a Beckman Conductivity Bridge, Model RC-18A with an oscillating frequency

of 1 KHz.

Melting Point Apparatus. A Mel-temp unit was used to obtain all melting points in degrees Centigrade using an uncalibrated thermometer.

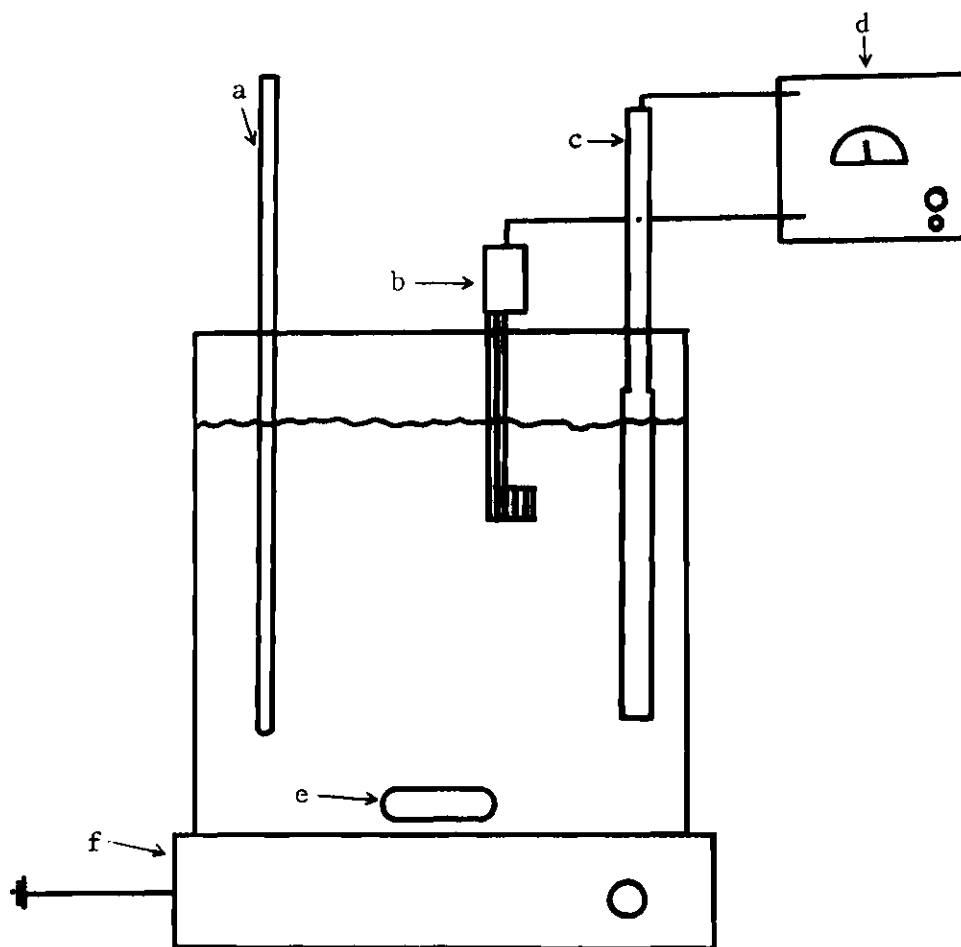
Weighing Balance. A 5 place Mettler H 20 T balance was used for weighing all potassium salts and thiourea. A Mettler type H-15, and a Mettler K-7 macro balance were used for all other weighings.

Conductance Cell. A conductance cell, No. 3403, K = 1.0 from Yellow Springs Instrument Company was used for all kinetic runs.

Infra-red Spectrophotometer. A Beckman IR-12 spectrophotometer was used for all infra-red work.

Constant Temperature Bath. A Precision Temperature Controller, Model 116, from Bayley Instrument Company along with a small immersion heater, were used to control the temperature (Figure 2) to the nearest 0.05°C. The container for the bath was a tall form, 1000 ml Pyrex beaker wrapped with tinfoil to help insulate the solution. A Fisher magnetic stirrer, along with a 1-1/2" x 1/2" stirring bar was used to agitate the constant temperature bath.

Sealing Benzyl Tosylate in Glass Bulbs. Glass bulbs were made from 6mm glass tubing such that the bulb was approximately 15mm in diameter with a 20mm stem. The bulbs were allowed to cool, then numbered using a Magic Marker and weighed. Under dry nitrogen atmosphere, the benzyl tosylate was placed in the glass bulbs then removed from the dry box one at a time and quickly sealed. After cooling the bulbs were weighed again to obtain the amount of benzyl tosylate present then were stored in a refrigerator until required. The benzyl



- a -10 to 55°C Thermometer
- b Heater
- c Thermocouple
- d Temperature Controller
- e Stirring Bar
- f Magnetic Stirrer

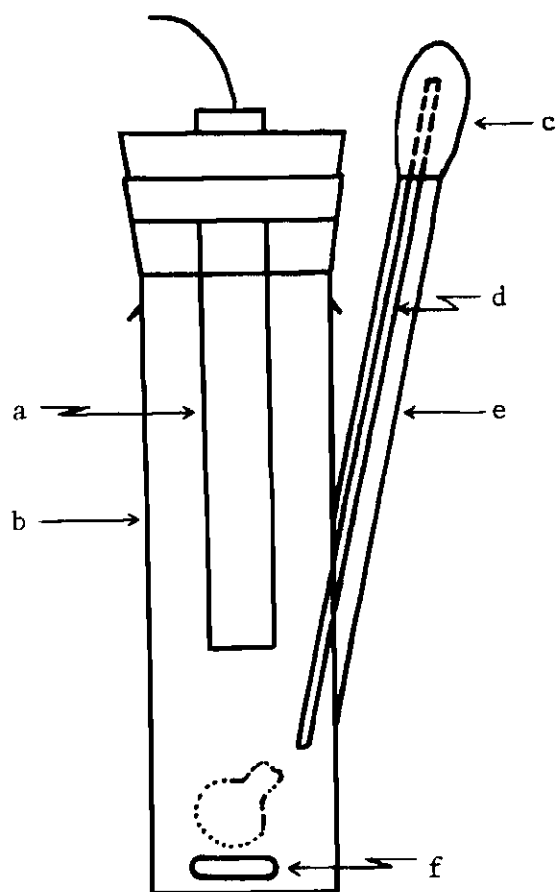
Figure 2. Constant Temperature Bath

tosylate was stored for as long as 3-4 weeks without decomposing.

Kinetic Procedure

The following procedure was used for the preparation of all reactions in which the kinetic measurements were performed. For the thiourea experiment the same procedure was followed except 18-crown-6 was not added. The potassium salt was added to a preweighed 1 ml weighing bottle, stoppered, removed from the dry box, and weighed. It was then quickly returned to the dry box and this procedure continued until a weight was obtained which would result in a concentration of $(4-8) \times 10^{-4} \text{ M}$. To a clean, dry 50 ml volumetric flask was added 1.33 g. $(5.28 \times 10^{-3} \text{ M})$ 18-crown-6 and freshly distilled acetonitrile which had been refluxed over CaH_2 added to the mark. A small stirring bar (1/2" x 1/8") along with the 1 ml weighing bottle containing the potassium salt was added then the flask was stoppered and allowed to stir overnight (ca. 15-20 hours). Any error induced by adding the potassium salt to the already filled volumetric flask was felt to be negligible due to the small quantities of salt compared to the volume being used. Also the salt was added to the 18-crown-6/acetonitrile solution in a weighing bottle to remove any error which might be caused by transferring the salt from the weighing bottle to the volumetric flask.

The following procedure was used in all kinetic experiments and all operations were performed in a dry box. After stirring the salt/18-crown-6 solution, it was poured into the reaction vessel (Figure 3). One glass bulb containing the substrate benzyl tosylate and a medium stirring bar (1-1/2" x 1/2") were also added. The vessel was sealed



- a Conductance Cell
- b Reaction Vessel
- c Rubber Diaphragm
- d Glass Rod
- e Side Arm
- f Stirring Bar

Figure 3. Reaction Vessel and Conductance Cell

by inserting the conductance cell and securing tightly with two rubber bands. The reaction vessel was then removed from the dry box and placed in the constant temperature bath (30°C) and connected to the conductance bridge. Equilibrium of the reaction solution was obtained with the constant temperature bath by following the conductance and noting when it became constant. This usually required about 15 minutes. Once the system equilibrated and the initial ($t=0$) conductance recorded, the benzyl tosylate was released to the solution by breaking the glass bulb with the glass rod in the vessel's side arm. The time was recorded when the bulb was broken and then at one-minute increments, the time and conductance were recorded. As the reaction slowed down, conductance readings were taken at larger intervals, usually with the sequence of two minutes, five minutes, ten minutes, fifteen minutes, etc. When conductance readings failed to change, it was assumed the reaction was complete.

Preliminary kinetic experiments for each nucleophile studied, except thiourea, were run in order to develop an easy, efficient method to be used for each nucleophile. The final rate constants are an average of three or more runs except for the fluoride ion (2) and thiourea (1). One reaction with thiourea was run in order to determine if its reactivity would be less than all other nucleophiles investigated, since it is a much weaker base than all others and it appeared that the reactivity order of the nucleophiles was following their basicity order.

Contamination by water proved to be the major problem in obtaining reproducible data. To insure minimum effects from the presence of water, each reaction was conducted in freshly distilled acetonitrile

which had been refluxed over CaH_2 . It has been estimated [42] this will reduce a water concentration to about 10^{-5}M . All salts were dried just prior to use. Also all solutions were made up in a nitrogen filled dry box. After each reaction the conductance cell, weighing bottle, reaction vessel, and 50 ml volumetric flask were washed with acetone and demineralized water. The conductance cell was dried with air from a heat gun, and the reaction vessel, weighing bottle, and 50 ml volumetric flask were dried in an oven at 100°C .

All readings taken from the conductance bridge were in conductance (mhos). In order to be able to relate directly to concentration, the conductance was transformed to equivalent conductance using the equation

$$\Lambda = \frac{1000 \text{ kL}}{C_s} \quad (4)$$

where Λ = equivalent conductance ($\text{cm}^3/\text{equiv-ohm}$)

L = conductance (mho)

k = cell constant (1.077)

C_s = salt concentration

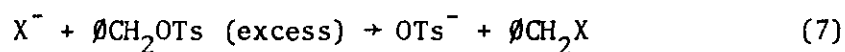
All kinetic studies were performed under pseudo first order conditions, i.e., the substrate benzyl tosylate was always at least 10 times the salt concentration. Since equivalent conductance (Λ) is proportional to concentration, conductance values can be used in place of concentration for the pseudo first order equation:

$$\text{Log } C = \text{Log } C_o - \frac{k't}{2.3} \quad (5)$$

If Λ_0 is the conductance of the nucleophile at zero time, Λ_t , the conductance at time (t), and Λ_∞ the conductance at infinite time, the equation would be,

$$\text{Log } \frac{(\Lambda_t - \Lambda_\infty)}{a - b} = \text{Log } \frac{(\Lambda_0)}{a} - \frac{k't}{2.3} . \quad (6)$$

The derivation of this equation [33] is readily obtained by applying the conductance principle to the following equation which represents the reaction of interest.



Let

$$\Lambda_0 = a(X^-)_0 \quad (8)$$

$$\Lambda_t = a(X^-)_t + b(\text{OTs}^-)_t \quad (9)$$

$$\Lambda_\infty = b(\text{OTs}^-)_\infty \quad (10)$$

(a and b are proportionality constants relating conductance to concentration)

If at infinite time it is assumed that the concentration of the tosylate ion formed is equal to the concentration of nucleophile (X^-) reacted, then,

$$b(\text{OTs}^-)_\infty = b(x^-)_0 \quad (11)$$

$$b(\text{OTs}^-)_t = b(X^-)_0 - b(X^-)_t \quad (12)$$

Therefore, substituting into equations (9) and (10) the following equations are obtained.

$$\Lambda_t = a(X^-)_t + b(OTs^-)_t = a(X^-)_t + b(X^-)_o - b(X^-)_t \quad (13)$$

$$\Lambda_\infty = b(OTs^-)_\infty = b(X^-)_o \quad (14)$$

Subtracting (14) from (13)

$$\Lambda_t - \Lambda_\infty = a(X^-)_t - b(X^-)_t \quad (15)$$

therefore, since $C_t = (X^-)_t = \Lambda_t - \Lambda_\infty/a - b$ and $C_o = \Lambda_o/a$, substituting into the pseudo first order equation one obtains the required equation,

$$\text{Log } \frac{(\Lambda_t - \Lambda_\infty)}{a - b} = \text{Log } \frac{(\Lambda_o)}{a} = \frac{-k't}{2.3} \quad (16)$$

Pseudo first order rate constants were obtained by plotting the $\text{Log } (\Lambda_t - \Lambda_\infty)$ versus time then determining the slope of the line (i.e., $-k'/2.3$) by the method of least squares. The pseudo first order rate constant was then equal to 2.3 times the slope (i.e., $k' = -2.3 \times$ slope). All pseudo first order rate constants were determined from data points taken over a minimum of 75% of the reaction except for thiourea which was over 45%.

To obtain the second order rate constant (k), the pseudo first order rate constant was divided by the concentration of benzyl tosylate,

$$k = \frac{k'}{C_{OTs}} = 1/m\text{-sec} . \quad (17)$$

It should be noted that although care was taken to obtain accurate concentrations for the potassium salts and thiourea, high accuracy for the salts concentration is not needed since when a measurement of $\Lambda(t)$ relative to Λ_0 and Λ_∞ is made so the slope is independent of the salt concentration; however, this is only true when the salts are completely dissociated.

The following procedure was used to determine which of the two nucleophilic atoms (sulfur or nitrogen) of the thiocyanate ion is the end which displaces the tosylate group from benzyl tosylate. A 5 ml beaker containing 0.0294 g. (1.1×10^{-4} mol) 18-crown-6 was charged with 1 ml 0.10M KSCN solution and 1 ml freshly distilled acetonitrile containing 0.0206 g. (7.86×10^{-4} mol) benzyl tosylate. After stirring for about one minute, a portion of the mixture was transferred to a KBr liquid IR cell using a disposable pipette. The remaining solution was covered securely with a strip of parafilm and stored in the dry box. A second KBr liquid cell, to be used as a blank, was filled with a fresh solution of 0.05M 18-crown-6 in acetonitrile. The cells were then quickly transferred to the Beckman IR-12 spectrophotometer at Georgia State University, and the growth and decline of peaks at 2157 cm^{-1} and 2060 cm^{-1} , respectively, were followed using both the transmittance and absorbance modes. This same procedure was used initially to find the product peak(s) between 2250 cm^{-1} and 1950 cm^{-1} for the benzyl derivative [39, 40]. The infra-red spectrum of benzyl tosylate, acetonitrile, and KSCN/18-crown-6 were also recorded between $1000\text{--}2500\text{ cm}^{-1}$.

Preparation of 0.10M KSCN Solution. Freshly distilled

acetonitrile was added to the mark in a 50 ml volumetric flask. To the acetonitrile was added 0.485 g. (4.99×10^{-3} mol) KSCN in a 1 ml weighing bottle. The solution was stoppered tightly and stirred overnight in the dry box.

CHAPTER III

RESULTS AND DISCUSSION

The kinetic study reported herein was performed to determine an order of nucleophilicities for the anions: SCN^- , I^- , Cl^- , Br^- , F^- , CN^- , OAc^- , and N_3^- in dry acetonitrile containing 0.10M 18-crown-6 at 30°C. An experiment run in the absence of 18-crown-6 with the neutral nucleophile thiourea was also conducted to determine how its reactivity would compare to the anions already studied. Table 6 shows the nucleophile, its concentration at $t=0$, pseudo first order rate constant, and calculated second order rate constant for the reaction with benzyl tosylate. Table 7 summarizes the average second order rate constants for each nucleophile and gives their relative rates corresponding to a relative rate of one for SCN^- . The inherent error for any one particular first order rate constant is estimated to be 10%. The standard deviation for each second order rate constant is less than 5% of the rate constant.

The order of reactivity obtained here follows the results published by Songstad and Engemyr [17, 18] and concurs with other results obtained for nucleophilic orders in dipolar aprotic solvents [12, 20, 34]. The reactivity of the nucleophiles varies by only a factor of 50 if thiourea is neglected. This is very small when compared to similar systems such as Songstad and Engemyr [18] (10^3 for methyl tosylate as the substrate in acetonitrile) or Fuchs and coworkers [20] (10^4 for *n*-propyl tosylate as the substrate in DMSO). The reversal in order of reactivity from that found in protic solvents, is typical of dipolar

Table 6. Summary of Concentrations, Pseudo First Order Rate Constants, and Second Order Rate Constants for the Reaction of Potassium Salts, plus Thiourea, with Benzyl Tosylate in Acetonitrile Containing 0.10M 18-Crown-6 at 30°C

Salt	Concentration (M)	k' (sec ⁻¹)	k (1/m-sec)
KN ₃	5.22 x 10 ⁻⁴	9.69 x 10 ⁻³	1.07
KN ₃	4.71 x 10 ⁻⁴	6.58 x 10 ⁻³	0.96
KN ₃	4.58 x 10 ⁻⁴	6.90 x 10 ⁻³	1.01
KOAC	5.60 x 10 ⁻⁴	1.03 x 10 ⁻²	0.96
KOAC	3.95 x 10 ⁻⁴	9.73 x 10 ⁻³	0.92
KOAC	5.07 x 10 ⁻⁴	5.98 x 10 ⁻³	0.96
KCN	5.41 x 10 ⁻⁴	2.37 x 10 ⁻³	0.22
KCN	6.17 x 10 ⁻⁴	2.08 x 10 ⁻³	0.21
KCN	7.98 x 10 ⁻⁴	3.64 x 10 ⁻³	0.26
KF	3.32 x 10 ⁻⁴	1.46 x 10 ⁻³	0.15
KF	6.59 x 10 ⁻⁴	1.47 x 10 ⁻³	0.12
KCl	5.53 x 10 ⁻⁴	2.66 x 10 ⁻³	0.12
KCl	5.90 x 10 ⁻⁴	1.34 x 10 ⁻³	0.11
KCl	5.61 x 10 ⁻⁴	2.52 x 10 ⁻³	0.13
KCl	7.59 x 10 ⁻⁴	1.75 x 10 ⁻³	0.13
KBr	6.74 x 10 ⁻⁴	1.75 x 10 ⁻³	0.13
KBr	6.57 x 10 ⁻⁴	1.42 x 10 ⁻³	0.11
KBr	7.56 x 10 ⁻⁴	7.67 x 10 ⁻⁴	0.11
KI	7.26 x 10 ⁻⁴	2.13 x 10 ⁻³	0.091
KI	7.02 x 10 ⁻⁴	9.81 x 10 ⁻⁴	0.084
KI	7.75 x 10 ⁻⁴	9.20 x 10 ⁻⁴	0.088
KSCN/C.E.	5.59 x 10 ⁻⁴	2.61 x 10 ⁻⁴	0.020
KSCN/C.E.	5.89 x 10 ⁻⁴	1.40 x 10 ⁻⁴	0.021
KSCN/C.E.	6.81 x 10 ⁻⁴	3.75 x 10 ⁻⁴	0.020
KSCN w/o C.E.	7.32 x 10 ⁻⁴	3.35 x 10 ⁻⁴	0.022
KSCN w/o C.E.	6.28 x 10 ⁻⁴	2.84 x 10 ⁻⁴	0.020
KSCN w/o C.E.	7.80 x 10 ⁻⁴	1.76 x 10 ⁻⁴	0.020
Thiourea	5.75 x 10 ⁻⁴	2.05 x 10 ⁻⁴	0.0013

Table 7. Second Order Rate Constants and Relative Rates for the Reaction of Potassium Salts, plus Thiourea, with Benzyl Tosylate in Acetonitrile Containing 0.10M 18-Crown-6 at 30°C.

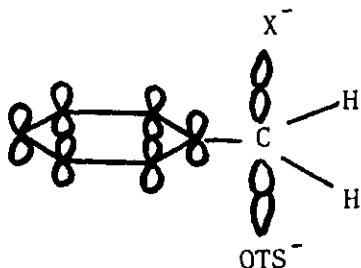
Nucleophile	k (l/m-sec)	Relative Rates
N_3^-	1.01 ^a	50.5
OAc^-	0.95 ^a	47.5
CN^-	0.23	11.5
F^-	0.14 ^b	7.0
Cl^-	0.12 ^b	6.0
Br^-	0.11 ^b	5.5
I^-	0.088	4.4
$\text{SCN}^-/\text{C.E.}$	0.020	1.0
SCN^- w/o C.E.	0.020	1.0
Thiourea	0.0013	0.065

^{a,b} Because of the inherent error in the experiments, the second order rate constants and thus their relative rates can be envisioned as being identical.

aprotic solvents.

The Songstad and Engemyr results are an interesting comparison since they used tetraphenylarsonium salts which should be mostly dissociated in acetonitrile. Comparing the results reported herein to Songstad's (Table 4), it can be seen that the magnitude of their series (methyl tosylate as the substrate) is larger by a factor of 20 and in all cases the nucleophiles are less reactive than those in 18-crown-6 solutions. The greater difference in reactivities for the larger, more polarizable anions is probably due to the ability of the benzyl group

to stabilize the transition state more readily than the methyl group (see below).



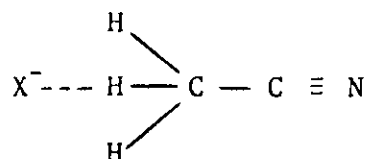
Undoubtedly some ion pairing does occur for the smaller anions (*i.e.*, Cl^- , OAc^-), which would cause a decrease in their reactivity. The higher reactivity of anions in 18-crown-6 also concurs with Sam and Simmons' [25] work. They found that Br^- and I^- in acetone containing dicyclohexyl 18-crown-6 to be more reactive than the corresponding tetra(*n*-butyl)ammonium salts and lithium bromide in acetone without the crown ether. They attribute this difference in reactivity to "significant ion association" (see Table 8).

Table 8. Degree of Dissociation for 0.04M Salts in Acetone at 25°C

Salt	α
KBr/crown ether	0.75 - 0.80
KI/crown ether	0.58 - 1.0
$(\text{Bu})_4\text{NCl}$	0.58
$(\text{Bu})_4\text{NBr}$	0.70
$(\text{Bu})_4\text{NI}$	0.84
LiBr	0.23

Only a slight difference in reactivity of the anions for the halide series was observed as can be seen from Table 7. Some evidence

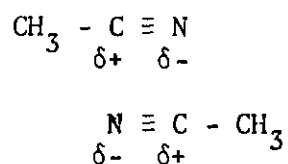
for the similarity in reactivities has been provided by reactions conducted in the gas phase [15] which showed that the nucleophiles (F^- , H^- , NH_2^- , OH^-) had similar reactivities within experimental error ($\pm 30\%$). These results raise the question of how much solvation occurs for anions in acetonitrile containing 18-crown-6 since solvation effects are absent in the gas phase. Some solvation undoubtedly does occur as it has been observed that acetonitrile forms a strong complex with halide ions even in the gas phase [14]. Coetzee and Sharpe [35] have also shown that the presence of halide ions causes a shift to lower wave numbers in the infrared spectrum for the methyl protons of acetonitrile. They propose this shift to be caused by direct interaction between the halide ions and the acetonitrile protons as shown below. Roche and Van Houg [36] made a similar study and came to the same conclusion.



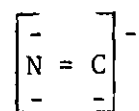
Grimsrud and Kratochvil [37] using conductance methods have observed similar relative reactivities for the anions Cl^- , Br^- , and SCN^- to those listed in Table 7 by reacting n-butyl iodide with the salts, tetraethylammonium chloride and bromide, potassium and sodium bromide, and potassium and sodium thiocyanate in acetonitrile at 25°C. The relative rates observed by Grimsrud and Kratochvil are Cl^- (6.7), Br^- (5.8), SCN^- (1), whereas for this study they are Cl^- (6), Br^- (5.5), SCN^- (1). Corrections were made for ion association in the work by Grimsrud and Kratochvil.

As can be seen from Table 7 the nucleophilic order obtained in this study follows the basicity (towards the proton) of the anions ($\text{CN}^- > \text{N}_3^- \approx \text{OAc}^- > \text{F}^- > \text{Cl}^- \approx \text{Br}^- \approx \text{I}^- \approx \text{SCN}^- > \text{thiourea}$) in aqueous solution except for CN^- , which falls below N_3^- and OAc^- , but above the halides. This result obtained for the reactivity of cyanide ion is contrary to the results obtained by Songstad and Engemyr [17]. They observed that cyanide ion was much greater in reactivity when methyl iodide was the substrate, than all other nucleophiles investigated. Several possible explanations can be made for this anomaly in the reactivity of cyanide ion. First, it is possible that water was a contaminate for all the cyanide experiments resulting in hydrolysis to form hydrocyanic acid and hydroxide ion, which in turn would give an erroneous rate constant due to the reaction of benzyl tosylate with hydroxide ion. This source of error seems improbable, however, since freshly distilled acetonitrile was used for each experiment and the precision for the rate constants obtained was good. All three experiments would have to have similar amounts of water to force the accuracy off, to account for the results obtained herein.

A second possible explanation may be found in Kebarle and Yamdagni's [14] gas phase study of halide solvation by acetonitrile. They pointed out that several workers [38a,b,c,d] have postulated the existence of an acetonitrile dimer (see below) in the gas phase and



gave supporting evidence, i.e., the outer shell solvation enthalpies ($\Delta H_{n,n-1}$) for Cl^- , Br^- , and F^- are about 5 Kcal/mol where as the dissociation energy of the dimer has been estimated to be in the range of 4-7 Kcal/mol. The idea of an acetonitrile dimer can be extended to an acetonitrile-cyanide ion adduct, $\text{CH}_3 - \text{C} \equiv \text{N}$, for a cyanide anion



free of association with its counter ion potassium (K^+). The formation of such an adduct might then reduce the reactivity of the cyanide anion significantly to account for its position in the nucleophilic order shown in Table 7.

The thiocyanide ion is known to be one of the better nucleophiles in protic solvents. As can be seen in Table 7, it was found to be the least reactive in the series of anions when reacted with benzyl tosylate both with and without the presence of 18-crown-6. The facts that addition of 18-crown-6 to the reaction did not change its reactivity, and that Grimsrud and Kratochvil have shown that KSCN is greater than 98% dissociated in acetonitrile at 25°C, confirm that SCN^- in acetonitrile containing 18-crown-6 is essentially free from association with its counter ion potassium (K^+). Also this result confirms earlier reports [11, 17, 18] that in acetonitrile and other aprotic solvents, thiocyanide ion is a poor nucleophile.

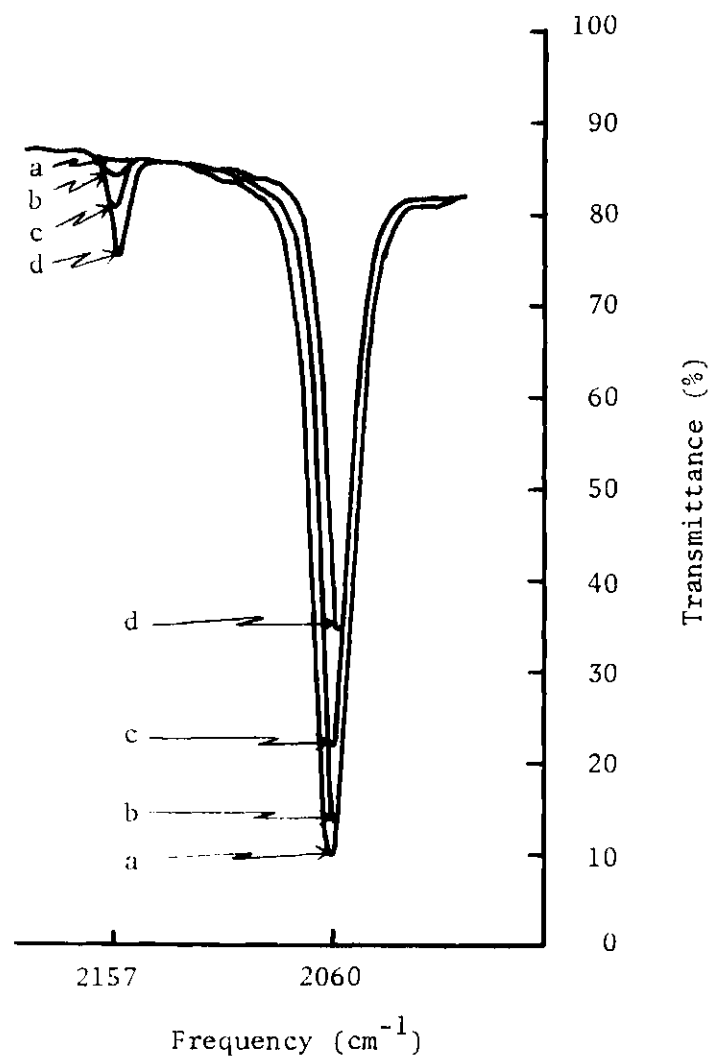
The reaction of thiocyanide ion with benzyl tosylate may produce two possible products, benzyl thiocyanide and benzyl isothiocyanide. In trying to elucidate which nucleophilic atom, sulfur or nitrogen, is the attacking species infra-red spectroscopy was used. It was observed

that a peak became visible at 2157 cm^{-1} (see Figures 4 and 5) while the original peak due to SCN^- decreased in intensity. Benzyl thiocyanide (in carbon tetrachloride) is characterized by one peak at approximately 2140 cm^{-1} (strong) [39], while benzyl isothiocyanide (in carbon tetrachloride) is characterized by two peaks, 2100 cm^{-1} (strong) and 2200 cm^{-1} (moderate) [40]. Since only a peak at 2157 cm^{-1} was found, benzyl thiocyanide is believed to be the product formed.

The above concurs with results obtained by Fava and coworkers [43] who used isotopic labeling techniques to study the isomerization of benzyl thiocyanate in acetonitrile at temperatures ranging from $50\text{--}70^\circ\text{C}$. They observed the sulfur atom to be more reactive than the nitrogen atom by a factor of 10^3 . Other studies [44a,b,c,d] by Fava and coworkers with benzhydryl and allylic thiocyanates in acetonitrile have indicated that the more electrophilic the reaction center is, the more reactive the nitrogen atom is with respect to the sulfur atom.

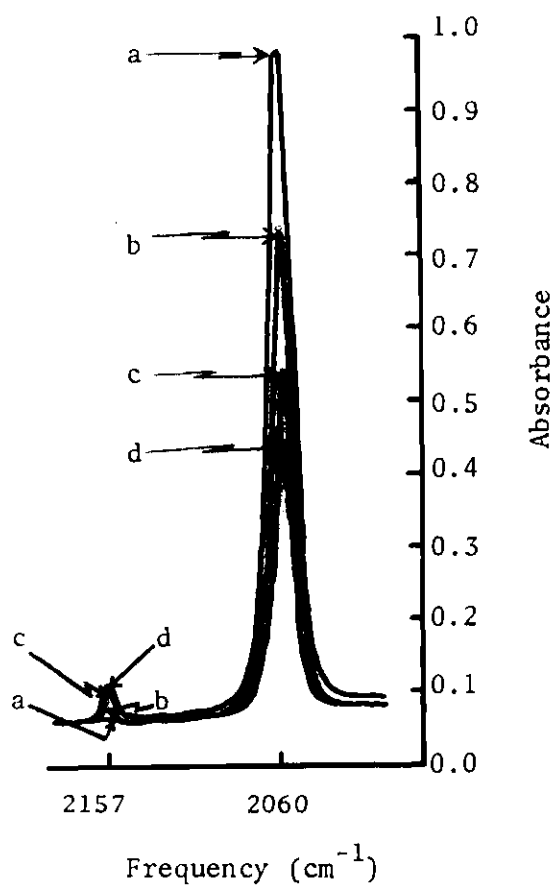
One reaction was run with thiourea in the absence of 18-crown-6 and it was found the thiourea was much less reactive than all the other nucleophiles investigated. This is to be expected if the nucleophilic order follows basicity (in water) since thiourea is the weakest base of those nucleophiles studied. This result provides another example of a nucleophile which is very reactive in protic solvents, but much less reactive in acetonitrile.

The complete reversal of nucleophilic order from that found in protic solvents lends support to Parker's [10, 11, 12] suggestion that hydrogen bonding is a major factor in determining nucleophilic order for protic solvents and in light of the small magnitude of the order



- a 4 minutes
- b 24 minutes
- c 64 minutes
- d 108 minutes

Figure 4. Transmittance Spectrum for the Reaction of 0.05M Benzyl Tosylate with 0.10M KSCN in Acetonitrile Containing 0.10M 18-Crown-6 at 25°C



- a 2 minutes
- b 17 minutes
- c 47 minutes
- d 104 minutes

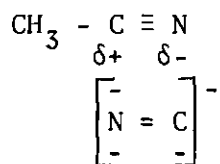
Figure 5. Absorbance Spectrum for the Reaction of 0.05M Benzyl Tosylate with 0.10M KSCN in Acetonitrile Containing 0.10M 18-Crown-6 at 25°C

determined herein, that dipolar aprotic solvents have much weaker solvation effects.

CHAPTER IV

CONCLUSION

The work reported herein has confirmed that nucleophilic order is reversed when going from protic to dipolar aprotic solvents for chloride, bromide, fluoride, iodide, azide, acetate, cyanide, and thiocyanide ions, and thiourea. The order of reactivity follows the basicity of the nucleophiles, the most reactive being the most basic, except for cyanide ion which falls between acetate and fluoride ions. This anomaly may be due to increased solvation of the cyanide ion over other ions, by interaction between it and the cyano group of acetonitrile



The small magnitude of the nucleophilic order obtained in this study provides evidence that minimal difference in solvation and ion pairing occur when potassium salts are solubilized by 18-crown-6 in acetonitrile.

Finally, only one peak was found between 2250 cm^{-1} and 1950 cm^{-1} in the infra-red upon formation of the benzyl derivative which could be attributed to the thiocyanate group. This shows that sulfur is the attacking species and not nitrogen.

CHAPTER V

RECOMMENDATIONS

In the area of determining relative nucleophilicities in the presence of 18-crown-6, much work still must be done. A large number of nucleophiles (e.g., Ph-S^- , $\text{S}_2\text{O}_4^{2-}$, OH^- , etc.) is still needed to be studied. Solvent effects and leaving group effects also provide areas of research. Various families of salts, such as sodium and lithium salts, should also be studied to determine nucleophilic order of anions in the presence of 18-crown-6.

As yet, little work has been done on relative nucleophilicities of anions in the presence of other crown ethers. A comparison of the nucleophilic orders obtained with various crown ethers will eventually be needed.

The effect of temperature on the nucleophiles reactivity and on the magnitude of the nucleophilic order needs to be determined in different solvents and at various temperatures in the presence of crown ethers. This will provide a better understanding of solvation effects on the "free" anion. Also, determination of the activation enthalpies (ΔH^*), entropy (ΔS^*), and free energy (ΔG^*) of solvation in various solvents and different temperatures would be beneficial.

APPENDIX

Chart 1. Pseudo First Order Rate Data for the Reaction of
 $1.50 \times 10^{-2}M$ Benzyl Tosylate with $7.32 \times 10^{-4}M$
 Potassium Thiocyanate in Acetonitrile at 30° .

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	123.2	181.6	18.7
2	121.8	179.5	16.7
4	120.2	177.2	14.3
7	119.5	176.2	13.3
12	118.6	174.8	11.9
17	117.9	173.8	10.9
27	116.6	171.9	9.0
37	115.4	170.1	7.2
47	114.6	168.9	6.0
57	113.8	167.8	4.9
72	112.9	166.4	3.5
87	112.3	165.5	2.7
122	111.4	164.2	1.3
152	110.8	163.3	0.4
212	110.6	163.0	0.1
242	110.5	162.9	-

Chart 2. Reaction of $1.50 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $7.32 \times 10^{-4} \text{ M}$ Potassium Thiocyanate in Acetonitrile
 at 30°

Linear Correlation Coefficient = -1.00

$$\text{Slope} = \frac{-k'}{2.3} = -8.75 \times 10^{-3} \text{ min}^{-1}$$

$$k' = 3.35 \times 10^{-4} \text{ sec}^{-1}$$

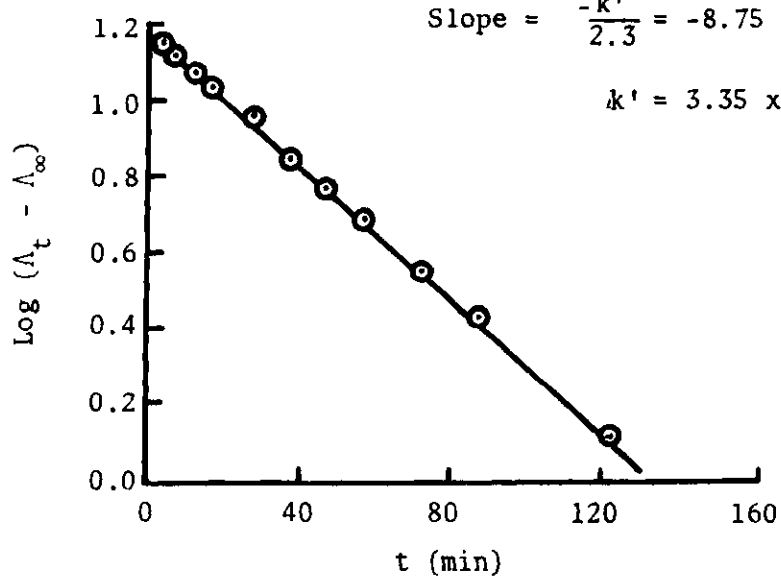


Chart 3. Pseudo First Order Rate Data for the Reaction of
 $1.45 \times 10^{-2}M$ Benzyl Tosylate with $6.28 \times 10^{-4}M$
 Potassium Thiocyanate in Acetonitrile at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	121.8	208.8	29.6
6	120.3	206.3	27.1
11	119.0	204.1	24.9
16	117.8	202.0	22.8
22	116.4	199.6	20.4
26	115.6	198.3	19.0
31	114.7	196.7	17.5
41	113.1	194.0	14.8
51	111.9	191.9	12.7
61	110.7	189.8	10.6
71	109.7	188.1	8.9
86	108.5	186.1	6.9
101	107.3	184.0	4.8
116	106.7	183.0	3.8
151	105.5	180.9	1.7
181	104.9	179.9	0.7
211	104.6	179.4	0.2
241	104.5	179.2	-

Chart 4. Reaction of $1.45 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $6.28 \times 10^{-4} \text{M}$ Potassium Thiocyanate in Acetonitrile
 at 30°

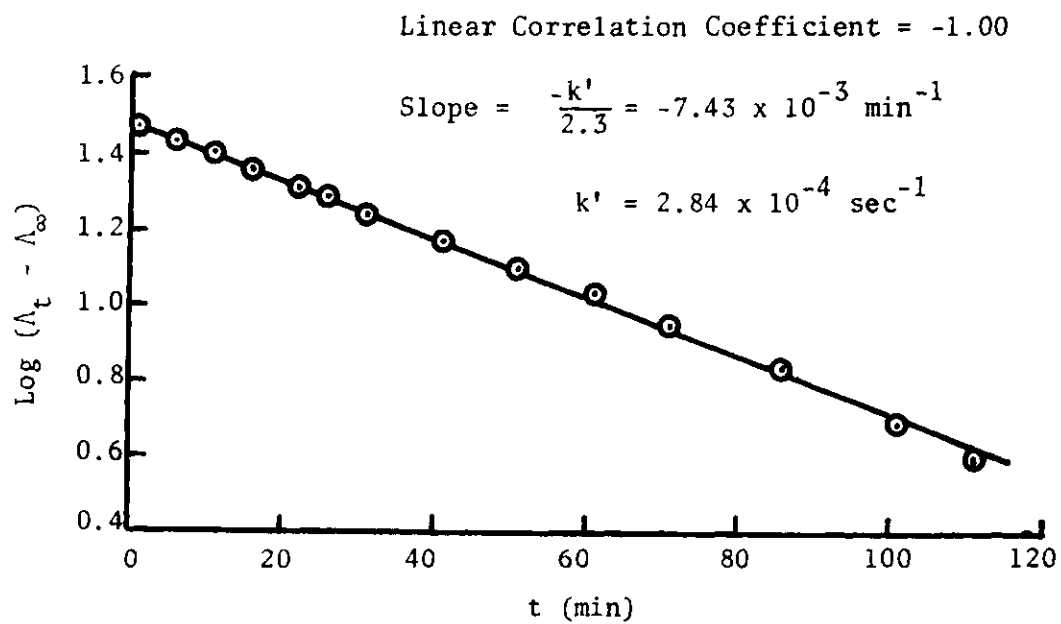


Chart 5. Psuedo First Order Rate Data for the Reaction of
 $8.91 \times 10^{-3}\text{M}$ Benzyl Tosylate with $7.80 \times 10^{-4}\text{M}$
 Potassium Thiocyanate in Acetonitrile at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
29	128.5	177.4	28.4
34	127.5	176.0	27.1
39	126.4	174.5	25.5
44	125.4	173.1	24.2
49	124.5	171.9	22.9
54	123.7	170.8	21.8
59	122.9	169.7	20.7
69	121.3	167.5	18.5
79	120.0	165.7	16.7
89	118.8	164.0	15.1
99	117.7	162.5	13.5
109	116.8	161.3	12.3
124	115.5	159.5	10.5
139	114.3	157.8	8.8
154	113.4	156.6	7.6
169	112.6	155.5	6.5
189	111.7	154.2	5.2
219	110.7	152.9	3.9
249	109.8	151.6	2.6
279	109.2	150.8	1.8
412	108.2	149.4	0.4
451	107.9	149.0	-

Chart 6. Reaction of $8.91 \times 10^{-3} \text{M}$ Benzyl Tosylate with
 $7.80 \times 10^{-4} \text{M}$ Potassium Thiocyanate in Acetonitrile
 at 30°

Linear Correlation Coefficient = $-.499$

$$\text{Slope} = \frac{-k'}{2.3} = -4.59 \times 10^{-3} \text{ min}^{-1}$$

$$k' = 1.76 \times 10^{-4} \text{ sec}^{-1}$$

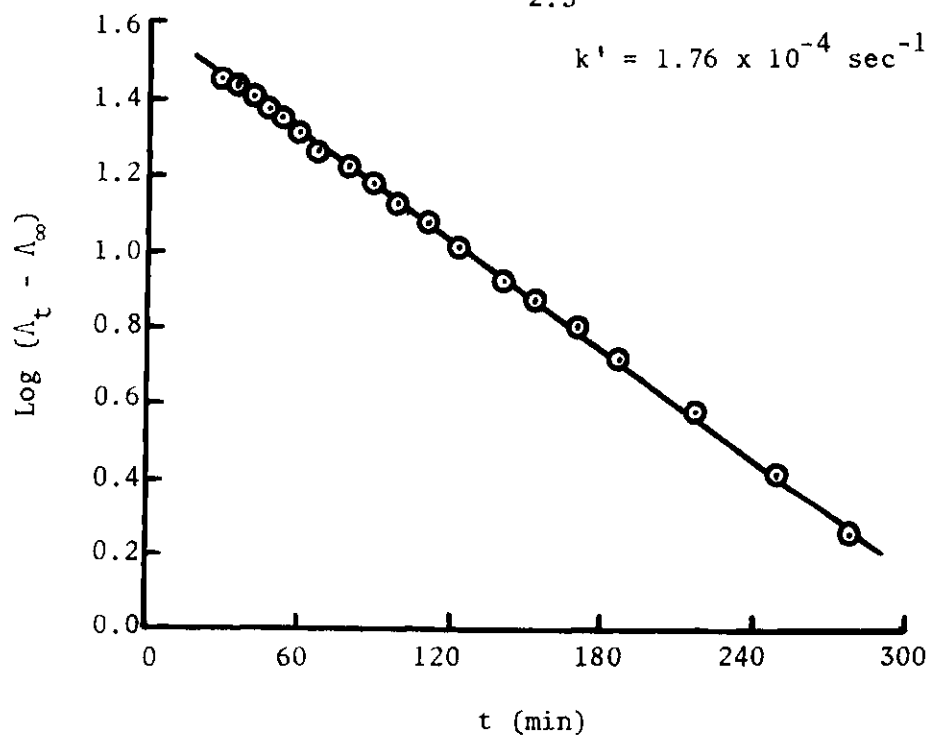


Chart 7. Pseudo First Order Rate Data for the Reaction of
 $1.87 \times 10^{-2}\text{M}$ Benzyl Tosylate with $6.81 \times 10^{-4}\text{M}$
 Potassium Thiocyanate in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
5	117.9	186.5	35.0
10	116.0	183.5	32.0
15	114.2	180.6	29.1
25	112.4	177.8	26.3
30	110.8	175.2	23.7
35	109.2	172.7	21.2
40	107.9	170.6	19.1
45	106.3	167.4	15.9
50	105.6	167.0	15.5
55	104.5	165.3	13.8
65	102.8	162.6	11.1
75	101.5	160.5	9.0
85	100.3	158.6	7.1
95	99.50	157.4	5.9
105	98.70	156.1	4.6
120	97.80	154.7	3.2
135	97.10	153.6	2.1
183	96.10	152.0	0.5
215	95.90	151.7	0.2
235	95.80	151.5	-

Chart 8. Reaction of $1.87 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $6.81 \times 10^{-4} \text{M}$ Potassium Thiocyanate in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

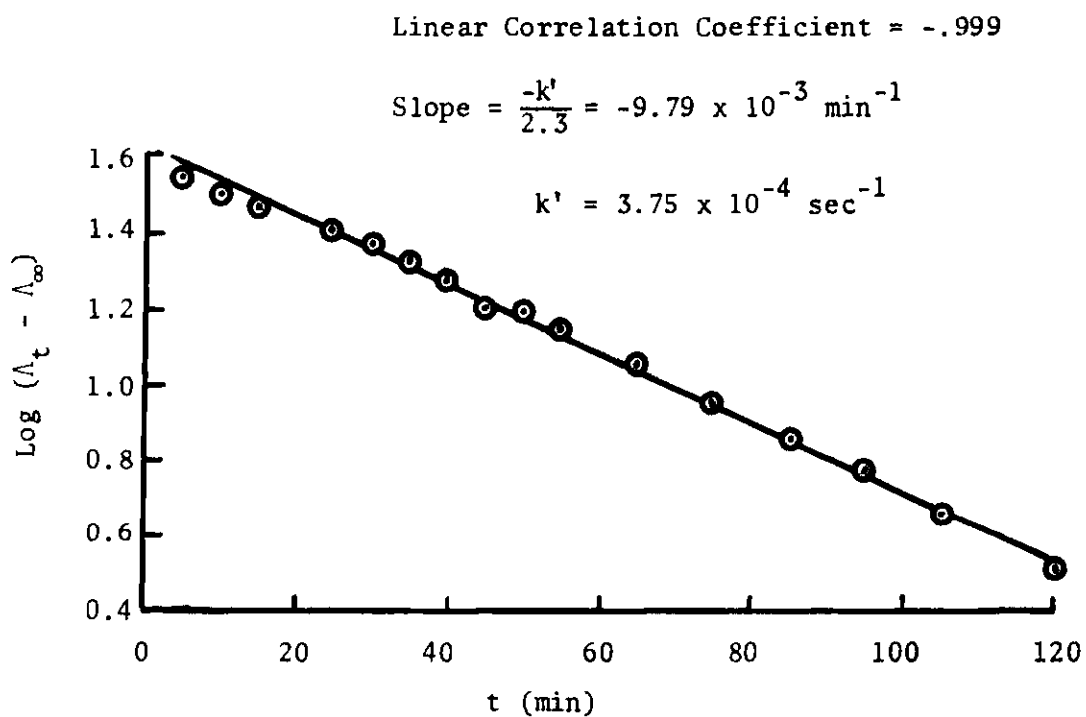


Chart 9. Pseudo First Order Rate Data for the Reaction of
 $6.77 \times 10^{-3}M$ Benzyl Tosylate with $5.89 \times 10^{-4}M$
 Potassium Thiocyanate in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($cm^3/equiv\text{-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	92.20	168.6	24.7
4	92.10	168.4	24.5
9	91.90	168.0	24.1
14	91.50	167.3	23.4
19	91.00	166.4	22.5
24	90.60	165.7	21.8
29	90.20	164.9	21.0
34	89.70	164.0	20.1
39	89.30	163.3	19.4
44	88.90	162.6	18.7
49	88.50	161.8	17.9
54	88.10	161.1	17.2
64	87.80	160.5	16.6
69	87.40	159.8	15.9
74	87.00	159.1	15.2
79	86.70	158.5	14.6
84	86.40	158.0	14.1
89	86.00	157.3	13.4
99	85.40	156.2	12.3
109	84.80	155.1	11.2
119	84.20	154.0	10.1
129	83.70	153.1	9.2
139	83.40	152.4	8.5
149	83.00	151.6	7.7
165	82.20	150.3	6.4
180	81.70	149.4	5.5
195	81.20	148.5	4.6
210	80.80	147.7	3.8
225	80.40	147.1	3.2
240	80.10	146.5	2.5
270	79.60	145.6	1.7
300	79.20	144.8	0.9
330	78.90	144.3	0.3
360	78.70	143.9	-

Chart 10. Reaction of $6.77 \times 10^{-3} \text{ M}$ Benzyl Tosylate with
 $5.89 \times 10^{-4} \text{ M}$ Potassium Thiocyanate in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.995$

$$\text{Slope} = \frac{-k'}{2.3} = -3.66 \times 10^{-3} \text{ min}^{-1}$$

$$k' = 1.40 \times 10^{-4} \text{ sec}^{-1}$$

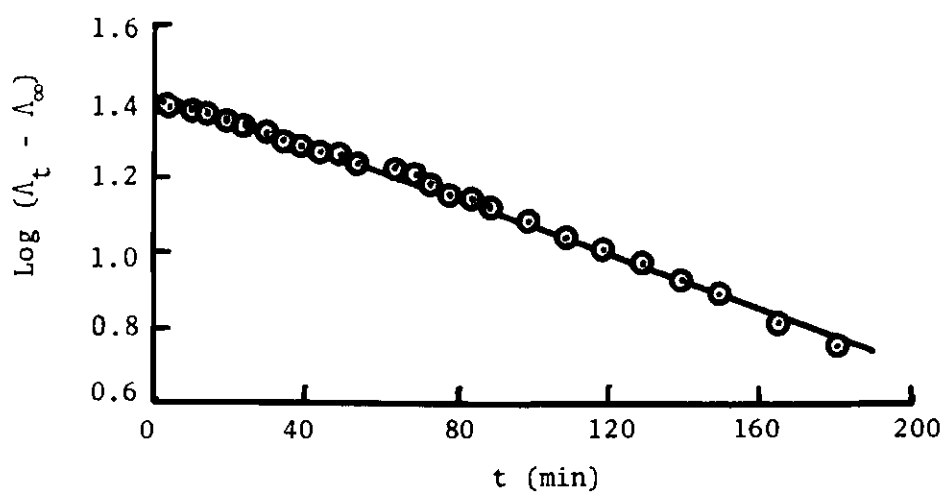


Chart 11. Pseudo First Order Rate Data for the Reaction of
 $1.31 \times 10^{-2}M$ Benzyl Tosylate with $5.59 \times 10^{-4}M$
 Potassium Thiocyanate in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($cm^3/equiv\text{-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	90.70	174.8	32.4
2	90.40	174.2	31.8
3	90.10	173.6	31.2
5	89.60	172.6	30.3
7	89.20	171.9	29.5
9	88.80	171.1	28.7
11	88.30	170.1	27.8
13	87.80	169.2	26.8
15	87.40	168.4	26.0
20	86.50	166.7	24.3
25	85.50	164.7	22.4
30	84.70	163.2	20.8
35	83.90	161.6	19.3
40	83.20	160.3	17.9
45	82.50	158.9	16.6
50	81.80	157.6	15.2
55	81.20	156.4	14.1
60	81.00	156.1	13.7
65	80.40	154.9	12.5
70	79.90	153.9	11.6
75	79.50	153.2	10.8
85	78.70	151.6	9.3
95	77.90	150.1	7.7
105	77.30	148.9	6.6
115	76.70	147.8	5.4
125	76.30	147.0	4.6
135	75.90	146.2	3.9
148	75.50	145.5	3.1
151	75.10	144.7	2.3
161	74.50	143.5	1.2
191	74.10	142.8	0.4
221	73.90	142.4	-

Chart 12. Reaction of $1.31 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $5.59 \times 10^{-4} \text{ M}$ Potassium Thiocyanate in Acetonitrile
Containing 0.10 M 18-Crown-6 at 30°

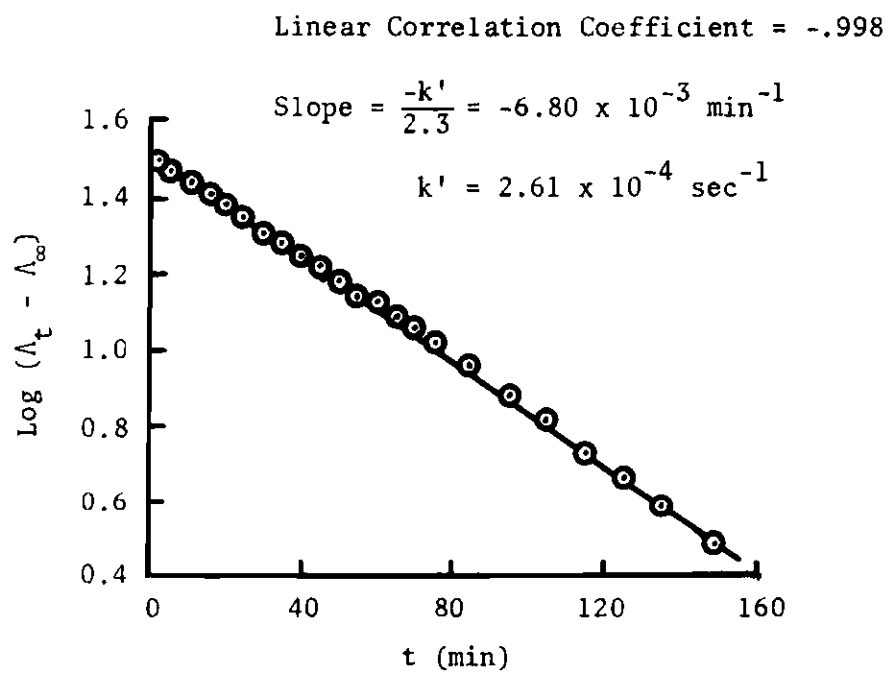


Chart 13. Pseudo First Order Rate Data for the Reaction of
 $1.04 \times 10^{-2}M$ Benzyl Tosylate with $7.75 \times 10^{-4}M$
 Potassium Iodide in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ (cm^3 /equiv-ohm)	$\Lambda_t - \Lambda_\infty$
2	118.3	164.4	26.7
3	117.3	163.0	25.3
4	116.2	161.5	23.8
5	115.3	160.2	22.5
6	114.4	159.0	21.3
7	113.5	157.7	20.0
8	112.7	156.6	18.9
9	112.0	155.6	17.9
11	110.7	153.8	16.1
13	109.4	152.0	14.3
15	108.3	150.5	12.8
17	107.4	149.3	11.5
21	105.8	147.0	9.3
25	104.5	145.2	7.5
29	103.4	143.7	6.0
33	102.6	142.6	4.9
38	101.7	141.3	3.6
48	100.6	139.8	2.1
58	100.0	139.0	1.3
73	99.50	138.3	0.6
103	99.20	137.9	0.1
133	99.10	137.7	-

Chart 14. Reaction of $1.04 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $7.75 \times 10^{-4} \text{ M}$ Potassium Iodide in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -2.40 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 9.20 \times 10^{-4} \text{ sec}^{-1}$$

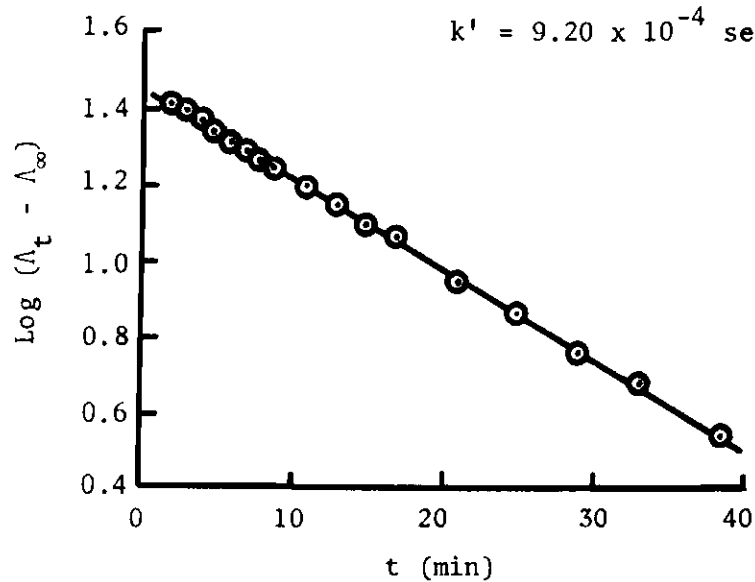


Chart 15. Pseudo First Order Rate Data for the Reaction of
 $2.34 \times 10^{-2}\text{M}$ Benzyl Tosylate with $7.26 \times 10^{-4}\text{M}$
 Potassium Iodide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
3	133.2	197.6	25.8
4	131.4	194.9	23.1
5	129.6	192.3	20.5
6	128.2	190.2	18.4
7	126.7	188.0	16.2
8	125.5	186.2	14.4
9	124.4	184.5	12.8
10	122.6	181.9	10.1
12	121.3	179.9	8.2
14	120.0	178.0	6.2
16	119.1	176.7	4.9
18	118.3	175.5	3.7
20	117.7	174.6	2.8
25	116.9	173.4	1.6
35	116.1	172.2	0.5
45	115.8	171.8	-

Chart 16. Reaction of $2.34 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $7.26 \times 10^{-4} \text{M}$ Potassium Iodide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -5.57 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 2.13 \times 10^{-3} \text{ sec}^{-1}$$

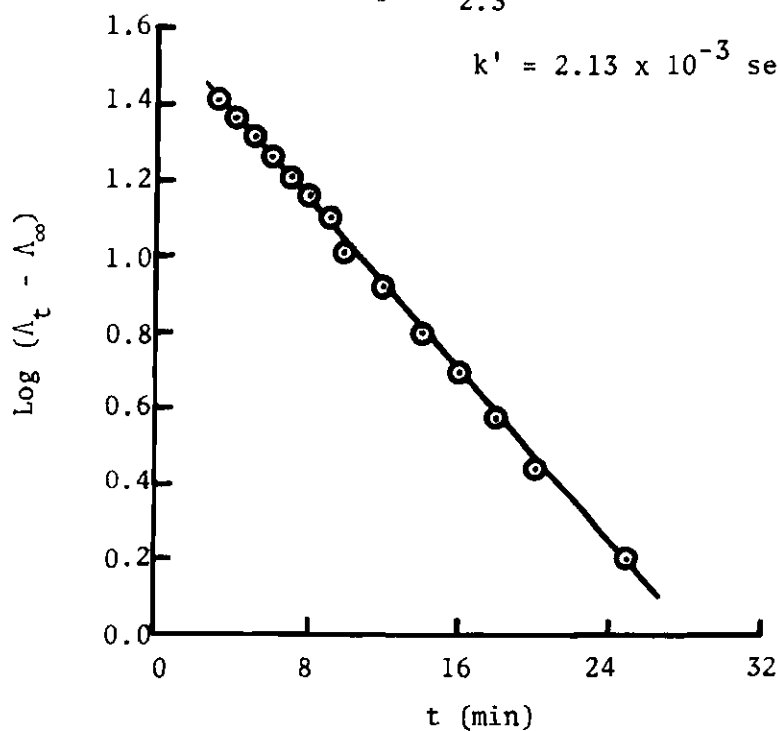


Chart 17. Pseudo First Order Rate Data for the Reaction of
 $1.17 \times 10^{-2}M$ Benzyl Tosylate with $7.02 \times 10^{-4}M$
 Potassium Iodide in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ (cm ³ /equiv-ohm)	$\Lambda_t - \Lambda_\infty$
1	114.7	176.0	27.3
2	113.7	174.4	25.8
3	112.8	173.1	24.4
4	112.0	171.8	23.2
5	111.1	170.4	21.8
6	110.1	168.9	20.3
9	108.0	165.7	17.0
11	106.8	163.9	15.2
13	105.6	162.0	13.4
15	104.8	160.8	12.1
17	103.8	159.2	10.6
19	103.2	158.3	9.7
23	101.7	156.0	7.4
27	100.7	154.5	5.8
32	99.60	153.0	4.0
37	98.90	151.7	3.1
48	97.80	150.0	1.4
85	96.90	148.6	-

Chart 18. Reaction of $1.17 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $7.02 \times 10^{-4} \text{M}$ Potassium Iodide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.999

$$\text{Slope} = \frac{-k'}{2.3} = -2.56 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 9.81 \times 10^{-4} \text{ sec}^{-1}$$

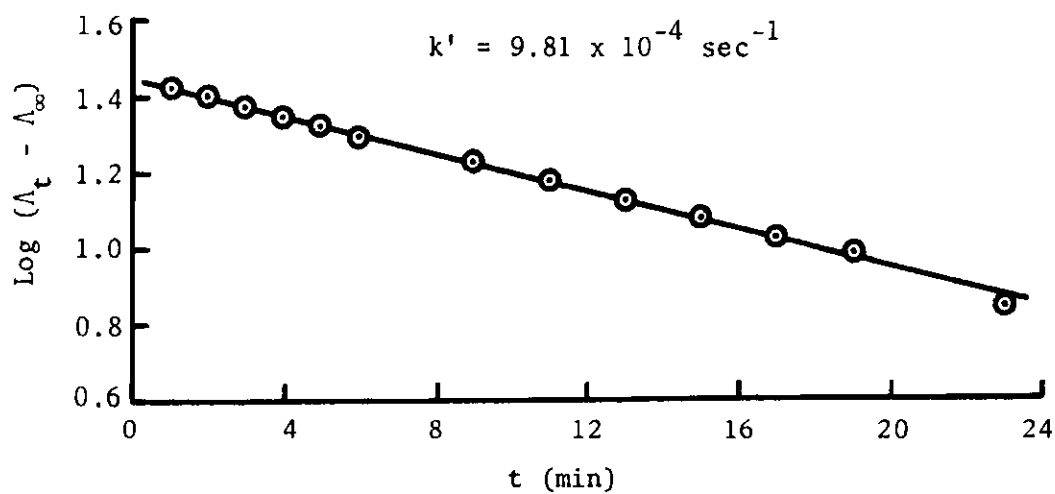


Chart 19. Pseudo First Order Rate Data for the Reaction of
 $7.28 \times 10^{-3}\text{M}$ Benzyl Tosylate with $7.56 \times 10^{-4}\text{M}$
 Potassium Bromide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
3	103.2	147.0	22.7
5	100.9	143.7	19.4
6	99.80	142.1	17.8
7	98.90	140.9	16.5
8	98.50	140.3	16.0
9	98.00	139.6	15.3
10	97.80	139.3	15.0
12	97.20	138.5	14.1
13	96.30	137.2	12.8
14	95.90	136.6	12.3
15	95.50	136.1	11.7
17	95.30	135.8	11.4
18	95.10	135.5	11.1
20	94.50	134.6	9.9
22	93.80	133.6	9.3
24	93.20	132.8	8.4
26	92.80	132.2	7.8
28	92.30	131.5	7.1
30	91.80	130.8	6.4
32	91.40	130.2	5.8
34	91.00	129.6	5.3
36	90.70	129.2	4.9
38	90.30	128.6	4.3
40	90.10	128.4	4.0
45	89.50	127.5	3.2
50	88.90	126.6	2.3
55	88.60	126.2	1.9
60	88.30	125.8	1.4
65	88.00	125.4	1.0
70	87.80	125.1	0.7
75	87.60	124.8	0.4
90	87.30	124.4	-

Chart 20. Reaction of $7.28 \times 10^{-3} \text{ M}$ Benzyl Tosylate with
 $7.56 \times 10^{-4} \text{ M}$ Potassium Bromide in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.998$

$$\text{Slope} = \frac{-k'}{2.3} = -2.00 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 7.67 \times 10^{-4} \text{ sec}^{-1}$$

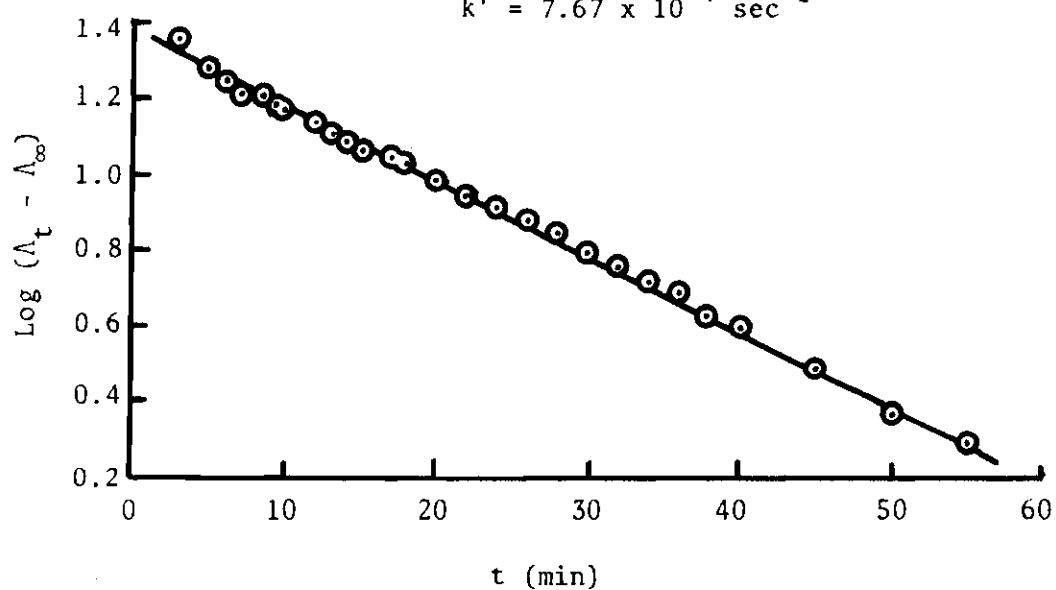


Chart 21. Pseudo First Order Rate Data for the Reaction of
 $1.32 \times 10^{-2} \text{M}$ Benzyl Tosylate with $6.57 \times 10^{-4} \text{M}$
 Potassium Bromide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
5	107.1	175.6	16.7
6	106.6	174.7	15.9
7	106.0	173.8	14.9
8	105.3	172.6	13.8
9	104.7	171.6	12.8
10	103.9	170.3	11.5
11	103.4	169.5	10.7
12	102.9	168.7	9.8
13	102.5	168.0	9.2
14	102.0	167.2	8.4
16	101.2	165.9	7.1
18	100.6	164.9	6.1
20	100.0	163.9	5.1
22	99.50	163.1	4.3
24	99.00	162.3	3.4
26	98.80	161.9	3.1
28	98.50	161.5	2.6
33	97.90	160.5	1.6
43	97.60	160.0	1.2
53	97.00	159.0	0.2
73	96.90	158.8	-

Chart 22. Reaction of $1.32 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $6.57 \times 10^{-4} \text{M}$ Potassium Bromide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -3.71 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 1.42 \times 10^{-3} \text{ sec}^{-1}$$

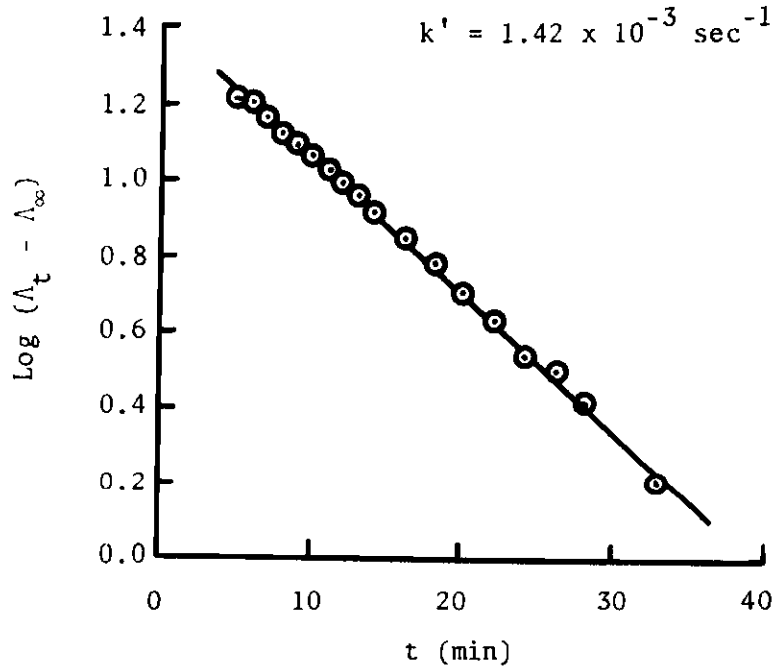


Chart 23. Pseudo First Order Rate Data for the Reaction of
 $1.36 \times 10^{-2} \text{M}$ Benzyl Tosylate with $6.74 \times 10^{-4} \text{M}$
 Potassium Bromide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
2	104.7	167.3	19.8
3	103.5	165.4	17.9
5	101.0	161.4	13.9
7	99.10	158.4	10.8
9	97.80	156.3	8.8
11	97.00	154.9	7.5
13	96.00	153.4	5.9
15	95.40	152.4	5.0
19	94.20	150.2	2.8
22	93.50	149.4	1.9
24	92.80	148.3	0.8
26	92.30	147.5	-

Chart 24. Reaction of $1.36 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $6.74 \times 10^{-4} \text{ M}$ Potassium Bromide in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

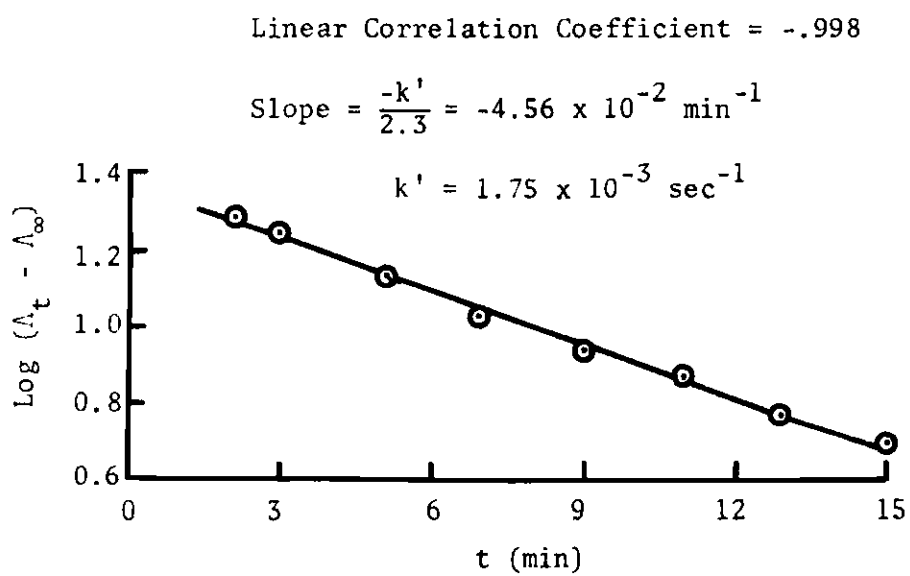


Chart 25. Pseudo First Order Rate Data for the Reaction of
 $1.34 \times 10^{-2} \text{M}$ Benzyl Tosylate with $7.59 \times 10^{-4} \text{M}$
 Potassium Chloride in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	142.6	202.3	26.4
2	140.8	199.8	23.8
3	139.3	197.7	21.7
4	138.0	195.8	19.9
5	136.7	194.0	18.0
6	135.5	192.3	16.3
7	134.4	190.7	14.8
8	133.5	189.4	13.5
9	132.6	188.2	12.2
10	131.8	187.0	11.1
11	130.5	185.2	9.2
13	129.3	183.5	7.5
15	128.5	182.3	6.4
17	127.7	181.2	5.3
22	126.2	179.1	3.1
27	125.3	177.8	1.8
32	124.7	176.9	1.0
37	124.3	176.4	0.4
42	124.2	176.2	0.3
52	124.0	176.0	-

Chart 26. Reaction of $1.34 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $7.59 \times 10^{-4} \text{ M}$ Potassium Chloride in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.999

$$\text{Slope} = \frac{-k'}{2.3} = -4.56 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 1.75 \times 10^{-3} \text{ sec}^{-1}$$

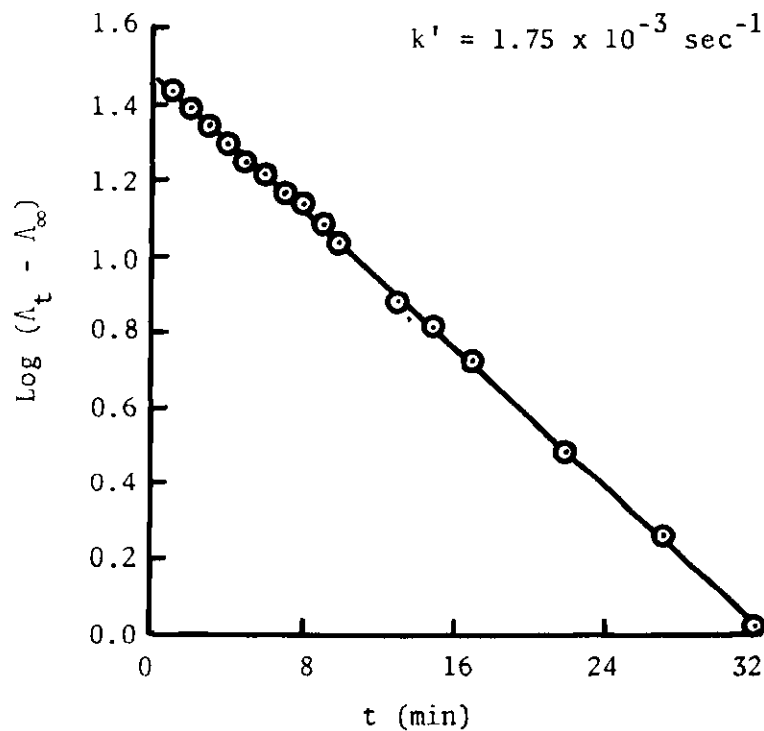


Chart 27. Pseudo First Order Rate Data for the Reaction of
 $1.94 \times 10^{-2} \text{M}$ Benzyl Tosylate with $5.61 \times 10^{-4} \text{M}$
 Potassium Chloride in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	130.1	249.8	29.2
2	128.1	245.9	25.3
3	126.6	243.0	22.5
4	125.0	240.0	19.4
5	123.6	237.3	16.7
6	122.4	235.0	14.0
7	121.3	232.9	12.3
8	120.3	231.0	10.0
9	119.7	229.8	9.2
10	119.0	228.5	7.9
12	117.9	226.3	5.8
14	117.1	224.5	3.9
16	116.5	223.7	3.1
18	116.1	222.9	2.3
20	115.8	222.3	1.7
25	115.2	221.2	0.6
30	115.0	220.8	0.2
35	114.9	220.6	-

Chart 28. Reaction of $1.94 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $5.61 \times 10^{-4} \text{M}$ Potassium Chloride in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -6.57 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 2.52 \times 10^{-3}$$

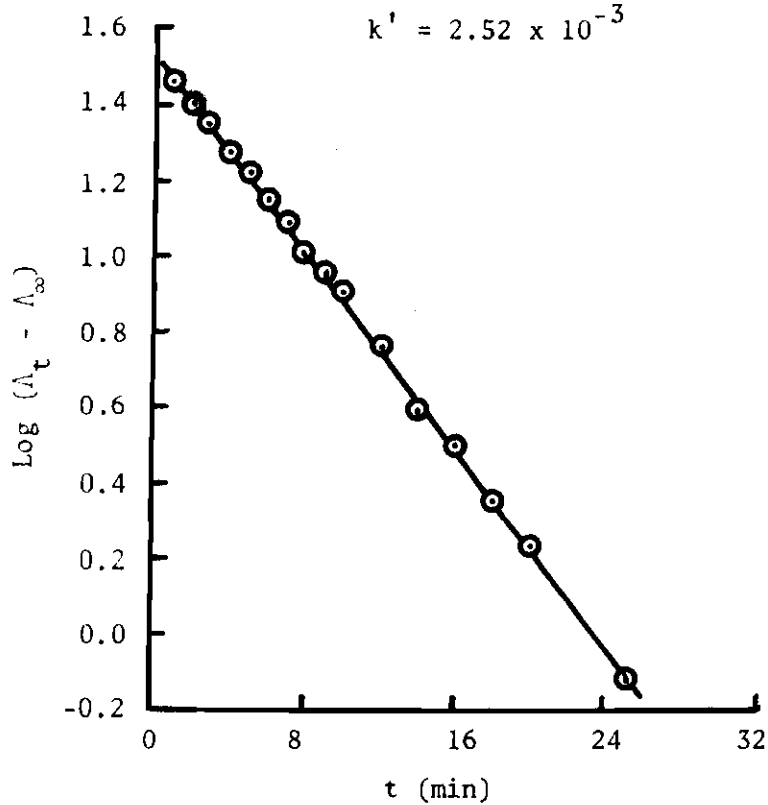


Chart 29. Pseudo First Order Rate Data for the Reaction of
 $1.26 \times 10^{-2} \text{M}$ Benzyl Tosylate with $5.90 \times 10^{-4} \text{M}$
 Potassium Chloride in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	114.8	209.6	25.9
2	114.0	208.1	24.5
3	113.1	206.5	22.8
4	112.0	204.4	20.8
5	111.1	202.8	19.2
6	110.3	201.4	17.7
7	109.6	200.1	16.4
8	108.9	198.8	15.2
9	108.2	197.5	13.9
10	107.6	196.4	12.8
12	106.6	194.6	11.0
14	105.8	193.1	9.5
16	105.0	191.7	8.0
19	104.1	190.0	6.4
22	103.3	188.6	4.9
25	102.7	187.5	3.8
28	102.2	186.6	2.9
31	101.9	186.0	2.4
35	101.5	185.3	1.7
40	101.1	184.6	0.9
45	100.9	184.2	0.6
50	100.7	183.8	0.2
55	100.6	183.6	-

Chart 30. Reaction of $1.26 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $5.90 \times 10^{-4} \text{M}$ Potassium Chloride in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.999

$$\text{Slope} = \frac{-k'}{2.3} = -3.50 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 1.34 \times 10^{-3} \text{ sec}^{-1}$$

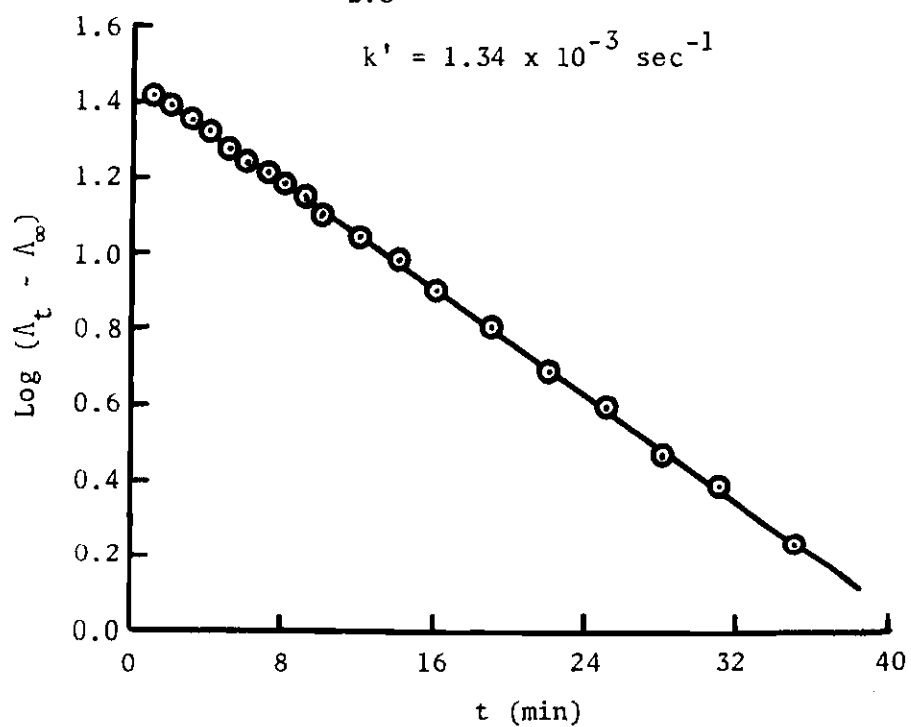


Chart 31. Pseudo First Order Rate Data for the Reaction of
 $2.15 \times 10^{-2}\text{M}$ Benzyl Tosylate with $5.53 \times 10^{-4}\text{M}$
 Potassium Chloride in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	117.3	228.4	24.2
2	116.1	226.1	21.8
3	114.5	223.0	18.7
4	113.0	220.1	15.8
5	111.7	217.5	13.2
6	110.8	215.8	11.5
7	110.0	214.2	9.9
8	109.2	212.7	8.4
9	108.6	211.5	7.2
10	108.0	210.3	6.1
11	107.5	209.4	5.1
12	107.1	208.6	4.3
14	106.4	207.2	2.9
16	105.9	206.2	2.0
18	105.5	205.5	1.2
23	105.1	204.7	0.4
28	104.9	204.3	-

Chart 32. Reaction of $2.15 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $5.53 \times 10^{-4} \text{ M}$ Potassium Chloride in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -6.93 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 2.66 \times 10^{-3} \text{ sec}^{-1}$$

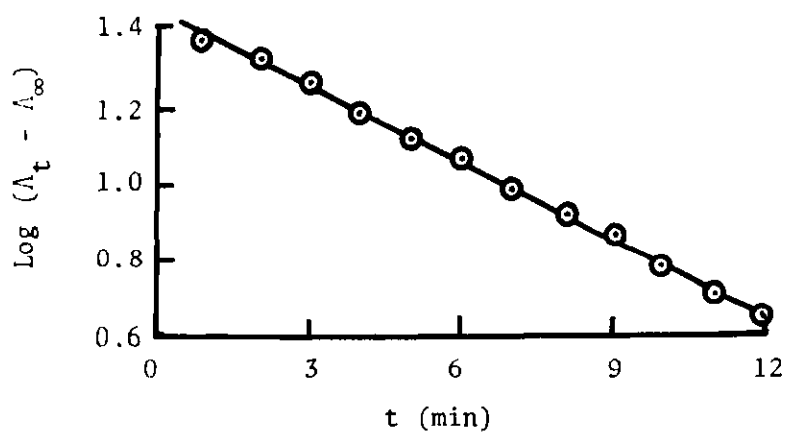


Chart 33. Pseudo First Order Rate Data for the Reaction of
 $1.22 \times 10^{-2}M$ Benzyl Tosylate with $6.59 \times 10^{-4}M$
 Potassium Fluoride in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	104.4	170.6	10.0
2	103.7	169.5	8.8
3	103.2	168.7	8.0
4	102.7	167.8	7.2
5	102.3	167.2	6.5
6	102.0	166.7	6.0
7	101.6	166.0	5.4
8	101.4	165.7	5.1
9	101.1	165.2	4.6
11	100.7	164.6	3.9
13	100.4	164.1	3.4
17	99.70	162.9	2.3
22	99.40	162.4	1.8
30	98.90	161.6	1.0
37	98.50	161.0	0.3
52	98.30	160.7	-

Chart 34. Reaction of $1.22 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $6.59 \times 10^{-4} \text{M}$ Potassium Fluoride in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.998

$$\text{Slope} = \frac{-k'}{2.3} = -3.85 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 1.47 \times 10^{-3} \text{ sec}^{-1}$$

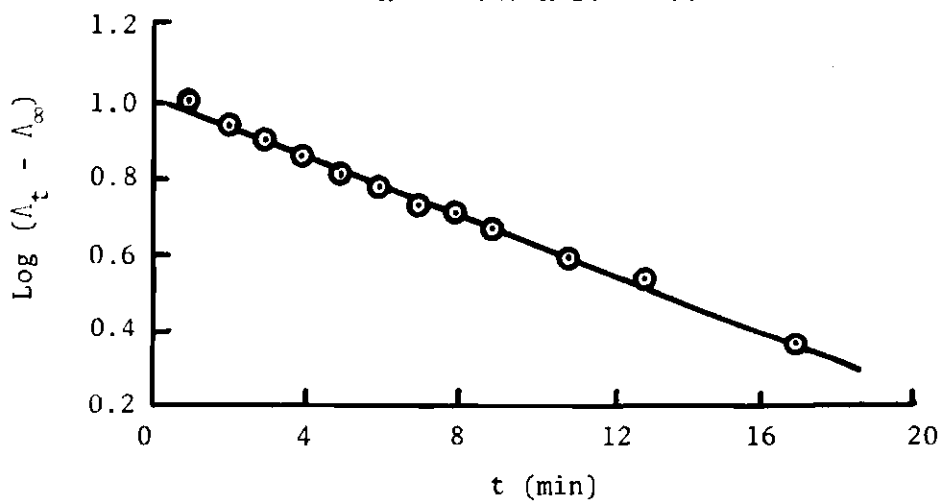


Chart 35. Pseudo First Order Rate Data for the Reaction of
 $9.71 \times 10^{-3}\text{M}$ Benzyl Tosylate with $3.32 \times 10^{-4}\text{M}$
 Potassium Fluoride in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
8	60.20	195.3	2.9
10	60.00	194.6	2.3
14	59.91	194.3	2.0
17	59.70	193.7	1.3
20	59.60	193.3	1.0
25	59.50	193.0	0.7
35	59.30	192.4	-

Chart 36. Reaction of $9.71 \times 10^{-3} \text{ M}$ Benzyl Tosylate with
 $3.32 \times 10^{-4} \text{ M}$ Potassium Fluoride in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

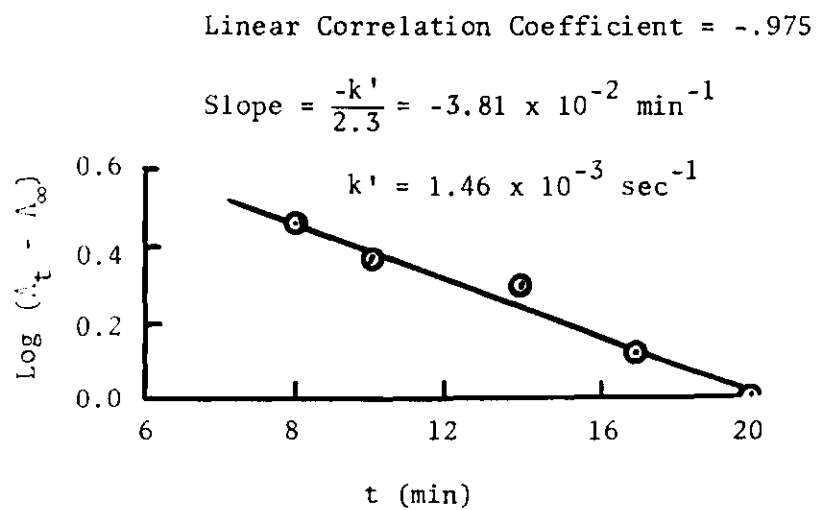


Chart 37. Pseudo First Order Rate Data for the Reaction of
 $1.42 \times 10^{-2}M$ Benzyl Tosylate with $7.98 \times 10^{-4}M$
 Potassium Cyanide in Acetonitrile Containing
 $0.10M$ 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($cm^3/equiv\text{-}ohm$)	$\Lambda_t - \Lambda_\infty$
1	98.80	133.3	12.4
2	97.00	130.9	10.0
3	95.60	129.0	8.1
4	94.50	127.5	6.6
5	93.60	126.3	5.4
6	92.90	125.4	4.5
7	92.20	124.4	3.5
8	91.50	123.5	2.6
10	90.90	122.7	1.8
14	90.00	121.5	0.5
32	89.60	120.9	-

Chart 38. Reaction of $1.42 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $7.98 \times 10^{-4} \text{M}$ Potassium Cyanide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.998

$$\text{Slope} = \frac{-k'}{2.3} = -9.49 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 3.64 \times 10^{-3} \text{ sec}^{-1}$$

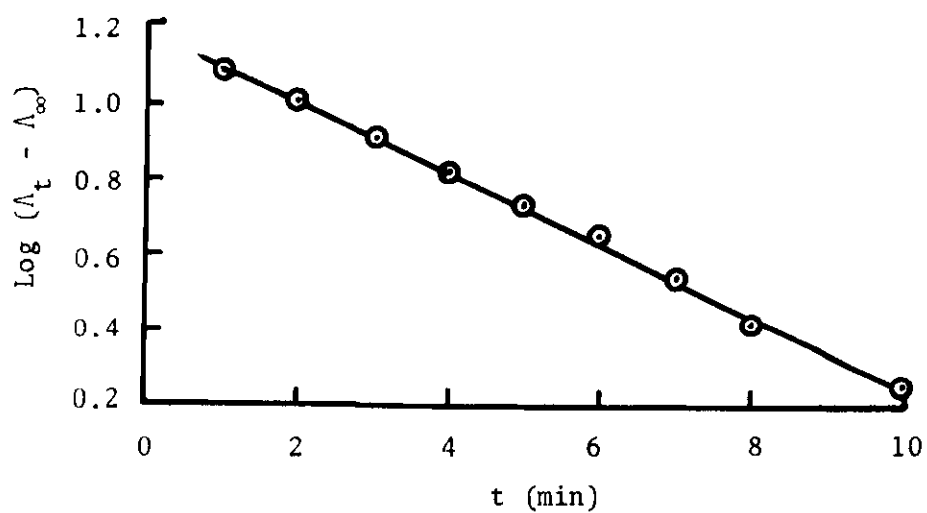


Chart 39. Pseudo First Order Rate Data of the Reaction of
 $1.09 \times 10^{-2} \text{M}$ Benzyl Tosylate with $5.41 \times 10^{-4} \text{M}$
 Potassium Cyanide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	84.50	168.2	20.1
2	81.90	163.0	14.9
3	81.10	161.5	13.3
4	80.30	159.9	11.7
5	79.40	158.1	10.0
6	78.70	156.7	8.6
7	78.10	155.5	7.4
8	77.60	154.5	6.4
9	77.20	153.7	5.6
11	76.50	152.3	4.2
13	76.00	151.3	3.2
15	75.60	150.5	2.4
19	75.20	149.7	1.6
24	74.80	148.9	0.8
29	74.60	148.5	0.4
39	74.40	148.1	-

Chart 40. Reaction of $1.09 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $5.41 \times 10^{-4} \text{M}$ Potassium Cyanide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -6.17 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 2.37 \times 10^{-3} \text{ sec}^{-1}$$

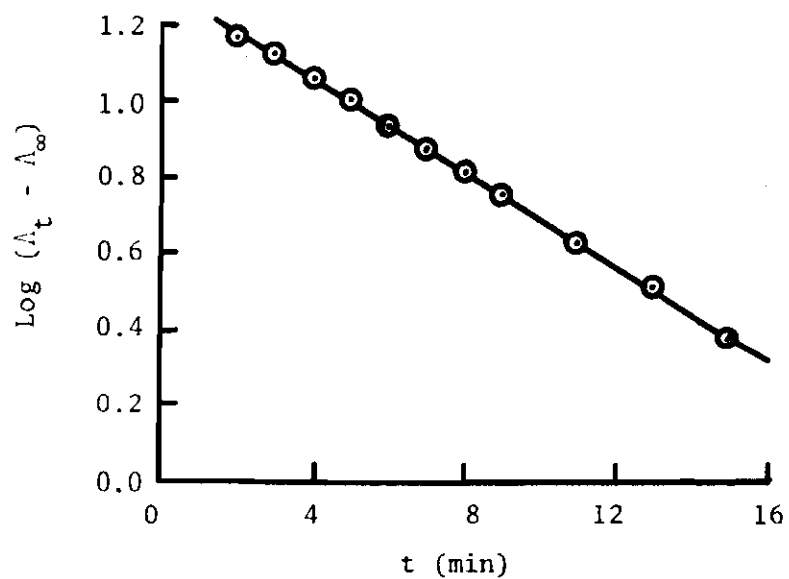


Chart 41. Pseudo First Order Rate Data for the Reaction of
 $9.88 \times 10^{-3}\text{M}$ Benzyl Tosylate with $6.17 \times 10^{-4}\text{M}$
 Potassium Cyanide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	88.60	154.7	16.9
2	87.10	152.0	14.3
3	86.00	150.1	12.4
4	85.10	148.5	10.8
5	84.30	147.1	9.4
6	83.70	146.1	8.4
7	82.70	144.4	6.6
8	82.20	143.4	5.7
9	81.80	142.8	5.1
10	81.50	142.3	4.5
12	81.00	141.4	3.7
14	80.50	140.5	2.8
16	80.20	140.0	2.3
18	79.90	139.5	1.7
22	79.50	138.8	1.1
27	79.20	138.2	0.5
37	79.00	137.9	0.2
52	78.90	137.7	-

Chart 42. Reaction of $9.88 \times 10^{-3} \text{M}$ Benzyl Tosylate with
 $6.17 \times 10^{-4} \text{M}$ Potassium Cyanide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.998$

$$\text{Slope} = \frac{-k'}{2.3} = -5.42 \times 10^{-2} \text{ min}^{-1}$$

$$k' = 2.08 \times 10^{-3} \text{ sec}^{-1}$$

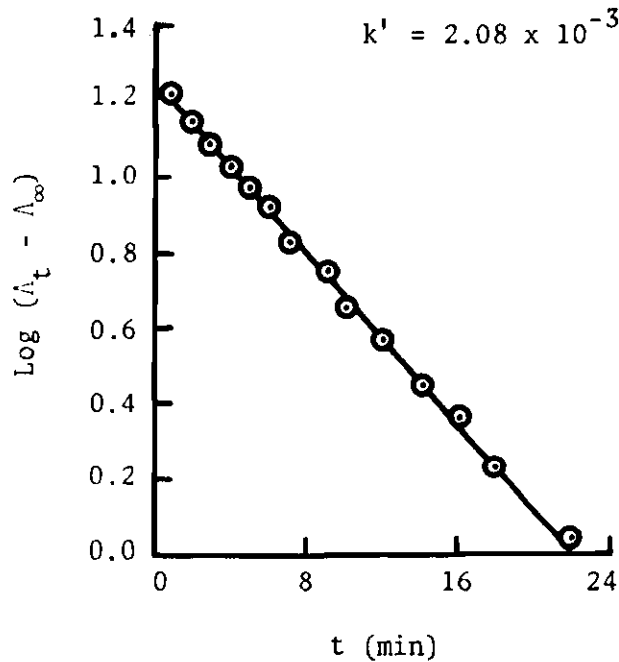


Chart 43. Pseudo First Order Rate Data for the Reaction of
 $6.18 \times 10^{-3}\text{M}$ Benzyl Tosylate with $5.07 \times 10^{-4}\text{M}$
 Potassium Acetate in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	56.10	119.2	5.5
2	55.50	117.4	3.8
3	54.90	116.2	2.5
4	54.50	115.3	1.7
5	54.30	114.9	1.3
7	54.00	114.3	0.6
11	53.90	114.0	0.4
13	53.70	113.6	-

Chart 44. Reaction of $6.18 \times 10^{-3} \text{M}$ Benzyl Tosylate with
 $5.07 \times 10^{-4} \text{M}$ Potassium Acetate in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.997$

$$\text{Slope} = \frac{-k'}{2.3} = -1.56 \times 10^{-1} \text{ min}^{-1}$$

$$k' = 5.98 \times 10^{-3} \text{ sec}^{-1}$$

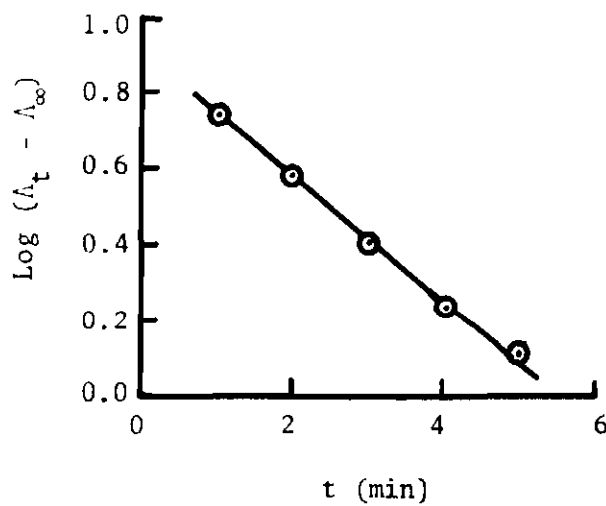


Chart 45. Pseudo First Order Rate Data for the Reaction of
 $1.06 \times 10^{-2} \text{M}$ Benzyl Tosylate with $3.95 \times 10^{-4} \text{M}$
 Potassium Acetate in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	48.40	132.0	4.6
2	47.60	129.8	2.5
3	47.20	128.7	1.4
4	47.00	128.1	0.8
6	46.70	127.3	-

Chart 46. Reaction of $1.06 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $3.95 \times 10^{-4} \text{M}$ Potassium Acetate in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.999$

$$\text{Slope} = \frac{-k'}{2.3} = -2.45 \times 10^{-1} \text{ min}^{-1}$$

$$k' = 9.73 \times 10^{-3} \text{ sec}^{-1}$$

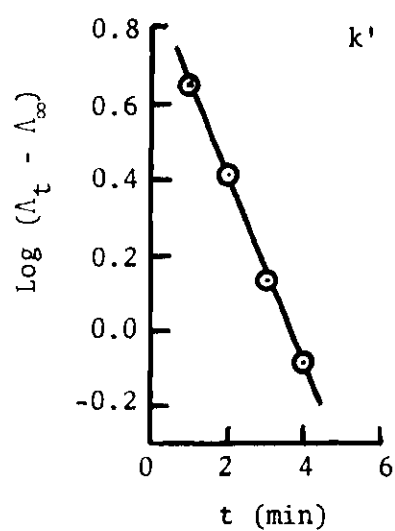


Chart 47. Pseudo First Order Rate Data for the Reaction of
 $1.08 \times 10^{-2} \text{M}$ Benzyl Tosylate with $5.60 \times 10^{-4} \text{M}$
 Potassium Acetate in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	79.90	136.2	5.2
2	78.80	134.3	3.3
3	77.80	132.6	1.6
4	77.40	131.9	0.9
5	77.10	131.4	0.4
6	76.90	131.0	-

Chart 48. Reaction of $1.08 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $5.60 \times 10^{-4} \text{M}$ Potassium Acetate in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.993$

$$\text{Slope} = \frac{-k'}{2.3} = -2.70 \times 10^{-1} \text{ min}^{-1}$$

$$k' = 1.03 \times 10^{-2} \text{ sec}^{-1}$$

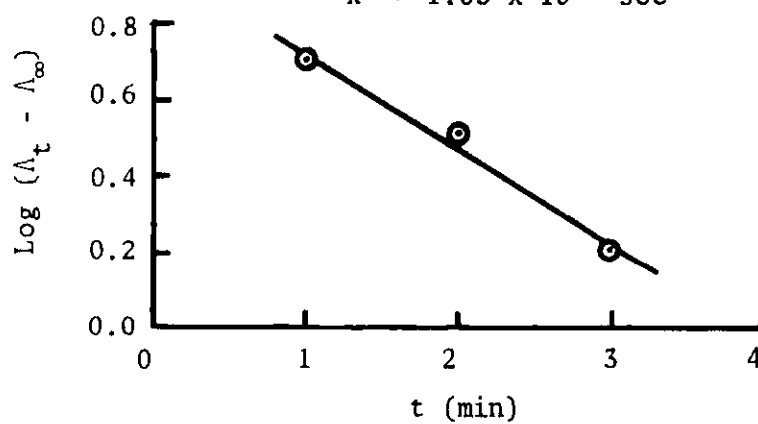


Chart 49. Pseudo First Order Rate Data for the Reaction of
 $1.36 \times 10^{-2} \text{M}$ Benzyl Tosylate with $4.71 \times 10^{-4} \text{M}$
 Potassium Azide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	70.30	160.8	16.5
2	65.80	150.5	6.2
3	64.30	147.0	2.7
4	63.70	145.7	1.4
5	63.40	145.0	0.7
6	63.30	144.7	0.5
7	63.20	144.5	0.2
9	63.10	144.3	-

Chart 50. Reaction of $1.36 \times 10^{-2} \text{M}$ Benzyl Tosylate with
 $4.71 \times 10^{-4} \text{M}$ Potassium Azide in Acetonitrile
 Containing 0.10M 18-Crown-6 at 30°

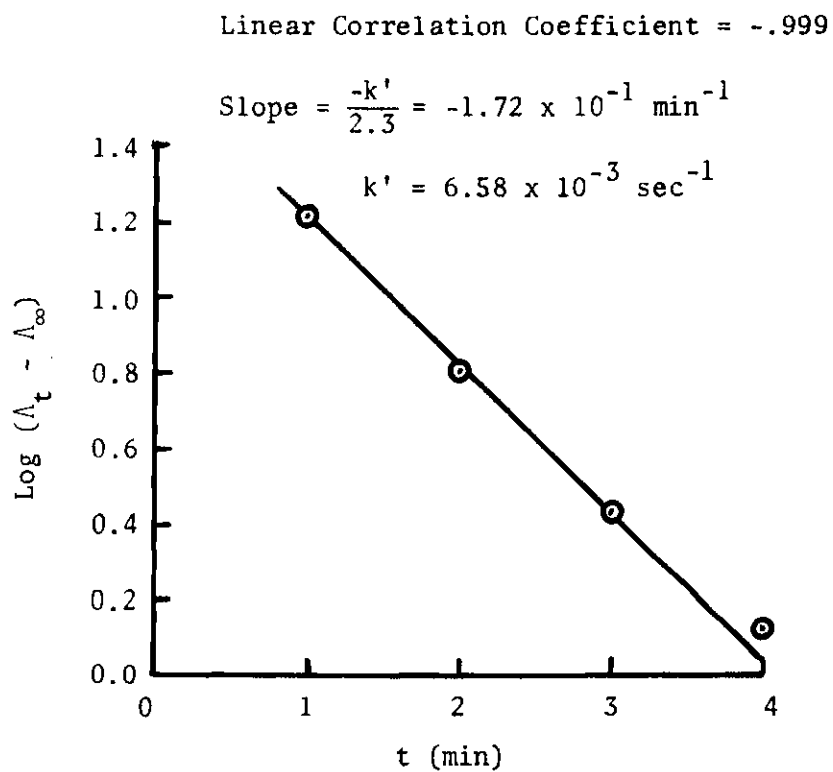


Chart 51. Pseudo First Order Rate Data for the Reaction of
 $6.83 \times 10^{-3}\text{M}$ Benzyl Tosylate with $4.58 \times 10^{-4}\text{M}$
 Potassium Azide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	81.10	190.7	19.0
2	78.40	184.4	12.7
3	76.70	180.3	8.7
4	75.40	177.3	5.6
5	74.70	175.7	4.0
6	74.00	174.0	2.4
7	73.70	173.3	1.6
8	73.50	172.8	1.2
9	73.30	172.4	0.7
10	73.20	172.1	0.5
11	73.10	171.9	0.2
14	73.00	171.7	-

Chart 52. Reaction of $6.83 \times 10^{-3} \text{ M}$ Benzyl Tosylate with
 $4.58 \times 10^{-4} \text{ M}$ Potassium Azide in Acetonitrile
 Containing 0.10 M 18-Crown-6 at 30°

Linear Correlation Coefficient = -0.999

$$\text{Slope} = \frac{-k'}{2.3} = -1.80 \times 10^{-1} \text{ min}^{-1}$$

$$k' = 6.90 \times 10^{-3} \text{ sec}^{-1}$$

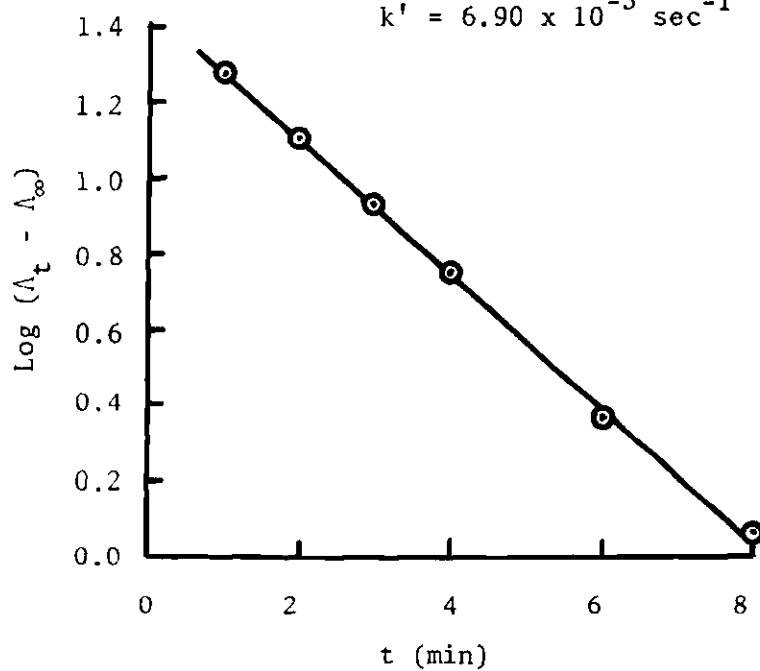


Chart 53. Pseudo First Order Rate Data for the Reaction of
 $9.00 \times 10^{-3}\text{M}$ Benzyl Tosylate with $5.22 \times 10^{-4}\text{M}$
 Potassium Azide in Acetonitrile Containing
 0.10M 18-Crown-6 at 30°

Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_t - \Lambda_\infty$
1	70.50	145.5	10.3
2	69.10	142.6	7.4
3	67.50	139.3	4.1
4	66.60	137.4	2.2
5	66.00	136.2	1.0
6	65.70	135.6	0.4
8	65.50	135.1	-

Chart 54. Reaction of $9.00 \times 10^{-3} \text{M}$ Benzyl Tosylate with $5.22 \times 10^{-4} \text{M}$ Potassium Azide in Acetonitrile Containing 0.10M 18-Crown-6 at 30°

Linear Correlation Coefficient = $-.990$

$$\text{Slope} = \frac{-k'}{2.3} = -2.53 \times 10^{-1} \text{ min}$$

$$k' = 9.69 \times 10^{-3} \text{ sec}^{-1}$$

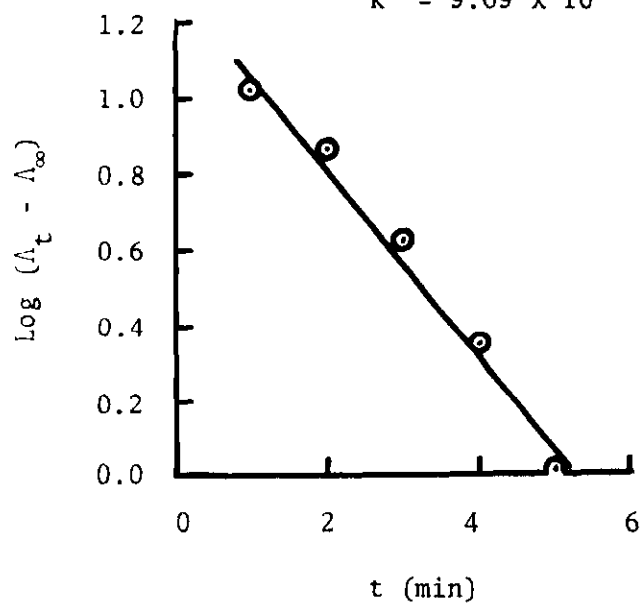


Chart 55. Pseudo First Order Rate Data for the Reaction of
 $1.57 \times 10^{-2} \text{M}$ Benzyl Tosylate with $5.75 \times 10^{-4} \text{M}$
 Thiourea in Acetonitrile at 30°

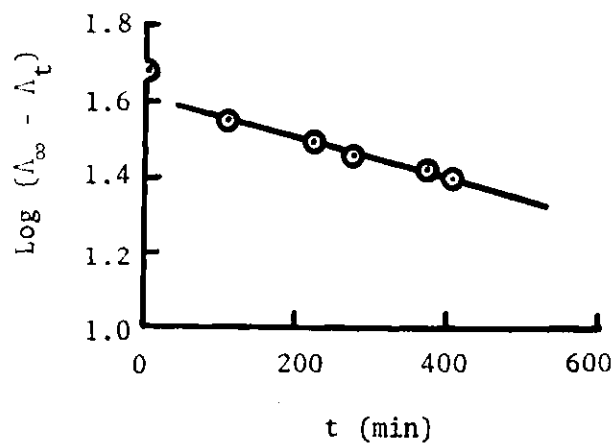
Time (min)	L (mho)	Λ ($\text{cm}^3/\text{equiv-ohm}$)	$\Lambda_\infty - \Lambda_t$
2	40.4	75.7	50.0
59	46.3	86.7	39.7
108	48.0	89.9	36.5
163	49.4	92.5	33.9
224	50.8	95.2	31.3
284	51.9	97.2	29.2
376	53.3	99.8	26.6
410	53.9	100.9	25.5
1366	61.2	114.6	11.8
2818	67.5	126.4	-

Chart 56. Reaction of $1.57 \times 10^{-2} \text{ M}$ Benzyl Tosylate with
 $5.75 \times 10^{-4} \text{ M}$ Thiourea in Acetonitrile at 30°

Linear Correlation Coefficient = $-.993$

$$\text{Slope} = \frac{-k'}{2.3} = -5.35 \times 10^{-4} \text{ min}^{-1}$$

$$k' = 2.05 \times 10^{-5} \text{ sec}^{-1}$$



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