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SALT EFFECTS IN NUCLEOPHILIC SUBSTITUTION REACTIONS

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ABSTRACT

The effect of electrolytes on the rates of SN1 reactions was attributed by the Hughes-Ingold electrostatic theory to their effect on the stability of the transition state, their effect on the initial state being considered as negligibly small. More recently Grunwald put forward a theory in which the effect of electrolytes on the initial as well as the transition state was considered to be important. Experimental support for the latter theory was rather weak as it consisted solely of results obtained using different organic compounds for the solubility and rate determinations (the solubility data showing the effect of electrolytes on the initial state).

It was therefore thought desirable to study the effect of electrolytes on the solubility and on the rate of hydrolysis of the same organic compound (p-nitrobenzhydryl chloride). The results show that the effect of electrolytes on the solubility of the initial state is certainly not negligibly small, and that the requirements of Grunwald's quantitative treatment are obeyed for many of the electrolytes studied. However factors not taken into account by this treatment appear to be of importance for some of the electrolytes employed (e.g. $NaClO_4$, $HClO_4$). These factors may arise from short-range interactions between the electrolyte and the substrate.

CHAPTER I

INTRODUCTION

The Range Of Nucleophilic Substitution Reactions

According to Ingold(1)(2) organic substitution reactions may occur in one of two ways, depending on the electron distribution on fission of the bond R - X, viz;

$$\text{(i)}\quad \text{R}\ \cdot\vdots\cdot\ \text{X} \longrightarrow \text{R}\cdot + \text{X}\cdot \qquad \text{Homolytic fission}$$

$$\text{(ii)}\quad \text{R}\ \vdots\cdot\cdot\ \text{X} \longrightarrow \text{R}^{+} + \text{X}\colon^{-} \qquad \text{Heterolytic fission}$$

where the dots represent electrons.

The type of fission that does occur is governed by the experimental conditions, and the nature of R, X, and the substituting atom, or group, Y. In homolysis the distribution of the bonding electrons facilitates attack by a free radical (Y·), i.e.

$$\text{Y}\cdot + \text{R}\ \cdot\vdots\cdot\ \text{X} \longrightarrow \text{Y} - \text{R} + \text{X}\cdot$$

Although common in the gaseous state, this type of substitution is rarely favoured in solution.

Substitution in solution usually involves heterolysis ; there are two possibilities. If the group R retains the bonding electrons the reaction is termed electrophilic, i.e.

$$\text{Y} + \text{R}\ \cdot\ \cdot\vdots\text{X} \longrightarrow \overbrace{\text{Y}\cdot\cdot\text{R}}^{-} + \text{X}^{+} \qquad \text{Electrophilic substitution (SE)}$$

On the other hand if the bonding electrons are retained by the departing group X the reaction is termed nucleophilic, i.e.

$$\text{Y} + \text{R}\vdots\cdot\ \cdot\ \text{X} \longrightarrow \overbrace{\text{Y} - \text{R}}^{+} + \text{X}\colon^{-} \qquad \text{Nucleophilic substitution (SN)}$$

As this thesis is concerned with nucleophilic substitution, only the latter type of reaction will be discussed.

In SN reactions the expelled group carries the bonding electrons away with it, the attacking nucleophilic group making up the electron deficiency on R. The overall reaction therefore involves the losing of one electron by Y, and the gaining of one electron by X. Consequently for a reaction to be regarded as a nucleophilic substitution reaction, it is irrelevant whether the substituting atom, or group, is a charged or neutral entity, as long as the transfer of charge ensues, e.g.

Finkelstein reaction $I^- + RCl \rightarrow RI + Cl^-$

Menschutkin reaction $NR'_3 + RCl \rightarrow \overbrace{R.NR'_3}^{+} + Cl^-$

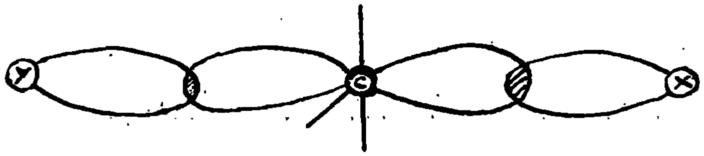
The Bimolecular And Unimolecular Mechanisms

Several theories (3)(4)(5)(6)(7) concerning substitution at a saturated carbon atom had been put forward before Hughes, Ingold, and their co-workers showed that there was a common mechanistic pattern for all nucleophilic substitution reactions (1). Experimental data led them to propose that such reactions could proceed via one of two mechanisms.

The bimolecular mechanism (SN2) involves only one stage, the two molecules undergoing simultaneous covalency change, i.e.

$$Y + R - X \rightarrow \overset{\delta+}{Y} --- R --- \overset{\delta-}{X} \rightarrow \overbrace{Y - R}^{+} + X^- \qquad (SN2)$$

The transition state in this mechanism may be formulated in terms of molecular orbitals (8), and the structure written as follows :



On this view there is a rehybridisation of the four original sp^3 orbitals of the central carbon atom on passage into the activated complex. The three bonds not undergoing reaction consist of three sp^2 orbitals of the central carbon atom, the remaining p orbital being perpendicular to the plane of these three. Finally an orbital of both the entering and leaving groups combine with this p orbital as shown.

The alternative mechanism occurs via two stages. The first stage involves a heterolytic fission of the R – X linkage without any participation by the nucleophilic reagent Y. The resulting carbonium ion undergoes rapid combination with this reagent in the second stage, i.e.

$$\left.\begin{array}{ll}(i) & R \overset{\curvearrowright}{-} X \overset{\text{slow}}{\rightleftharpoons} R^{+} + X^{-} \\ (ii) & Y + R^{+} \xrightarrow{\text{rapid}} \overbrace{R - Y}^{+}\end{array}\right\} ------- (SN1)$$

The rate of reaction is entirely controlled by the first step, and as there is only one molecule undergoing covalency change in this step, the reaction is regarded as unimolecular. The activation energy of the ionisation, stage (i), is considerable. However in solution the energy maximum is reduced to accessible values by solvation forces, which increase as the charge transfer increases$^{(9)}$. It is envisaged that the transition state involves a loosening of the covalent bond between R and X, and a partial charge transfer, i.e.

$$R^{\delta +} - - - - X^{\delta -}$$

Methods of distinguishing between the SN1 and SN2 mechanisms.

As the bimolecular mechanism proceeds via one stage, involving both RX and the nucleophile, such a reaction should follow second order kinetics, *viz.*,

$$\text{Rate} = k_2 [Y] . [RX]$$

On the other hand, the ionisation of RX is the rate-determining stage in the unimolecular mechanism. Consequently a reaction of this type should follow first order kinetics, *viz.*,

$$\text{Rate} = k_1 [RX]$$

This kinetic criterion of mechanism is only applicable if the reactants are present in small and controllable concentrations. In solvolytic reactions, where the concentration of the substituting agent may be regarded as constant, both mechanisms should yield first order kinetics. However, small deviations from first order kinetics may occur in the unimolecular mechanism due to the reversibility of the rate-determining ionisation (see page 5).

Several indirect methods for determining the mechanism of solvolytic reactions have been discussed by Hughes, Ingold and their co-workers.(10)(11)(12)(13) One of these involves the effect of electrolytes on the rate of reaction. As the present investigation entailed a study of electrolyte effects in SN1 reactions, their views are discussed in some detail below.

<u>The effect of electrolytes on the rate of reaction.</u>

Hughes, Ingold and their co-workers (13), considered that the addition of an electrolyte altered the rate of an SN solvolysis by invoking one (or both) of two effects : the ionic strength effect (shown by all electrolytes) and the mass-law effect (shown by a limited number of anions and only possible in SN1 solvolysis).

<u>The ionic strength effect.</u> - It was assumed that the transition state in SN reactions was so much more polar that the initial state that the effect of electrolytes on the stability of the latter could be ignored. The addition of electrolytes was considered to produce an ionic atmosphere round the polar transition state analagous to the ionic atmosphere postulated by Debye and Hückel for a fully developed ion. This ion atmosphere stabilises the transition state in the same way as it stabilises an ion in solution and hence all electrolytes should accelerate the reaction by this effect.

Acceleration of SN1 and SN2 reactions differ in that added salts have a weaker effect on the latter because of the greater diffusion of charge in the transition state.

The mass-law effect. - The rate-determining ionisation step in reaction by mechanism SN1 was considered by Hughes, Ingold and their co-workers to be reversible, i.e.

$$\text{(i)}\quad RCl \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ + Cl^-$$

$$\text{(ii)}\quad R^+ \xrightarrow[H_2O]{(3)} ROH + H^+$$

R^+ was considered to be so highly reactive that it disappeared by process (2) or (3) as soon as it was formed. Thus the concentration of R^+ was small at all times and the stationary state principle could therefore be applied

$$\text{i.e.}\quad \frac{d[R^+]}{dt} = 0$$

$$\text{Hence}\quad \frac{-d[RCl]}{dt} = \frac{d[ROH]}{dt} = k_3[R^+]$$

$$= \frac{k_1[RCl]}{1+\alpha[Cl^-]} \quad \text{-------} \quad (1.1)$$

$$\text{where } \alpha = \frac{k_2}{k_3}$$

As the reaction proceeds chloride ions are produced and the denominator in equation (1.1) therefore increases, leading to retardation of the reaction. This effect, which arises from the reversibility of the rate-determining ionisation, is called the mass-law effect, and the parameter α (called the mass-law constant) is a measure of its magnitude. If the effect is large the first order rate falls as the reaction proceeds, similarly the addition of a chloride ion electrolyte will reduce the rate.

The reaction of other ions with the carbonium ion will only have a small effect on the rate of disappearance of RCl but may cause a significant reduction in the rate of hydrolysis. For example if an added ion Y is such that RY is not hydrolysed, the rate of hydrolysis is decreased because some carbonium ions form RY.

Combination of the mass-law and ionic strength effects - In practice mass-law and ionic strength effects cannot be considered separately. With added common-ion electrolytes the mass-law effect reduces the rate in unimolecular reactions, but this reduction may or may not be greater than the acceleration due to the ionic strength effect. Thus the addition of common-ion electrolytes to benzhydryl halides caused a retardation of hydrolysis, while with tert-butyl bromide an acceleration was observed (14).

Quantitative Treatment Of The Ionic Strength Effect.

According to the transition state theory the specific rate in the presence of an electrolyte is given by the equation,

$$k_1 = k_1^{\circ} \frac{\gamma_{RX}}{\gamma_{\neq}}$$

where k_1° is the rate constant in the absence of electrolytes, and γ_{RX}, $\gamma_{\neq}$, the activity coefficients of RX and the transition state in the presence of the electrolyte, relative to unity when no electrolyte is present.

Hughes, Ingold and their co-workers (13), assumed that the effect of electrolytes on γ_{RX} was negligibly small. They calculated $\gamma_{\neq}$ by treating the transition state as two point charges, $\pm ze$, separated by a fixed distance, d, and then proceeded in a manner similar to that employed by Debye for the calculation of the activity coefficients of fully developed ions.

Using analagous approximations, they found that for uni-univalent electrolytes

$$\log ({}^{k_1'}/k_1^{\circ}) = 0.912 \times 10^{16} \frac{\sigma \mu}{D^2 T^2} \qquad (1.2)$$

where D is the dielectric constant, σ $(= z^2 d)$ is called the ionic strength constant, and μ is the ionic strength.

Thus for a given compound RX undergoing an SN1 reaction under a constant set of conditions, the magnitude of the ionic strength effect (i.e. the acceleration caused by added electrolytes) should depend only on the ionic strength, and be independent of the nature of the uni-univalent electrolyte.

This conclusion has been the subject of much discussion and, contrary to the requirements of equation (1.2), a number of workers have reported specific electrolyte effects in solvolysis and related reactions. Hughes, Ingold, and their co-workers, have however stressed that equation (1.2) arises from a limiting law which is, strictly, only applicable to very dilute solutions (13). This could account for small differences in the accelerating effects of electrolytes at experimental concentrations. Moreover, association of the electrolyte into ion pairs may occur, particularly in solvents of relatively low dielectric constant (14). Under these conditions the "true" ionic strength of the solution will depend on the nature of the electrolyte as well as on its concentration. This may account for the observation of specific electrolyte effects in the acetolysis of esters of toluene p-sulphonic acid (15)(16), in the racemisation and radio-chloride exchange of p-chlorobenzhydryl chloride (17), and in the hydrolysis of tert.-butyl bromide in mixed solvents of low water content.(18)

The suggestion of a linear relation between μ and k_1(19), instead of μ and log k_1, may also be connected with a significant degree of ion-pair formation in poor ionising solvents and it is noteworthy that the effect of verying amounts of bromide ions on the rate of hydrolysis of tert.-butyl chloride in 90% aqueous acetone is given by equation (1.2) if the association of the electrolyte is taken into account (20); it must however be stressed that this conclusion was reached by neglecting the retarding mass-law effect which should also be invoked in this system, though this effect may well have been small.

Kohnstam, Bensley, and Shillaker(21)(22), studied the reactions of dichlorodiphenylmethane with aqueous acetone and concluded that the observed electrolyte effects were consistent with the quantitative treatment of Hughes and Ingold. However these workers were mainly concerned with the mass-law effect which was very large in their system. Consequently the fact that the ionic strength constant, σ, was rather small (and also that the work was carried out in fairly dilute solutions) may well have obscured a specificity of electrolyte effects on the rate of ionisation.

On the other hand, there is some evidence for specific electrolyte effects in good ionising solvents. Lucas and Hammett (24) found the rate of reaction of tert.-butyl nitrate in aqueous dioxane was accelerated by perchlorate ions and retarded by the non-common hydroxide ions, while other anions had intermediate effects. These observations led them to suggest an alternative theory to that of Hughes and Ingold. They proposed that the different degrees of hydration of different electrolytes would alter the "effective" solvent composition, and thus affect the rate.

On this view the retarding action of the hydroxide ion arises from its "drying" effect on the solvent. Benfey, Hughes and Ingold (24) showed that if the plausible theory of Lucas and Hammett was correct, it could not account for the retardation of SN1 solvolysis by common-ions to the exclusion of the mass-law effect. They did however confirm the retarding effect of hydroxide ions, but proposed that lyate ions were a special case, being inferior to a chloride or azide ion in penetrating the solvation shell around a carbonium ion.

Further evidence of specific electrolyte effects in good ionising solvents has recently become available. Winstein, Hojo and Smith (25) observed that lithium and tetrabutyl-ammonium salts had widely different effects on the solvolysis of p-chlorobenzhydryl chloride in 80% aqueous acetone. Duynstee, Grunwald and Kaplan (26), found that the effect of sodium salts on the SN1 solvolysis and racemisation of sulphonic esters in 50% aqueous dioxane depended on the nature of the anion. Pocker (27) has also reported specific electrolyte effects for the hydrolysis of triphenylmethyl chloride in aqueous dioxane, and similar effects have been observed by Queen (28), and Shillaker (29) for the reaction of benzhydryl halides with aqueous acetone.

Since a modification of the original scheme for SN1 reactions has recently been proposed, it is necessary to consider it briefly in order to see whether it can account for the specific electrolyte effects that have been reported.

1. Ionisation of RX via ion-pair intermediates.

Winstein and his co-workers(30)(31)(32)(33)(34) observed that racemization occurred more rapidly than chemical reaction for a variety of compounds in non-aqueous solvents. This phenomenon has also been reported by Pocker(35) for the S_N1 reactions of aralkyl halides in nitromethane and sulphur dioxide as solvents. Recently excess racemization has also been demonstrated for reactions carried out in aqueous solvents(25)(36)(37). Winstein concluded from these observations that ionisation proceeded via a meta-stable intermediate, the internal ion pair, in which the carbonium and chloride ions are in contact. It was envisaged that this intermediate could undergo racemization but could not react with any other reagent.

A study of electrolyte effects on the S_N1 acetolysis of sulphonic esters led Winstein(15) to postulate the existence of a further meta-stable intermediate, the solvent-separated or external ion pair which could react with added nucleophiles in acetic acid. The acetolysis of a number of systems has afforded Winstein and his co-workers with evidence for the existence of this latter intermediate.(38)(39)(40)(41)(42)(43) The reaction scheme envisaged by these workers can therefore be represented as follows :-

$$\begin{tikzcd}
RX \arrow[r, shift left] & R^{+}X^{-} \arrow[l, shift left] \arrow[r, shift left] & R^{+}/\!/X^{-} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, dash] & R^{+}+X^{-} \arrow[l, shift left] \arrow[d, dash] \\
 & \text{Internal ion pair} & \text{External ion pair} \arrow[d] & \text{Dissociated ions} \arrow[d] \\
 & & ROH & ROH
\end{tikzcd}$$

However the evidence for the intervention of the external ion pair in solvolysis is based almost entirely on work in systems favourable to the formation of ion-pairs.

There is no evidence for this effect in hydroxylic solvents. Indeed Kohnstam and Shillaker (22) concluded from their work on the hydrolysis of dichlorodiphenylmethane in aqueous acetone that any reaction between water, or anions, and the external ion pair contributed nothing to the total rate. It will therefore be assumed that SN1 reactions in aqueous solvents occur via the fully developed carbonium ion, as the internal ion pair is not envisaged to undergo chemical reaction.

Grunwald's theory of electrolyte effects

Hughes, Ingold, and their co-workers assumed that electrolytes only affected the stability of the transition state (13). Grunwald and his co-workers have recently attempted to account for the specific nature of electrolyte effects ; their treatment allows the electrolyte to affect the stabilities of both the initial and the transition states (26). Their studies of the effect of electrolytes on the solubility of organic substrates showed that the ion-non-electrolyte interaction coefficient, k_s is given by the expression (44);

$$k_s = Ai + Bi \cdot \frac{dG^\circ i}{dZw} \cdot \frac{dG^\circ s}{dZw} \qquad (1.3)$$

where Ai and Bi are constants characteristic of the solvent and the non-electrolyte, G°i and G°s are the standard chemical potentials of the non-electrolyte and electrolyte respectively, and Zw is the mole fraction of water in the solvent. The ion-non-electrolyte interaction coefficient is related to the activity coefficient of the non-electrolyte by the expression

$$\ln \gamma_i = k_s C_s$$

where γi is the activity coefficient of the non-electrolyte relative to unity at zero ionic strength, and C_s is the concentration of the electrolyte.

Equation (1.3) therefore shows that the activity coefficient of an organic substrate depends on the term $\frac{dG^\circ_s}{dZw}$, i.e. on the nature of the electrolyte.

Grunwald and his co-workers assumed that a similar expression held true for the activity coefficient of the activated complex in an SN1 reaction (26). Substitution in the Brønsted equation then yielded

$$S_G = A + BRT \cdot \frac{d \ln k_1^\circ}{dZw} \cdot \frac{dG^\circ_s}{dZw} \quad \text{-----} (1.4)$$

where $S_G = \frac{1}{C_s} \cdot \log (k_1/k_1^\circ)$, and A and B are now parameters characteristic of the reactant, the transition state, and the solvent. The term S_G in equation (1.4) in effect shows the influence of electrolyte additions on the rate of reaction. Since the magnitude of S_G depends on the magnitude of $\frac{dG^\circ s}{dZw}$ which in turn depends on the nature of the electrolyte, equation (1.4) predicts specific electrolyte effects on the rates of SN1 reactions.

This approach requires a linear relationship between S_G and $\frac{dG^\circ s}{dZw}$. The latter term had been evaluated independently from fugacity measurements by Grunwald, Baughman, and Kohnstam (45) and therefore the validity of the equation could be tested. The results of Grunwald and his co-workers for the effect of simple inorganic electrolytes on the SN1 solvolysis of a sulphonic ester gave the predicted relationship; those obtained on the racemization of a similar compound were not in such good agreement.

The investigations of Grunwald and his co-workers involved the use of two different non-electrolytes for the solubility measurements, and a further two for the rate determinations. It was therefore thought desirable to determine the effect of electrolytes on the solubility and the rate of reaction of the same material. p-Nitrobenzhydryl chloride was suitable for this purpose. Hydrolysis proceeds by mechanism SN1 (46) and the reaction at 0°C is sufficiently slow to allow the solubility to be determined. This temperature is below the melting point of the compound and there is therefore no uncertainty about the composition of the undissolved material. However before the results of this investigation can be discussed, it is necessary to consider the effect of electrolytes on the solubility of non-electrolytes, i.e. on their activity coefficients.

CHAPTER II

The Effect Of Electrolytes On Solubility

The effect of added electrolytes on the activity coefficient of a non-electrolyte, present in low concentration, is given by the equations, (47)

$$\log \frac{\gamma_i}{\gamma_i^\circ} = \log \frac{S_i^\circ}{S_i} = K_s C_s + K_i (S_i - S_i^\circ) \quad \text{---}(2.1)$$

where γ_i° and γ_i are the activity coefficients in the pure solvent and in the solvent with added electrolyte, respectively, S_i° and S_i are the corresponding solubilities, K_s is the ion-non-electrolyte interaction coefficient, and K_i that for the interaction of the non-electrolyte with itself.

If S_i and S_i° are small the last term can be neglected and equation (2.1) reduces to,

$$\log \frac{\gamma_i}{\gamma_i^\circ} = \log \frac{S_i^\circ}{S_i} = K_s C_s \quad \text{---}(2.2)$$

which is a form of the well known Setschenow equation (48). On the other hand if S_i and S_i° are large, then equation (2.2) can often be applied by replacing K_s by another constant K.

Values of K_s and K have been interpretated in a variety of ways which are conveniently considered under three main headings.

1. Electrostatic theories

The electrostatic theories treat the solvent as a continuous dielectric, and any departures from ideality are assumed to arise from electrostatic interaction involving ionic charges. The most widely known of these theories are those of Debye and McAulay (49) and Debye (50). The former related electrolyte effects to the influence of the non-electrolyte on the dielectric constant of the solvent, and predicted a linear dependence of $\log \gamma_i$ on electrolyte concentration, viz.,

$$\ln \gamma_i = \frac{\delta_i \varepsilon^2}{2kTD_o} \sum_j c_j z_j^2/b_j \text{ - - - - - - } (2.3)$$

where δ_i is defined by $D = D_o(1 - \delta_i C_i)$, D_o, D are the dielectric constants of the pure solvent and the solution containing the non-electrolyte, respectively, C_j is the molar concentration of ionic species j, Z_j is the valence and b_j the radius of ionic species j.

The later more exact theory of Debye took into account the heterogeneity of the mixture of solvent and neutral solute, and required a linear dependence of $1/\gamma_i$ on electrolyte concentration, viz.,

$$\frac{1}{\gamma_i} = 1 - \frac{4\pi N}{1000} \sum_j J_j c_j \qquad (2.4)$$

where $J_j = \int_{b_j}^{\infty} (1 - e^{-(R_j)^4/r^4})\, r^2 . dr$, r represents the possible separation between an ion and a molecule of the non-electrolyte, and R_j^4 is defined by

$$R_j^4 = \frac{\varepsilon^2 Z_j^2 \, 1000}{8 \pi R T D_o} \cdot \delta_i$$

Similar approaches have been proposed by Altshuller and Everson (51), Butler (52), and Belton (53). A linear dependence of log γ_i on the electrolyte concentration was also predicted by Kirkwood (54). According to the electrostatic approach K_s should be entirely independent of the nature of the electrolyte for ions of the same valence type (13), or only small variations should be expected. Moreover the addition of electrolytes should give rise to a salting out of the non-electrolyte if the latter decreases the dielectric constant of the solvent, while salting-in should occur if the dielectric constant of the solvent is increased by the non-electrolyte. (The terms "salting-out" and "salting-in" are used to denote an increase and a decrease in the activity coefficient of the non-electrolyte respectively).

Albright and Williams (55)(56) determined the dielectric constants of aqueous systems for which reliable salting-out data were available. At low electrolyte concentration they found solubilities, calculated from dielectric constant measurements, to be in good agreement with the observed values. Wright, Stuber, and Albright (57) noted that the addition of phenylthiourea to ethanol increased the dielectric constant of the latter. Thus if equations (2.3) and (2.4) are correct then the addition of electrolytes will salt-in phenylthiourea, an effect observed in practice. However Long, McDevit, and Dunkle (58), found that the requirements of the electrostatic approach were not obeyed in the γ-butyrolactone-water system. Thus while some uni-univalent electrolytes cause salting-out of γ-butyrolactone others give rise to salting-in.

Deviations of this kind may be due to non-electrostatic interaction between ions and the non-electrolyte, a factor not allowed for in the electrostatic theories.

2. Short-range interaction theories.

The electrostatic theories cannot explain the marked variation in the effects of different electrolytes on the activity coefficients of, for example, the aniline-water (59), and diacetone alcohol-water (60) systems. Moreover they are totally inadequate when there is a change from salting-out to salting-in of the non-electrolyte in the same system (58).

McDevit and Long (61) attempted to explain such observations by postulating short-range interactions between electrolytes and the non-electrolyte, in agreement with the earlier ideas of Kortüm (62). On this basis McDevit and Long derived the equation : -

$$\log \gamma i = A \sum z^2_j c_j - B \sum \alpha_j c_j \quad ---(2.5)$$

where A and B are parameters which depend on the non-electrolyte and to a small extent on the electrolyte, and αj is the polarizability of ion j.

A more detailed equation than (2.5) was later proposed by Bockris and his co-workers (63), but the two equations are similar in that the second term in each makes allowance for a salting-in effect. It follows therefore that the many observations of salting-in by large cations or by large anions (64)(65)(66)(67)(68) when salting-out would be predicted by the electrostatic theories, can be accomodated by equation (2.5). Nevertheless the short-range interaction theories fail to indicate the anomolously low salting-out effect of certain ions. Thus in the ammonia-water system lithium ions have a much smaller salting-out effect than sodium or potassium ions (69), while a similar low salting-out effect by hydrogen ions has been reported for boric, benzoic, and salicyclic acids (70)(71).

It would therefore appear that the short-range interaction theories offer an important contribution to the effect of electrolytes on solubility, although they cannot accomodate all the experimental results.

3. Salt-induced medium effects.

The short-range interaction approach cannot account for the fact that the sequence of electrolyte effects, for simple inorganic electrolytes, is almost independent of the non-electrolyte. Various workers have attempted to account for this by assuming that the addition of electrolytes alters the properties of the solvent, which in turn effect the solubility of the non-electrolyte. Such approaches may be discussed under the heading of salt-induced medium effects.

One of the earliest approaches involved the assumption of preferential attraction of water by ions (72). However as this work involved aqueous solutions it is difficult to envisage a change in solvent resulting from the removal of water molecules by ions. Later Lucas and Hammett (23) suggested that a change of composition in a two-component system may be brought about by the strong attraction of water by electrolytes. This in effect would increase the concentration of the organic solvent, and could therefore accomodate the phenomenon of salting-in in a two-component system.

A different approach was proposed by McDevit and Long (66) who assumed that the effect of the non-electrolyte was simply one of occupying volume. They derived a limiting law which related the magnitude of the electrolyte effects to the volume changes which occur when electrolytes and water are mixed. Such an effect creates variations in the internal pressure of the solvent and hence can accomodate salting-out or salting-in of the non-electrolyte. Application of their limiting law to the benzene-water system satisfactorily fitted the low salting-out observed with lithium and hydrogen ions, and the salting-out with large ions such as perchlorate and tetramethyl ammonium ions, as well as the normal salting-out usually observed in aqueous solutions with sodium and potassium salts. These experimental results of McDevit and Long have been confirmed by other workers. (67)(73) Results obtained by Paul (68) from his study of the solubilities of naphthalene and diphenyl in aqueous solutions of electrolytes were in agreement with McDevit and Long's theory. He found that for a given electrolyte the magnitude of the salting-out effect increased progressively from benzene to naphthalene to diphenyl - apparently paralleling the increase in the liquid volume of the non-electrolyte.

The addition of sodium chloride to benzoic acid in water resulted in salting-out of the organic compound, but the presence of organic solvents resulted in salting-in, the effect increasing with decreasing water content of the solvent. Bockris and Egan (74) explained this phenomenon by assuming a preferential solvation of the sodium and chloride ions by water molecules, thus increasing the effective concentration of the organic solvent ; this would clearly increase the solubility of the non-electrolyte. Confirmation of this view was provided by Butler and Grunwald (75). They observed that whereas the addition of sodium and potassium chlorides to the naphthalene-water system resulted in salting-out, salting-in occurred with 50% aqueous dioxane as solvent.

More recently Grunwald and Butler (44) have studied the effect of electrolytes on the solubilities of naphthalene and 1-naphthoic acid in 50% aqueous dioxane.

This work again illustrated the marked differences in the properties of one- and two-component systems. Previous observations (47) in water had shown that electrolyte effects on solubility could be described by the Setschenow equation up to quite large electrolyte concentrations (> 1M). This was not found to be the case in the two-component systems studied by Grunwald and Butler. In such systems it was found that the Setschenow equation only held for electrolyte concentrations of the order of 0.1 M.

However observations made in aqueous (76)(77)(78) and in partially aqueous (74)(75) systems have indicated that local solvent structure is a significant factor when the effect of electrolytes on the solubility of non-electrolytes is considered. A solvation effect together with an electrostatic effect was incorporated in Grunwald's recent treatment of salt effects. This treatment led to equation (1.3) viz.,

$$k_s = Ai + Bi \frac{dGi^\circ}{dZw} \quad \frac{dG^\circ s}{dZw}$$

where Ai allows for electrostatic effects and the last term for solvation effects. k_s and K_s are related by the expression

$$k_s = \frac{K_sC_s + KiCi}{C_s}$$

where Ci is the concentration of the non-electrolyte i in a salt solution. Thus $k_s = K_s$ when the concentration of the non-electrolyte is very low, or when the value of Ki itself is small. It has been pointed out previously (see page 11) that since

$$\ln \gamma_i = K_sC_s$$

the activity coefficient of the non-electrolyte is dependent on the term $\frac{dG^\circ s}{dZw}$, i.e. on the nature of the electrolyte.

The validity of equation (1.3) could be tested by the linearity of a plot of k_s against $\frac{dG^{o}s}{dZw}$. An independent investigation (45) had determined values of this latter term and had also shown that some ions were preferentially solvated by water molecules - others by organic molecules. A plot of the independently obtained values of $\frac{dG^{o}s}{dZw}$ against k_s gave a straight line for simple inorganic electrolytes, as required by equation (1.3).

Grunwald and Butler found the salting order of simple inorganic electrolytes to be almost the reverse of that found in water (47)(68). However electrolytes with large organic ions were found to give negative k_s values in aqueous dioxane similar to those previously obtained with water (47)(65). They suggested that short-range electrolyte-non-electrolyte interaction could account for the results observed with large organic ions but did not attempt a quantitative explanation. At present therefore no simple theory has been postulated that can account for all the observed changes in the solubility of non-electrolytes on the addition of electrolytes.

CHAPTER III

RESULTS AND DISCUSSION

Kinetic Experiments

The effect of electrolytes on the rate of reaction of p-nitrobenzhydryl chloride with 50% aqueous acetone was studied at 20.03°C and 39.75°C. In order to eliminate the possibility of a change in the solvent composition during a kinetic run the sealed ampoule technique was employed. The low solubility of sodium fluoride in 50% aqueous acetone and of p-nitrobenzhydryl chloride in 45% aqueous acetone necessitated the use of stoppered flasks for these runs. All the runs were carried out in duplicate, and the reactions followed by observing the development of acidity or chloride ions in the solutions.

The effect of electrolytes on the rate of hydrolysis of p-nitrobenzhydryl chloride.

The effect of electrolytes on the first order rate coefficient for the disappearance of p-nitrobenzhydryl chloride with 50% aqueous acetone at 39.75°C is summarised in Table I. The percentage increase in rate on the addition of electrolytes is quoted. This percentage is given by $100\left(\frac{k_1}{k_1^{0}} - 1\right)$, where the k_1's are the mean coefficients for the rate of disappearance of p-nitrobenzhydryl chloride, and 0 refers to the absence of electrolytes.

Table I. The effect of electrolytes on the rate of reaction of p-nitrobenzhydryl chloride in 50% aqueous acetone at 39.75°C. (The figures reported refer to the percentage change in rate caused by the addition of electrolytes).

Electrolyte	Concentration 0.05 M	Concentration 0.1 M
* NaF	- 4.64[≠] ± 0.34	
LiCl	- 2.93 ± 0.19	- 6.97 ± 0.21
NaCl	- 2.64 ± 0.20	- 6.52 ± 0.25
KCl	- 1.74 ± 0.27	- 5.72 ± 0.23
NaO_3SPh	+ 1.43 ± 0.21	+ 2.25 ± 0.16
$NaNO_3$	+ 4.73 ± 0.29	+ 7.78 ± 0.32
$NaClO_4$	+ 3.28 ± 0.27	+ 8.02 ± 0.35
KNO_3	+ 4.63 ± 0.33	+ 8.57 ± 0.35
NaBr	+ 5.83 ± 0.28	+ 8.72 ± 0.33
$KClO_4$	+ 3.57 ± 0.31	+ 8.93 ± 0.38
$LiNO_3$	+ 4.50 ± 0.20	+ 9.05 ± 0.21
KBr	+ 4.08 ± 0.41	+ 9.44 ± 0.42
LiBr	+ 5.94 ± 0.22	+10.03 ± 0.33
* HNO_3	+10.18 ± 0.38	+19.81 ± 0.42
* $HClO_4$	+13.36 ± 0.36	+22.42 ± 0.39

[≠] This was twice the value obtained on addition of 0.025 M NaF.

* These systems were followed by noting the production of chloride ions.

The results in Table I show that electrolytes generally do not have a large effect on the rate. Doubling the electrolyte concentration often doubles the change in rate but this does not always apply, e.g. KCl, $NaNO_3$, $NaBr$, $LiBr$, $HClO_4$. It is noteworthy that the acceleration caused by 0.1 M electrolyte is sometimes more and sometimes less than twice the acceleration caused by 0.05 M, cf. $NaBr$-$NaClO_4$, $LiBr$ - KBr.

The apparently anomalous observations may result from the fact that k_1° (the first order rate constant in the absence of electrolytes) was not determined at the same time as k_1 (the first order rate constant in the presence of electrolytes with the same solvent). The composition of the solvent altered on standing and although attempts were made to compensate for this by frequent monitoring, small changes in composition occurring over a period of a few days may have been missed. If the values taken for k_1° are in error by 0.5% this would bring the 0.05 M results in line with the 0.1 M results. An 0.5% error in the k_1° value causes a smaller error in the results observed for 0.1 M electrolyte solutions than for 0.05 M, and the former results will therefore be used in the discussion of salt effects ; differences of less than 1% will be neglected.

It can be seen in Table I that the alkali metal bromides, nitrates, and perchlorates, have much the same effect, although the bromides probably accelerate more than the others. Lithium salts appear to have a greater accelerating effect than sodium or potassium salts. However the fluoride ion has a large retarding effect, the benzene sulphonate ion is not as accelerating as other anions, and hydrogen ions accelerate much more than lithium, sodium, or potassium ions. Chloride ions retard but this is probably due to the operation of the mass-law effect.

The effect of temperature on the change in rate caused by the addition of electrolytes to the reaction of p-nitrobenzhydryl chloride in 50% aqueous acetone is shown in Table II.

Table II. The effect of salts on the rate of reaction of p-nitrobenzhydryl chloride in 50% aqueous acetone at 20.03°C and 39.75°C. (The figures reported refer to the percentage change in rate caused by the addition of electrolytes).

Electrolyte		Concentration 0.05 M	Concentration 0.1 M
NaCl	20.03°C	− 3.35 ± 0.26	− 5.83 ± 0.26
	39.75°C	− 2.64 ± 0.20	− 6.52 ± 0.23
$NaNO_3$	20.03°C	+ 2.64 ± 0.36	+ 6.58 ± 0.40
	39.75°C	+ 4.73 ± 0.29	+ 7.78 ± 0.32
$NaClO_4$	20.03°C	+ 3.89 ± 0.31	+ 7.44 ± 0.31
	39.75°C	+ 3.28 ± 0.27	+ 8.02 ± 0.35
NaBr	20.03°C	+ 6.69 ± 0.41	+12.06 ± 0.43
	39.75°C	+ 5.83 ± 0.28	+ 8.72 ± 0.33

The results in Table II show that, in general, the effect of electrolytes on the rate is fairly insensitive to changes in temperature. Sodium chloride, nitrate, and perchlorate, seem to have the same effects on the rate at 20.03°C and 39.75°C within the limits of experimental error. The greater acceleration caused by sodium bromide at the lower temperature appears to be anomolous.

Hughes and Ingold's electrostatic treatment of the ionic strength effect has been discussed previously (see page 6).

It requires that for a compound undergoing an SN1 reaction under a given set of conditions, the acceleration caused by added electrolytes should depend only on the ionic strength, and be independent of the nature of the uni-univalent electrolyte. The results obtained from the present systems cannot, however, be explained by their treatment. Admittedly this treatment is strictly only applicable to very dilute solutions and so some specificity may be expected on addition of 0.1 M electrolyte. However it is most unlikely that this limitation can account for the range of about 9% retardation by the fluoride ions to 20% acceleration by acids. Moreover, retardation by any electrolyte is not envisaged in the Hughes-Ingold scheme.

Nevertheless for many simple non-common ion electrolytes the increase in rate is approximately constant. These results are therefore in accordance with equation (1.2) derived by Hughes and Ingold. This equation indicates that there should be a logarithmic dependence of k_1 on the molar concentration of the uni-univalent electrolyte. Fainberg and Winstein (19) have however claimed that k_1 should vary linearly with electrolyte concentration but the present results do not allow this difference of opinion to be resolved, since the addition of electrolytes causes only relatively small changes in the rate. Hence equation (1.2) may be expressed as follows :

$$k_1/k_1^{\circ} = \text{antilog} - B\sigma\mu = e^{-2.303\, B\sigma\mu}$$

$$= 1 - 2.303\, B\sigma\mu$$

since $2.303\, B\sigma\mu \ll 1$; B is a constant dependent only on the solvent and temperature.

A comparison of the effects of electrolytes on the rates of reaction of benzhydryl chloride in 70% aqueous acetone and p-nitrobenzhydryl chloride in 50% aqueous acetone.

Queen (28) and Shillaker (29) have studied the effect of electrolytes on the reaction of benzhydryl chloride in 70% aqueous acetone at 20°C. Their results, together with those obtained in the present investigation at 39.75°C are given in Table III.

Table III . The effect of electrolytes on the rate of reaction of (a) benzhydryl chloride in 70% aqueous acetone at 20°C, and (b) p-nitrobenzhydryl chloride in 50% aqueous acetone at 39.75°C. (The figures reported refer to the percentage change in rate caused by the addition of electrolytes).

Electrolyte	Benzhydryl chloride 70% aqueous acetone, 20°C 0.05 M electrolyte	p-Nitrobenzhydryl chloride 50% aqueous acetone, 39.75°C 0.1 M electrolyte
NaCl	- 8.18	- 6.52
LiCl	- 7.63	- 6.97
NMe_4F	- 5.65	-
NaF	-	- 9.28 *
NaO_3SPh	+ 5.70	+ 2.25
$NaNO_3$	+ 6.85	+ 7.78
LiBr	+ 6.95	+10.03
NaBr	+ 8.60	+ 8.72
KBr	+ 9.15	+ 9.44
$NaClO_4$	+15.07	+ 8.02
$HClO_4$	+21.06	+22.42

* This was 4 x the value obtained on addition of 0.025 M NaF.

The results in Table III clearly show that the electrolyte effects are larger in the benzhydryl chloride system but this may arise, at least partly, from the change in solvent composition. Application of the Hughes-Ingold theory indicates that the decrease in dielectric constant could account for this, and the possibility of a greater charge distance ($\sigma = z^2d$) must also be taken into consideration. The greater retardation by chloride ions also evident in the benzhydryl chloride system is consistent with a stabler carbonium ion, i.e. a longer time interval between the stages of the unimolecular substitution reaction. A decrease in dielectric constant has also been observed to increase the mass-law effect (22).

However specific electrolyte effects are clearly evident in Table III and moreover the two systems yield a similar pattern for such effects. In particular fluoride ions retard, replacement of a sodium ion by a hydrogen ion causes marked acceleration, and sodium benzene sulphonate does not accelerate as much as other alkali metal salts. The apparent anomolies in the two systems are the low acceleration caused by lithium bromide in the benzhydryl chloride system (probably due to ion-association because of the decrease in dielectric constant of the solvent), and the low acceleration caused by sodium perchlorate in the p-nitrobenzhydryl chloride system.

<u>Specificity of electrolyte effects.</u>

A number of workers in addition to Queen and Shillaker have observed specific salt effects (see page 9). The most recent attempt to account for such effects was made by Grunwald and his co-workers (26), who proposed equation (1.4), *viz.*

$$S_G = A + BRT \frac{d \ln k_1^0}{dZw} \cdot \frac{dG^\circ_s}{dZw}$$

where $S_G = \frac{1}{C_s} \log (k_1/k_1^\circ)$.

This equation demands that the acceleration caused by added electrolyte depends on the term $\frac{dG^\circ_s}{d2w}$, i.e. on the nature of the electrolyte. Values of this term were available for electrolytes in 50% aqueous dioxane (45), and as this solvent was used by Grunwald in his work he was able to demonstrate the validity of equation (1.4).

$\frac{dG^\circ_s}{d2w}$ values were not available for electrolytes in 50% aqueous acetone, the solvent used in the present investigation. However if $\frac{dG^\circ_s}{d2w}$ values in 70% aqueous acetone follow roughly the same sequence as in 50% aqueous dioxane Queen and Shillaker's results are in qualitative agreement with this recent treatment, and therefore the results from the present investigation (except those with sodium perchlorate) are also in qualitative agreement. Thus although the retardation by fluoride ions cannot be accounted for by the Hughes-Ingold theory, the recent treatment which allows for salt-induced medium effects offers a ready explanation of the retarding effect exerted by the highly hydrated fluoride ion.

Solubility Experiments.

The effects of electrolytes on the solubility of p-nitrobenzhydryl chloride and p-nitrobenzyl chloride in 50% aqueous acetone were studied at 0°C. This was accomplished by addition of excess of organic halide and a known concentration of an electrolyte to 50 ml. of 50% aqueous acetone in a stoppered tube. The tube was then strapped on to a wheel which rotated beneath the surface of an ice-bath. Samples were removed after equilibrium had been reached and analysed by titrating with either 0.005 N sodium hydroxide solution or 0.005 N silver nitrate solution.

The effect of electrolytes on the solubility of p-nitrobenzhydryl chloride.

The effects of electrolytes on the solubility of p-nitrobenzhydryl chloride in 50% aqueous acetone at 0°C are summarised in Table IV. The percentage increase in solubility $100(^{S}/S^{o} - 1)$ is quoted.

Table IV. The effect of electrolytes on the solubility of p-nitrobenzhydryl chloride in 50% aqueous acetone at 0°C. (The figures reported refer to the percentage change in solubility caused by the addition of electrolytes).

Electrolyte	Concentration 0.05 M	Concentration 0.1 M
HNO_3	- 1.23 ± 0.32	- 6.05 ± 0.35
LiCl	0.00 ± 0.50	0.72 ± 0.46
$NaNO_3$	1.31 ± 0.20	1.31 ± 0.27
KNO_3	- 0.44 ± 0.50	1.55 ± 0.27
KBr	1.32 ± 0.47	3.52 ± 0.21
NaBr	1.43 ± 0.20	4.39 ± 0.18
NaCl	3.09 ± 0.20	4.62 ± 0.21
KCl	3.10 ± 0.27	4.68 ± 0.21
$HClO_4$	2.26 ± 0.38	5.65 ± 0.38
NaO_3SPh	4.66 ± 0.23	7.29 ± 0.56
≠ $KClO_4$	6.83 ± 0.33	10.79 ± 0.49
≠ NaF	*8.14 ± 0.21	——
$NaClO_4$	8.45 ± 0.21	14.85 ± 0.22

* This was twice the value obtained on addition of 0.025 M NaF.

≠ 0.1 M $KClO_4$ and 0.025 M NaF were not completely soluble in 50% aqueous acetone at 0°C and presumably have a larger value than that reported.

The results in Table IV show that the effect of electrolytes on the solubility of the non-electrolyte in this system are small, however it is noteworthy that a doubling of the electrolyte concentration approximately doubles the effect on solubility. Nitric acid causes salting-out, the alkali metal nitrates, bromides, and chlorides, all have a salting-in effect, sodium benzene sulphonate salts-in rather more, while sodium perchlorate, potassium perchlorate, and sodium fluoride have a much larger salting-in effect. Replacement of an alkali metal ion with a hydrogen ion markedly reduces the salting-in effect.

The effect of electrolytes on the solubility of p-nitrobenzyl chloride was also studied, the results are given in Table V.

<u>Table V.</u> The effect of electrolytes on the solubility of p-nitrobenzyl chloride in 50% aqueous acetone at 0°C. (The figures reported refer to the percentage change in solubility caused by the addition of electrolytes).

Electrolyte	Concentration 0.05 M	Concentration 0.1 M
HNO_3	0.20 ± 0.18	- 2.01 ± 0.16
$NaNO_3$	0.65 ± 0.13	1.15 ± 0.10
≠ NaCl	———	1.7
$HClO_4$	1.87 ± 0.14	3.54 ± 0.20
≠ $NaClO_4$	3.9	9.20
NaF	*7.64 ± 0.23	———

* This was twice the value obtained on addition of 0.025 M NaF

≠ Measurements by J. Fox (79).

The results in Table V show that the effects are less marked than with p-nitrobenzhydryl chloride, an observation paralleled by measurements of the solubilities of the organic halides in solvents of varying composition without added electrolytes. The results in Table VI show that changes in solvent composition have a smaller effect on the solubility of p-nitrobenzyl chloride than on the solubility of p-nitrobenzhydryl chloride.

<u>Table VI</u>. The effect of a change in solvent composition on the solubilities of p-nitrobenzhydryl chloride and p-nitrobenzyl chloride at 0°C.

Organic halide	Solubility at 0°C in		
	55% aqueous acetone	50% aqueous acetone	45% aqueous acetone
p-nitrobenzhydryl chloride	0.01000 M	0.00513 M	0.00172 M
p-nitrobenzyl chloride	0.02270 M	0.01472 M	0.00655 M

A comparison of the results in Tables IV and V shows that although the electrolyte effects are less marked in the p-nitrobenzyl chloride system they follow roughly the same sequence as in the p-nitrobenzhydryl chloride system. It has been shown that with 50% aqueous acetone as solvent, hydrolysis of p-nitrobenzyl chloride proceeds by mechanism SN2 and that of p-nitrobenzhydryl chloride by mechanism SN1 (46).

Hughes and Ingold considered that electrolytes would accelerate reaction by mechanism SN1 more than SN2 solvolysis because the latter reaction is associated with a greater diffusion of charge in the transition state. However the results from the two systems above indicate that the effect on the rate could be at least partly due to an initial state effect, as proposed by Grunwald and his co-workers. The similar pattern of electrolyte effects on solubility observable in the two systems may be due to the similarity in structure of the two organic compounds.

A comparison of the effects of electrolytes on the solubilities of naphthalene and 1-naphthoic acid in 50% aqueous dioxane, and p-nitrobenzhydryl chloride in 50% aqueous acetone.

Grunwald and Butler (44) have recently obtained results for the effects of electrolytes on the solubility of naphthalene and 1-naphthoic acid in 50% aqueous dioxane. The results obtained with p-nitrobenzhydryl chloride in 50% aqueous acetone in the present investigation were found to follow a similar pattern to that observed by these workers. Thus alkali metal bromides and chlorides had about the same salting-in effect, while HX had a smaller salting-in effect than MX. However the results on the addition of sodium and potassium perchlorates differed widely, a much greater salting-in effect being observed in the present investigation. This could possibly be due to complex formation with the organic compound, and it is noteworthy that attractive interaction between perchlorate ions and organic compounds is well known, e.g., sodium perchlorate is very soluble in acetone (80) and perchlorate salts crystallise from aqueous dioxane with dioxane of crystallisation. (45)

Possibly, attractive interaction occurs with a phenyl group carrying a slight positive charge, the result of electron withdrawal by a p-nitro substituent.

Comparison Of The Effects Of Electrolytes On The Rate Of Reaction And Solubility Of p-Nitrobenzhydryl Chloride In 50% Aqueous Acetone.

The effects of electrolytes on the rate of reaction and solubility of an organic compound, RX, can be expressed as follows :-

$$\text{(a)} \quad \ln {}^{k_1}/{}_{k_1^\circ} = \ln \gamma_{RX} - \ln \gamma_{\ddagger}$$

$$\text{(b)} \quad \ln {}^{S^\circ}/{}_{S} = \ln \gamma_{RX}$$

The effect of electrolyte on the activity coefficient of the transition state can therefore be found by comparing equations (a) and (b), i.e.

$$\ln {}^{S^\circ}/{}_{S} - \ln {}^{k_1}/{}_{k_1^\circ} = \ln \gamma_{\ddagger}$$

The variation of activity coefficients with temperature are usually small and consequently a comparison of the kinetic results at 39.75°C and solubility measurements at 0°C obtained in the present work will afford a good approximation of the effects of electrolytes on the activity coefficient of the transition state. Table VII gives results obtained on the addition of electrolytes to p-nitrobenzhydryl chloride in 50% aqueous acetone.

Table VII. The effects of electrolytes on (a) the rate of reaction of p-nitrobenzhydryl chloride at 39.75°C, and (b) the solubility of p-nitrobenzhydryl chloride at 0°C, in 50% aqueous acetone.

Electrolyte (0.1M)	ln k_1/k_1°	ln S/S°	ln γ_{RX}	ln $\gamma_\mp$	$\frac{\ln \gamma_{RX}}{\ln \gamma_\mp}$
+ NaF	- 0.0974*	0.1509*	- 0.1509	- 0.0535	2.82
$NaNO_3$	0.0746	0.0129	- 0.0129	- 0.0875	0.14
NaO_3SPh	0.0221	0.0705	- 0.0705	- 0.0926	0.76
KNO_3	0.0822	0.0152	- 0.0152	- 0.0974	0.16
HNO_3	0.1808	-0.0624	0.0624	- 0.1184	-0.53
KBr	0.0901	0.0343	- 0.0343	- 0.1244	0.28
NaBr	0.0834	0.0431	- 0.0431	- 0.1265	0.34
+ $KClO_4$	0.0852	0.1025	- 0.1025	- 0.1877	0.55
$NaClO_4$	0.0769	0.1382	- 0.1382	- 0.2151	0.64
$HClO_4$	0.2022	0.0550	- 0.0550	- 0.2572	0.21
HCl	- 0.0587	0.0456	- 0.0456	0.0131	-3.47
NaCl	- 0.0675	0.0451	- 0.0451	0.0224	-2.02
LiCl	- 0.0907	0.0067	- 0.0067	0.0840	-0.11

* From 4X the percent change in k_1 and S in the presence of 0.025 M NaF.

\+ 0.025 M NaF and 0.1 M $KClO_4$ were not completely soluble in 50% aqueous acetone at 0°C and the reported values of ln $\gamma_\mp$ are therefore subject to a positive error.

The results in Table VII show that $\ln \gamma_{\neq}$ is always negative, i.e. electrolytes stabilise the activated complex. (The results with alkali metal chlorides are only included for completeness. In these cases, as k_1 is subject to a mass-law effect, values of $\ln \gamma_{\neq}$ are not real). Contrary to the electrostatic approach of Hughes and Ingold the effects of electrolytes on the stability of the transition state are not independent of the electrolyte, $-\ln \gamma_{\neq}$ increasing from NaF to $HClO_4$. Moreover the effects of electrolytes on the activity coefficient of the initial state ($\ln \gamma_{RX}$) are not negligible (the effect of fluoride ions is greater on the activity coefficient of the initial state than on the activity coefficient of the transition state) and are an important factor in controlling the rate. Acceleration of the rate of reaction is comparable for perchlorate, bromide, and nitrate ions, however the former have a larger effect on the solubility, possibly due to a short-range interaction effect (see page 33). NaF also has a relatively large effect on the initial state but retards the rate of reaction. $\frac{\ln \gamma_{RX}}{\ln \gamma_{\neq}}$ is large for perchlorate and benzene sulphonate ions. In the case of the former this again indicates their large effect on the stability of the initial state, with the latter it arises mainly from their comparatively small accelerating effect on the rate of reaction.

It is of interest to see how the results fit the quantitative treatment of Grunwald and his co-workers(26)(44) who proposed that the effects of electrolytes on the rate of reaction and solubility of an organic compound could be expressed in the form :

$$(i)\ \frac{1}{C_s} \ln. \frac{k_1}{k_1^\circ} = \frac{1}{C_s} \ln. \frac{\gamma_{RX}}{\gamma_{\neq}} = A' + B' RT \frac{dG^\circ_s}{d2w} \cdot \frac{d\ln k_1^\circ}{d2w}$$

$$\text{(ii)}\ \frac{1}{C_s}\ \ln.\ \frac{S^\circ}{S} = \frac{1}{C_s} \ln \gamma_{RX} = A - BRT \cdot \frac{dG^\circ_s}{dZw} \cdot \frac{d\ln S^\circ}{dZw}$$

It follows from the equations that

$$\frac{1}{C_s}\ \ln \frac{k_1}{k_1^\circ} = A'' + \left(\frac{B'\ d\ln k_1{}^\circ/dZw}{B\ d\ln S^\circ/dZw}\right) \frac{1}{C_s} \cdot \ln \frac{S}{S^\circ}$$

$$\text{where } A'' = A' + A\left(\frac{B'\,d\ln k_1{}^\circ/dZw}{B\ d\ln S^\circ/dZw}\right).$$

Thus a straight line plot of ln ${}^{k_1}/{k_1}^\circ$ against ln ${}^{S}/{S^\circ}$ would illustrate the existence of a relationship between the effects of electrolytes on the stabilities of the transition-and initial-states, as well as proving the validity of the Grunwald approach.

The terms $\frac{d\ln k_1{}^\circ}{dZw}$ and $\frac{d\ln S^\circ}{dZw}$ have been evaluated, see Table VIII.

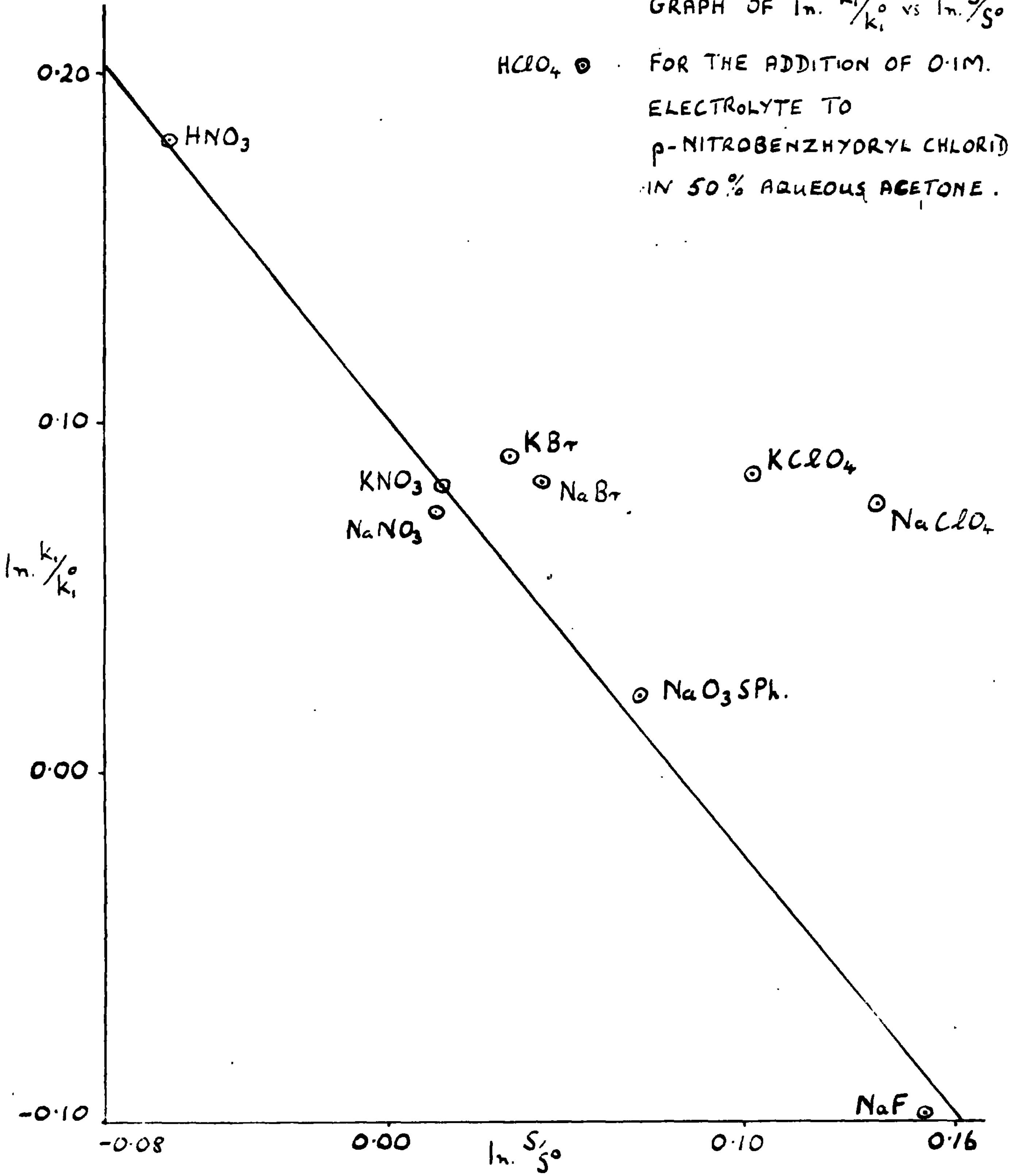
<u>Table VIII.</u> The effect of a change in solvent composition on the rate of reaction at 39.75°C and solubility at 0°C of p-nitrobenzhydryl chloride.

	55% aqueous acetone	50% aqueous acetone	45% aqueous acetone
Weight % H_2O	50.82	55.81	60.68
Zw	0.7693	0.7989	0.8326
$k_1{}^\circ \times 10^{-5}$ sec $^{-1}$	2.683	5.522	11.800
$\frac{d\ln k_1{}^\circ}{dZw}$	+ 24.4	+ 22.4	
S° (M)	0.01000	0.00513	0.00172
$\frac{d\ln S^\circ}{dZw}$	- 23.6	- 32.4	

The results in Table VIII show that the variation of rate with solvent composition is entirely a consequence of the effect on the stability of the initial state. Of course, the results refer to different temperatures but as variation of activity coefficients with temperature are usually small, this factor can be assumed to have only a small effect.

FIGURE I

GRAPH OF ln. k_1/k_1^0 vs ln. S/S^0 FOR THE ADDITION OF 0·1M. ELECTROLYTE TO p-NITROBENZHYDRYL CHLORIDE IN 50% AQUEOUS ACETONE.



A plot of $\ln {}^{k_1}/{k_1^{\circ}}$ against $\ln {}^{S}/{S^{\circ}}$ is shown in Figure I and it is evident that the results with nitric acid, sodium and potassium nitrates, sodium benzene sulphonate, and sodium fluoride are consistent with Grunwald's approach, and those with alkali metal bromides are in reasonable agreement (slight variances may arise because of ion-pair intervention). The results with perchlorate ions are in complete disagreement, possibly due to short-range interaction effects which were not allowed for in the original Grunwald treatment.

The slope of the straight line in Figure I,

$$\frac{B' \, d\ln k_1^{\circ}/dZw}{B \, d\ln S^{\circ}/dZw} = -1.25$$

Substituting mean values of ${}^{d\ln k_1^{\circ}}/dZw$ and ${}^{d\ln S^{\circ}}/dZw$ it follows that,

$$\frac{B'}{B} = 1.04.$$

This value is reasonable as Grunwald (26)(44) considers that B, B' are not very sensitive to the species in question and depend mainly on the solvent and temperature.

Thus, assuming the variation of activity coefficients with temperature to be small, it can be concluded that the results are consistent with the quantitative treatment based on salt-induced medium effects, at least for many electrolytes. Exceptions do occur (e.g. with perchlorate ions) possibly due to short-range interaction effects which were not allowed for in this treatment.

CHAPTER IV

EXPERIMENTAL

Preparation And Purification Of Materials

p-Nitrobenzhydryl chloride.

p-Nitrobenzhydryl chloride was prepared via the following reaction scheme :

(a) $O_2N\,C_6H_4COCl + C_6H_6 \xrightarrow[\text{Friedel-Crafts (81)}]{AlCl_3} O_2N\,C_6H_4\,CO\,C_6H_5 + HCl$

(b) $O_2N\,C_6H_4\,CO\,C_6H_5 \xrightarrow[\text{Meerwein-Ponndorf (82)}]{Al(OHC(CH_3)_2)_3} O_2N\,C_6H_4\,CHOH\,C_6H_5$

(c) $O_2N\,C_6H_4\,CHOH\,C_6H_5 \xrightarrow{ZnCl_2} O_2N\,C_6H_4\,CHCl\,C_6H_5 + H_2O$

Several preparations were carried out, details of a typical one are as follows. A mixture of 80g. of p-nitrobenzoyl chloride, 70g. of freshly sublimed aluminium chloride, and 400 ml. of sodium dried A.R. benzene was refluxed for 4 hours. The resulting benzene solution was poured into 500 ml. of an ice-water-hydrochloric acid mixture from which it was later separated, washed with sodium hydroxide solution, followed by water, and dried over calcium chloride. Removal of the benzene by distillation yielded p-nitrobenzophenone which was purified by refluxing with activated charcoal in acetone, filtering, and recrystallising from acetone. The final product had a m. pt. of 137°C (uncorrected), the literature value being 138°C. (83)

Aluminium isopropoxide for stage (b) was prepared by refluxing 50 g. of aluminium foil with 600 ml. of isopropanol (previously dried over calcium oxide) for 6 hours, 2.5 g. of mercuric chloride being added to facilitate the reaction.

After cooling, more isopropanol was added until the volume was 2 ℓ., i.e. an approximately 1 M solution. 92 ml. of this solution were then refluxed with 35 g. of p-nitrobenzophenone for 20 minutes. The acetone produced in the reaction was distilled over slowly, the distillation being stopped when the distillate no longer gave a precipitate with 2:4 dinitrophenylhydrazine solution. The residue was refluxed for 6 hours, the excess isopropanol distilled off under reduced pressure, and dilute sulphuric acid added to the cooled residue. Extraction of this mixture with ether removed the p-nitrobenzhydryl, which was isolated after washing with sodium bicarbonate solution, water, and distilling off the ether. Several recrystallisations of the alcohol from benzene yielded a product of m.pt. 74 - 75.5°C (84). Infra-red analysis of the final product indicated the purity to be > 99%.

Stage (c) involved dissolving 10 g. of p-nitrobenzhydrol in 100 ml. of benzene, adding approximately 10 g. of zinc chloride, and passing dry hydrogen chloride gas through for 6 hours. The benzene solution was then separated, washed with sodium bicarbonate solution, water, and dried over calcium chloride. Distillation of the benzene left a yellow, viscous oil which was dissolved in a petroleum ether (60 - 80 B.P.) - diethyl ether solvent. This solution was passed down a small glass column (10" x ½") packed with celite, and after distilling off the solvent, the oil was dried in vacuo. Cooling with Drikold caused the oil to solidify. On standing in a dessicator at room temperature most of the solid melted and then slowly resolidified.

Almost colourless needle-like crystals were formed which on crushing yielded an off-white solid, m.pt. 41.5 - 42.5°C (uncorrected) the literature value being 41 - 42°C.(85).

The purity, determined by hydrolysis, was within the range 99 - 100%.

p-Nitrobenzyl chloride.

p-Nitrobenzyl chloride was recrystallised from ethanol and dried in vacuo, m.pt. 71.2 °C (uncorrected), literature value 71°C (86).

Electrolytes.

Electrolytes were usually dried either in air or in vacuo at elevated temperatures, A.R. products being used when possible. Sodium perchlorate was recrystallised from aqueous dioxane and dried in vacuo at an elevated temperature to constant weight. Sodium benzene sulphonate was recrystallised from ethanol and dried in air at an elevated temperature.

Solutions of acid were prepared by adding a calculated amount of acid of known strength to a known volume of 50% aqueous acetone. A volume of pure acetone, equal to the amount of water in the acid, was then added, so that the final solution corresponded to the anhydrous acid in 50% aqueous acetone.

Solvent acetone (87)

A.R. grade acetone was refluxed over potassium hydroxide pellets and potassium permanganate for two hours and then distilled, the distillate being distilled again from hydroquinone through a fractionating column. Generous head and tail fractions were discarded.

The addition of 50, 55 and 45 volumes of distilled water to 50, 45 and 55 volumes of acetone, respectively, gave 50%, 45% and 55% aqueous acetone.

Titration acetone.

Commercial acetone was refluxed for two hours over potassium hydroxide pellets and potassium permanganate and then distilled. Lacmoid indicator was added and the acetone neutralised before use.

Rate Measurements.

p-Nitrobenzhydryl chloride

Kinetic runs were carried out at 20.03°C and 39.75°C. A mercury toluene regulated type of thermostat was used and temperatures were constant to ± 0.02°C. A layer of oil was used to prevent evaporation of water from the bath at the higher temperature. An approximately 0.01 M solution of the organic halide in 100 ml. of 50% aqueous acetone was prepared, and the necessary amount of electrolyte to give a 0.05 or 0.1 M solution added. Runs with sodium fluoride contained only 0.025 M of the salt because of its low solubility in 50% aqueous acetone. In order to eliminate any change in the composition of the solvent by evaporation of acetone, the sealed ampoule technique was employed for the kinetic runs. However the runs containing sodium fluoride had to be carried out in stoppered flasks because of the low solubility of this salt in 50% aqueous acetone at room temperature. A similar solubility problem with a 0.01 M solution of p-nitrobenzhydryl chloride in 45% aqueous acetone also necessitated the use of stoppered flasks for these runs. The results obtained from runs carried out in flasks and in sealed ampoules gave constant first order rate coefficients.

For runs carried out at 39.75°C the tubes were introduced into a bath at 35°C for 3-4 minutes before being placed into the thermostat, for runs at 20.03°C the tubes were placed into the thermostat without preheating. The tubes were shaken in the thermostat for 3-4 minutes during which time no tubes were removed, thus giving the thermostat time to regain its nominal value and the tubes to reach the temperature of the thermostat. Tubes were withdrawn from the thermostat from time to time and the reaction stopped by freezing in an acetone-Drikold mixture. After cleaning, the tubes were broken under about 200 ml. of neutral acetone. The reaction was followed either by determining the development of acidity by titration with 0.005 N sodium hydroxide solution using lacmoid as indicator, or by determining the production of chloride ions by potentiometric titrations using 0.005 N silver nitrate solution with a glass electrode and a silver reference electrode.

Usually two samples were taken in each kinetic run to determine the first or "zero time" reading, and three to determine the "infinity" reading or initial concentration of the organic halide, the latter after heating several tubes in a boiling water-bath for at least ten half-lives. Twelve tubes, removed at different times, enabled values of ki to be calculated, ki being the first order rate coefficient. On average ten or eleven of these ki's were within 5% of the mean value, k_1', for the run, k_1' and k_1" from identical runs agreeing to within 0.5%.

As several batches of solvent were used, each batch was standardised by examining the rate of solvolysis of p-nitrobenzhydryl chloride without added electrolyte, the k_1° value thus obtained being used in determining the k_1/k_1° ratios for runs carried out with this solvent.

Calculation of kinetic results.

The reactions studied were kinetically of the first order, and the rate constants were therefore calculated from the normal first-order integrated rate equation, viz.,

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

where t is the time, 'a' is the initial concentration of the organic halide (t = 0), and a-x is the concentration of the organic halide remaining after time t.

The first reading was taken as "zero time", and 'a' was calculated from this and the "infinity" reading.

Solubility Measurements.

p-Nitrobenzhydryl chloride and p-nitrobenzyl chloride.

Solubility runs were carried out at 0°C. No variations from this temperature could be measured on using a well-stirred bath of crushed ice. An excess of the organic halide was introduced into each of four 120 ml. Pyrex tubes containing 50 ml. of 50% aqueous acetone and placed in the ice-bath. Sufficient electrolyte to give a 0.05 M or 0.1 M solution was added to three of the tubes and all four tubes stoppered. (Solubility runs with added sodium fluoride contained only 0.025 M of the salt in order that a comparison with the corresponding kinetic runs could be made. It was noted that 0.025 M sodium fluoride and 0.1 M potassium perchlorate were not completely soluble in this solvent at 0°C). After stoppering the tubes they were strapped on to a wheel which rotated at 40 revolutions per min. beneath the surface of the 0°C thermostat.

After 6 hours (and after 24 hours) the tubes were removed from the wheel, clamped in the ice-bath, and the stoppers removed, care being taken that no water entered the tube and thus changed the composition of the solvent. Approximately 25 ml. of the supernatant liquid were pipetted for analysis through a sintered glass filter, the pipette then being inverted into a bottle clamped in the ice-bath. 5 ml. of this solution were pipetted into about 200 ml. of neutral acetone and titrated immediately. It was found that after 24 hours in 50% aqueous acetone at 0°C p-nitrobenzhydryl chloride had undergone solvolysis to an extent $\leq 5\%$. Under identical conditions solvolysis of p-nitrobenzyl chloride was non-detectable. Appropriate corrections for solvolytic reactions were applied to the solubility results in the p-nitrobenzhydryl chloride system. The concentration of the organic halide present in the supernatant liquid was determined in the following manner. Three sealed tubes each containing 5 ml. of the liquid were placed into a boiling water bath or into an oil-bath, depending upon whether the solubility of p-nitrobenzhydryl chloride or p-nitrobenzyl chloride was being investigated, for at least ten half-lives. On removing, and after cooling, each tube was broken under about 200 ml. of neutral acetone and titrated with either 0.005 N sodium hydroxide solution or 0.005 N silver nitrate solution.

Thus for each solubility run six results were obtained (three after 6 hours and three after 24 hours in the thermostat) of which at least five were usually within 2% of the mean, the mean values of two identical solubility runs being within 2% of each other.

The tube containing only the organic halide in the solvent was a "blank", and one was always run side by side with each set of electrolyte solutions. The mean solubility found in this run was then used to calculate the $^{S}/S^{\circ}$ values for the electrolyte solutions, the solubility of which had been determined at the same time. The mean S° values determined from a number of runs carried out on different days were within ± 1% of the mean value($S^{\circ}m$), for a particular solvent.

Statistical Treatment Of Errors.

Errors in rate coefficient.

In the calculation of the errors in the rate coefficients all kinetic results for one set of conditions (temperature, solvent, and the nature and concentration of the electrolyte) were considered as one for statistical purposes. Thus if one set of experimental conditions gave n different rate coefficients ki, the final mean rate coefficient is given by

$$k_1 = \frac{\sum_{i=0}^{n} ki}{n}$$

and the standard deviation of each individual ki is obtained from

$$\sigma = \left[\frac{\sum (k_i - k_1)^2}{n} \right]^{\frac{1}{2}}$$

where k_1 is the statistical mean rate coefficient. For Gaussian distribution of errors more than 99% of all the ki's should be within $3\,\sigma$ of k_1. Any ki value not within this limit was discarded and a new k_1 and σ calculated. This was only rarely necessary.

The standard error of the final mean is given by

$$\sigma_m = \frac{\sigma}{n^{\frac{1}{2}}}$$

In all the runs carried out (with the exception of those with added sodium bromide at 20.03°C),

$$\frac{\sigma_m}{k_1} < 0.003.$$

The effect of electrolyte addition on the rate of hydrolysis is expressed by the ratio k_1/k_1°, where 0 refers to the absence of electrolytes. This ratio is subject to a standard error

$$\sigma'_m = \frac{k_1}{k_1^\circ}\left[\left(\frac{\sigma_m}{k_1}\right)^2 + \left(\frac{\sigma^\circ_m}{k_1^\circ}\right)^2\right]^{\frac{1}{2}}$$

The percentage change in rate caused by the addition of electrolytes is given by $100\left(k_1/k_1^\circ - 1\right)$ and is subject to a standard error of $100\,\sigma'_m$

Error in solubilities

In the solubility runs the results needed to calculate the mean solubilities S', S'_0 were obtained on the same day (the subscript 0 refers to the absence of electrolytes). The value of S'_0 in the ratio S'/S'_0 was variable (see page 46) even though the same solvent was used. If n' acceptable solubility measurements were made for one run and n'' for an identical run (both runs containing electrolyte) then the mean solubility ratio, S/S°, is given by

$$\frac{S}{S^\circ} = \frac{n'\,\frac{S'}{S_0'} + n''\,\frac{S''}{S_0''}}{n' + n''}$$

where S', S'' are the mean solubilities of identical runs containing added electrolytes, and S_0', S_0'' those of the corresponding runs without added electrolytes.

The standard errors of the final means (σ', σ'_o, σ'', σ''_o) were calculated in the same manner as in the kinetic section, e.g.

$$\sigma' = \frac{\left[\sum (S'_o - S'_s)^2 \right]^{1/2}}{n}$$

where S'_s is an acceptable solubility result.

However the results from identical runs were treated separately as the values of So', So" varied slightly. The ratio $S'/S'o$ is subject to a standard error

$$\sigma_1 = \pm \frac{S'}{S'o} \left[\left(\frac{\sigma'}{S'} \right)^2 + \left(\frac{\sigma' o}{S' o} \right)^2 \right]^{1/2}$$

and similarly the standard error of S''/So'' is given by

$$\sigma_2 = \pm \frac{S''}{So''} \left[\left(\frac{\sigma''}{S''} \right)^2 + \left(\frac{\sigma'' o}{So''} \right)^2 \right]^{1/2}$$

The mean solubility ratio S/S^o is subject to a standard error

$$\sigma m = \frac{(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}}{2}$$

The percentage change of solubility caused by the addition of electrolytes is given by

$$100 \left(\frac{S}{S^o} - 1 \right)$$

and this is subject to a standard error of $100\sigma m$.

APPENDIX

Details Of Kinetic Runs.

First order rate constants, ki, were calculated from the integrated rate equation,

$$ki = \frac{2.303}{t} \log \frac{a}{a - x}$$

where the symbols have their usual meaning.

Details of one run for each set of experimental conditions are given and the mean rate coefficient, k_1^{*}, of the duplicate run quoted, together with the statistical mean k_1 of the two runs.

Unless stated otherwise the solvent refers to 50% aqueous acetone.

The initial concentration reported in each run is that of the non-electrolyte.

p-Nitrobenzhydryl chloride + 0.1 M NaBr at 39.73°C

Solvent C Run 44

Initial concentration = 0.00970 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.41	-
3287	7.78	(5.788)
5087	7.00	5.817
6910	6.28	5.852
8762	5.62	5.884
10698	5.00	5.910
12438	4.52	5.898
14537	3.95	5.971
16665	3.46	6.006
18964	3.06	5.924
21458	2.59	6.013
23904	2.23	6.025
26408	1.93	5.999
29268	1.56	(6.142)

$k_1' = 5.935 \times 10^{-5} sec^{-1}$

$k_1'' = 5.928 \times 10^{-5} sec^{-1}$

$k_1 = 5.932 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M $NaNO_3$ at 39.76°C

Solvent B Run 37

Initial concentration = 0.01036 M

t (secs)	(a - x)	k x 10^{-5} sec $^{-1}$
0	10.00	-
3200	8.29	5.859
4780	7.59	5.773
6578	6.89	5.842
8099	6.20	5.903
9728	5.65	6.008
11506	5.07	5.903
13502	4.49	5.933
15600	3.96	5.939
17890	3.44	5.967
20522	2.93	5.982
23646	2.42	6.002

$k_1' = 5.919 \times 10^{-5}$ sec $^{-1}$

$k_1'' = 5.926 \times 10^{-5}$ sec $^{-1}$

$k_1 = 5.922 \times 10^{-5}$ sec $^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M $NaClO_4$ at 39.77°C

Solvent L   Run 171

Initial concentration = 0.01014 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.86	-
3078	8.25	5.792
4771	7.45	5.875
6542	6.71	5.886
8480	6.00	5.857
10119	5.45	5.861
12254	4.78	5.910
13849	4.35	5.909
15418	3.99	5.869
17676	3.46	5.927
20418	2.93	5.944
22297	2.60	5.978
25288	2.16	6.006

$k_1' = 5.901 \times 10^{-5} sec^{-1}$

$k_1'' = 5.915 \times 10^{-5} sec^{-1}$

$k_1 = 5.908 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M NaCl at 39.75°C

Solvent E Run 85

Initial concentration = 0.00966 M

t (secs)	(a - x)	$k \times 10^{-5} \text{sec}^{-1}$
0	9.34	-
3310	7.90	5.058
5236	7.16	5.074
7051	6.47	5.206
8915	5.89	5.171
10840	5.36	5.122
12881	4.81	5.152
14999	4.31	5.154
17102	3.88	5.139
19561	3.43	5.123
21881	2.98	5.222
24335	2.63	5.208
28210	2.13	5.241
31755	1.77	5.237

$k_1' = 5.162 \times 10^{-5} \text{sec}^{-1}$

$k_1'' = 5.140 \times 10^{-5} \text{sec}^{-1}$

$k_1 = 5.153 \times 10^{-5} \text{sec}^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M NaO_3SPh at 39.76°C

Solvent J   Run 138

Initial concentration = 0.00946 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.31	-
2767	7.95	5.702
4585	7.19	5.635
6376	6.47	5.709
8173	5.84	5.707
10106	5.25	5.670
12100	4.66	5.719
13865	4.20	5.741
15986	3.75	5.711
18012	3.36	5.659
20435	2.89	5.727
22990	2.53	5.667
25921	2.11	5.728
29347	1.76	5.689

$$k_1' = 5.697 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.702 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.700 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M NaBr at 39.75°C

Solvent C Run 53

Initial concentration = 0.00978 M

t(secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.55	-
3340	7.89	5.718
5146	7.12	5.706
6958	6.43	5.685
8785	5.76	5.757
10611	5.17	5.785
12531	4.59	5.848
14801	4.03	5.830
17204	3.49	5.853
19617	3.06	5.803
23085	2.52	5.773
26719	2.03	5.797

$k_1' = 5.778 \times 10^{-5} sec^{-1}$

$k_1'' = 5.769 \times 10^{-5} sec^{-1}$

$k_1 = 5.774 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M $NaNO_3$ at 39.75°C

Solvent C — Run 51

Initial concentration = 0.00957 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.31	-
3373	7.70	5.626
5192	6.94	5.654
6990	6.23	5.745
8789	5.67	5.641
10601	5.10	5.676
12538	4.53	5.746
14942	3.96	5.720
17763	3.36	5.737
20763	2.83	5.735
24475	2.29	5.732
27904	1.86	5.772

$$k_1' = 5.708 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.719 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.714 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M NaClO$_4$ at 39.75°C

Solvent C Run 47

Initial concentration = 0.00945 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.24	-
3300	7.69	5.569
5110	6.94	5.602
6901	6.27	5.620
8704	5.65	5.667
10532	5.13	5.589
12404	4.63	5.572
14634	4.07	5.603
16833	3.58	5.632
19454	3.09	5.631
22484	2.62	5.608
25685	2.15	5.678
29258	1.72	5.748

$k_1' = 5.627 \times 10^{-5} sec^{-1}$

$k_1'' = 5.643 \times 10^{-5} sec^{-1}$

$k_1 = 5.635 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M NaCl at 39.75°C

Solvent E **Run 88**

Initial concentration = 0.00963 M

t(secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.32	-
3318	7.80	5.379
5154	7.09	5.310
6987	6.41	5.356
9010	5.75	5.360
11149	5.13	5.357
13243	4.60	5.332
15445	4.08	5.350
17787	3.59	5.364
20722	3.08	5.343
24140	2.52	5.419
27140	2.14	5.423
30313	1.81	5.403

$$k_1' = 5.367 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.370 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.368 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M NaO_3SPh at 39.76°C

Solvent J　　　　Run 137

Initial concentration = 0.00945 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.23	-
3011	7.79	5.637
4806	7.03	5.665
6605	6.34	5.689
8402	5.74	5.654
10212	5.17	5.676
12163	4.66	5.620
14486	4.08	5.635
16649	3.61	5.639
18901	3.17	5.654
21927	2.68	5.643
25888	2.16	5.610
29564	1.73	5.665

$$k_1' = 5.649 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.660 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.654 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.025 M NaF at 39.77°C

Solvent H — Run 160

Initial concentration = 0.00975 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.46	-
3105	8.00	5.399
4756	7.31	5.424
6513	6.70	5.298
8430	5.98	5.443
10275	5.46	5.351
12167	4.91	5.391
14223	4.38	5.414
16625	3.85	5.408
19317	3.30	5.454
22269	2.80	5.468
25218	2.39	5.458
27832	2.01	(5.567)

$k_1' = 5.410 \times 10^{-5} sec^{-1}$

$k_1'' = 5.376 \times 10^{-5} sec^{-1}$

$k_1 = 5.394 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M KBr at 39.75°C

Solvent D Run 76

Initial concentration = 0.00964 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.31	-
3373	7.61	5.974
5176	6.82	6.010
6990	6.11	6.026
8800	5.45	6.084
10812	4.84	6.052
12653	4.32	6.067
14520	3.82	6.135
16415	3.41	6.119
18677	2.99	6.081
21829	2.46	6.096
25018	2.00	6.149
27965	1.64	6.212

$k_1' = 6.084 \times 10^{-5} \text{sec}^{-1}$

$k_1'' = 6.091 \times 10^{-5} \text{sec}^{-1}$

$k_1 = 6.087 \times 10^{-5} \text{sec}^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M KNO_3 at 39.74°C

Solvent C Run 63

Initial concentration = 0.00970 M

t (secs)	(a - x)	k x 10^{-5}sec^{-1}
0	9.52	-
3323	7.91	(5.573)
5233	7.03	5.803
6904	6.44	(5.662)
8819	5.69	5.836
10622	5.10	5.876
12446	4.55	5.932
14348	4.09	5.891
16285	3.61	5.955
18132	3.29	5.861
20484	2.80	5.974
22828	2.45	5.947
25901	2.02	5.985
29415	1.61	6.043

$k_1' = 5.918 \times 10^{-5} \text{sec}^{-1}$

$k_1'' = 5.930 \times 10^{-5} \text{sec}^{-1}$

$k_1 = 5.924 \times 10^{-5} \text{sec}^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M $KClO_4$ at 39.78°C

Solvent D   Run 70

Initial concentration = 0.00962 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.04	-
2972	7.57	5.974
4674	6.81	6.064
6501	6.08	6.102
8328	5.44	6.101
10167	4.82	6.189
11968	4.28	(6.250)
13813	3.92	6.050
15555	3.53	6.046
17590	3.08	6.124
20060	2.71	6.008
22787	2.30	6.010
25795	1.90	6.047
29295	1.56	5.998

$$k_1' = 6.059 \times 10^{-5} sec^{-1}$$

$$k_1'' = 6.059 \times 10^{-5} sec^{-1}$$

$$k_1 = 6.059 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.1 M KCl at 39.73°C

Solvent C Run 55

Initial concentration = 0.00972

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.40	-
3330	7.91	5.181
5145	7.21	5.157
6984	6.57	5.126
8957	5.95	5.107
10959	5.31	5.212
12981	4.80	5.178
15317	4.27	5.152
17568	3.81	5.141
20080	3.36	5.125
23214	2.83	5.170
26907	2.39	5.089
30474	1.95	5.163

$k_1' = 5.150 \times 10^{-5}\, sec^{-1}$

$k_1'' = 5.135 \times 10^{-5}\, sec^{-1}$

$k_1 = 5.143 \times 10^{-5}\, sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M KBr at 39.77°C

Solvent D Run 68

Initial concentration = 0.00965 M

t (secs)	(a - x)	$k \times 10^{-5}$ sec^{-1}
0	9.43	-
3372	7.80	(5.627)
5407	6.95	5.643
7218	6.27	5.654
9025	5.63	5.716
10941	5.03	5.744
13098	4.42	5.785
15493	3.82	5.833
17685	3.32	5.905
20024	2.91	5.873
22156	2.60	5.816
24375	2.28	5.826
27449	1.89	5.856
30821	1.56	5.838

$k_1' = 5.791 \times 10^{-5}$ sec^{-1}

$k_1'' = 5.788 \times 10^{-5}$ sec^{-1}

$k_1 = 5.789 \times 10^{-5}$ sec^{-1}

p-Nitrobenzhydryl chloride + 0.05 M KNO_3 at 39.76°C

Solvent C Run 60

Initial concentration = 0.00988 M

t (secs)	(a − x)	$k \times 10^{-5} sec^{-1}$
0	9.57	–
3302	8.00	(5.426)
5119	7.18	5.614
7000	6.43	5.680
8809	5.89	(5.511)
10705	5.22	5.662
12792	4.66	5.626
14939	4.06	5.740
17287	3.57	5.705
20153	3.03	5.705
23103	2.54	5.742
26183	2.09	5.812
29642	1.78	5.675

$k_1' = 5.696 \times 10^{-5} sec^{-1}$

$k_1'' = 5.721 \times 10^{-5} sec^{-1}$

$k_1 = 5.709 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M $KClO_4$ at 39.75°C

Solvent D Run 72

Initial concentration = 0.00957 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.22	-
3357	7.61	5.751
5372	6.76	5.779
7181	6.08	5.797
9137	5.44	5.775
10976	4.89	5.775
12876	4.41	5.715
15041	3.85	5.806
17772	3.34	5.702
20833	2.78	5.744
23061	2.43	5.785
25787	2.06	5.815
29344	1.67	5.824

$$k_1' = 5.769 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.751 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.761 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M KCl at 39.75°C

Solvent C **Run 57**

Initial concentration = 0.00983 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.57	-
3445	7.95	5.381
5268	7.22	5.351
7086	6.55	5.352
8887	5.93	5.387
10975	5.34	5.316
13222	4.69	5.403
15365	4.16	5.424
17507	3.74	5.369
20038	3.27	5.362
22881	2.84	5.311
26342	2.37	5.299
29837	1.94	5.351

$$k_1' = 5.359 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.362 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.361 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.1 M LiBr at 39.75°C

Solvent D Run 80

Initial concentration = 0.00940 M

t (secs)	(a - x)	$k \times 10^{-5}$ sec^{-1}
0	9.22	-
3247	7.59	5.995
5068	6.77	6.092
6883	6.07	6.073
8711	5.44	6.057
10340	4.94	6.037
12709	4.23	6.132
14922	3.68	6.158
17419	3.15	6.027
19917	2.72	6.131
22785	2.25	6.193
26270	1.77	6.284
29168	1.48	6.272

$k_1' = 6.121 \times 10^{-5}$ sec^{-1}

$k_1'' = 6.118 \times 10^{-5}$ sec^{-1}

$k_1 = 6.120 \times 10^{-5}$ sec^{-1}

p-Nitrobenzhydryl chloride + 0.1 M $LiNO_3$ at 39.74°C

Solvent E Run 89

Initial concentration = 0.00943 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.18	-
3311	7.59	(5.746)
5137	6.75	5.985
6937	6.04	6.057
8736	5.42	6.032
10620	4.83	6.047
12487	4.30	6.074
14302	3.88	6.024
16123	3.48	6.017
18163	3.04	6.085
20252	2.71	6.026
22602	2.35	6.030
25892	1.97	5.946
29643	1.48	(6.158)

$$k_1' = 6.027 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.995 \times 10^{-5} sec^{-1}$$

$$k_1 = 6.012 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.1 M LiCl at 39.75°C

Solvent D   Run 75

Initial concentration = 0.00946 M

t (secs)	(a − x)	$k \times 10^{-5}$ sec^{-1}
0	9.03	-
3572	7.61	5.075
5291	6.89	5.114
6905	6.32	5.170
8960	5.67	5.195
10768	5.16	5.187
12594	4.70	5.187
15223	4.10	5.188
17915	3.55	5.212
20805	3.03	5.248
24152	2.59	5.184
27440	2.18	5.180
31451	1.79	5.146

$$k_1' = 5.174 \times 10^{-5} \text{sec}^{-1}$$

$$k_1'' = 5.176 \times 10^{-5} \text{sec}^{-1}$$

$$k_1 = 5.175 \times 10^{-5} \text{sec}^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M LiBr at 39.75°C

Solvent D Run 81

Initial concentration = 0.00948 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.22	-
3306	7.63	(5.727)
5126	6.87	(5.737)
6922	6.14	5.872
8727	5.52	5.880
10528	4.96	5.889
12326	4.48	5.896
14272	3.98	5.888
16198	3.55	5.892
18088	3.16	5.923
20050	2.81	5.927
22216	2.48	5.912
25324	2.05	5.937
28890	1.65	5.955

$$k_1' = 5.903 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.880 \times 10^{-5} sec^{-1}$$

$$k_1 = 5.892 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M $LiNO_3$ at 39.75°C

Solvent E   Run 92

Initial concentration = 0.00959 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.22	-
3323	7.62	5.732
5070	6.93	(5.632)
6657	6.29	5.742
9095	5.47	5.741
10891	4.93	5.749
12570	4.48	5.742
14633	3.96	5.776
16527	3.56	5.759
19253	3.04	5.762
22163	2.59	5.729
25605	2.10	5.779
29224	1.70	5.786

$k_1' = 5.754 \times 10^{-5} sec^{-1}$

$k_1'' = 5.768 \times 10^{-5} sec^{-1}$

$k_1 = 5.761 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M LiCl at 39.75°C

Solvent D Run 78

Initial concentration = 0.00949 M

t(secs)	$(a - x)$	$k \times 10^{-5} \text{sec}^{-1}$
0	9.24	-
3510	7.74	5.358
5118	7.04	5.315
6921	6.37	5.376
9003	5.69	5.388
10793	5.16	5.401
13586	4.44	5.396
15957	3.93	5.358
18640	3.36	5.430
21335	2.91	5.417
23904	2.59	5.369
26672	2.18	5.417
30219	1.80	5.414

$$k_1' = 5.386 \times 10^{-5} \text{sec}^{-1}$$

$$k_1'' = 5.413 \times 10^{-5} \text{sec}^{-1}$$

$$k_1 = 5.400 \times 10^{-5} \text{sec}^{-1}$$

p-Nitrobenzhydryl chloride + 0.1 M HNO$_3$ at 39.76°C

Solvent H Run 163

Initial concentration = 0.00987 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.52	-
2549	8.06	6.533
3547	7.53	6.610
4847	6.95	6.491
6188	6.34	6.567
7857	5.72	6.483
9488	5.12	6.537
11293	4.52	6.598
13035	4.02	6.616
15151	3.44	6.719
17538	2.94	6.704
20524	2.42	6.674
24051	1.88	6.745

$k_1' = 6.606 \times 10^{-5} \text{ sec}^{-1}$

$k_1'' = 6.627 \times 10^{-5} \text{ sec}^{-1}$

$k_1 = 6.616 \times 10^{-5} \text{ sec}^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M $HClO_4$ at 39.74°C

Solvent B Run 168

Initial concentration = 0.00995 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.60	-
2360	8.20	6.685
3425	7.61	6.704
4695	6.97	6.812
5858	6.49	6.695
7065	5.98	6.704
8570	5.39	6.736
10362	4.82	6.653
12816	4.00	6.831
15803	3.29	6.778
18490	2.72	6.823
20866	2.30	6.848
23574	1.90	6.873

$$k_1' = 6.766 \times 10^{-5} sec^{-1}$$

$$k_1'' = 6.752 \times 10^{-5} sec^{-1}$$

$$k_1 = 6.760 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M HNO_3 at 39.76°C

Solvent H Run 161

Initial concentration = 0.00975 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.43	-
3000	7.90	(5.903)
4542	7.19	5.998
6021	6.58	5.977
7402	6.02	6.064
8898	5.51	6.039
10647	4.98	5.999
12358	4.41	6.152
14537	3.90	6.074
16925	3.31	6.187
19482	2.83	6.180
22394	2.39	6.131
25878	1.90	6.190

$k_1' = 6.090 \times 10^{-5} sec^{-1}$

$k_1'' = 6.078 \times 10^{-5} sec^{-1}$

$k_1 = 6.084 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M $HClO_4$ at 39.76°C

Solvent H   Run 165

Initial concentration = 0.00986 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.52	-
3005	7.91	6.163
4450	7.21	6.246
5948	6.59	6.184
7250	6.09	6.163
8568	5.61	6.170
10172	5.03	6.273
11963	4.48	6.301
13846	3.99	6.279
16028	3.44	6.352
18674	2.92	6.350
21785	2.40	6.299
25394	1.83	(6.454)

$k_1' = 6.251 \times 10^{-5} sec^{-1}$

$k_1'' = 6.269 \times 10^{-5} sec^{-1}$

$k_1 = 6.260 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M NaBr at 20.03°C

Solvent F Run 116

Initial concentration = 0.00937 M

t (secs)	(a − x)	$k \times 10^{-6}$ sec^{-1}
0	9.25	-
29400	7.91	(5.320)
40920	7.43	(5.353)
76260	6.06	5.546
94920	5.46	5.552
110880	5.00	5.549
126960	4.56	5.568
163020	3.68	5.654
187320	3.26	5.569
213900	2.82	5.555
248640	2.25	5.684
266040	2.02	5.719
285540	1.81	5.714
335280	1.36	5.719

$k_1' = 5.621 \times 10^{-6}$ sec^{-1}

$k_1'' = 5.601 \times 10^{-6}$ sec^{-1}

$k_1 = 5.612 \times 10^{-6}$ sec^{-1}

p-Nitrobenzhydryl chloride + 0.1 M $NaNO_3$ at 20.03°C

Solvent F Run 119

Initial concentration = 0.00935 M

t (secs)	(a - x)	$k \times 10^{-6} sec^{-1}$
0	9.21	-
40740	7.44	5.241
60900	6.71	5.207
76860	6.16	5.234
92880	5.63	5.302
127380	4.66	5.346
152220	4.10	5.319
179040	3.55	5.326
213660	2.93	5.363
231900	2.64	5.391
250560	2.37	5.419
300240	1.82	5.403
324780	1.59	5.411

$k_1' = 5.330 \times 10^{-6} sec^{-1}$

$k_1'' = 5.346 \times 10^{-6} sec^{-1}$

$k_1 = 5.338 \times 10^{-6} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.1 M NaClO$_4$ at 20.03°C

Solvent G Run 123

Initial concentration = 0.00939 M

t (secs)	(a - x)	k x 10^{-6} sec^{-1}
0	9.26	-
30240	7.88	5.338
40320	7.49	5.261
75360	6.20	5.323
92220	5.68	5.302
111780	5.12	5.302
130440	4.67	5.250
161880	3.94	5.282
189600	3.36	5.348
212940	2.92	5.420
248700	2.41	5.412
299940	1.90	5.281
334740	1.54	5.362

$$k_1' = 5.323 \times 10^{-6} \text{ sec}^{-1}$$

$$k_1'' = 5.338 \times 10^{-6} \text{ sec}^{-1}$$

$$k_1 = 5.330 \times 10^{-6} \text{ sec}^{-1}$$

p-Nitrobenzhydryl chloride + 0.1 M NaCl at 20.03°C

Solvent F Run 104

Initial concentration = 0.00942 M

t (secs)	(a - x)	$k \times 10^{-6} sec^{-1}$
0	9.33	-
40980	7.70	4.687
76440	6.51	4.709
92820	6.05	4.670
110100	5.63	(4.588)
128340	5.11	4.691
162780	4.33	4.718
188160	3.85	4.705
213840	3.36	4.777
250080	2.85	4.743
301740	2.22	4.754
362100	1.69	4.739

$$k_1' = 4.719 \times 10^{-6} sec^{-1}$$
$$k_1'' = 4.715 \times 10^{-6} sec^{-1}$$
$$k_1 = 4.717 \times 10^{-6} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M NaBr at 20.03°C

Solvent F Run 114

Initial concentration = 0.00939 M

t (secs)	(a - x)	$k \times 10^{-6} \text{sec}^{-1}$
0	9.23	-
34140	7.83	(4.814)
45660	7.24	5.320
80940	6.04	5.242
99600	5.46	5.271
115620	5.05	5.216
131760	4.64	5.220
167520	3.74	5.393
193020	3.27	5.378
219240	2.83	5.393
254400	2.30	5.456
270900	2.17	5.346
291240	1.88	5.466
349920	1.43	5.471

$k_1' = 5.348 \times 10^{-6} \text{sec}^{-1}$

$k_1'' = 5.338 \times 10^{-6} \text{sec}^{-1}$

$k_1 = 5.343 \times 10^{-6} \text{sec}^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M $NaNO_3$ at 20.03°C

Solvent F Run 113

Initial concentration = 0.01010 M

t (secs)	(a - x)	$k \times 10^{-6} sec^{-1}$
0	9.93	-
39660	8.15	5.093
57360	7.44	5.030
74820	6.77	5.219
91980	6.20	5.121
126540	5.16	5.174
138540	4.85	5.174
156120	4.43	5.170
171600	4.10	5.154
213060	3.31	5.157
265260	2.54	5.141
299940	2.07	5.229
320820	1.90	5.156

$$k_1' = 5.143 \times 10^{-6} sec^{-1}$$

$$k_1'' = 5.138 \times 10^{-6} sec^{-1}$$

$$k_1 = 5.140 \times 10^{-6} sec^{-1}$$

p-Nitrobenzhydryl chloride + 0.05 M $NaClO_4$ at 20.03°C

Solvent G Run 120

Initial concentration = 0.00938 M

t (secs)	(a - x)	$k \times 10^{-6} sec^{-1}$
0	9.26	-
34140	7.87	(4.762)
45240	7.34	5.136
80460	6.10	5.189
97320	5.66	5.059
117480	5.05	5.163
135360	4.61	5.153
167340	3.90	5.168
194400	3.44	5.094
218640	2.95	5.232
254460	2.48	5.181
272400	2.24	5.212
305700	1.90	5.182
339540	1.58	5.207

$k_1' = 5.165 \times 10^{-6} sec^{-1}$

$k_1'' = 5.145 \times 10^{-6} sec^{-1}$

$k_1 = 5.154 \times 10^{-6} sec^{-1}$

p-Nitrobenzhydryl chloride + 0.05 M NaCl at 20.01°C

Solvent F Run 107

Initial concentration = 0.00969 M

t (secs)	(a - x)	$k \times 10^{-6}\,\text{sec}^{-1}$
0	9.52	-
42120	7.76	4.850
58140	7.21	4.781
77100	6.54	4.868
94800	6.03	4.818
128520	5.10	4.856
149160	4.64	4.818
177840	4.03	4.833
215040	3.32	4.900
233280	3.07	4.851
268260	2.58	4.870
301740	2.18	4.887
327060	1.96	4.835

$k_1' = 4.847 \times 10^{-6}\,\text{sec}^{-1}$

$k_1'' = 4.834 \times 10^{-6}\,\text{sec}^{-1}$

$k_1 = 4.841 \times 10^{-6}\,\text{sec}^{-1}$

p-Nitrobenzhydryl chloride in SOLVENT B at 39.75°C

Run 35

Initial concentration = 0.00983 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.59	-
3512	7.97	(5.266)
5309	7.17	5.479
7093	6.48	5.526
8904	5.89	5.475
10696	5.33	5.492
12608	4.78	5.524
14648	4.28	5.509
16780	3.79	5.534
19410	3.29	5.513
22617	2.65	(5.689)
26066	2.27	5.530
29537	1.87	5.537

$$k_1' = 5.512 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.481 \times 10^{-5} sec^{-1}$$

$$k_1^{o} = 5.495 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride in SOLVENT C at 39.75°C

Run 42

Initial concentration = 0.00952 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.40	-
3291	7.88	5.360
5094	7.13	5.426
6898	6.45	5.462
8700	5.87	5.414
10506	5.32	5.420
12615	4.74	5.428
14669	4.18	5.524
16716	3.73	5.530
19298	3.24	5.520
22525	2.74	5.473
25938	2.26	5.496
29554	1.86	5.484

$$k_1' = 5.461 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.491 \times 10^{-5} sec^{-1}$$

$$k_1^{\circ} = 5.456 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride in SOLVENT D at 39.75°C

Run 64

Initial concentration = 0.00973 M

t (secs)	(a - x)	k x 10^{-5}sec^{-1}
0	9.50	-
3289	7.93	5.489
5719	6.96	5.441
6926	6.45	5.589
9328	5.65	5.573
11132	5.10	5.590
12941	4.65	5.521
14934	4.15	5.547
17236	3.64	5.568
19640	3.21	5.525
22047	2.79	5.559
24980	2.35	(5.723)
27492	2.03	5.614
30248	1.71	5.671

$k_1' = 5.557 \times 10^{-5}$sec^{-1}

$k_1'' = 5.568 \times 10^{-5}$sec^{-1}

$k_1^{*} = 5.562 \times 10^{-5}$sec^{-1}

p-Nitrobenzhydryl chloride in SOLVENT E at 39.75°C

Run 83

Initial concentration = 0.00968 M

t (secs)	(a - x)	k x 10^{-5} sec^{-1}
0	9.35	-
3320	7.80	5.461
5109	7.08	5.444
6897	6.42	5.454
9043	5.67	5.533
10849	5.14	5.514
12675	4.65	5.509
14593	4.17	5.535
16646	3.72	5.539
18666	3.32	5.549
21492	2.85	5.530
24283	2.42	5.554
27252	2.06	5.551
30588	1.70	5.573

$k_1' = 5.519 \times 10^{-5}$ sec^{-1}

$k_1'' = 5.506 \times 10^{-5}$ sec^{-1}

$k_1^{\circ} = 5.513 \times 10^{-5}$ sec^{-1}

p-Nitrobenzhydryl chloride in SOLVENT H at 39.76°C

Run 158

Initial concentration = 0.00986 M

t (secs)	(a - x)	$k \times 10^{-5}\text{sec}^{-1}$
0	9.53	-
3163	7.93	(5.811)
4918	7.24	5.591
6700	6.61	5.463
8506	5.91	5.619
10472	5.31	5.586
12059	4.92	5.484
14334	4.33	5.505
16652	3.81	5.508
18935	3.39	5.461
21654	2.89	5.511
26298	2.21	5.558

$$k_1' = 5.529 \times 10^{-5}\text{sec}^{-1}$$
$$k_1'' = 5.516 \times 10^{-5}\text{sec}^{-1}$$
$$k_1^{\circ} = 5.522 \times 10^{-5}\text{sec}^{-1}$$

p-Nitrobenzhydryl chloride in SOLVENT J at 39.76°C

Run 133

Initial concentration = 0.00972 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.46	-
3303	7.88	5.537
5119	7.13	5.525
7035	6.40	5.555
8711	5.84	5.540
10627	5.24	5.560
12266	4.77	5.585
14606	4.19	5.576
16805	3.71	5.571
20047	3.11	5.550
23250	2.60	5.556
26939	2.08	5.623
29992	1.78	5.571

$$k_1' = 5.562 \times 10^{-5} sec^{-1}$$

$$k_1'' = 5.585 \times 10^{-5} sec^{-1}$$

$$k_1^{\circ} = 5.574 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride in SOLVENT L at 39.79°C

Run 169

Initial concentration = 0.01019 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	10.08	-
3136	8.54	(5.281)
4938	7.72	5.401
6734	7.02	5.373
8833	6.26	5.393
10864	5.57	5.459
12902	4.97	5.479
15266	4.36	5.491
17515	3.84	5.511
19833	3.37	5.524
22525	2.88	5.562
25580	2.47	5.498
28982	2.00	5.581

$k_1' = 5.479 \times 10^{-5} sec^{-1}$

$k_1'' = 5.458 \times 10^{-5} sec^{-1}$

$k_1^{\circ} = 5.469 \times 10^{-5} sec^{-1}$

p-Nitrobenzhydryl chloride in SOLVENT F at 20.05°C

Run 102

Initial concentration = 0.00935 M

t (secs)	(a - x)	$k \times 10^{-6} sec^{-1}$
0	9.25	-
37620	7.67	4.977
48240	7.29	4.937
81300	6.17	(4.866)
97860	5.67	5.000
116160	5.17	5.007
133320	4.74	5.013
167640	3.97	5.047
191220	3.57	4.979
218400	3.07	5.051
255180	2.56	5.036
286980	2.26	4.911
341280	1.66	5.032
367560	1.41	(5.118)

$k_1' = 4.999 \times 10^{-6} sec^{-1}$

$k_1'' = 5.020 \times 10^{-6} sec^{-1}$

$k_1^{\circ} = 5.008 \times 10^{-6} sec^{-1}$

p-Nitrobenzhydryl chloride in SOLVENT G at 20.03°C

Run 127

Initial concentration = 0.00982 M

t (secs)	(a − x)	$k \times 10^{-6}\,\mathrm{sec}^{-1}$
0	9.65	–
35400	8.08	5.017
46860	7.68	4.871
81360	6.47	4.914
99480	5.89	4.964
117600	5.42	4.906
133680	4.96	4.978
168480	4.21	4.923
193560	3.70	4.953
219600	3.26	4.943
255540	2.69	4.999
306960	2.06	5.031
341760	1.73	5.029

$k_1' = 4.961 \times 10^{-6}\,\mathrm{sec}^{-1}$

$k_1'' = 4.961 \times 10^{-6}\,\mathrm{sec}^{-1}$

$k_1^{\circ} = 4.961 \times 10^{-6}\,\mathrm{sec}^{-1}$

p-Nitrobenzhydryl chloride in 55/45 acetone/water at 39.76°C

Run 98

Initial concentration = 0.00989 M

t (secs)	(a - x)	$k \times 10^{-5} sec^{-1}$
0	9.74	-
5940	8.34	2.614
9060	7.64	2.682
12720	7.08	(2.509)
16320	6.37	2.604
20460	5.65	2.663
24180	5.08	2.693
27600	4.65	2.679
31500	4.18	2.686
35820	3.70	2.705
39600	3.32	2.719
45060	2.89	2.698
49920	2.51	2.717
54720	2.20	2.719

$$k_1' = 2.681 \times 10^{-5} sec^{-1}$$

$$k_1'' = 2.686 \times 10^{-5} sec^{-1}$$

$$k_1^{\circ} = 2.683 \times 10^{-5} sec^{-1}$$

p-Nitrobenzhydryl chloride in 45/55 acetone/water at 39.76°C

Run 144

Initial concentration = 0.00484 M

t (secs)	(a - x)	k x 10^{-4} sec^{-1}
0	4.62	-
1348	3.94	1.180
2062	3.63	1.169
2786	3.34	1.165
3588	3.02	1.185
4397	2.74	1.188
5280	2.48	1.179
6240	2.23	1.168
7329	1.95	1.177
8410	1.69	1.196
9548	1.45	(1.237)
10748	1.25	1.189
11945	1.10	1.201
13173	0.91	(1.234)

$k_1' = 1.182 \times 10^{-4} sec^{-1}$

$k_1'' = 1.179 \times 10^{-4} sec^{-1}$

$k_1^\circ = 1.180 \times 10^{-4} sec^{-1}$

Details Of Solubility Runs.

Details of one solubility run and "blank" are given. The mean solubilities, S'' and S''_{o}, of a duplicate run and "blank", respectively are reported, together with the standard error of the final mean in each case.

RCl = p-Nitrobenzhydryl chloride

All runs were carried out at 0°C, and unless stated otherwise the solvent was 50% aqueous acetone.

0.01 M RCl

Run 22

t (hrs)	Concn.
6	0.00489 M
"	0.00491
"	0.00492
24	0.00491
"	0.00492
"	0.00492

S'_0 = 0.00491 ± 1

S''_0 = 0.00489 ± 1

0.01 M RCl + 0.1 M $NaClO_4$

Run 19

t (hrs)	Concn.
6	0.00555 M
"	0.00556
"	0.00556
24	0.00556
"	0.00558
"	0.00559

S' = 0.00557 ± 1

S'' = 0.00570 ± 1

0.01 M RCl = 0.05 M $NaClO_4$

Run 20

t (hrs)	Concn.
6	(0.00520)M
"	0.00529
"	0.00529
24	0.00528
"	0.00529
"	0.00531

S'_0 = 0.00529 ± 1

S''_0 = 0.00539 ± 1

0.01 M RCl + 0.1 M NaCl

Run 21

t (hrs)	Concn.
6	0.00513M
"	0.00513
"	0.00511
24	0.00511
"	0.00511
"	-

S' = 0.00512 ± 1

S'' = 0.00513 ± 1

0.01 M KCl

Run 30

t (hrs)	Concn.
6	0.00492 M
"	0.00492
"	0.00493
24	0.00497
"	0.00496
"	-

S'_o =0.00494 ± 1

S''_o =0.00500 ± 1

0.01 M KCl + 0.1 M $NaNO_3$

Run 26

t (hrs)	Concn.
6	0.00498 M
"	0.00499
"	0.00500
24	0.00509
"	0.00507
"	0.00506

S' = 0.00503 ± 2

S'' = 0.00504 ± 1

0.01 M KCl + 0.05 M NaCl

Run 27

t (hrs)	Concn.
6	0.00506 M
"	0.00511
"	0.00509
24	0.00510
"	0.00511
"	0.00511

S' = 0.00510 ± 1

S'' = 0.00514 ± 1

0.01 M KCl + 0.05 M $NaNO_3$

Run 29

t (hrs)	Concn.
6	0.00501 M
"	0.00503
"	0.00504
24	0.00505
"	0.00503
"	0.00503

S' = 0.00503 ± 1

S'' = 0.00504 ± 1

0.01 M RCl

Run 38

t (hrs)	Concn.
6	0.00492 M
"	0.00492
"	0.00495
24	0.00496
"	0.00497
"	0.00495

S'_o = 0.00494 ± 1

S''_o = 0.00487 ± 1

0.01 M RCl + 0.1 M NaBr

Run 35

t (hrs)	Concn.
6	(0.00494) M
"	-
"	-
24	0.00513
"	0.00513
"	0.00513

S' = 0.00513

S'' = 0.00511 ± 1

0.01 M RCl + 0.05 M NaBr

Run 36

t (hrs)	Concn.
6	0.00496 M
"	0.00501
"	0.00497
24	0.00502
"	0.00502
"	0.00502

S' = 0.00500 ± 1

S'' = 0.00496 ± 1

0.01 M RCl + 0.1 M KCl

Run 37

t (hrs)	Concn.
6	0.00511 M
"	0.00512
"	0.00514
24	0.00517
"	0.00516
"	0.00518

S' = 0.00515 ± 1

S'' = 0.00514 ± 1

0.01 RCl

Run 42

t (hrs)	Conc.
6	0.00478 M
"	0.00479
"	0.00480
24	0.00485
"	0.00486
"	0.00483

$S'_o = 0.00482 \pm 1$

$S''_o = 0.00493 \pm 1$

0.01 M RCl + 0.05 M KCl

Run 39

t (hrs)	Concn.
6	0.00506 M
"	0.00510
"	0.00511
24	0.00503
"	0.00502
"	0.00503

$S' = 0.00506 \pm 1$

$S'' = 0.00499 \pm 1$

0.01 M RCl + 0.1 M $KClO_4$

Run 40

t (hrs)	Concn.
6	(0.00529) M
"	0.00536
"	0.00537
24	0.00542
"	0.00538
"	0.00541

$S' = 0.00539 \pm 1$

$S'' = 0.00541 \pm 3$

0.01 M RCl + 0.05 M $KClO_4$

Run 41

t (hrs)	Concn.
6	0.00513 M
"	0.00513
"	0.00511
24	0.00523
"	(0.00496)
"	0.00525

$S' = 0.00517 \pm 2$

$S'' = 0.00525 \pm 2$

0.01 M KCl

Run 54

t (hrs)	Concn.
6	0.00492 M
"	0.00495
"	0.00493
24	0.00489
"	0.00493
"	0.00485

S'_o = 0.00491 ± 1

S''_o = 0.00495 ± 1

0.01 M KCl + 0.1 M KBr

Run 51

t (hrs)	Concn.
6	(0.00499) M
"	0.00506
"	0.00508
24	0.00512
"	0.00513
"	0.00512

S' = 0.00510 ± 1

S" = 0.00511 ± 1

0.01 M KCl + 0.05 M KBr

Run 52

t (hrs)	Concn.
6	(0.00482) M
"	0.00492
"	0.00491
24	0.00502
"	0.00502
"	0.00503

S' = 0.00498 ± 2

S" = 0.00501 ± 4

0.01 M KCl + 0.1 M KNO_3

Run 53

t (hrs)	Concn.
6	0.00490 M
"	0.00490
"	0.00489
24	0.00501
"	0.00500
"	0.00499

S' = 0.00495 ± 2

S" = 0.00507 ± 1

0.01 M HCl

Run 58

t (hrs)	Concn.
6	0.00497 M
"	0.00495
"	0.00499
24	0.00499
"	0.00496
"	0.00498

$S'_0 = 0.00497 \pm 1$

$S''_0 = 0.00504 \pm 2$

0.01 M HCl + 0.05 M KNO_3

Run 55

t (hrs)	Concn.
6	(0.00473) M
"	0.00496
"	0.00498
24	0.00491
"	0.00487
"	(0.00463)

$S' = 0.00493 \pm 2$

$S'' = 0.00503 \pm 4$

0.01 M HCl + 0.1 M LiCl

Run 56

t (hrs)	Concn.
6	0.00506 M
"	0.00505
"	0.00505
24	(0.00484)
"	0.00506
"	0.00508

$S' = 0.00506 \pm 1$

$S'' = 0.00503 \pm 4$

0.01 M HCl + 0.05 M LiCl

Run 57

t (hrs)	Concn.
6	0.00495 M
"	0.00494
"	0.00494
24	0.00494
"	0.00502
"	0.00502

$S' = 0.00497 \pm 2$

$S'' = 0.00504 \pm 4$

0.01 M RCl

Run 85

t (hrs)	Concn.
6	0.00483 M
"	0.00485
"	0.00486
24	0.00489
"	0.00491
"	0.00491

S'_o = 0.00487 ± 1

S''_o = 0.00487 ± 1

0.01 M RCl + 0.1 M NaO_3SPh

Run 83

t (hrs)	Concn.
6	0.00516 M
"	0.00517
"	0.00517
24	0.00531
"	0.00536
"	0.00536

S' = 0.00526 ± 4

S" = 0.00519 ± 3

0.01 M RCl + 0.05 M NaO_3SPh

Run 84

t (hrs)	Concn.
6	0.00508 M
"	0.00509
"	0.00508
24	0.00513
"	0.00515
"	0.00515

S' = 0.00511 ± 1

S" = 0.00507 ± 1

0.01 M RCl

Run 96

t (hrs)	Concn.
6	0.00480 M
"	0.00483
"	0.00484
24	0.00488
"	0.00489
"	0.00497

S'_0 = 0.00487 ± 2

S''_0 = 0.00487 ± 2

0.01 M RCl + 0.1 M $HClO_4$

Run 93

t (hrs)	Concn.
6	0.00510 M
"	0.00511
"	0.00511
24	0.00514
"	0.00512
"	0.00513

S' = 0.00512 ± 1

S" = 0.00517 ± 2

0.01 M RCl + 0.05 M $HClO_4$

Run 94

t (hrs)	Concn.
6	0.00489 M
"	0.00489
"	0.00489
24	0.00506
"	0.00499
"	0.00500

S' = 0.00495 ± 2

S" = 0.00501 ± 1

0.01 M RCl + 0.1 M HNO_3

Run 95

t (hrs)	Concn.
6	0.00456 M
"	0.00457
"	0.00457
24	0.00454
"	0.00454
"	0.00457

S' = 0.00456 ± 1

S" = 0.00459 ± 2

0.01 M RCl

Run 106

t (hrs)	Concn.
6	0.00489 M
"	0.00489
"	0.00485
24	0.00489
"	0.00490
"	0.00489

S'_o = 0.00489 ± 1

S''_o = 0.00494 ± 2

0.01 M RCl + 0.05 M HNO_3

Run 104

t (hrs)	Concn.
6	0.00490
"	0.00490
"	0.00489
24	0.00480
"	0.00480
"	0.00477

S' = 0.00484 ± 2

S'' = 0.00487 ± 1

0.01 M RCl + 0·025 M NaF

Run 105

t (hrs)	Concn.
6	0.00510 M
"	0.00509
"	0.00509
24	0.00509
"	0.00509
"	0.00509

S' = 0.00509

S'' = 0.00514 ± 1

0.01 M RCl

Run 103

t (hrs)	Concn.
6	0.00514 M
"	0.00512
"	0.00513
24	0.00513
"	0.00515
"	0.00515

$S'_o = 0.00514 \pm 1$

$S''_o = 0.00512 \pm 1$

0.01 M RCl
in 45/55 acetone/water

Run 101

t (hrs)	Concn.
6	0.00173 M
"	0.00172
"	0.00174
24	0.00167
"	0.00172
"	0.00171

$S'_o = 0.00172 \pm 1$

$S''_o = 0.00173 \pm 1$

0.01 M RCl
in 55/45 acetone/water

Run 102

t (hrs)	Concn.
6	0.00996 M
"	0.01004
"	0.00996
24	0.00998
"	0.00998
"	0.00999

$S'_o = 0.00999 \pm 1$

$S''_o = 0.01001 \pm 1$

R'Cl = p-Nitrobenzyl chloride

All runs were carried out at 0°C, and unless stated otherwise the solvent was 50% aqueous acetone.

Excess R'Cl

Run 130

t (hrs)	Concn.
6	0.01396 M
"	0.01397
"	0.01392
24	0.01399
"	0.01395
"	0.01392

$S'_0 = 0.01395 \pm 1$

$S''_0 = 0.01403 \pm 4$

Excess R'Cl + 0.1 M HNO_3

Run 127

t (hrs)	Concn.
6	0.01370 M
"	0.01377
"	0.01378
24	0.01371
"	0.01361
"	0.01368

$S' = 0.01371 \pm 2$

$S'' = 0.01371 \pm 1$

Excess R'Cl + 0.05 M HNO_3

Run 128

t (hrs)	Concn.
6	0.01408 M
"	0.01408
"	0.01407
24	0.01397
"	0.01400
"	0.01403

$S' = 0.01404 \pm 2$

$S'' = 0.01399 \pm 2$

Excess R'Cl + 0.1 M $HClO_4$

Run 129

t (hrs)	Concn.
6	0.01444 M
"	0.01437
"	0.01448
24	0.01438
"	0.01438
"	0.01439

$S' = 0.01441 \pm 2$

$S'' = 0.01456 \pm 3$

Excess R'Cl

Run 138

t (hrs)	Concn.
6	0.01388 M
"	0.01383
"	0.01383
24	0.01390
"	0.01385
"	—

S'_o = 0.01386 ± 1

S''_o = 0.01387 ± 1

Excess R'Cl + 0.05 M HClO$_4$

Run 135

t (hrs)	Concn.
6	0.01432 M
"	0.01418
"	0.01418
24	0.01402
"	0.01409
"	0.01400

S' = 0.01409 ± 3

S" = 0.01416 ± 2

Excess R'Cl + 0.025 M NaF

Run 136

t (hrs)	Concn.
6	0.01445 M
"	0.01443
"	0.01452
24	0.01441
"	0.01437
"	0.01433

S' = 0.01444 ± 2

S" = 0.01435 ± 6

Excess R'Cl

Run 141

t (hrs)	Concn.
6	0.01387 M
"	0.01396
"	0.01385
24	0.01388
"	0.01380
"	0.01383

$S'_0 = 0.01387 \pm 2$

$S''_0 = 0.01387 \pm 1$

$S'''_0 = 0.01386 \pm 1$

Excess R'Cl + 0.1 M $NaNO_3$

Run 139

t (Hrs)	Concn.
6	0.01402 M
"	0.01408
"	0.01408
24	0.01400
"	0.01402
"	0.01402

$S' = 0.01404 \pm 1$

$S'' = 0.01402 \pm 1$

Excess R'Cl + 0.05 M $NaNO_3$

Run 140

t (hrs)	Concn.
6	0.01400 M
"	0.01399
"	0.01401
24	0.01390
"	0.01390
"	0.01393

$S' = 0.01396 \pm 2$

$S''' = 0.01395 \pm 2$

Excess R'Cl

Run 119

t (hrs)	Concn.
6	0.01476 M
"	0.01484
"	0.01483
24	0.01468
"	0.01471
"	0.01465

$S'_o = 0.01474 \pm 3$

$S''_o = 0.01470 \pm 5$

Excess R'Cl in 45/55 acetone/water

Run 116

t (hrs)	Concn.
6	0.00650 M
"	0.00648
"	0.00651
24	0.00648
"	0.00647
"	0.00643

$S'_o = 0.00648 \pm 1$

$S''_o = 0.00662 \pm 3$

Excess R'Cl in 55/45 acetone/water

Run 117

t(hrs)	Concn.
6	0.02282 M
"	0.02284
"	0.02285
24	0.02256
"	0.02261
"	0.02257

$S'_o = 0.02271 \pm 5$

$S''_o = 0.02270 \pm 6$

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